Dedicated to:

My **Parents**, **Mr. Mumtaz Hussain** and **Mrs. Shaheen Mumtaz,** for their continuous support throughout my career.

To my **whole family**, especially my **Sisters** and late Aunt **Ms. Suraya Ishaque**.

To my friends**—Hanna Plewa, Fawad, Shakir-ul-Azam, Faizan, Kamran,** and **Shanza Zaib.**

Without your support, this journey would have been impossible.

DEPARTMENT OF THERMAL TECHNOLOGY
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Experimental analysis of the waste hydrothermal treatment process

Ph.D. thesis of

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Abstract

The increasing prevalence of polymeric and composite waste from wind turbine blades (WTBs), personal protective equipment (PPEs) used in the medical sector, end-of-life photovoltaic (PV) panels, and municipal solid waste (MSW), necessitates the development of effective recycling technologies to uphold the principles of a circular economy. Traditional approaches, such as mechanical recycling, incineration, and pyrolysis, encounter challenges, including significant energy consumption, downcycling, emissions of pollutants, and suboptimal material recovery. This research thesis introduces oxidative liquefaction as a method to selectively degrade polymeric waste, facilitating the production of liquid chemical compounds and valuable secondary materials.

A systematic experimental matrix was established for each waste type utilizing a specific experimental design approach to assess the impact of reaction parameters, i.e., temperature, pressure, reaction time, oxidant concentration, and waste-to-liquid ratio on the degradation of selected waste types. After the oxidative liquefaction process, the total solid reduction (TSR), or total polymer degradation (TPD), was calculated for the obtained solid fraction, and the resulting liquid was subjected to analysis through gas chromatography with flame ionization detection (GC-FID) to identify the individual chemical fraction as well as to quantify overall yield of oxygenated chemical compounds (OCCs). Statistical modelling of obtained results and response surface methodology (RSM) were utilized to study the effect of each reaction parameter on overall process efficiency and to identify the optimal reaction conditions to enhance the resource recovery while reducing energy input. The inside reactor temperature profiles were drawn, and inverse analyses were performed to identify the reaction stages resulting in major waste degradation and determine the reaction's nature.

The investigation commenced with the detailed characterization of raw waste samples achieved through a series of analytical techniques, including ultimate and proximate analysis, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The analyses indicated notable variations in composition, highlighting that PPEs are rich in polymers, MSW and WTBs display heterogeneity, and PV panels consist of a substantial proportion of inorganic residues. The TGA results validated single-stage degradation for PPEs, highlighting uniform composition, while the multi-stage decomposition behaviour was observed for remaining waste types.

In addition to producing OCCs, the successful recovery of glass fibers from WTBs highlights the potential of oxidative liquefaction as a viable method for material recovery, especially in the context of fiber-reinforced composites. The results highlight oxidative liquefaction as a practical and scalable approach to waste management, providing an alternative to traditional disposal methods and supporting circular economy principles. Nonetheless, additional investigation is necessary to improve process efficiency, refine reactor designs, and examine catalytic enhancements for applications on an industrial scale. This thesis aims to enhance sustainable waste-to-resource technologies, tackling significant environmental issues and facilitating the shift towards a more resilient and resource-efficient future

Streszczenie

Rosnąca ilość odpadów polimerowych i kompozytowych pochodzących z łopat turbin wiatrowych (WTB), środków ochrony osobistej (PPE) stosowanych w sektorze medycznym, wyeksploatowanych paneli fotowoltaicznych (PV) oraz odpadów komunalnych (MSW) wymaga opracowania efektywnych technologii recyklingu, wspierających zasady gospodarki o obiegu zamkniętym. Tradycyjne metody, takie jak recykling mechaniczny, spalanie czy piroliza, napotykają ograniczenia, w tym wysokie zużycie energii, degradację jakości materiału, emisję zanieczyszczeń oraz nieoptymalny odzysk surowców. Niniejsza praca doktorska proponuje proces oksydatywnego upłynniania polimerów jako metodę selektywnej degradacji odpadów polimerowych, umożliwiającą uzyskiwanie ciekłych związków chemicznych oraz cennych materiałów wtórnych.

Dla każdego typu odpadów opracowano macierz eksperymentalną z wykorzystaniem zaawansowanych metod planowania eksperymentu, aby ocenić wpływ parametrów procesowych, takich jak temperatura, ciśnienie, czas reakcji, stężenie utleniacza oraz stosunek odpadów do cieczy reakcyjnej, na degradację frakcji organicznej. Dokonano pomiarów temperatury wewnątrz komory reaktora, a analizy odwrotne przeprowadzono w celu identyfikacji etapów reakcji prowadzących do głównej degradacji odpadów oraz określenia charakteru reakcji. Po procesie oksydatywnego upłynniania obliczano całkowitą redukcję masy stałej (TSR) lub całkowitą degradację polimerów (TPD), a produkty ciekłe poddano analizie chromatografii gazowej z detekcją płomieniowo-jonizacyjną (GC-FID), aby zidentyfikować poszczególne frakcje chemiczne oraz określić ogólny uzysk związków zawierających tlen (OCC). Zastosowano modelowanie statystyczne wyników oraz metodykę powierzchni odpowiedzi (RSM), by ocenić wpływ każdego parametru reakcji na efektywność procesu i wyznaczyć optymalne warunki prowadzenia reakcji, maksymalizujące odzysk surowców przy minimalnym zużyciu energii.

Badania rozpoczęto od szczegółowej charakterystyki surowych próbek odpadów z wykorzystaniem szeregu technik analitycznych, w tym analiz technicznej i elementarnej, spektroskopii w podczerwieni z transformacją Fouriera (FTIR), skaningowej mikroskopii elektronowej (SEM) oraz analizy termograwimetrycznej (TGA). Analizy wykazały istotne różnice w składzie materiałowym: PPE charakteryzuje się wysoką zawartością polimerów, MSW i WTB są materiałami wysoce heterogenicznymi, natomiast panele PV zawierają znaczący udział składników nieorganicznych. Wyniki TGA potwierdziły jednofazową degradację PPE, wskazując na jednorodny charakter materiału, podczas gdy pozostałe rodzaje odpadów wykazywały wieloetapowy przebieg dekompozycji.

Oprócz uzyskiwania związków tlenowych (OCC) wykazano skuteczny odzysk włókien szklanych z WTB, co podkreśla potencjał oksydatywnego upłynniania jako praktycznej metody odzysku materiałów — zarówno włókien, jak i wypełniaczy — szczególnie w przypadku kompozytów wzmacnianych włóknem. Wyniki badań wskazują, że analizowana metoda stanowi skalowalne i efektywne podejście do gospodarowania odpadami, będące alternatywą dla tradycyjnych metod utylizacji i wspierające zasady gospodarki o obiegu zamkniętym. Niemniej konieczne są dalsze prace nad poprawą efektywności procesu, udoskonaleniem konstrukcji reaktorów oraz oceną możliwości katalitycznych usprawnień w zastosowaniach przemysłowych. Celem niniejszej pracy jest rozwój zrównoważonych technologii przetwarzania odpadów w wartościowe surowce, co przyczynia się do rozwiązywania istotnych problemów środowiskowych i wspiera transformację w kierunku bardziej odpornej i efektywnej gospodarki zasobami.

Thesis Organization

This doctoral dissertation is structured in an **article-based format**, consisting of seven peer-reviewed publications rather than a standard monograph-style thesis structure. The thesis consists of nine chapters, and each chapter is considered as standalone unit with provided background and excluding chapter 1&2, each chapter provide the summary of results from published research article focusing on a distinct element of the investigation into oxidative liquefaction as a viable waste management approach for various waste streams, such as WTBs, PPEs, MSW and PV waste.

The structure of the thesis is outlined as follows:

Chapter 1: General Introduction

This chapter offers a comprehensive overview of the overall research landscape, highlighting the critical issues related to plastic or polymeric waste production (PPEs), composite waste arising from the renewable energy sector (such as WTBs and PV panels), and the management of heterogeneous MSW. The study examines the environmental consequences of inadequate waste disposal and highlights the shortcomings of current waste management approaches. This chapter identifies significant research gaps and establishes the aim and objectives of the doctoral study, thereby laying the groundwork for future experimental research.

Chapter 2: Materials and Methods

In Chapter 2, the materials examined in this study, comprising WTBs, PPE, MSW, and PV panels, are detailed alongside their baseline characterization. This chapter delineates the experimental configuration and the operational parameters utilized for oxidative liquefaction. Additionally, it outlines the analytical techniques and elemental analysis implemented to evaluate the chemical and structural modifications observed during the process. The application of statistical analysis, specifically RSM and Analysis of Variance (ANOVA), for the purposes of process optimization and results evaluation is comprehensively outlined.

Chapter 3: Experimental Investigation of Oxidative Liquefaction of Wind Turbine Blades

This chapter introduces the initial experimental investigation into the oxidative liquefaction of WTBs, emphasizing the degradation of resin and the recovery of glass fibers. The chapter outlines the materials used, the reactor design, and the experimental procedures employed, concluding with an examination of energy usage and optimization of the process. The results demonstrate the technical viability of oxidative liquefaction for WTBs and underscore its promise for material recovery and energy efficiency.

Chapter 4: Product Analysis from Oxidative Liquefaction of Wind Turbine Blades

This section expands upon the previous chapter by performing a thorough chemical and structural analysis of the products obtained from oxidative liquefaction. Methods including FTIR, SEM-EDS, and chromatography are utilized to analyze liquid products (VFAs, OCCs) and evaluate the structural alterations in WTBs prior to and following treatment. This chapter further delineates the optimal reaction conditions that enhance product yields to their maximum potential.

Chapter 5: Comparative Analysis of Oxidative Liquefaction Process (WTBs vs. PPEs)

This chapter explores the oxidative liquefaction method applied to PPE waste, analysing its degradation characteristics and product yields in comparison to WTBs. TGA compositional studies, and energy efficiency assessments are performed to assess variations in polymer degradation patterns and the production of OCCs. The findings offer valuable perspectives on the adaptability of processes when dealing with various waste categories.

Chapter 6: An Overview of MSW Generation, Globally and in Poland

This chapter examines trends in waste generation, composition, and disposal practices, with a specific focus on MSW management at both global and regional levels, particularly in Poland. The section emphasizes the difficulties associated with MSW treatment and underscores the necessity for alternative approaches such as oxidative liquefaction, connecting this discourse to the following experimental investigation.

Chapter 7: Comparative Analysis of Oxidative Liquefaction for MSW and PPEs

This chapter examines the application of oxidative liquefaction to MSW samples, analyzing the outcomes in relation to those obtained from PPEs processes. The analysis focuses on key parameters including TSR, OCC yields, and energy efficiency. This research delineates the optimal parameters for MSW treatment and examines the potential for scaling the process to accommodate diverse waste streams.

Chapter 8: End-of-Life Disposal Of Photovoltaic Panels, Outcomes And Challenges

The final experimental chapter investigates the utilization of oxidative liquefaction in the context of PV waste. The evaluation of degradation behaviour and product recovery is conducted using SEM-EDS, TGA, and inverse analysis of the heating process. This chapter examines the challenges associated with PV waste recycling and suggests enhancements to processes for better large-scale implementation.

Chapter 9: Summary of Thesis, General Conclusions, and Future Perspectives

The thesis wraps up by summarizing the main findings from all studies, highlighting the adaptability of oxidative liquefaction for various waste streams. The chapter delineates constraints, industrial ramifications, and prospective avenues for investigation, encompassing pilot-scale validation and assessments of economic viability.

During the Ph.D. study, the candidate Hamza Mumtaz was listed in 12 scientific articles published in high-impact-factor journals, with 8 papers as the leading author. According to the Scopus data base total number of citations starting from 2022 is 175 with h-index = 6 (access on 10th of September 2025). The list of publications is given below

1. H. Mumtaz, S. Sobek, M. Sajdak, R. Muzyka, S. Werle, An experimental investigation and process optimization of the oxidative liquefaction process as the recycling method of the end-of-life wind turbine blades, Renew Energy 211 (2023) 269–278. https://doi.org/10.1016/J.RENENE.2023.04.120.

2. H. Mumtaz, S. Sobek, M. Sajdak, R. Muzyka, S. Drewniak, S. Werle, Oxidative liquefaction as an alternative method of recycling and the pyrolysis kinetics of wind turbine blades, Energy 278 (2023) 127950. https://doi.org/10.1016/J.ENERGY.2023.127950.

3. H. Mumtaz, S. Sobek, S. Werle, M. Sajdak, R. Muzyka, Hydrothermal treatment of plastic waste within a circular economy perspective, Sustain Chem Pharm 32 (2023) 100991. https://doi.org/10.1016/J.SCP.2023.100991.

4. H. Mumtaz, S. Werle, S. Sobek, M. Sajdak, R. Muzyka, An in-depth study of the oxidative liquefaction process for polymeric waste reduction and chemical production from wind turbine blades and personal protective equipment used in the medical field, J Environ Manage 365 (2024) 121668. https://doi.org/10.1016/J.JENVMAN.2024.121668.

5. S. Sobek, L. Lombardi, B. Mendecka, H. Mumtaz, M. Sajdak, R. Muzyka, S. Werle, A life cycle assessment of the laboratory—scale oxidative liquefaction as the chemical

recycling method of the end-of-life wind turbine blades, J Environ Manage 361 (2024) 121241. https://doi.org/10.1016/J.JENVMAN.2024.121241.

6. H. Mumtaz, S. Werle, R. Muzyka, S. Sobek, M. Sajdak, Oxidative Liquefaction, an Approach for Complex Plastic Waste Stream Conversion into Valuable Oxygenated Chemicals, Energies 2024, Vol. 17, Page 1086 17 (2024) 1086.https://doi.org/10.3390/EN17051086.

7. H. Mumtaz, S. Sobek, M. Sajdak, R. Muzyka, S. Werle, Optimizing advanced oxidative liquefaction of municipal solid waste and personal protective equipment of medical sector for solid reduction and secondary compounds production, *Renewable Energy* 255 (2025) 123831. https://doi.org/10.1016/j.renene.2025.123831.

8. H. Mumtaz, S. Sobek, M. Sajdak, R. Muzyka, S. Werle, M. Procek, Innovative recycling of end-of-life photovoltaic panels with the aim of polymer degradation and valuable chemical production, Renew Energy (2025) 123535. https://doi.org/10.1016/J.RENENE.2025.123535.

9. R. Muzyka, H. Mumtaz, S. Sobek, S. Werle, J. Adamek, D. Semitekolos, C.A. Charitidis, T. Tiriakidou, M. Sajdak, Solvolysis and oxidative liquefaction of the end-of-life composite wastes as an element of the circular economy assumptions, J Clean Prod 478 (2024) 143916. https://doi.org/10.1016/J.JCLEPRO.2024.143916.

10. H. Mumtaz, S. Werle, S. Sobek, A waste wet oxidation technique as a solution for chemical production and resource recovery in Poland, Clean Technologies and Environmental Policy 26 (2024) 1363–1382. https://doi.org/10.1007/s10098-023-02520-4.

11. S. Sobek, S. Schmölzer, H. Mumtaz, M. Sajdak, R. Muzyka, S. Werle, Kinetic study of the decommissioned wind turbine blade oxidative liquefaction based on differential scanning calorimetry, Energy 316 (2025) 134651. https://doi.org/10.1016/J.ENERGY.2025.134651.

12. R. Muzyka, M. Sajdak, S. Sobek, H. Mumtaz, S. Werle, The application of chromatographic methods in optimization and the enhancement of the oxidative liquefaction process to wind turbine blade recycling, Clean Technol Environ Policy 27 (2024) 1799–1808. https://doi.org/10.1007/S10098-024-02988-8/FIGURES/7.

Author's Contribution to Included Publications

Throughout his doctoral research, the candidate, Hamza Mumtaz, contributed as an author or co-author to 12 peer-reviewed publications. Nonetheless, this thesis comprises only 7 articles presented as distinct chapters. The selection was made due to the candidate's substantial contributions to these articles.

Below is a comprehensive outline of the candidate's specific contributions to each publication included.

Chapter 1 – Article 1

Title: Hydrothermal treatment of plastic waste within a circular economy perspective
Type: Review Article
Journal: Sustainable Chemistry and Pharmacy
Authors: Hamza Mumtaz, Szymon Sobek, Marcin Sajdak, Roksana Muzyka, Sebastian Werle

Candidate's Contribution: This review article was solely authored by Hamza Mumtaz as a lead author. The study was conceptualized, a comprehensive literature review was conducted, the thematic structure was organized, critical data analysis was performed, and the entire manuscript was drafted by him. The co-authors mentioned played a role in evaluating the technical and scientific dimensions of the article, as well as offering editorial insights. The candidate managed all revisions and secured final approval.

Chapter 3 – Article 2

Title: An experimental investigation and process optimization of the oxidative liquefaction process as the recycling method of the end-of-life wind turbine blades
Type: Research article
Journal: Renewable Energy
Authors: Hamza Mumtaz, Szymon Sobek, Marcin Sajdak, Roksana Muzyka, Sebastian Werle

Candidate's Contribution: The manuscript was predominantly prepared by Hamza Mumtaz, who also led the research process. The experimental plan was independently designed by candidate, with consultation from Marcin Sajdak. He constructed and customized the reactor setup and took full responsibility for sample preparation. The WTBs samples were prepared by Hamza Mumtaz and Marcin Sajdak. The ultimate and proximate analyses were conducted by laboratory technicians, with Hamza Mumtaz responsible for the interpretation and evaluation of the results that followed.

The entire data processing and thorough analysis were carried out by him, along with the development of figures and tables. He was solely accountable for formulating the results and discussions. Szymon Sobek played a key role in enhancing the introduction section and improving the quality of the draft. The candidate oversaw the complete publication process, which involved addressing reviewers' feedback, implementing revisions, and finalizing the manuscript for publication. Sebastian Werle and Roksana Muzyka performed a thorough review of the article.

Chapter 4 – Article 3

Title: Oxidative liquefaction as an alternative method of recycling and the pyrolysis kinetics of wind turbine blades
Type: Research article
Journal: Renewable Energy
Authors: Hamza Mumtaz, Szymon Sobek, Marcin Sajdak, Roksana Muzyka, Sabina Drewniak, Sebastian Werle

Candidate's Contribution: This article is divided into two distinct sections, with only the part concerning the oxidative liquefaction of End-of-Life (EoL) WTBs being relevant to this thesis and the candidate's contribution. The portion addressing the pyrolysis kinetics of WTBs was created autonomously by co-authors and is excluded from this thesis chapter.

This work was conducted primarily by Hamza Mumtaz. Preparation of end-of-life WTB samples, Development and assembly of the high-temperature, high-pressure batch reactor for conducting oxidative liquefaction experiments, formulation and implementation of the Design of Experiments strategy, procedure for conducting experiments on oxidative conversion and processing samples, calculations about the yield of resin degradation, enhancing process parameters to achieve the highest possible yield of VFAs, preparation of all components pertaining to experimental design, methodology, results, and discussion associated with oxidative liquefaction.

While laboratory technicians conducted elemental analysis, thermogravimetric analysis (TGA), FTIR, and Py-GC-MS, the candidate chose not to include these pyrolysis-related results in this chapter, as they fall outside the realm of his direct contributions. The GC-FID analysis was conducted by Dr. Roksana Muzyka, while the interpretation, visualization, and discussion of the data were carried out by Hamza Mumtaz.

The candidate took charge of the entire publication process, which involved drafting the manuscript, integrating feedback from co-authors, responding to all reviewer comments, and finalizing the manuscript for publication.

Chapter 5 – Article 4

Title: An in-depth study of the oxidative liquefaction process for polymeric waste reduction and chemical production from wind turbine blades and personal protective equipment used in the medical field
Type: Research article
Journal: Journal of Environmental Management
Authors: Hamza Mumtaz, Sebastian Werle, Szymon Sobek, Marcin Sajdak, Roksana Muzyka

Candidate's Contribution: The entirety of this article was composed by Hamza Mumtaz, who undertook the responsibilities of conceptualization, experimental design, sample preparation, execution, and data analysis. The candidate conducted all essential research activities concerning the oxidative liquefaction of end-of-life WTBs and PPEs, which included the comparative study.

The ultimate and proximate analyses, along with TGA-DTG thermal characterization, were carried out in an external laboratory. The GC-FID analysis was executed by Roksana Muzyka and Marcin Sajdak. The candidate independently processes, interprets, and integrates all analytical data into the final manuscript. The analytical results were interpreted and the comparative analysis of WTBs and PPEs was comprehensively developed by Hamza Mumtaz, culminating in the scientific conclusions presented in the article.

The candidate assumed complete responsibility for the preparation of the manuscript, integrating feedback from co-authors, addressing comments from reviewers, and managing the revision and final submission of the article.

Chapter 6 – Article 5

Title: A waste wet oxidation technique as a solution for chemical production and resource recovery in Poland – a review
Type: Review article
Journal: Clean Technologies and Environmental Policy
Authors: Hamza Mumtaz, Sebastian Werle, Szymon Sobek

Candidate's Contribution: This chapter draws upon the insight of a review article that was fully conceptualized, structured, and authored by Hamza Mumtaz. The candidate executed the literature review, carried out a thorough assessment of current research, and constructed the thematic structure and scholarly narrative of the paper. The candidate conducted a thorough analysis of all pertinent data, interpreted trends, created graphical representations, and ensured that the review was comprehensive, methodologically robust, and aligned with the dynamic research environment.

The co-authors engaged in a comprehensive technical and editorial review of the manuscript, offering constructive feedback aimed at refining the language, enhancing clarity, and bolstering the scientific rigor of the final version.

The comprehensive management of the manuscript preparation, submission, response to reviewers, and revision process was conducted by Hamza Mumtaz.

Chapter 7 – Article 6

Title: Optimizing advanced oxidative liquefaction of municipal solid waste and personal protective equipment of the medical sector for solid reduction and secondary compounds production

Type: Research article
Journal: Renewable Energy
Authors: Hamza Mumtaz, Szymon Sobek, Marcin Sajdak, Roksana Muzyka, Sebastian Werle

Candidate's Contribution: The primary author of this article is Hamza Mumtaz, who managed both the experimental and analytical components of the research. The candidate conducted the preparation of waste materials, which involved generating representative samples from two different categories of waste. The experimental rig and the comprehensive experimental matrix necessary for the process evaluation were also designed by the candidate. Hamza Mumtaz executed the experimental runs, gathered operational data, and carried out the inverse analysis of process heating to evaluate the thermal behaviour of the process. The TSR and OCCs yields were calculated and compared, with energy consumption recorded for each scenario. ANOVA was employed to assess the statistical significance of the findings. Additionally, the candidate conducted a comparison of the optimal conditions of to attain the highest process efficiency for both types of waste.

The ultimate and proximate analyses, along with FTIR spectroscopy, were carried out by laboratory technicians. Meanwhile, Roksana Muzyka and Marcin Sajdak conducted the GC-FID and chromatographic analyses. However, all resulting data were comprehensively interpreted, visualized, and presented by Hamza Mumtaz in the manuscript. He took full responsibility for managing the complete manuscript preparation, overseeing the revision process in response to reviewer feedback, and ensuring the final submission for publication.

Chapter 8 – Article 7

Title: Innovative recycling of end-of-life photovoltaic panels with the aim of polymer degradation and valuable chemical production
Type: Research article
Journal: Renewable Energy
Authors: Hamza Mumtaz, Szymon Sobek, Marcin Sajdak, Roksana Muzyka, Sebastian Werle, Marcin Procek

Candidate's Contribution: The entirety of this article was conceived, structured, and composed by Hamza Mumtaz. The intricate and composite characteristics of end-of-life PV panels necessitated significant attention to material handling and sample preparation. The candidate, in collaboration with Marcin Sajdak, undertook the task of cutting and preparing the samples to guarantee both representativeness and experimental reliability.

The elemental analysis, SEM, and FTIR analysis were conducted by laboratory technicians. The comprehensive interpretation of these analytical results, encompassing data processing, graphical representation, and integration into the scientific discourse, was conducted by Hamza Mumtaz. The analysis utilizing GC-FID was conducted by Roksana Muzyka, with the subsequent data being analysed and contextualized in the manuscript by the candidate.

In addition to leading all research planning and experimental execution relevant to this study, Hamza Mumtaz prepared the manuscript independently, addressed all co-author and reviewer comments, and finalized the article for journal submission.

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Nomenclature

Acronym		Parameters and Variables	
EJ	Exajoule	Reaction Temperature (T)	°C
WTBs	Wind Turbine Blades	Oxidant Concentration (C)	wt.%
PPEs	Personal Protective Equipment	Pressure (P)	MPa
PV	Photovoltaic	Waste-to-Liquid Ratio (W/L)	wt.%
MSW	Municipal Solid Waste	Total Solid Reduction (TSR)	%
FRPs	Fiber-Reinforced Polymers	Total Polymer Degradation (TPD)	%
OCCs	Oxygenated Chemical Compounds	Oxygenated Chemical Compounds Yield (OCCs)	g/kg-waste
HTC	Hydrothermal Carbonization	Ultimate Analysis	wt.%
HTL	Hydrothermal Liquefaction	Proximate Analysis	wt.%
HTG	Hydrothermal Gasification	Heating Value (HV)	MJ/kg
TSR	Total Solid Reduction	Thermal Decomposition Temperature	°C
TPD	Total Polymer Degradation	Fourier Transform Infrared Spectroscopy (FTIR)	-
TGA	Thermogravimetric Analysis	Scanning Electron Microscopy with Energy-Dispersive Spectroscopy (SEM-EDS)	-
FTIR	Fourier Transform Infrared Spectroscopy	Thermogravimetric Analysis (TGA)	% weight loss
SEM-EDS	Scanning Electron Microscopy with Energy-Dispersive Spectroscopy	Inverse Heating Analysis	-
ANOVA	Analysis of Variance	Glass Fiber Recovery	%
RSM	Response Surface Methodology	Statistical Optimization (ANOVA, RSM)	-
HDPE	High-Density Polyethylene		
LDPE	Low-Density Polyethylene		
PP	Polypropylene		
PS	Polystyrene		
PVC	Polyvinyl Chloride		

Chapter 1

1 General Introduction

Paper I (Appendix A): Hydrothermal treatment of plastic waste within a circular economy perspective

1.1 Background

The global economy is experiencing a critical transformation influenced by the essential needs of climate mitigation and sustainable resource management, and the core of the transition is fundamentally driven by the necessity to tackle the energy crisis and mitigate the escalating amount of global waste generation. It is projected that global waste generation will escalate to 3.4 billion tonnes each year by 2050, with MSW, plastics, and biomass residues representing the most significant portions [1]. On the other hand, the demand for energy worldwide has surged exponentially in recent decades, with total energy consumption hitting 595 exajoules (EJ) in 2022, marking a 14% rise since 2010 [2]. Technologies in renewable energy, especially wind and solar PVs, have experienced significant expansion to reduce reliance on fossil fuels. The current installed capacity of wind energy has exceeded 906 GW, and solar PV capacity has attained 1.2 TW, representing almost 12% of global electricity generation [3,4]. Nonetheless, the extensive implementation of these technologies has given rise to a significant environmental issue: the management of WTBs and PV panels at the end of their life cycle.

Simultaneously, the production and consumption of plastic materials have increased significantly, with global plastic production surpassing 400 million metric tons each year [5]. If current disposal trends persist, nearly 12 billion metric tons of plastic waste are expected by 2050 [6]. A considerable amount of this waste originates from single-use plastics, especially PPEs, which experienced an extraordinary increase during the COVID-19 pandemic. At the height of the pandemic, an alarming 129 billion face masks and 65 billion gloves were disposed of each month, intensifying the existing polymer waste crisis [7]. Furthermore, the generation of MSW has surpassed 2 billion metric tons annually, with plastic-based components accounting for 12–14% of the overall waste stream [8].

1.1.1 EU policy frameworks: from waste reduction to resource valorization

The European Union (EU) has implemented a detailed policy framework that combines climate action, energy security, and principles of a circular economy. The Waste Framework Directive (2008/98/EC) serves as the legislative foundation for waste prevention, reuse, and recycling among member states [9]. It establishes the concept of the "*waste hierarchy*" and mandates that member states take measures to reduce landfill waste. Additionally, the Landfill Directive (1999/31/EC) requires a systematic decrease in the amount of biodegradable waste directed to landfills, thereby increasing the necessity for alternative treatment approaches [10]. Recently, the European Green Deal and the Circular Economy Action Plan 2.0 have established systemic objectives aimed at separating economic growth from resource consumption [11,12]. The Renewable Energy Directives (REDII and REDIII) have progressed the adoption of sustainable bioenergy while establishing binding targets for renewable energy consumption, with a goal of 32% by 2030 under REDII, which has been raised to 42.5% under REDIII [13–15]

The International Energy Agency (IEA) highlights the importance of incorporating bio-based technologies in the transition to net-zero emissions, advocating for advancements in waste-to-energy systems, carbon capture, and circular material flows [16]. In 2023, the EU reported a 37% decrease in net greenhouse gas emissions relative to 1990 levels, indicating progress towards its interim goal of a 55% reduction by 2030 as stipulated by the European Climate Law [17]. The primary factors behind these reductions include the decarbonization of the energy sector, the growth of renewable energy sources, and legislative initiatives like the “Fit for 55” package and the EU Green Deal [18,19]. Moreover, recent advancements in EU energy policy—including the extension of the Emissions Trading System (ETS), the implementation of the Carbon Border Adjustment Mechanism (CBAM), and the establishment of sustainability criteria for waste-to-energy—are generating regulatory and economic incentives for the adoption of circular technologies [20]. The combination of these frameworks establishes a strong policy justification for investing in thermochemical valorization technologies, which have the potential to recover energy and materials from waste streams that are typically unrecyclable.

1.1.2 Composite and polymer-based waste materials management in a circular economy perspective

An essential aspect of the presented legislative framework and strategies involves shifting from a linear to a circular economy, emphasizing the importance of resource recovery and material reuse rather than relying on landfilling and incineration. This transition is especially significant considering the increasing challenge faced by the EU regarding composite and polymer-based waste materials stemming from renewable energy infrastructure, PPEs, and urban solid waste streams. The swift implementation of wind and PV technologies, which are crucial for the decarbonization of energy in the EU, is anticipated to result in a significant increase in the number of decommissioned WTBs and PV panels by the years 2030 to 2040 [21,22]. In a similar vein, the COVID-19 pandemic has intensified the buildup of PPE waste, primarily made up of thermoplastics such as polypropylene (PP), which has now become a lasting pollutant in urban waste systems [23,24]. MSW, even with enhanced separation and recycling initiatives in the EU, continues to comprise a notable portion of non-recyclable and energy-dense materials that have the potential to be valorised via advanced thermochemical processes [26].

Plastics and composite materials, such as those present in WTBs, PPEs, PV panels, and MSW, exhibit high calorific values, between 25–45 MJ/kg, positioning them as a viable option for energy recovery [27]. Nevertheless, current waste management strategies exhibit considerable shortcomings. Mechanical recycling represents a mere 12-20% of the global plastic waste treatment landscape facing challenges such as material contamination, polymer degradation, and the complications associated with downcycling [28]. Incineration accounts for 19% of plastic waste disposal and produces hazardous emissions, including dioxins, furans, and CO_2, with global emissions from this process surpassing 850 million metric tons each year [29,30]. Pyrolysis has the potential to transform plastics into liquid fuels; however, it necessitates elevated temperatures ranging from 400 to 800°C and substantial energy input, presenting significant economic and environmental hurdles [31]. Currently, landfilling continues to be the primary method of disposal, with approximately 79% of plastic waste being deposited in landfills or the surrounding environment, resulting in persistent pollution and microplastic contamination.

1.2 Discussion of Relevant Studies

1.2.1 Plastic waste generation and associated environmental repercussions

The issue of environmental pollution stands as a significant challenge confronting human societies in the present day. Among various pollutants, plastic waste poses a considerable threat owing to its extensive utilization and growing presence in the environment. The wide-ranging uses of plastics in packaging, film formation, container manufacturing, construction, and electrical and renewable energy industries can be traced back to their affordability, remarkable mechanical characteristics, lightweight composition, and exceptional durability. The term "plastic" has its roots in the Greek word *plastikos*, which translates to "fit for moulding" [32]. Plastics consist of long-chain synthetic or semi-synthetic polymers that originate from petrochemical sources. They are frequently combined with additives, inert fillers, and plasticizers to improve their mechanical and rheological characteristics [33,34]. Plastics are generally categorized into two main types according to their thermal response: thermosets and thermoplastics. Thermoplastics, including polystyrene (PS), PP, polyvinyl chloride (PVC), high-density polyethylene (HDPE), and low-density polyethylene (LDPE), possess the ability to be melted and reshaped repeatedly while maintaining their chemical integrity. In contrast, thermosetting plastics, such as Bakelite and Melamine, experience irreversible chemical bonding when subjected to heat, rendering them inappropriate for reprocessing [35]. Plastics can be categorized according to the process of polymerization, including addition, condensation, and cross-linking polymers. The accurate identification of plastic types is essential for effective recycling. In 1988, the Society of Plastic Industry implemented a resin identification code system to facilitate sorting and recycling processes. PET is designated as resin code 1, HDPE as 2, PVC as 3, LDPE as 4, PP as 5, PS as 6, while other plastics are categorized under resin code 7 [36,37].

Plastics find extensive application in various sectors owing to their lightweight nature, resilience, affordability, and versatility in technology. The plastic industry employs around 1.5 million individuals and adds about 30 billion EUR to the European economy [38]. Global production statistics indicate that plastic production surpassed 320 million metric tons in 2015 and rose to 335 million metric tons in 2016, accounting for more than 8% of the world's crude oil supply [39]. As outlined in a report by PlasticsEurope from 2017, the production hierarchy of different plastic types is as follows: PP at 19.3 wt%, LDPE at 17.5 wt%, HDPE at 12.3 wt%, PVC at 10 wt%, PET at 7.4 wt%, and PS at 6.7 wt% [40].

Significant risks to the ecosystem

The rising levels of plastic production and consumption have resulted in a growing waste crisis, posing significant threats to ecosystems and biodiversity. Most plastics, characterized by their high molecular weight and chemically stable structure, are non-biodegradable and can persist in the environment for centuries. Significant environmental issues related to plastic waste encompass:

Effects on soil and agricultural Output – The incineration of plastic waste diminishes the availability of crucial soil nutrients, such as dissolved nitrogen and phosphorus, leading to a decline in soil fertility [41]. Furthermore, the presence of plastic fragments within the soil hinders root absorption, which diminishes the uptake of water and nutrients, consequently leading to a decrease in crop yields [42].

Impact on wildlife – Plastic waste disposed of in open landfills and aquatic environments frequently gets ingested by animals, leading to intestinal blockages, malnutrition, and mortality [43].

Impact of toxic substances on biological entities – Plastics incorporate various additives, dyes, and stabilizers that have the potential to leach into the environment, thereby presenting biological hazards to both plants and animals. Microplastics, characterized as plastic particles smaller than 5 mm, raise significant concerns due to their ability to infiltrate biological membranes and interfere with genetic expression, oxidative stress responses, and cellular transport mechanisms [44]. Microplastics possess a significant surface area, which enables them to function as carriers for pollutants by adsorbing heavy metals and organic toxins, thus exacerbating environmental risks [45].

Visual pollution & urban aesthetic damage – The unchecked buildup of plastic waste leads to "white pollution," which deteriorates both landscapes and urban settings.

Marine pollution & ecosystem disruption – The introduction of plastic waste into oceanic environments leads to processes such as hydrolysis, oxidation, and microbial attack, which enhance its hydrophilicity and render it increasingly vulnerable to microbial degradation into microplastics [46]. These particles accumulate in marine food chains, impacting aquatic life. Research indicates that fish subjected to microplastics exhibit false satiety, resulting in decreased food consumption, hindered growth, and diminished biomass production [47]. Furthermore, microplastics taken up by crops make their way into the human food chain, leading to potential intestinal infections and developmental health risks.

1.2.2 Circular economy framework in the context of 6R waste management hierarchy, and advanced waste management techniques

Effective waste management plays a crucial role in addressing the environmental and economic challenges associated with the rising generation of plastic and composite waste. Contemporary waste management practices are progressively shaped by structured frameworks that emphasize resource efficiency, environmental protection, and the tenets of a circular economy. A 10R waste management hierarchy is already in practice, but a simplified version is presented in Table 1.1.

Table 1.1 6R waste management hierarchy [48,49]

Priority	Strategy	Description
R1	Refuse	Avoid unnecessary products or materials
R2	Reduce	Minimize material and energy consumption
R3	Reuse	Use again without significant changes
R4	Recycle	Convert waste into new materials
R5	Recover	Energy recovery
R6	Residuals	Landfilling or final disposal

Although waste prevention (refuse, reduce, and reuse) is a prioritized strategy within the EU waste hierarchy, its application is frequently limited when it comes to composite, or complex waste materials like PPEs, WTBs, and aging PV panels. In these instances, carbonization and gasification (rather old), advanced waste management techniques such as mechanical recycling, incineration, pyrolysis, and hydrothermal treatment act as an essential and complementary solution within the larger circular economy framework. Every approach presents unique benefits and drawbacks regarding energy efficiency, potential for material recovery, and environmental sustainability. This section presents a comprehensive evaluation of the advance waste management strategies, emphasizing their effectiveness, challenges, and suitability for different waste types.

Mechanical recycling vs. Thermal treatment: Mechanical recycling transforms waste plastics into new products while maintaining their molecular structure. Although thermoplastics such as polyethylene terephthalate (PET), HDPE, and polypropylene (PP) can be recycled efficiently, the sorting process is essential to ensure quality preservation [50]. Methods encompass manual or mechanical separation, shredding, sieving, and the elimination of contaminants such as labels and adhesives. Nonetheless, the recycling of mixed plastics presents significant challenges, primarily due to phase separation occurring during the melting process, which subsequently impacts the strength of the final product [51,52]. The majority of recycled plastics consist of types 1, 2, and 3, whereas types 6 and 7 are infrequently recycled, primarily due to economic limitations [53]. Furthermore, inadequate recycling methods can subject workers to harmful emissions, leading to potential health hazards.

Incineration: Incineration represents a prevalent method in waste management, characterized by the combustion of waste materials in an oxygen-rich environment. This process not only generates energy but also significantly diminishes waste volume, achieving reductions of up to 90% [54]. The operation is conducted at elevated temperatures (900–1100°C) to achieve thorough combustion while effective management of emissions is very important [55,56]. Plastic polymers including HDPE, PP, and LDPE exhibit elevated calorific values (40 MJ/kg), rendering them appropriate for energy recovery applications [57]. Nonetheless, the process of incineration produces CO_2, NOx, and hazardous substances such as dioxins and furans, necessitating the implementation of modern filtration systems. Although it serves as an alternative to fossil fuels and contributes to the reduction of methane emissions from solid waste, stringent environmental regulations and elevated operational costs hinder its practicality. European policies emphasize the importance of recycling as a preferred method over incineration, driven by significant environmental considerations [58].

Pyrolysis: Pyrolysis is a thermal degradation process that transforms plastic waste into fuel through heating within the range of 300–900°C (depending upon the waste type) in an oxidant-free environment [59]. The process yields liquid oil (50–95% yield) depending upon the type of plastic, solid char, and syngas, which are contingent upon the specific conditions applied during the procedure. The calorific values of pyrolysis oils derived from PP, PS, and PVC are 44, 40.6, and 40 MJ/kg, respectively, indicating their potential as energy sources [60]. The process of co-pyrolysis utilizing biomass enhances both the liquid yield and the quality of the fuel produced. The process exhibits adaptability for various types of plastics, including those that are contaminated [61]. However, it faces challenges such as the need to optimize operating conditions, choose appropriate catalysts, and maintain a reliable supply of feedstock. While the potential is evident, additional refinement is necessary to enhance the stability and usability of oil in commercial applications.

Hydrothermal treatment HTC, HTL, HTG: Hydrothermal carbonization (HTC) is a process that involves wet torrefaction, transforming waste biomass and plastics into energy-dense hydrochar at temperatures ranging from 180 to 260°C, under pressures of 2 to 6 MPa [62,63]. The process involves two primary pathways: the polymerization of intermediates and a decomposition process akin to pyrolysis, resulting in the production of phenolic and polyaromatic chars. The carbon content of hydrochar is similar to that of lignite, ranging from 35% to 60%, which positions it as a significant solid fuel option [64]. HTC improves fuel characteristics through processes such as dehydration, carbonization, and dehalogenation, leading to enhanced combustion efficiency. This method can be utilized for the treatment of plastic waste, facilitating the removal of chlorine to generate cleaner fuels. Nonetheless, the design of reactors, the scalability of processes, and the economic viability continue to pose significant challenges for the large-scale implementation of HTC [65].

Hydrothermal Liquefaction (HTL) is a process that transforms solid carbonaceous waste into liquid fuels by utilizing subcritical or supercritical water conditions. This occurs within a temperature range of 280–450°C and under pressures of 7–30 MPa [66,67]. In these extreme conditions, water functions as a solvent, reactant, and catalyst, facilitating the effective breakdown of carbon-carbon bonds in organic compounds. This process encompasses various chemical reactions such as hydrolysis, free radical reactions, and cyclization, resulting in the production of bio-crude oil, solid residues, and aqueous byproducts [68].

HTL presents a notable advantage over pyrolysis due to its lack of dependence on heating rates, which positions residence time as a more significant factor in influencing the composition of the final product. At reduced temperatures, the process promotes the generation of liquid bio-oil, whereas at elevated temperatures (greater than 350°C), the reaction equilibrium transitions towards gaseous products [69]. Typical yields of bio-crude oil from HTL vary from 10% to 60% by weight, with certain instances surpassing 75%, influenced by the type of feedstock and the specific reaction conditions employed [70]. HTL has undergone significant investigation concerning biomass, encompassing woody biomass, agricultural waste, and MSW, resulting in the generation of bio-oils with elevated heating values (30–40 MJ/kg) [71–73]. The composition of bio-crude exhibits variability, encompassing phenols, nitrogen compounds, esters, and hydrocarbons. The potential of algae-based HTL is noteworthy, as the high moisture content of algae eliminates the need for pre-drying, thereby improving economic viability [74].

The HTL of plastics has attracted attention as a viable alternative to pyrolysis, yielding both aliphatic and aromatic hydrocarbons that hold potential for fuel applications. The selection of solvent significantly influences HTL efficiency, as ethanol-based HTL enhances bio-oil yield by 10–15% in comparison to water-based systems [75]. The process of co-liquefaction with biomass significantly improves both the yield and quality of oil, with research indicating a bio-oil yield exceeding 30% and a calorific value of 34.9 MJ/kg. The optimization of HTL performance for commercial applications is significantly influenced by operating parameters, including temperature, reaction time, catalyst type, and solvent choice.

Hydrothermal gasification (HTG) employs supercritical water at 22.1 MPa and 374 °C to transform biomass into hydrogen-rich synthesis gas [76]. The distinctive characteristics of supercritical water, including elevated diffusivity and improved solvation, facilitate enhanced mass transfer and reaction kinetics. HTG directly processes high-moisture feedstocks, eliminating the need for the energy-intensive drying step that is typically necessary for conventional gasification [77]. The gas yield and composition are significantly affected by key process parameters such as temperature, pressure, residence time, biomass-to-water ratio, and catalysts. The design of reactors, including fluidized bed technology, is essential for maintaining uniform temperatures and facilitating effective gas-solid interactions.

Cellulose is frequently chosen as a model compound because of its uniform conversion and notable role in hydrogen production [78,79]. The behaviours of hemicellulose and lignin under HTG conditions differ, which impacts the overall efficiency of gasification. HTG presents a streamlined approach for generating hydrogen-rich gas from diverse biomass feedstocks, all while maximizing energy efficiency.

The benefits of hydrothermal treatment include reduced energy demands. For instance, HTL operates at temperatures ranging from 250 to 400°C, which is considerably lower than the

500 to 800°C required for pyrolysis. This implies possible variations in energy demand; nevertheless, direct comparison is complex. The amount of energy used relies on more than just the temperature. It also depends on the medium being heated (for example, liquid water in HTL vs inert gases in pyrolysis), their heat capacities, and the general setup of the process [80].

1.3 Identification of Research Gaps (RGs)

Despite the significant progress in hydrothermal treatment research, several gaps remain:

RG-1: Limited details on the identification of reaction parameters affecting process output and optimization of the overall process.

RG-2: Limited application while treating complex waste types e.g. WTBs, PV panels

RG-3: Lack of comparative assessment of process efficiency to understand the effects of composition or nature of waste material

RG-4: Need for further research on enhancing process efficiency and product quality by introducing additional reactive species (oxidants), while treating complex waste streams.

RG-5: Lack of large-scale industrial applications due to economic and technical barriers.

1.4 Aim and Objectives of Doctoral Study

The primary aim of this doctoral study is to introduce and develop oxidative liquefaction as an advanced waste management technique for the efficient chemical recycling of complex WTBs, PPEs, PV panels, and MSW waste through degradation of the organic matrix in an oxidative environment, resulting in secondary compounds. The study seeks to maximize large polymer's degradation, while enhancing the yield of OCCs, contributing to a sustainable and circular economy approach for complex waste management.

Objectives

- To conduct a comprehensive characterization of selected waste materials to determine their chemical composition, elemental makeup, and thermal degradation behaviour through advanced analytical techniques to assess critical data for identifying effective oxidative liquefaction conditions
- The objective is to develop a statistically robust experimental matrix design aimed at exploring the oxidative liquefaction processes associated with selected waste materials. The experimental design aims to systematically assess the impacts of critical process parameters such as temperature, pressure, oxidant concentration, reaction time, and waste-to-liquid ratio, thereby facilitating thorough data collection for subsequent process analysis.
- Under the designed experimental matrix conditions, preparing the sample, and performing oxidative liquefaction process for all four waste kinds (WTBs, PPEs, PV, and MSW) in high temperature, high pressure reactor, setting arrangements for periodic monitoring and recording of the process parameters, analysing the obtained solid and liquid products.
- Statistically analyze the obtained results to identify the effect of each reaction parameter on process effectiveness, optimizing the overall experimental plan to make the process less resource intensive against achieving the maximum outputs.

Chapter 2

2 Materials and Methods

2.1 Feedstock Materials

This thesis examines the selected feedstock materials, which include end-of-life WTBs, PV panels, PPE from the medical sector, and MSW. These materials exemplify some of the most significant and diverse waste streams currently encountered. The decommissioning of WTBs, which are predominantly made from composite materials including fiberglass and carbon-fiber-reinforced polymers (CFRPs), is becoming a significant contributor to the waste stream as the renewable energy sector expands. Projections indicate that approximately 8.6 million tonnes of blade material will be retired globally by the year 2042, with an estimated 570 million tonnes anticipated in the European Union by 2030 under a business-as-usual model [81]. The volume of PPEs waste experienced a significant increase during the COVID-19 pandemic. According to data from the WHO, approximately 87,000 tonnes of PPE were procured globally between March 2020 and November 2021, excluding items such as masks discarded by households [82]. Furthermore, the administration of over 8 billion vaccine doses has resulted in an additional 144,000 tonnes of waste [83,84]. Currently, MSW continues to pose a significant environmental challenge, with projections indicating an increase in global generation from approximately 2.3 billion tonnes in 2023 to 3.8 billion tonnes by 2050. This escalation could result in a doubling of related costs to USD 640 billion annually, unless a substantial transition towards circular economy practices is implemented [85,86].

The treatment of these diverse yet critically significant waste types is essential, as it serves to mitigate the increasing reliance on landfills and reduce environmental degradation. Furthermore, it presents opportunities for material recovery, energy valorization, and the advancement of sustainable innovations. Their collective significance highlights the imperative for an advanced methodology in this thesis aiming to contribute a more sustainable management paradigm.

2.1.1 Wind turbine blades

The samples of end-of-life WTBs utilized in this study were provided by ANMET, a Polish company that has been engaged in WTBs recycling since the year 2015. In the context of this investigation, segments measuring approximately 25 × 30 cm were provided and subsequently processed at the Silesian University of Technology. The preliminary processing phase consisted of segmenting the blade components into smaller sections utilizing an angle grinder. This was succeeded by additional comminution in a shredder mill, resulting in the production of chips with dimensions varying from 0.5 to 2 cm in length (Figure 2.1).

Figure 2.1 Wind turbine blade sample used for oxidative liquefaction

The WTB fragments acquired appear to have originated predominantly from the high-end tips of the blades, which characteristically lack structural reinforcements, including metals. The samples primarily comprised glass fibre integrated within a polymer matrix, reflecting the composite structures commonly utilized in contemporary WTBs blade production. This approach guaranteed that the material under investigation accurately represented the predominant fraction of composite waste produced during the decommissioning of WTBs, while minimizing the risk of contamination from auxiliary components.

2.1.2 Personal protective equipment used in the medical sector

In order to reduce the potential risk of viral transmission associated with material handling, unused PPEs were procured from a local medical supplier. The inventory chosen comprised single-use face masks, N-95 respirators, polymer-based gloves, protective gowns, and disposable bedsheets, all of which exemplify the primary categories of PPEs frequently employed within the healthcare industry.

Figure 2.2 Personal protective equipment sample used for oxidative liquefaction

Before proceeding with additional processing, the PPEs items were systematically segmented into fragments measuring 1 to 3 centimetres using scissors to ensure uniformity in sample preparation. Recent investigations indicate that the predominant components of PPEs waste include PP, PE, PES, textiles, and HDPE. These materials are representative of the polymeric makeup found in the majority of single-use medical protective products [87,88]. This approach guaranteed that the feedstock utilized in this study faithfully reflected the actual composition of PPE waste streams produced during and subsequent to the COVID-19 pandemic.

2.1.3 End-of-life photovoltaic panels

The PV waste analysed in this study was acquired as a damaged PV panel from the local market. The panel was initially segmented into dimensions of approximately 6 × 6 inches utilizing an electrically powered circular saw. In light of the dimensional limitations imposed by the experimental reactor, the panel fragments were systematically reduced to 1 × 1 cm chips utilizing mechanical scissors as a cutting tool. The preparation of the feedstock within this specified size range resulted in an elevated surface area-to-volume ratio, thereby enhancing the efficiency of thermal treatment throughout the processing phase.

The waste generated from photovoltaic panels primarily comprises polymeric layers, glass, and silicon-based materials, in addition to lesser quantities of metals and additives commonly found in commercial photovoltaic modules. The presence of trace elements, including copper and rare earth elements such as cerium, praseodymium, and neodymium, suggests a potential resource value. However, the relatively low concentrations of these elements underscore the economic challenges associated with their recovery from waste materials. In this thesis, the primary emphasis is placed on the treatment and valorization of photovoltaic panel waste as a composite feedstock, rather than on the extraction of trace elements.

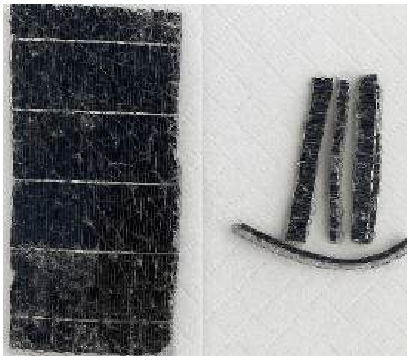


Figure 2.3 PV waste sample used in the current study

2.1.4 Municipal solid waste

This study examined MSW, which is characterized as a heterogeneous mixture of materials typical of urban and suburban regions in Poland. The analysed MSW samples exhibited a diverse stream of fractions, comprising polymers, organic matter, glass, metals, and various other components, thereby illustrating the intricate composition commonly observed in actual waste streams. In order to achieve representativeness and reliability, the test materials were sourced from proficiency testing suppliers, who meticulously prepared and standardized the samples in alignment with ISO guidelines pertinent to this category of material.

Figure 2.4 Municipal solid waste sample used for oxidative liquefaction

Before conducting the experimental investigation, a comprehensive sorting process was implemented on the waste to remove non-representative contaminants and ensure uniform feedstock characteristics. Considerable emphasis was placed on reducing the chlorine concentration, as elevated levels of chlorine have the potential to enhance the corrosion of reactor materials in oxidative environments. Through meticulous preparation of the MSW feedstock, the investigation guaranteed that the results would hold significance for practical waste-to-resource conversion systems, thereby providing valuable insights into their prospective environmental and economic advantages.

2.2 Characterization of Feedstock Materials

2.2.1 Ultimate and proximate analysis of waste samples

The comprehensive and detailed analyses of the chosen feedstocks were performed to ascertain their essential physicochemical characteristics. The analysis of the WTBs, PPEs, PV panels, and MSW samples encompassed the quantification of moisture (M^a), volatile matter (VM), ash content (A^a), and elemental composition including carbon (C^a), hydrogen (H^d), nitrogen (N^a), sulfur (S^a), and oxygen ($O_a.^{diff.}$). The proximate analysis was conducted utilizing thermogravimetric and gravimetric techniques, while the ultimate analysis was executed through high-temperature combustion, employing infrared (IR) and thermal conductivity (TC) detection methods.

Table 2.1 Standards and methods used for the ultimate and proximate analysis of the investigated waste types

Parameter	Standard	Method
Moisture, M^a	PN-G-04560:1998	Thermogravimetric
Ash, A^a	EN ISO 21656:2021-06	Weight method
Volatile matter, VM	EN 15402:2011	Weight method
Carbon, C^a	EN ISO 21663:2021-06	HT combustion with IR detection
Nitrogen, N^a	EN ISO 21663:2021-06	HT combustion with IR detection
Hydrogen, H^d	EN ISO 21663:2021-06	HT combustion with IR detection
Sulfur, S^a	EN ISO 21663:2021-06	HT combustion with TC detection

Oxygen, $O^{a.d.}$	EN ISO 16993:2016-09	Calculated as a difference

$^{diff.}$- calculated as a difference from the elementary balance

The determination of moisture content was conducted utilizing the thermogravimetric method as outlined in PN-G-04560:1998. Concurrently, the assessment of volatile matter and ash content was performed gravimetrically by EN 15402:2011 and EN ISO 21656:2021–06, respectively. The elemental composition, specifically carbon (C), hydrogen (H), nitrogen (N), and sulfur (S), was assessed utilizing an LECO 828 Combustion Series Analyzer in conjunction with the LECO TruSpec CHN analyzer, incorporating the SC 632 instrument, following the standards set forth in EN ISO 21663:2021–06. The calculation of oxygen content was performed by determining the difference, per the guidelines set forth in EN ISO 16993:2016–09. Furthermore, the composition of ash was analyzed utilizing a plasma spectrometer (Thermo iCAP 6500 Duo ICP), which facilitated the identification of inorganic elements contained within the residues. Summary of the adopted standards have been provided in Table 2.1, while the results of analysis have been provided in Table 2.2.

Table 2.2 Detail properties of the invested feedstock

Parameter	**WTB**	**PPE**	**MSW**	**PV**
wt.%		**U(X)**		
Moisture content in the analytical state (M_{ad})	1.3 ± 0.7	0.1 ± 0.2	2.5 ± 0.2	N.A
Ash content in the analytical state (A_{ad})	57.9 ± 0.2	8.7 ± 0.5	15.1 ± 0.8	93.2±4.8
Volatile matter (VM)	40.7 ± 0.3	97.0 ± 3.8	84.9 ± 0.3	6.3±0.2
Content of total carbon in the analytical state (C_{ad})	28.2 ± 8.0	80.1 ± 2.3	50.3 ± 2.3	6.4±0.2
Content of total hydrogen in the dry state (H_a)	2.7 ± 1.1	12.8 ± 0.6	7.2 ± 0.2	0.70±0.03
Content of nitrogen in the analytical state (N_{ad})	1.2 ± 0.5	0.17 ± 0.01	1.1 ± 0.1	0.03
Content of oxygen in the analytical state from differences ($O^{diff.}$)	8.7	0.0	23.3	0.0
Content of total sulphur in the analytical state ($w_{S,\ ad}$)	<0.5	<0.013	<0.5	<0.03
Content of total chlorine in the analytical state (Cl)	<0.01	0.04 ± 0.01	0.03 ± 0.01	0.014±0.003

2.2.2 Thermogravimetric analysis of waste samples

The TGA and DTG analysis of the chosen waste samples were conducted by an external operator. The subsequent interpretation, elaboration, and presentation of the results were executed by the author.

The thermal behavior of the selected waste materials was investigated utilizing a Netzsch TG 409 LUXX thermogravimetric analyzer, in conjunction with a QMS 403D Aeolos quadrupole mass spectrometer for the monitoring of evolved gases. Controlled experiments were conducted across a temperature spectrum of 30 to 800 °C, utilizing heating rates of 2, 4, 8, and 16 K/min. A continuous argon flow of 35 cm^3/min was established to maintain inert conditions, effectively inhibiting oxidative reactions and facilitating the evaluation of the intrinsic thermal decomposition mechanisms of the samples. The feedstocks underwent analysis in open alumina (Al_2O_3) crucibles, which facilitated uniform heating and ensured the reproducibility of results. This configuration facilitated a methodical assessment of the thermal degradation mechanisms associated with WTBs, PPEs, PV and MSW samples, yielding critical insights into the effects of heating rates and reaction environments on decomposition characteristics. The results obtained from TGA/DTG provide significant insights into the intrinsic stability of polymeric and composite wastes, while also functioning as a diagnostic instrument for oxidative liquefaction processes. Identifying the critical temperature intervals associated with major devolatilization and breakdown is essential for delineating the experimental window for the application of oxidizing agents. Moreover, the understanding of kinetic parameters obtained from multi-rate analyses plays a crucial role in the optimization of process conditions, including temperature, residence time, and oxidant concentration. This optimization is essential for achieving enhanced liquid yields and superior product quality in oxidative liquefaction processes. The obtained results will be presented in subsequent chapters.

2.2.3 Fourier transform infrared spectroscopy and scanning electron microscopy analysis

In accordance with reviewer recommendations to broaden the scope and deepen the structural analysis, FTIR and SEM examinations of selected waste materials were incorporated where necessary. These measurements were performed by a laboratory operator, while the interpretation and discussion of the results were carried out by the author. The characterization of functional groups in the examined feedstocks was conducted utilizing a Nicolet iS50-TRACE 1300 ISQ 7000 spectrometer (Thermo Scientific, USA). The spectra were obtained within the wavenumber range of 650–3200 cm^{-1}, employing a resolution of 0.05 cm^{-1}, and were measured at ambient temperature conditions. For each sample, an average of 15 to 21 measurements was obtained to ensure reproducibility and reduce spectral noise. The process of data acquisition was executed utilizing the attenuated total reflectance (ATR) technique, wherein the sample surface was applied to a single-reflection diamond crystal. The acquired spectra were subsequently subjected to processing and analysis using OMNIC software (version 9), facilitating the accurate identification of the characteristic absorption bands associated with the functional groups present in the materials.

The surface morphology and elemental composition of the selected samples were examined using SEM in combination with an EDAX/Octane Elect Plus energy dispersive spectroscopy (EDS) system. The examination was conducted utilizing an FEI INSPECT S50 SEM, sourced from Hillsboro, Oregon, USA. The experimental setup involved incident electron acceleration voltages of 5 kV and 15 kV, while the chamber pressure was consistently regulated to approximately 10^{-7} mbar. In order to achieve a comprehensive characterization, various measurements were conducted across different regions of the waste samples, with the findings expressed in atomic percent (at.%). The obtained results will be presented in the upcoming chapters.

2.3 Oxidative Liquefaction Framework

After characterizing the chosen feedstock, it is essential to present the oxidative liquefaction process, which constitutes the fundamental aspect of the experimental research detailed in this thesis. Oxidative liquefaction is a thermochemical conversion process that facilitates the transformation of solid waste materials into liquid products, achieved through the regulation of temperature, pressure, and the incorporation of an oxidizing agent [89]. In contrast to traditional pyrolysis or hydrothermal liquefaction processes, which predominantly operate under inert or reducing conditions, oxidative liquefaction employs a controlled introduction of oxygen or other oxidizing agents. This approach promotes bond cleavage, improves depolymerization efficiency, and mitigates the production of excessive char [90].

The procedure generally functions within a temperature range of 200–400 °C, frequently under increased pressures to facilitate liquid-phase reactions, utilizing oxygen, air, or peroxide-based oxidants administered in precisely measured amounts. The process of oxidative liquefaction involves the partial oxidation of complex polymers and composites, which serves to reduce activation energy barriers and enhance liquid yields. Additionally, this method introduces oxygenated functional groups that significantly affect the characteristics of the resultant bio-oils or chemical intermediates [91].

In the current investigation, oxidative liquefaction has been identified as a viable method for the valorization of end-of-life WTBs, PV panels, PPEs, and MSW, due to their heterogeneous and polymer-rich composition. Comprehending the foundational principles of oxidative liquefaction is crucial for establishing the necessary context for the following sections, which will elaborate on the experimental setup and planning.

2.3.1 Details of experimental setup and sample preparation

The experiments on oxidative liquefaction were performed using a high-pressure batch reactor system, which was specifically designed to maintain stringent control over the process conditions. A Parr 4650 series batch reactor (Parr Instruments, Moline, IL, USA), possessing a total capacity of 500 mL, was utilized for all experimental trials (Figure 2.5). The reactor incorporated a high-temperature spiral heating element, which facilitated the attainment of operating temperatures reaching 800 °C, thereby allowing for the treatment of various waste feedstocks under regulated conditions. The regulation of temperature was accomplished through the utilization of a Parr 4838 reactor controller, which provides a readout and setpoint resolution of 1 °C, alongside an overall system accuracy of ±2 °C. In order to enhance the precision and reproducibility of the experimental results, the reactor and controller underwent a calibration process before the initiation of the experiments. This calibration aimed to optimize the heating power, thereby ensuring the maintenance of stable process temperatures throughout the entire residence time.

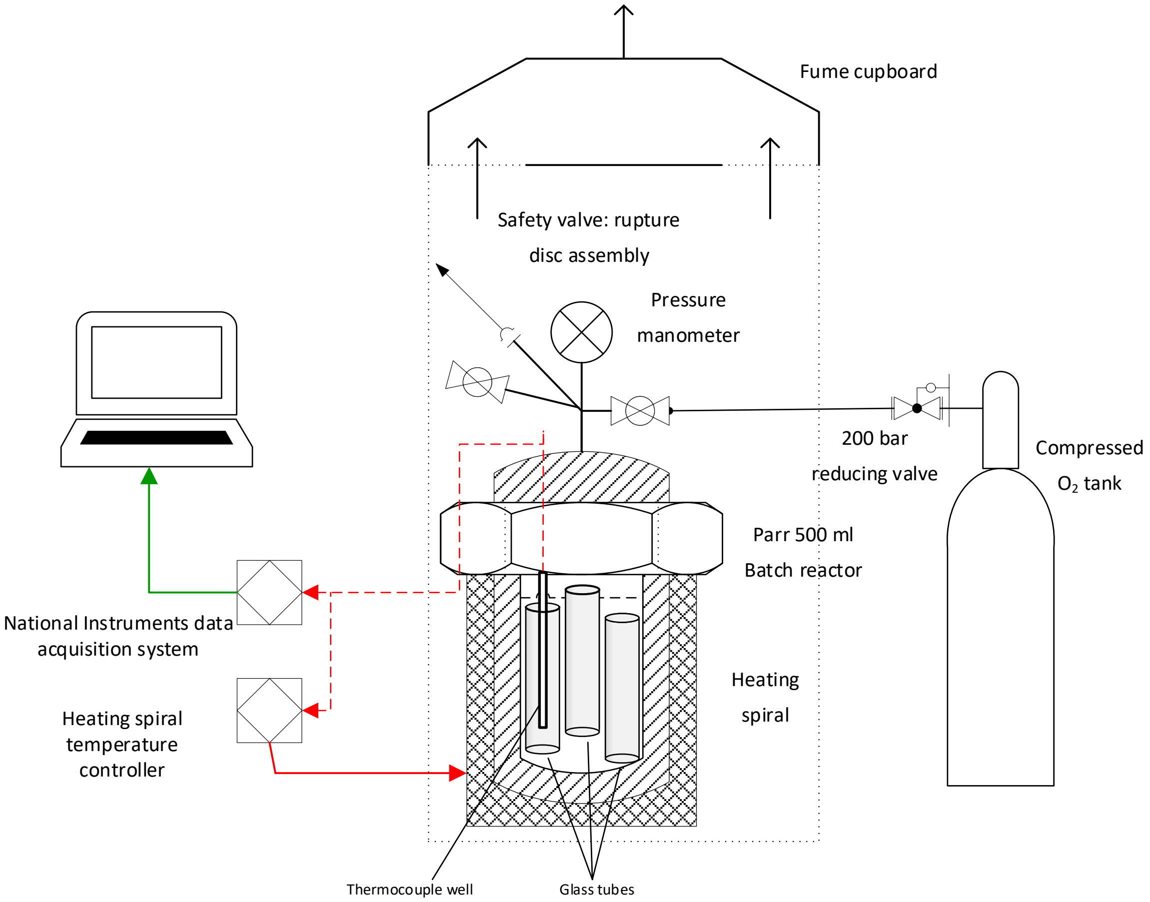


Figure 2.5 Reactor setup for oxidative liquefaction process

The reactor head was outfitted with various functional components designed to enable process monitoring and control. A J-type thermocouple was employed, positioned within a thermowell situated in the reactor head, to facilitate continuous measurement of the internal temperature. The pressure gauge, affixed to the reactor head, facilitated the monitoring of pressure levels up to 350 bar, thereby ensuring the safe attainment of high-pressure oxidative liquefaction conditions. The apparatus was equipped with two straight valves: the initial valve was linked to a gas inlet for the purpose of pressurization using an inert gas (nitrogen) before the commencement of experiments, whereas the subsequent valve functioned as an outlet for the regulated release of flue gases or the collection of product gases generated during the reaction process.

The management of temperature regulation during operation was achieved through the implementation of proportional–integral–derivative (PID) control groups integrated within the Parr 4838 controller. Each PID group was allocated a specific setpoint value, facilitating precise control of temperature variations during the liquefaction process. Nitrogen served dual functions in this context, acting as both a pressurizing medium and an inert atmosphere, thereby inhibiting undesired side reactions before the onset of oxidative conditions. Furthermore, the configuration was augmented with an auxiliary data acquisition system that included a cDAQ controller and an NI-9212 temperature recording module (National Instruments, USA), and K-type thermocouples, facilitating the continuous recording and archiving of process parameters. This configuration facilitated the monitoring of the dynamic evolution of process conditions with a high degree of precision.

The experiments on oxidative liquefaction were carried out utilizing pre-processed waste feedstocks, which included end-of-life PV panels, WTBs, PPEs and MSW, as outlined in the materials section. Before conducting the experiments, the WTB samples underwent milling with a blade grinder, resulting in chips measuring approximately 1.5–2 cm in length. In parallel, the PV and PPEs were similarly cut into comparable dimensions to maintain homogeneity.

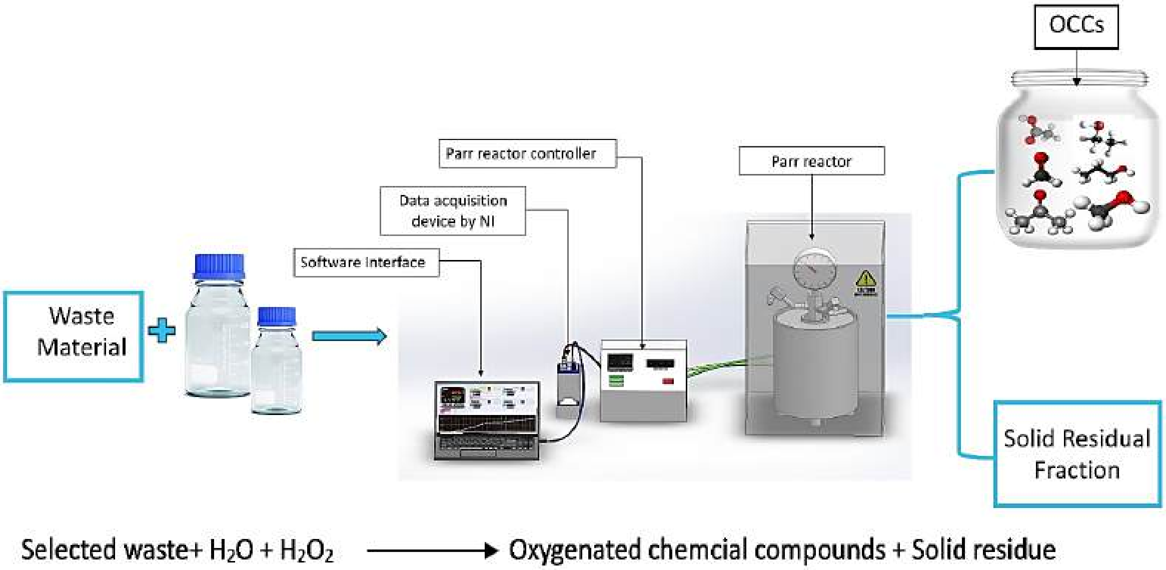


Figure 2.6 Sample processing approach for the oxidative liquefaction process

In each experimental run, a specific amount of the prepared waste sample was meticulously measured and placed into glass liners. Following this, the liners were filled with the liquid reaction medium, which comprised a defined H_2O/H_2O_2 mixture, formulated in accordance with the ratios detailed in Table 2.3. Following the loading of the samples and reaction medium, the glass liner was positioned within the Parr 4650 reactor, and the reactor head was fastened to create a sealed environment. The system was subsequently pressurized with nitrogen gas to an initial pressure, which is a crucial procedure to maintain the reaction mixture in a liquid state under the specified conditions. Subsequent to the pressurization process, the integrity of the reactor's airtightness was assessed through continuous observation of the pressure readout over a period of 30 minutes.

The reactor was heated via a spiral heater incorporated within the reactor system until the designated temperature was attained. The specified temperature was sustained throughout the duration outlined in the experimental matrix (Table 2.3), with meticulous monitoring of both temperature and pressure parameters. After attaining the required residence time, the heating spiral was turned off, and the reactor was permitted to cool naturally under ambient environmental conditions.

Subsequent to the cooling phase, the reactor was accessed, and the glass liner was extracted. The contents underwent processing to facilitate product recovery: the reaction mixture was subjected to filtration to isolate liquid and solid fractions. The liquid products were contained in sealed plastic bottles for future analytical characterization, whereas the solid residues underwent a comprehensive washing and drying process in an oven to eliminate any remaining moisture before proceeding with further analysis. A schematic illustration of the sample processing workflow is presented in Figure 2.5.

2.3.2 Design of experimental conditions/Plan

The experimental study on the oxidative liquefaction of selected waste samples was carried out utilizing a central composite face-centred design (CCF), which was created with the assistance of Statistica Software (v.13.3.0). The chosen statistical design methodology aims to effectively investigate the process variables while reducing the overall number of experimental runs. The CCF encompasses three distinct categories of design points: factorial points, which yield insights into the primary effects and two-way interactions among the variables; axial points, which facilitate the identification of curvature within the response surface; and centre points, which serve to estimate experimental error variance and to assess the adequacy of the model.

This investigation commenced with the consideration of five independent process variables: oxidative liquefaction temperature, initial pressure, residence time, waste-to-liquid ratio, and the concentration of the oxidant, specifically the amount of H_2O_2. Each variable was operationally defined at three distinct levels (−1, 0, +1), which correspond to low, medium, and high values, respectively. For $k = 5$ variables, the total number of experiments in the CCF design is calculated using the equation 2.1

$$2k + 2^{(k-1)} + n_{center} \qquad (2.1)$$

The outcome yielded a total of 29 runs. This design framework facilitated the estimation of linear, quadratic, and interaction terms, thereby enabling the capture of both direct and combined effects of the chosen parameters. The model demonstrated the ability to estimate a constant term, five linear terms, ten two-factor interactions, and five quadratic terms, thus facilitating a thorough statistical evaluation of the process conditions.

The experimental design was modified to accommodate the diverse structural and chemical robustness observed in the various categories of waste materials under investigation. The investigation focused on WTBs, which exhibit markedly superior physical and chemical durability relative to other waste fractions. A comprehensive five-factor CCF design was employed, necessitating a total of 29 experimental runs for thorough analysis. In contrast, for less complex wastes such as PPEs, MSW and PV waste, preliminary analyses indicated that certain process variables, particularly pressure, reaction duration had a minimal impact on liquefaction performance under the conditions tested. As a result, the quantity of independent variables was minimized to three specific factors: liquefaction temperature, oxidant concentration, and waste-to-liquid ratio. The observed reduction resulted in a streamlined three-factor CCF design, necessitating a total of 17 experimental runs.

The implementation of this customized methodology facilitated the optimization of the oxidative liquefaction process for WTBs, taking into account all pertinent process parameters. Concurrently, the treatment of PPEs, PV and MSW was executed utilizing a streamlined yet statistically robust design. This approach facilitated the efficient utilization of experimental resources while maintaining the integrity of the results obtained. The comprehensive experimental matrix is illustrated in Table 2.3.

Table 2.3 Process parameter levels compared to coded values using a central composite face-cantered plan

Sample type	**Variable/coded values**	**Temperature, °C**	**Initial pressure, bar**	**40% H_2O_2 addition, wt.%**	**Process time, min**	**Waste-Liquid ratio, wt.%**
WTB	-1	250	20	15	30	5
	0	300	30	30	60	15
	1	350	40	45	90	25
PPE	-1	200	30	30	45	3
	0	250		45		5
	1	300		60		7
MSW	-1	200	30	30	45	3
	0	250		45		5
	1	300		60		7
PV	-1	200	30	30	45	12.5
	0	250		45		25
	1	300		60		37.5

2.4 Analysis of Results:

2.4.1 Calculation of total solid reduction or resin degradation yield

Upon the completion of the oxidative liquefaction process, the contents of the reactor was a biphasic mixture. This mixture comprised a solid fraction, primarily consisting of inorganic residues, including alongside a liquid fraction. The separation of the mixture was achieved via simple filtration process employing standard laboratory filter paper. The liquid sample was collected in plastic containers, which were sealed to prevent evaporation, stabilized, and then stored under controlled conditions (freezer storage) for subsequent chemical and physicochemical evaluations. The isolated solid residue underwent a drying process in a laboratory oven (WGL-30B, Adverti, Poland) at a temperature of 105 °C for a duration of 8 hours, utilizing forced air circulation to eliminate any residual moisture. Subsequent to the drying process, the solid fraction was subjected to weighing to quantify the mass loss incurred during processing. The degree of waste degradation was assessed utilizing mass balance calculations. The TSR was quantified as follows, equation 2.2:

$$TSR = \frac{m_0 - m_s}{m_0 \cdot} \cdot 100\% \tag{2.2}$$

where m_o denotes the initial mass of the feedstock and m_s the dry mass of the solid residue subsequent to the liquefaction process. The thermal conversion efficiency is indicative of the proportion of the feedstock that is transformed into liquid and gaseous products.

Furthermore, the Resin (or Polymer) Degradation Yield (RDY) was determined by relating the TSR with ash content (A), which is presumed to remain constant throughout the liquefaction process and to signify the inorganic fraction of the selected waste. The RDY was ascertained utilizing the subsequent expression 2.3:

$$RDY = \frac{m_0 - m_s}{m_0 \cdot (1 - A)} = TSR \cdot (1 - A)^{-1} \qquad (2.3)$$

This parameter measures the effective degradation of the organic polymeric component of the waste, irrespective of the presence of inorganic residues. Through the correlation of TSR and RDY with the ash content present in various waste streams, a distinction was made between the degradation of the organic resin/polymer matrix and the inert inorganic fraction. This differentiation facilitated a comparative assessment of liquefaction efficiency among different waste materials.

2.4.2 Analysis of liquid products

The analysis of these liquid products was conducted by a trained laboratory operator, whereas the interpretation and discussion of the results were undertaken by the author to quantify the yield of OCCs obtained. The liquid products derived from the oxidative liquefaction of the examined waste feedstocks were subjected to analysis utilizing a gas chromatograph (Clarus 500, PerkinElmer, USA) that is equipped with a flame ionization detector (FID). A DB-FAT WAX UI capillary column (30 m × 0.25 mm × 0.25 µm, Agilent Technologies, USA) was utilized for the purpose of compound separation. Helium served as the carrier gas, maintained at a flow rate of 1.0 cm^3/min. The furnace temperature protocol commenced with a 4-minute isothermal hold at 40 °C, succeeded by a heating ramp of 5 °C/min until the target temperature of 240 °C was attained, at which point the temperature was sustained for a duration of 15 minutes. A split/splitless injection system was employed to guarantee the reproducibility of measurements.

The liquid fraction underwent quantitative analysis through the preparation of calibration curves for designated VFAs and aromatic hydrocarbons (AHs), achieving correlation coefficients that surpassed 0.99. The concentrations measured (expressed in µg/mL of the liquid phase) were subsequently normalized to the initial waste input, represented as g/kg of dry feedstock, utilizing the relevant conversion equation 2.4.

$$\sum \mathrm{OCCs} = \frac{\mathrm{OCC} \cdot V_{liq\_samp}}{m_{sample} \cdot 1000} \left[\frac{g}{kg_{waste}}\right] \qquad (2.4)$$

$\sum \mathrm{OCCs}$ - sum of OCCs [g/kg $_{Wastes}$]

OCC – OCC in the liquid sample from oxidative liquefaction [µg/mL]

V_{liq_samp} – the volume of the liquid sample from oxidative liquefaction in [mL]

m_{sample} – mas of waste sample used for oxidative liquefaction [g]

The analysis of the liquefied products revealed the presence of several compounds, including volatile fatty acids (C_2–C_{16}), aromatic carboxylic acids (ACAs), fatty acid methyl esters (FAMEs, C_2–C_{16}), aromatic hydrocarbons (AHs), and aromatic carboxylic acid esters (ACAEs). These compounds together are referred as OCCs. The identified groups of compounds serve as significant oxygenated and hydrocarbon derivatives that are characteristically produced during the process of oxidative liquefaction, thereby indicating the degree of depolymerization and oxidation of the initial waste samples.

2.4.3 Statistical analysis of results and optimization of experimental plan

The experimental data derived from the oxidative liquefaction of the examined waste feedstocks underwent thorough statistical analysis to optimize the process conditions and assess the impact of critical operational parameters. A comprehensive framework was employed, incorporating graphical, mathematical, and statistical methodologies to ascertain the most significant variables and establish optimal operational parameters. The investigation predominantly utilized ANOVA as a methodological framework to assess the statistical significance of distinct factors and their interactions. The independent variables examined in this study comprised reaction temperature, pressure, residence time, waste-to-liquid ratio, and oxidant concentration. In contrast, the dependent response variables assessed included TSR, resin RDY, yield of OCCs, and energy consumption. The determination of the significance of factor effects was conducted via p-values, where values less than 0.05 suggest a statistically significant influence on the response variables. Furthermore, a two-way ANOVA was employed to evaluate the interaction effects among the variables, with the null hypothesis positing that all factor levels exert equal influence, while the alternative hypothesis indicated that at least one factor had a distinct effect. In order to visually analyze the influence of experimental variables, Pareto charts depicting standardized effects were developed, facilitating the identification of parameters that exert the most significant impact on process outcomes. Profiles of predicted values were generated to facilitate a comparison between experimental responses and those predicted by the model, thereby serving to validate the accuracy of the model and to identify potential discrepancies for further refinement.

Additionally, RSM was utilized to investigate the relationships between factors and responses within a multidimensional framework. The incorporation of desirability functions alongside response surface plots facilitated the concurrent optimization of various response variables. The application of desirability functions facilitated the conversion of each response into a dimensionless scale, which spans from 0, indicating undesirable outcomes, to 1, representing the most desirable scenarios. This methodological approach enables the simultaneous optimization of conflicting objectives, exemplified by the need to maximize TSR, RDY, and OCC yield while concurrently minimizing energy consumption. In the context of this investigation, the linear desirability function was chosen as the optimal formulation, given its effectiveness in managing the trade-offs between dependent variables. The overall desirability was quantified as the geometric mean of the individual desirability functions, with weights assigned based on the relative significance of each response parameter.

The integration of ANOVA, Pareto analysis, response profiling, and desirability-based optimization establishes a comprehensive framework for elucidating the paramount parameters that affect oxidative liquefaction. Furthermore, it facilitates the identification of optimal operating conditions aimed at enhancing process efficiency across various waste categories.

2.4.4 Inverse analysis of process heating

The study aimed to examine the thermal decomposition characteristics of selected waste during the process of oxidative liquefaction, with a focus on identifying the temperature range linked to significant decomposition stages. An inverse analysis of the heating process was conducted to achieve this objective. Reactions were modelled at specific temperatures of 200 °C and 250 °C, with all other parameters held constant at their optimized levels. The internal reactor temperature, referred to as the reaction temperature, was subjected to continuous monitoring at intervals of 10 seconds. This was achieved through the utilization of K-type thermocouples interfaced with a National Instruments (NI) data acquisition system, which exhibited a measurement error of 0.75% and a resolution of 1 K.

Alongside the modelled runs utilizing waste feedstocks, two control experiments were conducted under the same conditions to determine reference thermal profiles:

(i) a combination of oxidant and water, aimed at quantifying the thermal contribution of the oxidant in the absence of waste,
(ii) water alone, serving as a representation of a purely endothermic baseline devoid of any chemical reactions.

The heating profile derived from the water-only experiment served as a reference point for detecting deviations linked to exothermic or endothermic reactions in the simulated runs. The temperature-time profiles obtained from both the modelled and dummy runs were systematically compared to evaluate discrepancies in heating behaviour. Additionally, the rate of temperature change (dT/dt, K s^{-1}) was graphically represented in relation to the internal reactor temperature to understand transient fluctuations in heating rates. Distinct peaks in dT/dt were observed in the modelled reactions, which were not present in the control runs. This observation suggests the release of additional thermal energy resulting from the exothermic decomposition of the waste materials. The analysis of the heating rate profiles through curve examination facilitated the identification of supplementary peaks, encompassing their quantity, intensity, and total area. This approach offers a quantitative framework for differentiating reaction-driven thermal effects from baseline heating phenomena.

Introduction to the next chapter

With outlining the research gaps, identification of feedstock materials and comprehensive understanding of the oxidative liquefaction process the next chapter presents the methodology for experimental investigations on hydrothermal treatment of WTBs (*RG-2*), in presence of oxidizing agent H_2O_2 (*RG-4*), and the overall process is called oxidative liquefaction. The experimental work aims to degrade the WTBs to recover the good quality glass fibers, identify the effective reaction parameters, optimize the process conditions *(RG-1)*, and contribute to the practical implementation of the oxidative liquefaction process for complex waste management and recycling.

Chapter 3

3 Experimental Investigation of Oxidative Liquefaction of Wind Turbine Blades

Paper II (Appendix B): An experimental investigation and process optimization of the oxidative liquefaction process as the recycling method of the end-of-life wind turbine blades

3.1 Background

The disposal of end-of-life WTBs poses a significant environmental and economic challenge due to their composite structure, which includes GFs embedded in a thermoset resin matrix [92]. The increasing deployment of wind energy has led to an escalating number of decommissioned WTBs, creating a pressing need for sustainable recycling solutions. In the literature, various recycling techniques for WTBs have already been reported (Table 3.1 A). Traditional recycling methods such as landfilling, incineration, and mechanical processing have limitations, including incomplete material recovery, high energy consumption, and environmental concerns [93]. These challenges necessitate the development of innovative and efficient recycling techniques.

Among emerging recycling technologies, oxidative liquefaction presents a promising method for addressing the limitations of conventional approaches [94]. By integrating hydrothermal treatment with an oxidizing agent, this process facilitates the breakdown of thermoset resins while preserving the integrity of reinforcing fibers. Compared to pyrolysis and mechanical grinding, oxidative liquefaction operates at lower temperatures, reducing energy demand and minimizing secondary pollution. Furthermore, this method aligns with circular economy principles by enabling the recovery and reuse of high-quality glass fibers for new composite applications.

Purpose of the experimental study

The aim of this study, titled “An experimental investigation and process optimization of the oxidative liquefaction process as the recycling method of the end-of-life WTBs,” is to evaluate the effectiveness of oxidative liquefaction in degrading WTBs. This will facilitate the recovery of glass fibers, identify key reaction parameters, and optimize the oxidative liquefaction process for WTBs, focusing on maximizing output while minimizing resource consumption. This study examines how temperature, residence time, pressure, waste-to-liquid ratio, and oxidant concentration affect resin degradation and fiber recovery. Determining the optimal parameters for achieving the highest resin degradation while minimizing energy usage evaluating the practicality of oxidative liquefaction for implementation as a novel complex waste recycling technique.

Alignment of the presented research with the PhD thesis objectives

This chapter expands upon the identified research gaps from Chapter 1 and detailed experimental investigations was carried out on hydrothermal treatment of WTBs (complex composite waste) using the oxidant H_2O_2, a process referred to as oxidative liquefaction. It highlights the key reaction parameters that influence the oxidative liquefaction of WTBs and offers comprehensive insights into the optimization of the overall process. This study's findings establish a basis for the future implementation of oxidative liquefaction in the recycling of composite waste on a larger scale.

3.2 Materials and Methods

The waste generated from decommissioned WTBs was analyzed through oxidative liquefaction to assess the degradation of resin and the recovery of glass fibers, with a focus on the influence of different process parameters. An experimental framework was systematically devised and refined, focusing on the parameters of resin degradation and energy utilization. Comprehensive details of the experimental setup, adopted methodologies, and analytical techniques are delineated in Chapter 2.

3.3 Results and Discussion

3.3.1 Resin degradation and glass fiber recovery *(RG-2)*

The research assessed the impact of various factors, including temperature, pressure, residence time, waste-to-liquid ratio, and oxidizer content, on TSR and resin degradation yield (RDY).

The highest TSR of 49% and a complete RDY were achieved under conditions of 350°C, 40 bar, for a duration of 30 minutes, with 45% oxidizer and a waste-to-liquid ratio of 5%. The obtained glass fibers are shown in Figure 3.1. At temperatures of 250 and 300 °C, similar TSR and RDY values were noted, with residence times adjusted while keeping a 5% waste-to-liquid ratio constant. A higher waste-to-liquid ratio of 25% and a 90-minute residence time resulted in lower TSR and RDY, highlighting its significant importance. The sample size was maintained at 1–2 cm, indicating that increasing the sample size could necessitate extended reaction times and elevated oxidant concentrations. At elevated temperatures, while the TSR showed enhancement, the energy consumption almost doubled in comparison to the process conducted at 250 °C. Enhancing reaction conditions to achieve optimal TSR and RDY, while concurrently reducing energy consumption, is crucial for ensuring commercial feasibility. Repetitive experiments demonstrated a standard deviation in RDY of approximately 2.9%, suggesting a commendable level of repeatability despite the intricacies of the process.

Figure 3.1 Pure glass fibres obtained from oxidative liquefaction of WTBs

3.3.2 Energy consumption analysis

The energy demand recorded at 350°C was 2.8 kWh, which is nearly twice the demand observed at 250°C, where it was 1.5 kWh. The ideal parameters include a temperature of 300°C, pressure of 30 bar, a duration of 30 minutes, a concentration of 30% H_2O_2, and a 15% waste-to-liquid ratio, achieving a balanced resin degradation rate of 97% while minimizing energy consumption. The details from RDY analysis, energy consumption during different runs, and complex interactions between tested parameters demand detailed process optimization.

3.3.3 Process optimization *(RG-1)*

A total of twenty-nine oxidative hydrothermal tests, along with additional repetitions, were performed under a range of conditions. These included temperatures varying from 250 to 350 °C, pressures between 20 and 40 bar, H_2O_2 concentrations spanning 6 to 18%, residence times of 30 to 90 minutes, and waste-to-oxygenated solution ratios from 5 to 25%. The study employed experimental design and ANOVA to determine that the ratio of waste to oxygenated solution, temperature, and the amount of oxidant, along with their interactions, have a significant impact on resin removal.

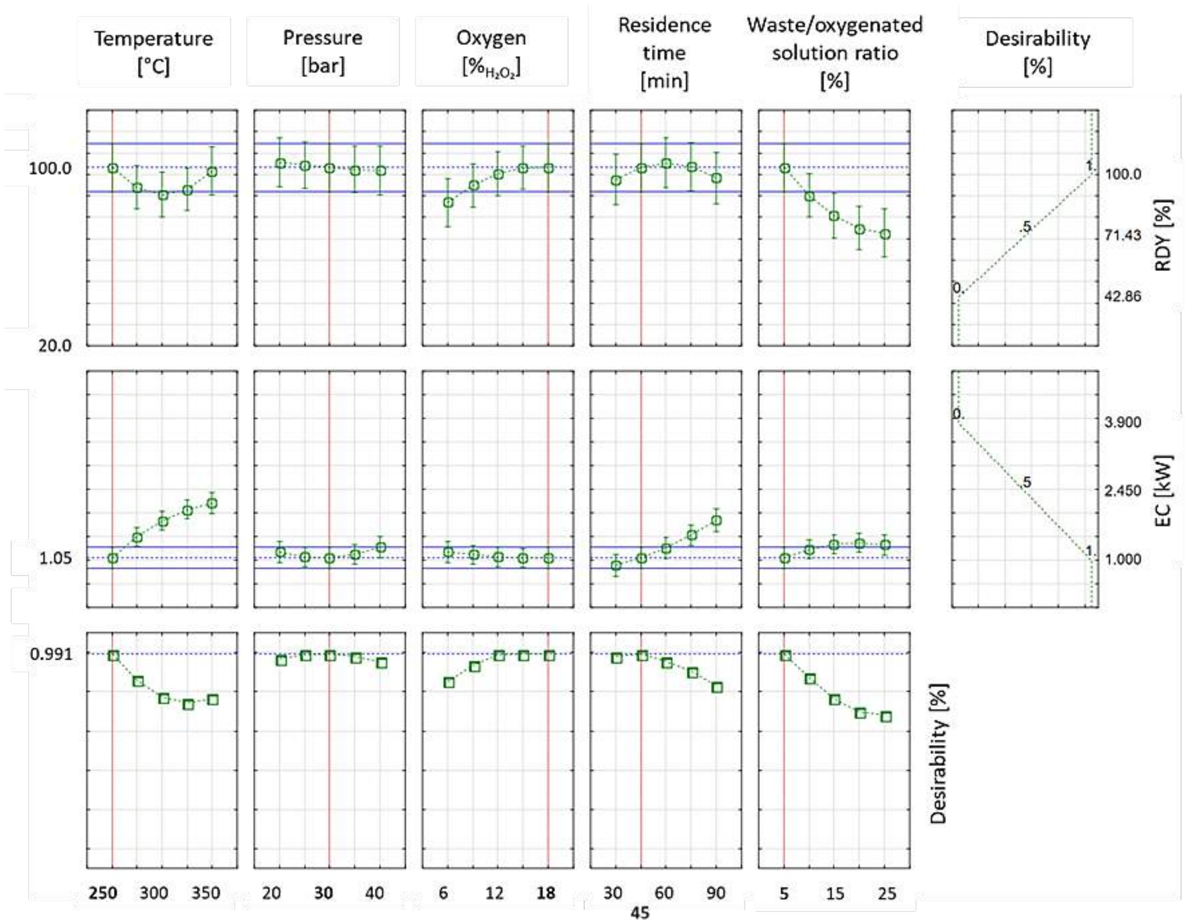


Figure 3.2 Optimal levels of tested parameters for oxidative liquefaction of WTBs

As shown in Figure 3.2, a higher ratio of waste to the oxygenated solution was observed to adversely affect resin degradation yield (RDY), whereas elevated oxidant levels enhanced RDY. The interaction of temperature with the waste ratio demonstrated a positive and significant impact on RDY. The achieved optimal process conditions resulted in an average RDY of 100.00% (±2.9%), while also minimizing energy consumption. The analysis indicated that process pressure did not exert a statistically significant influence on RDY, with variations from 20 to 40 bar leading to only negligible differences. Residence time, although not significant by itself, demonstrated a quadratic effect, with RDY reaching its maximum at 60 minutes before experiencing a decline. The findings underscore the significant influence of the waste-to-oxygenated solution ratio and oxidant concentration in enhancing the wet oxidation process for resin removal.

3.4 Summary of Outcomes

The structural makeup of WTBs generally comprises 60–70% reinforcing fibers, including glass, carbon, and aramid, alongside 30–40% thermoset resin, such as epoxy, polyester, and polyurethane. Under optimized conditions, the oxidative liquefaction process demonstrated a resin degradation efficiency ranging from 95% to 100%. The primary process parameters encompassed a temperature range of 250–350 °C, residence times varying from 30 to 90 minutes, operating pressures between 20 and 40 bar, oxidant concentrations of 15 to 45% H_2O_2, and a waste-to-liquid ratio ranging from 5 to 25%.

The optimization of energy consumption facilitated a beneficial equilibrium between significant resin degradation and minimized energy input, thereby illustrating the feasibility of oxidative liquefaction as a sustainable recycling method for WTBs recycling. The results of the experiment indicate that oxidative liquefaction facilitates the near-total removal of resin while simultaneously maintaining the mechanical integrity of the recovered glass fibers. The findings underscore the significant influence of oxidant concentration on facilitating efficient resin decomposition, concurrently contributing to a reduction in operational expenses.

This research demonstrates that oxidative liquefaction represents a viable approach for the recycling of composites, offering an efficient and energy-aware method for the management of end-of-life WTBs in the renewable energy sector.

Introduction to the next section

The next chapter is the continuation of the current studies, as it provides details of the solid structure of WTB sample before and after treatment, together with yields of OCCs that are produced through oxidative liquefaction of polymer matrix sample. It also provides details about the optimization of the overall process with goals of maximum OCCs and RDY against minimum energy consumption. These insights will support the implication of the oxidative liquefaction process in composite waste recycling.

Chapter 4

4 Product Analysis from Oxidative Liquefaction of WTBs

Paper III (Appendix C): Oxidative liquefaction as an alternative method of recycling and the pyrolysis kinetics of wind turbine blades

4.1 Background

WTBs which are predominantly constructed from glass fiber-reinforced polymer composites, present significant challenges for recycling owing to their intricate design. Annually, a substantial number of WTBs are taken out of service, presenting a considerable challenge in waste management. The existing methods for recycling encompass:

- Mechanical recycling: involves processes such as shredding and grinding that reduce the size of glass fibers as well as generate products of lower quality [95].
- Pyrolysis, defined as the thermal decomposition of the matrix at higher temperatures, but it is suspected to degrade the quality of glass fibers and generate undesirable byproducts [96].
- Chemical recycling processes, including solvolysis, have the capability to recover carbon fibers; however, they frequently result in the degradation of glass fibers [97].

This study offers a comprehensive examination of the oxidative liquefaction products, expanding upon the findings presented in the Chapter 3. The primary goals encompass the analysis of the chemical composition of recovered materials, the evaluation of the quality of separated glass fibers, and the exploration of the potential for utilizing volatile fatty acids (VFAs) as valuable byproducts. Grasping the structural, morphological, and chemical properties of these materials is essential for enhancing the recycling process and guaranteeing their suitability in secondary markets.

Purpose of the experimental study

The previous chapter highlighted the potential of the oxidative liquefaction process to recover glass fibers while this section aims to evaluate the efficacy of oxidative liquefaction in generating VFAs and to examine the chemical composition of the liquid and solid fractions to identify their possible applications. Structural and chemical analyses of obtained glass fibers were conducted to assess the quality and purity. The study aims to determine the optimal process parameters that enhance VFA production and RDY, all while reducing energy usage. This study seeks to enhance understanding of the conversion mechanisms that result in VFA formation by systematically varying essential parameters, including temperature, pressure, residence time, oxidant concentration, and waste-to-liquid ratio. This study employs statistical process optimization via ANOVA to elucidate the trade-offs between process efficiency and material recovery, thereby advancing the development of an optimized oxidative liquefaction method aimed at enhancing both material and chemical valorisation of WTB waste.

4.2 Materials and Methods

The oxidative liquefaction of end-of-life WTBs was conducted under controlled conditions to examine the degradation of resin and the formation of liquid products. The study employed a systematic approach involving experimental design, product characterization through SEM, FTIR and GC-FID, and statistical analyses, specifically ANOVA, to assess performance and energy efficiency in the context of process optimization. Comprehensive methodological details are delineated in Chapter 2.

4.3 Results and Discussion

4.3.1 Structural details of WTBs before and after oxidative liquefaction process *(RG-2)*

The analysis of the structural properties of raw and processed WTBs was conducted through SEM (Figure 4.1). The investigation demonstrated that unprocessed WTBs possess a polymer resin matrix that consistently envelops the glass fibers. Following oxidative liquefaction, the polymer matrix experienced significant degradation, resulting in the separation of glass fibers with only a minimal amount of residual resin remaining. The analysis of morphology validated the effective degradation of the epoxy matrix, revealing high-purity glass fiber.

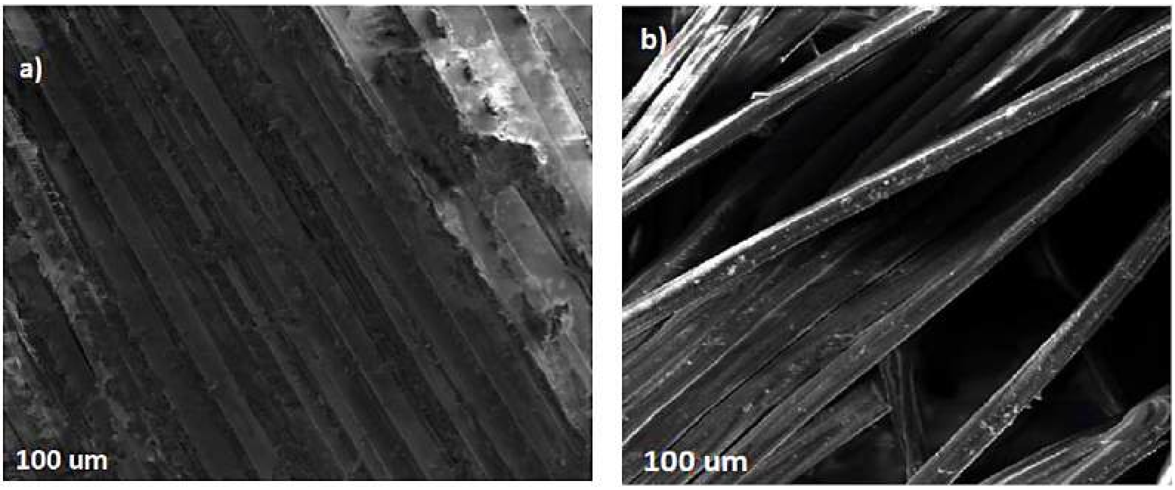


Figure 4.1 Structural details of WTBs sample before and after oxidative liquefaction

4.3.2 Chemical structure of WTBs sample subjected to oxidative liquefaction *(RG-2)*

The FTIR spectra of WTB waste shown in Figure 4.2 exhibit absorption bands that are indicative of different chemical bonds and functional groups. The band observed at 3020 cm^{-1} is linked to C–H stretching within the epoxy group, whereas the bands at 2950 and 2860 cm^{-1} are attributed to C–H stretching in the CH_2 and CH_3 groups found in aliphatic chains. The prominent band observed at 1720 cm^{-1} signifies the stretching of the C=O bond, while the less intense band at 1630 cm^{-1} corresponds to the C=C stretching associated with the aromatic ring. The bands observed at 1500 cm^{-1}, 1450 cm^{-1}, and 1340 cm^{-1} are indicative of N–H bending and C–N stretching in amines. The bands observed at 1220, 1120, and 1050 cm^{-1} are indicative of ether group vibrations, while the bands at 750 and 660 cm^{-1} are associated with C–H vibrations occurring outside the aromatic ring plane. The findings indicate the existence of intricate organic compounds, including epoxy, aromatic groups, and amines.

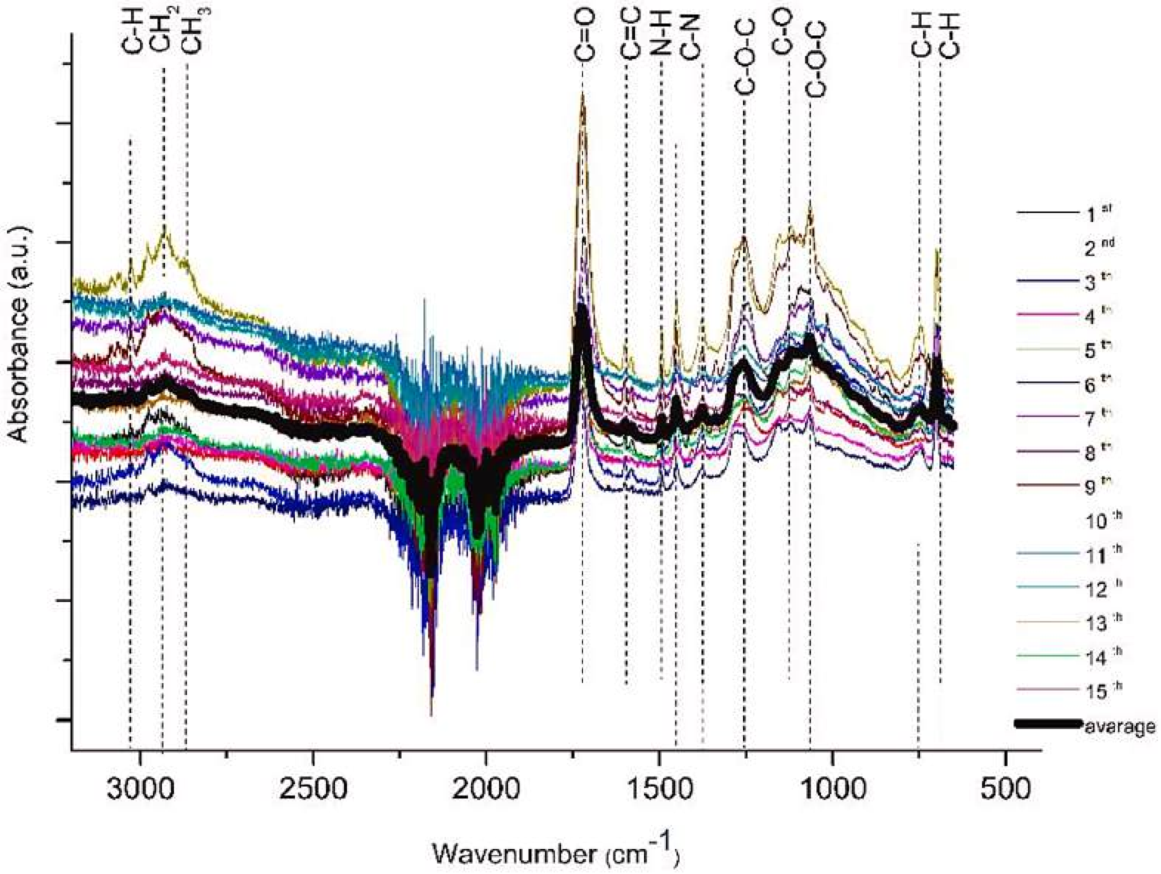


Figure 4.2 In-depth probing of the chemical structure of WTBs sample

This suggests that oxidative liquefaction would focus on the degradation of these bonds, resulting in the formation of smaller volatile products.

4.3.3 Enhancing RDY as a fundamental parameter for VFAs production *(RG-2)*

The RDY results, derived from various combinations (Figure 4.3) of temperature, pressure, oxidant concentration, residence time, and waste-to-liquid ratio, indicated that the peak RDY (100%) was attained at 350°C with a minimal residence time (30 or 60 min) and a low waste-to-liquid ratio (5%). The findings indicated a reduction in RDY at lower temperatures (300°C and 250°C), while the performance exhibited a relatively stable trend. The concentration of oxidants and pressure exhibited minimal influence on RDY, whereas the waste-to-liquid ratio emerged as the most significant factor in maximizing RDY. Increased temperatures lead to a reduction in the Hildebrand parameter, which in turn enhances the solubility of resin in near-critical water [98]. Conversely, lower waste-to-liquid ratios result in a higher concentration of liquid, thereby facilitating reactions and RDY. The standard deviation observed in the repeated experiments varied between 2.5% and 4.5%, suggesting a high level of reliability in the repeatability of the results.

At 350°C, the peak RDY values, reaching as high as 100%, were obtained with a minimal waste-to-liquid ratio of 5% and brief residence times of 30 to 60 minutes. Additionally, it was observed that the concentration of oxidants and pressure exerted minimal influence once they surpassed basic thresholds. Reducing the waste-to-liquid ratio elevates the concentration of reactive species, thereby enhancing the solvation power of water, which leads to improved degradation and ultimately increases RDY.

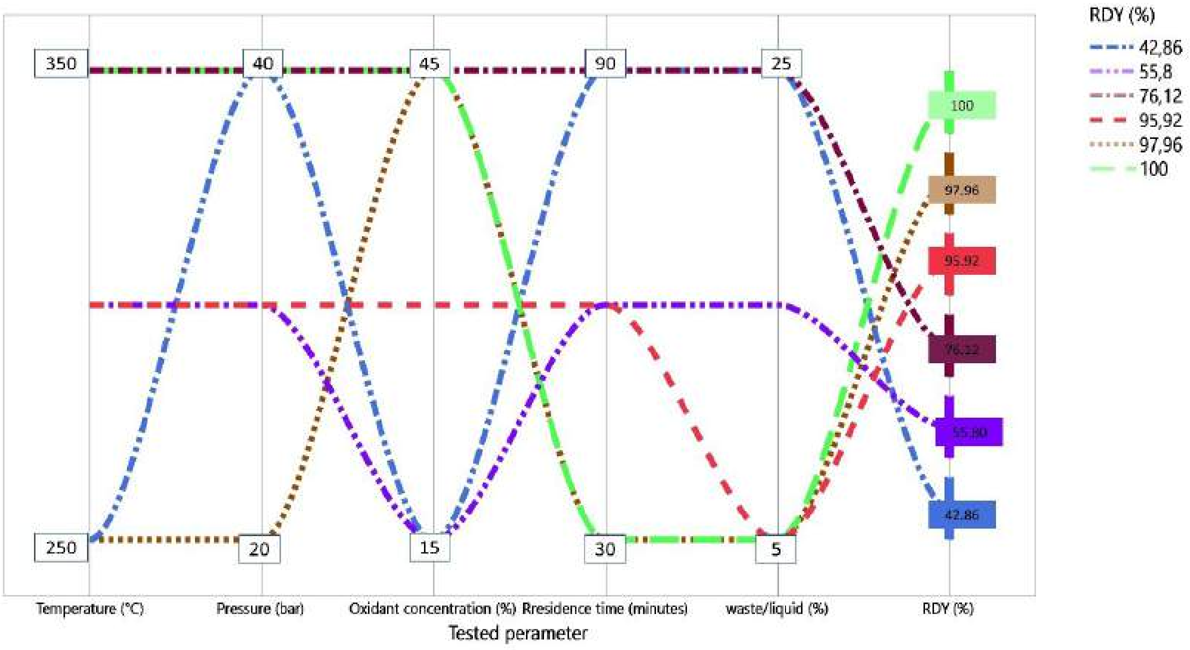


Figure 4.3 Different combinations of reaction parameters against minimum to maximum levels of RDY

4.3.4 Volatile fatty acid concentration in liquid products

The oxidative liquefaction of WTB produces VFAs that exhibit considerable variability (Figure 4.4) depending on the tested temperatures and parameter combinations. At a temperature of 250°C, the highest concentration of VFAs attained was 210.59 g/kg-WTB, achieved under conditions characterized by low oxygen concentration, minimal waste-to-liquid ratio, and reduced residence time, along with elevated pressure. Conversely, the lowest yield recorded was 28.90 g/kg-WTB, which occurred under conditions of high oxygen concentration, extended residence time, and increased pressure. At 300°C, the VFAs were observed to range from 60.92 to 158.54 g/kg-WTB, indicating that a minimal waste-to-liquid ratio is advantageous for achieving higher yields. At 350°C, the elevated temperature contributed to improved solvation properties; however, the maximum and minimum yields recorded were 163.50 and 36.31 g/kg-WTB, respectively, obtained under differing conditions. The data indicates a rise in energy consumption corresponding to temperature increments (1.6 kWh at 250°C, 2.41 kWh at 300°C, and 2.9 kWh at 350°C). This highlights the necessity for optimizing processes to achieve a balance between energy input, product yield, and commercial viability.

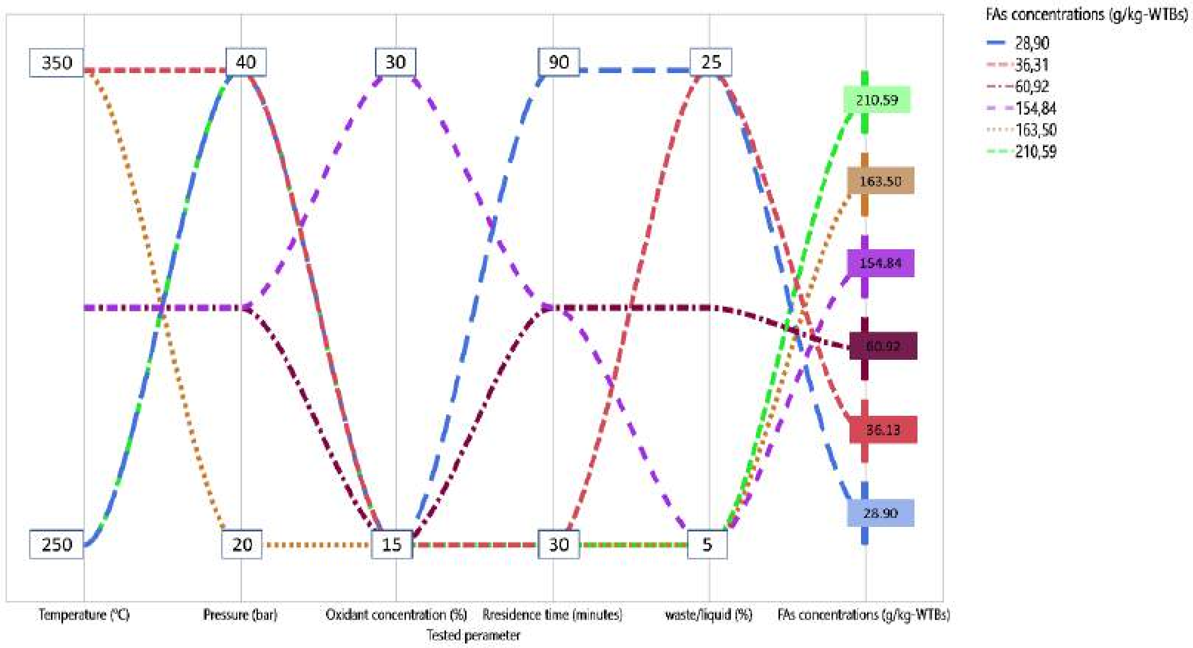


Figure 4.4 Different combinations of reaction parameters against minimum to maximum levels of VFAs achieved

4.3.5 Identification of optimal reaction conditions for effective recycling of WTBs for maximum material recovery and secondary product generation *(RG-1)*

The research examined the oxidative liquefaction of WTBs by conducting 29 experiments that altered temperature (250–350 °C), pressure (20–40 bar), H_2O_2 concentration (6–18%), residence time (30–90 min), and waste-to-liquid ratio (5–25%). A design of experiments integrated with ANOVA ($p < 0.05$) was employed to determine the significant factors affecting VFAs production and RDY, along with their interactions.

Figure 4.5 presents a Pareto chart of standardized effects, illustrating that the waste-to-liquid ratio emerges as the most significant parameter, exerting a negative influence on VFAs yield. This suggests that increased ratios result in diminished production. The oxygen concentration, when considered independently, exhibits a weak negative effect. However, its interaction with the waste-to-liquid ratio reveals a strong positive correlation, highlighting its significance particularly in conjunction with low waste-to-liquid ratios. Other parameters demonstrate both linear and quadratic behaviours; however, their overall contributions remain relatively minor.

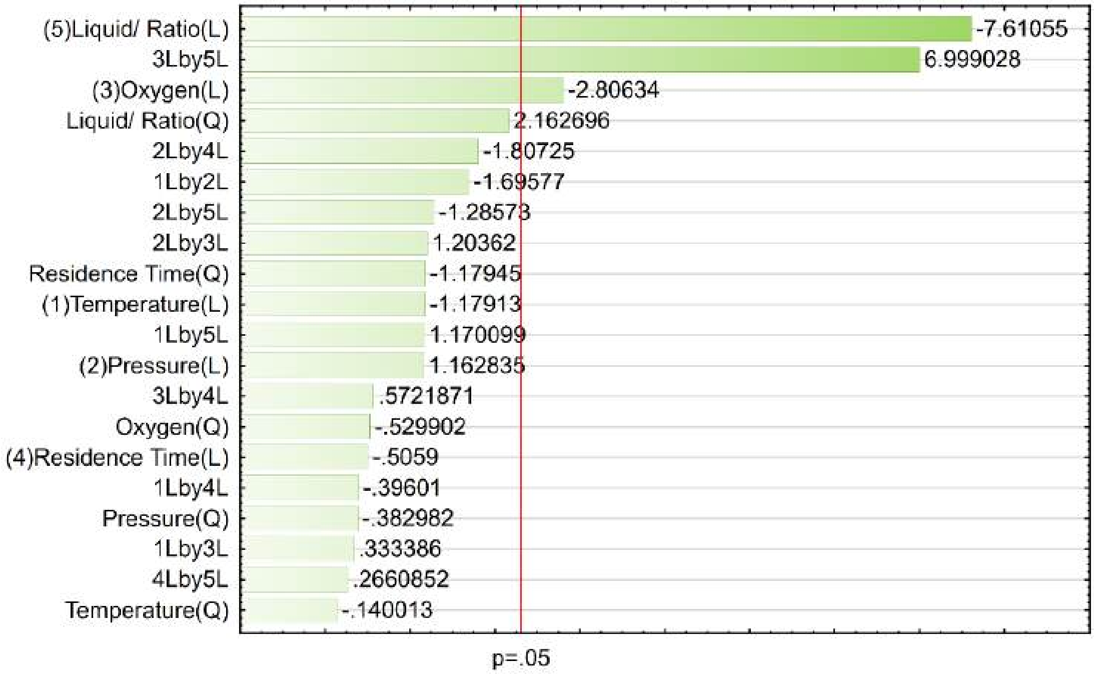


Figure 4.5 Identification of most effective parameters effecting oxidative liquefaction of WTBs

Figure 4.6 illustrates a strategic plan that integrates energy consumption into the assessment of process efficiency. This examination indicates that although elevated temperatures may enhance RDY, they concurrently require a substantially greater amount of energy. The optimization highlights the importance of sustaining a minimal waste-to-liquid ratio and a balanced oxidant concentration, which are essential for attaining high yields of VFAs and favourable energy economics. The effect of all tested parameters on recorded outcomes and related energy consumption, associated best scenarios, can be seen in Figure 4.6

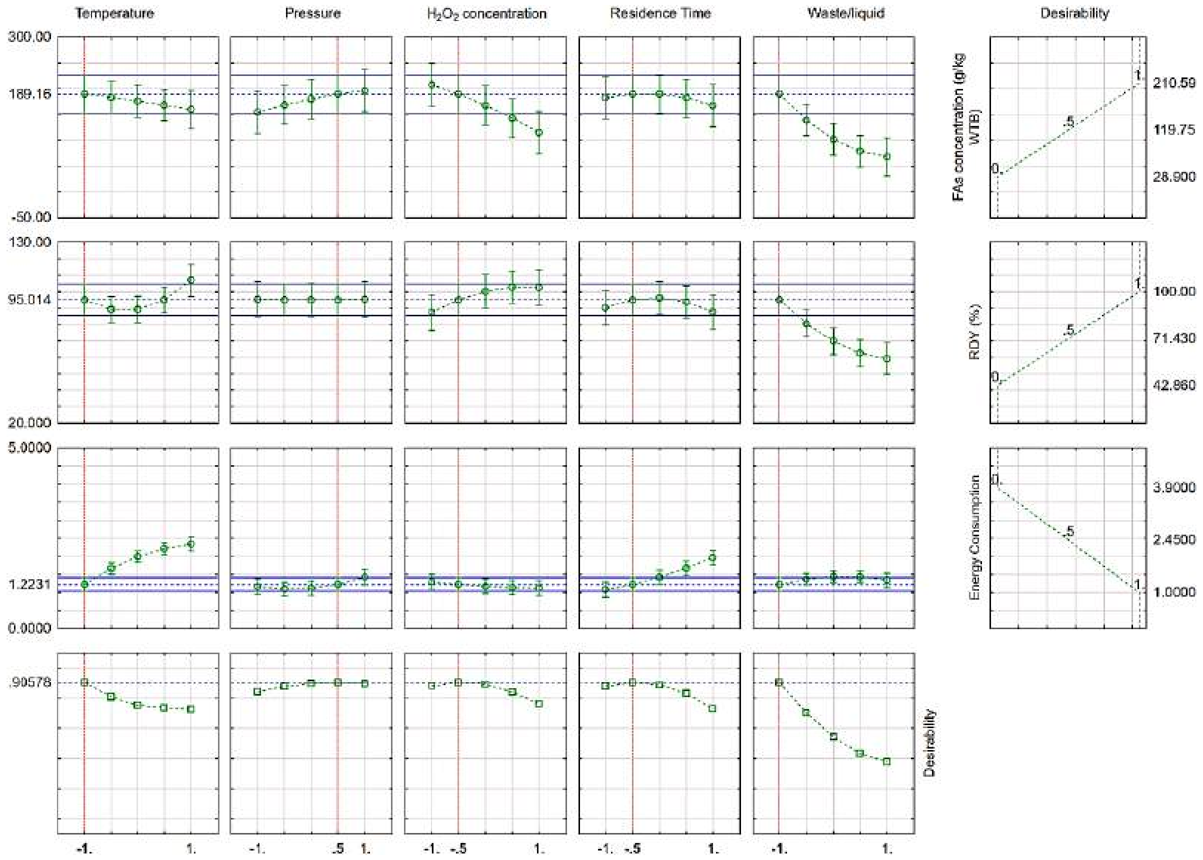


Figure 4.6 Complete optimization plan for oxidative liquefaction of WTBs considering RDY, VFAs yields, and energy consumption

Figure 4.7 illustrates response surface profiles that delineate the desirability of parameter combinations while maintaining the integrity of their individual effects. The profiles suggest that the best process performance, achieving a global maximum, takes place under conditions of 35 bar pressure and 250 °C temperature, alongside intermediate values for H_2O_2 concentration and residence time. The surfaces clarify the connections among the variables and assist in identifying the conditions that lead to the maximization of the process output.

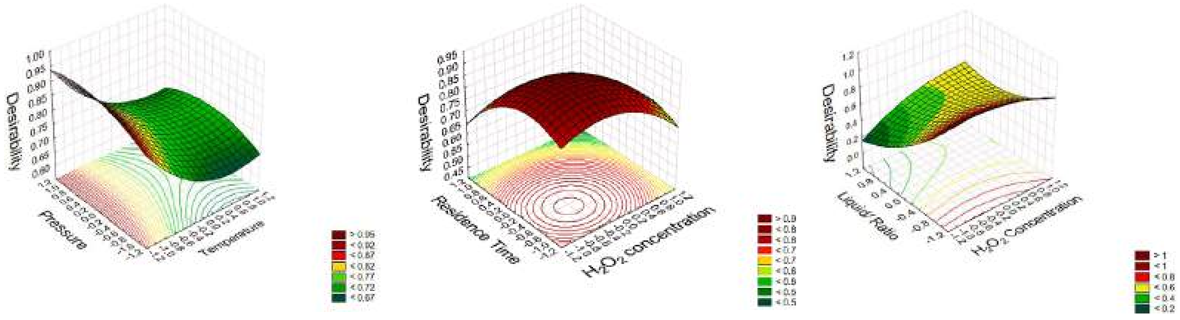


Figure 4.7 Response surface profiles showing the collective desirability of two targeted reaction parameters

So in general study systematically assessed the impact of critical process variables on the oxidative liquefaction of WTBs. The Pareto analysis underscored the significant importance of the waste-to-liquid ratio, while the optimization plan effectively balanced yield with energy input. Additionally, the response surface analysis showed the desirability of reaction parameters in oxidative liquefaction of WTBs, thereby offering a thorough framework for enhancing process efficiency and economic viability.

4.4 Summary of Outcomes

This research illustrates that the oxidative liquefaction of waste WTBs serves as an efficient method for the degradation of resins, the recovery of glass fibers, and the production of valuable liquid byproducts. The FTIR analysis substantiated the degradation of the polymer matrix, evidenced by the attenuation and displacement of specific epoxy and aromatic absorption bands. Concurrently, SEM observations indicated the elimination of polymer layers while maintaining the structural integrity of the fibers. The findings indicated that RDY and the production of VFAs were significantly affected by the ratios of waste to liquid and the concentration of oxidants. The attainment of the highest RDY at 350 °C underscores the importance of addressing the associated energy penalties through process optimization. The highest concentration of VFAs was observed at 210.59 g/kg of WTBs at a temperature of 250 °C, with acetic acid being recognized as the predominant product. The application of Pareto chart of standardized effects alongside response surface modelling has elucidated the waste-to-liquid ratio and oxidant concentration as the predominant factors influencing the system, with their interaction proving to be critical in optimizing the output of VFAs. The optimal process conditions were identified as 250 °C, 35 bar, 45 minutes, 22.5% H_2O_2, and a 5% waste-to-liquid ratio, indicating the most effective equilibrium between efficiency and energy utilization. The results obtained from this study collectively demonstrate that oxidative liquefaction represents a scalable and energy-efficient recycling approach for WTBs. This method facilitates the near-complete removal of resin, the generation of high-value VFAs, and the recovery of mechanically intact glass fibers.

Introduction to the next section

The current chapter is based upon the detailed discussion on oxidative liquefaction of WTBs, while the upcoming chapter will bring a comparative scenario for oxidative liquefaction potential of WTBs and PPEs used in the medical sector. PPEs are widely used in hospitals as well as their use was found to be more common during the pandemic. That resulted in a higher concentration of this polymeric waste in the environment. So, the upcoming discussion will be based on comparative mode for both waste composition, their degradation trends with increasing temperatures, yields of polymer degradation and oxygenated chemical production, possible challenges due to different compositions. Comparison of optimal reaction conditions, assessing the combined desirability of targeted reaction parameters during overall process to justify the use oxidative liquefaction potential for effectively managing different waste kinds with aims of waste reduction and valuable secondary compound generation.

Chapter 5

5 Comparative Analysis of Oxidative Liquefaction for Wind Turbine Blades and Personal Protective Equipments Used in Medical Sector

Paper IV (Appendix D): An in-depth study of the oxidative liquefaction process for polymeric waste reduction and chemical production from wind turbine blades and personal protective equipment used in the medical field

5.1 Background

As described in previous chapters, the swift advancement of the renewable energy industry, especially in wind energy, has resulted in a notable rise in the number of aging WTBs. The extensive use of PPEs in the healthcare sector, particularly during the COVID-19 pandemic, has intensified the issue of plastic waste. The essential role of PPEs in mitigating infection transmission is undeniable; however, their disposable characteristic has significantly exacerbated the issue of global plastic waste. At the height of the pandemic, there was a significant increase in the global demand for masks and gloves. In Asia, the daily consumption reached 3,716.20 million masks, which amounted to around 1,486.48 tonnes of waste [99]. Furthermore, there was a significant rise in medical waste generation, particularly evident in Wuhan, China, where daily production reached over 247 tonnes, which is nearly six times higher than the levels observed before the pandemic [100]. PPEs, primarily composed of polymers such as PP, PE, PC, and PVC, can remain in the environment for decades when not disposed of appropriately [101]. The inadequate disposal of this waste presents significant threats to both ecosystems and human health. In addressing this crisis, a range of waste treatment techniques has been investigated, including high-temperature incineration, pyrolysis, gasification, chemical liquefaction, and solvothermal methods. Nevertheless, each of these methods presents specific limitations, such as significant energy requirements, the production of hazardous byproducts, and intricate process demands [102–105].

A comparative analysis of oxidative liquefaction process in the context of recycling WTBs and PPEs reveals several advantages. The management of both waste streams presents significant challenges attributed to their polymeric compositions. WTBs are characterized by the presence of thermosetting resins and glass or carbon fibers, whereas PPEs predominantly consist of thermoplastics such as polypropylene and polyethylene. Evaluating the effectiveness of a single process in degrading these materials can reveal the potential to minimize the necessity for distinct recycling technologies.

This analysis further aids in refining process parameters, including temperature, pressure, and oxidant concentration, to enhance polymer degradation and resource recovery to offer a

circular economy solution by transforming PPEs into valuable hydrocarbons and WTB resins into reusable aromatic compounds. This process presents a potential energy-efficient and low-emission alternative to incineration or landfill disposal, thereby reducing environmental impact.
Analyzing the economic implications, implementing a unified oxidative liquefaction system for both waste categories has the potential to lower operational costs and draw in investments for scalable waste-to-resource facilities.

Purpose of the experimental study

Keeping this in mind this chapter examines the viability of oxidative liquefaction as an innovative approach for the effective recycling of polymer waste derived from PPEs and WTBs. The study seeks to identify the best reaction conditions—including temperature, pressure, residence time, waste-to-liquid ratio, and oxidant concentration—that enhance TPD and the production of OCCs, all while reducing energy consumption. Achieving these objectives could lead to an economical and energy-efficient solution for managing polymer waste, thereby contributing to the sustainability of the renewable energy and healthcare sectors.

Alignment of the presented research with PhD thesis objectives

This chapter expands upon earlier discussions centred on WTBs recycling by broadening the focus to include PPEs and examining oxidative liquefaction as a viable alternative to existing waste management technologies. The results offer valuable perspectives on the chemical transformation of polymeric waste streams into useful compounds, thereby supporting strategies for effective management of polymer based waste.

5.2 Materials and Methods

The oxidative liquefaction process of polymeric waste derived from PPEs and WTBs was conducted in batch-type reactors. This study utilized systematic experimental designs to assess TPD and the generation of OCCs. The analysis of liquid products focused on the concentration of OCC, employing statistical optimization techniques such as ANOVA to ascertain the conditions that enhance TPD and OCC yield, concurrently aiming to reduce energy consumption. Chapter 2 contains an extensive overview of the materials utilized, the configuration of the reactor, the design of the experiments, the procedures for analysis, and the statistical methodologies employed.

5.3 Results and Discussion

5.3.1 Compositional details of WTBs and PPEs *(RG-2)*

The elemental composition of WTBs and PPEs (Figure 5.1) shows notable differences that affect their potential for oxidative liquefaction. The characteristics of PPEs reveal a primarily organic and flammable composition, featuring a significant volatile matter content of 97.0% and a carbon content of 80.1%. Additionally, they display low levels of moisture at 0.1% and ash content at 8.7%. In comparison, WTBs exhibit a considerably elevated ash content of 57.9% and moisture levels at 1.3%. Conversely, their volatile matter is recorded at 40.7%, and carbon content stands at 28.2%, both of which are markedly lower than those of PPEs. Furthermore, PPEs exhibit a higher hydrogen content of 12.8% in contrast to WTBs, which contain 2.7%. Nitrogen levels are comparatively low in both materials, with PPEs at 0.2% and WTBs at 1.2%. The oxygen content in WTBs, measured at 8.0%, is significantly greater than that found in PPEs, which plays a role in their more inorganic and oxidized characteristics. The concentration of chlorine (0.04%) and sulfur (0.03%) in PPEs is relatively low, while wire transfer boxes exhibit a marginally elevated sulfur level of 0.1%.

The observed compositional differences indicate that PPEs are likely more advantageous for energy recovery and chemical production, attributed to their elevated carbon and volatile content. In contrast, WTBs, characterized by higher ash and oxygen levels, may encounter difficulties in oxidative liquefaction, primarily due to the increased formation of inorganic residues.

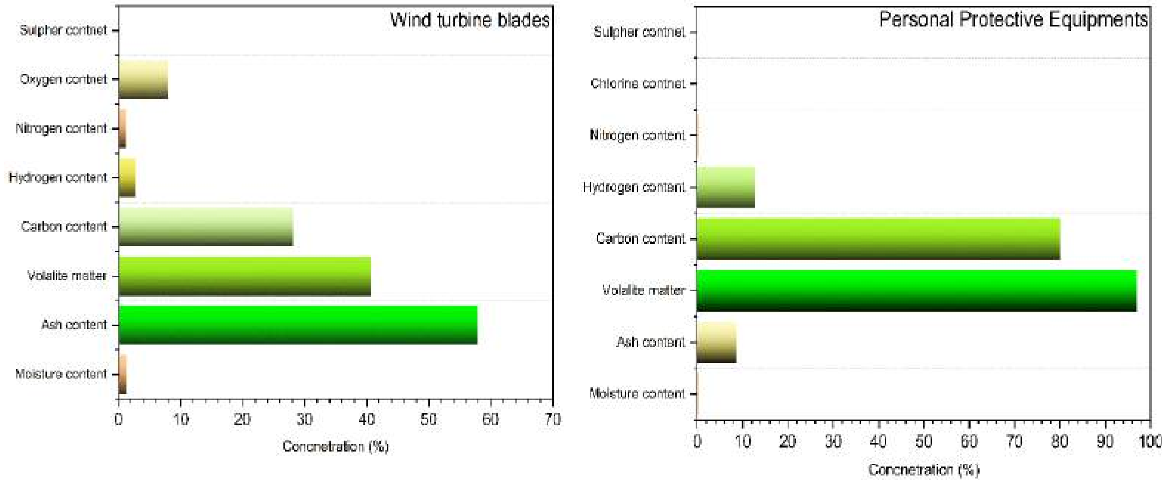

(a) (b)

Figure 5.1 Ultimate and Proximate analysis results for (a) WTBs and (b) PPEs

5.3.2 Thermal degradation pattern of WTBs and PPEs *(RG-2)*

The analysis of thermal degradation behaviour in WTBs and PPEs, conducted via TGA and DTG, demonstrates notable differences attributed to their material compositions. WTBs show several degradation peaks, which suggest various stages of thermal breakdown, while PPEs present a singular, distinct degradation peak (Figure 5.2 (a&b)).

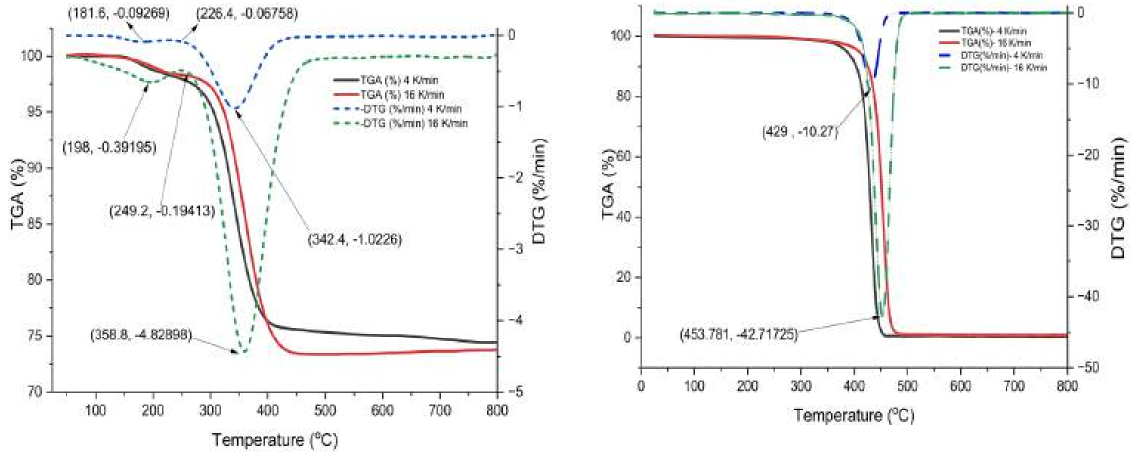

(a) (b)

Figure 5.2 TGA and DTG analysis of (a) WTBS (b) PPEs

In the case of WTBs, thermal decomposition takes place in a series of stages. The initial minor mass loss occurring between 181–250°C can be ascribed to the evaporation of moisture and the release of volatiles. Following peaks at 226°C and 324°C indicate the degradation of polymeric materials such as polyethylene, silicone acrylic resins, and epoxy resins. The most notable reduction in mass takes place within the temperature range of 275–420°C, attributed to the degradation of reinforcing materials and intricate polymers. Above

450°C, a gradual reduction in mass indicates the existence of thermally stable inorganic residues, like glass fibers, that exhibit minimal decomposition. Elevated heating rates (16 K/min) result in the displacement of degradation peaks to elevated temperatures and enhance decomposition rates.

PPEs demonstrate a swift and clear degradation process. At a heating rate of 4 K/min, a singular peak is observed at 429.3°C, accompanied by a mass change rate of 10.3%/min. In contrast, at 16 K/min, the peak shifts to 453.3°C, revealing a markedly increased decomposition rate of 42.8%/min. The mass loss is mainly attributed to the decomposition of thermoplastics such as polyethylene (PE), polypropylene (PP), and PVC, which undergo degradation within a specific temperature range of 350–480°C at a heating rate of 4 K/min and 380–480°C at 16 K/min.

The primary distinction between WTBs and PPEs is found in their thermal decomposition characteristics. WTBs, characterized by their intricate polymeric and inorganic makeup, undergo degradation in several phases (Table 5.1), each exhibiting unique peaks that indicate the presence of various constituent materials. PPEs primarily made of thermoplastics, undergoes rapid degradation within a specific temperature range, demonstrating a consistent breakdown process.

Table 5.1 Parametric details of oxidative liquefaction of WTBs and PPEs

			Stage 1			Stage 2			Stage 3		
	β, (K/min)	R_m (%)	r_m (%/min)	Δm_L (%)	T_{peak} (°C)	r_m (%/min)	Δm_L (%)	T_{peak} (°C)	r_m (%/min)	Δm_L (%)	ΔT (°C)
WTBs	4	74.4	-0.1	-1.7	181.5	-1.0	-22.5	342.4	N/A	-1.4	420-800
	16	71.6	-0.	-1.8	198.2	-4.8	-26.7	359.9	N/A	0.4	460-800
PPEs	4	0.	-10.3	N/A	429.3	N/A					
	16	0.8	-42.8	N/A	453.3						

R_m - Residual mass, %

r_m - Mass loss rate, %/min

Δm_L - Total Mass loss, %

T_{peak} - Peak Temperature, °C

ΔT - Gradual change in Temperature, °C

5.3.3 Comparative trends of polymer degradation through oxidative liquefaction of WTBs and PPEs *(RG-3)*

The degradation behaviour of polymers in WTBs and PPEs under experimental conditions shows notable variations in both magnitude and reliability (Figure 5.3). The analysis of WTBs revealed a polymer breakdown range between 21.1% and 49.0% across 29 trials, yielding an average degradation rate of roughly 37.0–38.0%. In Experiment 15, the highest TPD achieved was 49.0%. This experiment was conducted under conditions of high temperature at 350°C, maximum pressure, an oxygen concentration of 45 wt.%, a residence time of 30 minutes, and a minimal waste-to-liquid ratio. The observed conditions led to significant degradation, highlighting the material's vulnerability to controlled oxidative environments. In contrast, the minimum TPD recorded was 21.1% in Experiment 1, which was conducted under less extreme conditions, specifically at a temperature of 250°C, a pressure of 20 bar, an oxygen concentration of 15 wt.%, and a waste-to-liquid ratio of 25%. The results indicate that WTBs

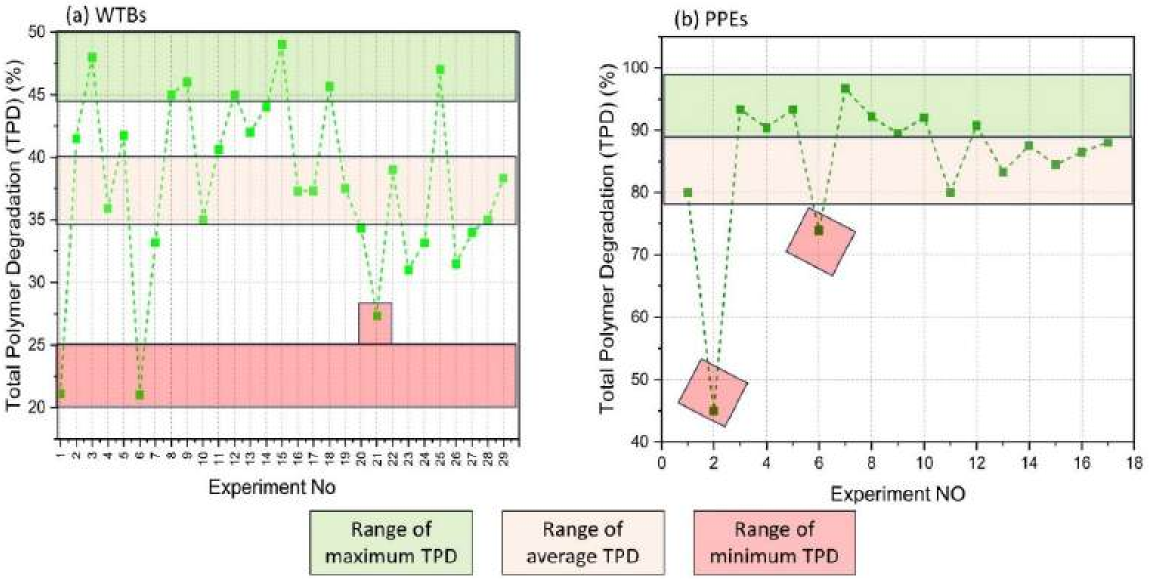


Figure 5.3 Comparative trends of polymer degradation through oxidative liquefaction of WTBs and PPEs

necessitate extreme reaction conditions for optimal degradation, and their disintegration is notably sensitive to changes in experimental parameters.
PPEs demonstrated a notably higher and more stable degradation range of 45.0% to 96.7% across 17 trials, with an average breakdown of approximately 85.0–90.0%. Experiment 7 yielded the highest TPD of 96.7% under optimal conditions, characterized by a temperature of 300°C, an oxygen concentration of 60 wt.% H_2O_2, and a low waste-to-liquid ratio of 3%. In Experiment 2, conducted under less favorable conditions (200°C, 30 wt.% H_2O_2, and a waste-to-liquid ratio of 7), PPEs still demonstrated a significant degradation of 45.0%. This suggests that PPEs exhibit a greater degree of degradability compared to WTBs, even when subjected to moderate experimental conditions, attributable to their less complex polymeric structure and elevated thermoplastic content.
The differences in material composition are further underscored by the variation in TPD results. WTBs displayed increased variability, characterized by standard deviation ranges from 1.5% to 4.3%. This variability can be attributed to their intricate polymer-fiber composition and differing levels of crosslinking. The degradation pattern of PPEs was notably more uniform, exhibiting standard deviations ranging from 0.5% to 3.5%. This consistency can be attributed to their standardized and less complex thermoplastic composition. This indicates that WTBs exhibit greater sensitivity to changes in parameters, whereas PPEs demonstrate enhanced stability in their degradation patterns. These findings highlight the distinct material reactivities of WTBs and PPEs. WTBs necessitate more extreme conditions for effective breakdown, while PPEs demonstrate efficient degradation even under moderate conditions.

5.3.4 Comparative trends of OCCs production through oxidative liquefaction of WTBs and PPEs *(RG-3)*

The oxidative liquefaction of WTBs and PPEs exhibited notable patterns in OCC production, shaped by critical experimental variables (Figure 5.4). The highest OCC yields were observed in WTBs at elevated temperatures of 350°C, utilizing a 45% oxidant concentration and prolonged reaction times ranging from 60 to 90 minutes. This indicates that increased thermal energy and extended exposure to oxidative environments facilitate greater material degradation and the formation of OCC. In contrast, PPEs reached peak OCC production at a significantly reduced temperature of 200°C, accompanied by a moderate oxidant concentration of 30%. Furthermore, reduced waste-to-liquid ratios were noted to significantly improve OCC yields, suggesting an alternative reaction mechanism in contrast to WTBs.

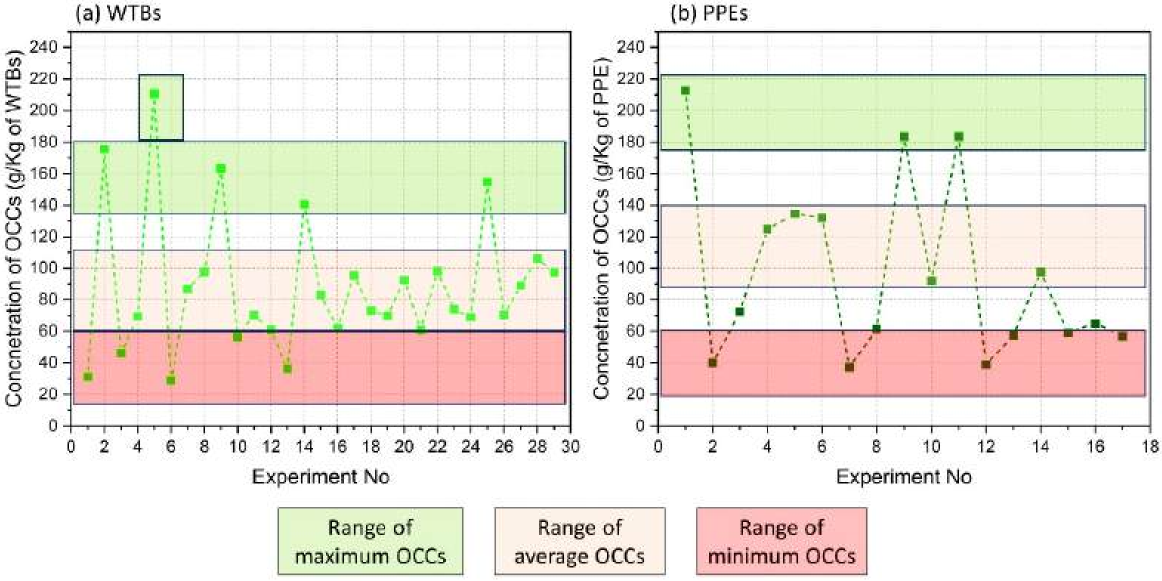


Figure 5.4 Yields of OCCs obtained during experiments for (a) WTBs, & (b) PPEs

The minimum OCC yields for WTBs were recorded at 250°C with an oxidant concentration of 15–30%, along with reduced reaction times of 30 minutes. The specified conditions constrained the degree of oxidation, thereby limiting the development of OCCs. In the case of PPEs, the lowest OCC values were observed at 200°C with an oxidant concentration of 60%. This indicates that excessive oxidation could impede the process by modifying degradation pathways or generating undesirable byproducts. The average OCC production for WTBs was observed over a wide temperature spectrum (250–350°C), with oxidant concentrations fluctuating between 30–45%, indicating a more intricate and variable decomposition process. Conversely, PPEs exhibited more stable OCC yields at 250°C with a 45% oxidant concentration, suggesting a more reliable and uniform degradation pattern.

The disparity in energy consumption between the two materials was also notable. WTBs necessitated an energy consumption ranging from 1.3 to 4 kWh for each experiment, whereas PPEs utilized only 0.7 to 1.2 kWh. The increased energy requirement for WTBs is linked to their intricate polymeric composition and the necessity for elevated temperatures to promote degradation. The results highlight the importance of optimizing processes to enhance energy efficiency and maximize OCC yields for both materials.

5.3.5 Optimizing overall process conditions with goals of maximum OCCs and TPD yields with maximum energy efficiency *(RG-4)*

The optimization of oxidative liquefaction for WTBs and PPEs concentrated on enhancing TPD and the production of OCCs (Figure 5.5 (a & b)). ANOVA was employed with a p-value threshold of 0.05 to optimize five reaction parameters for WTBs. In contrast, only three parameters were evaluated for PPEs, given that pressure and reaction time exhibited negligible effects on their degradation.

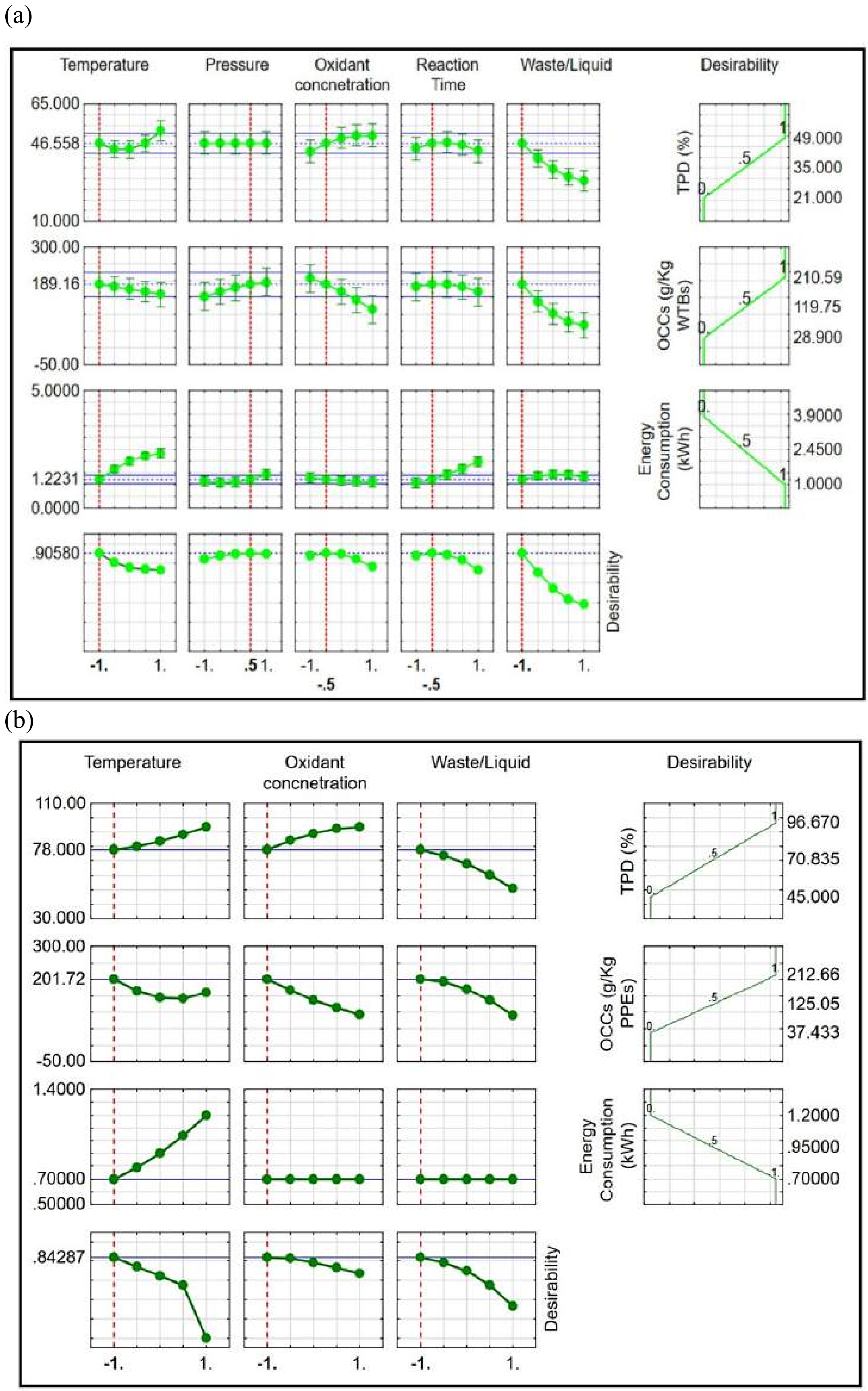


Figure 5.5 Comparison of optimal reaction conditions for oxidative liquefaction of (a) WTBs and (b) PPEs

WTBs displayed a nonlinear degradation pattern, characterized by an initial decrease in TPD followed by an increase at elevated temperatures, whereas PPEs showed a consistent degradation as temperature rose. Excessive temperatures, however, led to a reduction in OCC yields for both materials. Variations in pressure did not impact the degradation of PPE, while WTBs exhibited an optimal pressure threshold that did not influence energy consumption. Increased oxidant concentrations expedited the degradation of polymers yet resulted in diminished OCC yields. The performance of PPEs was optimal at reduced oxidant levels, whereas WTBs necessitated marginally elevated concentrations to achieve effective degradation. The duration of reaction time was crucial in WTBs, as extended periods initially enhanced degradation but subsequently led to efficiency declines and higher energy usage. Given that PPEs exhibited effective degradation at reduced reaction times, this parameter was maintained at a constant value.

An optimal waste-to-liquid ratio was observed for both materials, with increased waste concentrations leading to a decrease in TPD and OCC yields. WTBs necessitated increased energy consumption owing to elevated temperatures and extended reaction durations, while PPEs exhibited effective degradation with reduced energy input. In summary, WTBs require elevated temperatures, increased oxidant concentrations, and meticulous control of reaction times, whereas PPEs demonstrate effective degradation under less severe conditions. The results highlight the critical need for optimization tailored to specific materials in order to improve efficiency and minimize energy usage. Based on this discussion the comparative optimal reaction conditions for both WTBs and PPEs are presented in Table 5.2 below

Table 5.2 Listing optimal reaction conditions for WTBs and PPEs

	Temperature (°C)	**Initial pressure (bar)**	**H_2O_2 Concentration (wt.%)**	**Residence time (min)**	**Waste-to-Liquid ratio (wt.%)**
WTBs	250	35	22.5	45	5
PPEs	200	30	30	45	3

Figure 5.6 (a) demonstrates that the optimal combined desirability of the waste-to-liquid ratio and oxidant concentrations in the oxidative liquefaction of WTBs occurs at reduced values of these parameters. As either parameter increases, the additional gain in desirability decreases, highlighting the necessity for an optimal balance to maintain process efficiency. In a similar manner, Figure 5.6 (b) demonstrates that the combination of temperature and waste-to-liquid ratio also exhibits higher desirability at lower levels. When these parameters surpass specific thresholds, the desirability diminishes, highlighting the necessity of keeping them within an optimal range for enhanced process performance. This pattern is likewise evident in Figure 5.6 (b) emphasizes the appeal of the evaluated parameters for the oxidative liquefaction of PPEs. The primary observation across all figures highlights the significance of maintaining parameter levels at their minimum for optimal efficiency, noting that returns begin to diminish once they exceed certain thresholds.

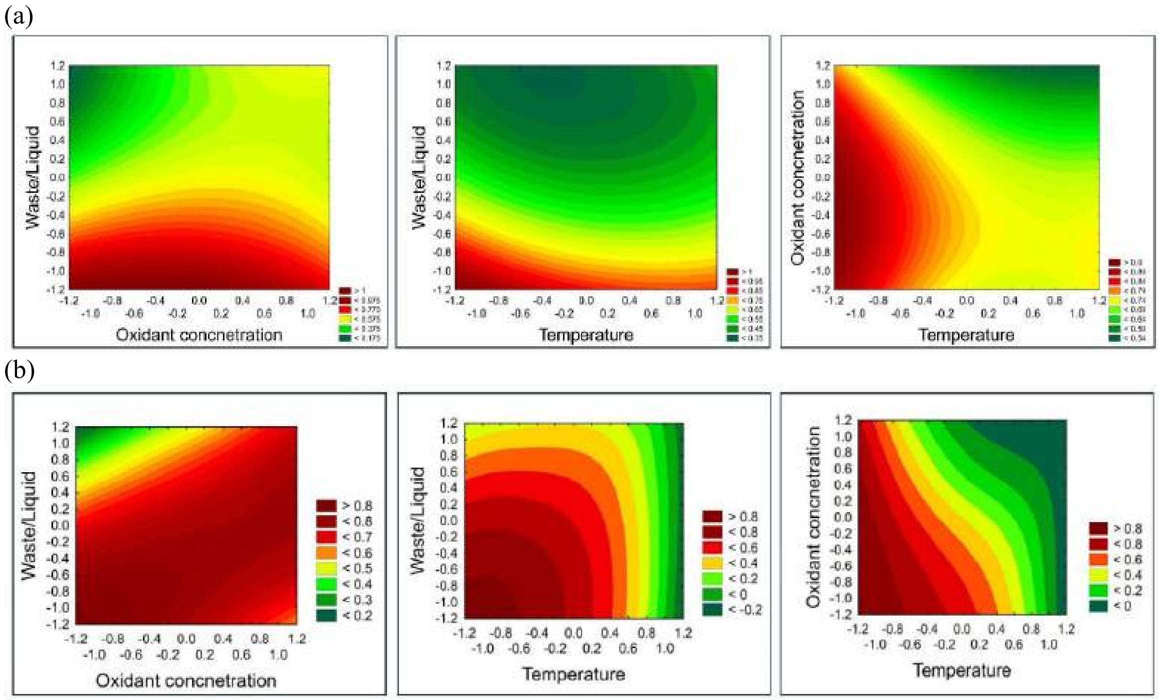


Figure 5.6 Assessing combined desirability of desired reaction parameters (a) WTBs, (b) PPEs

5.4 Summary of Outputs

The comparative analysis of oxidative liquefaction for WTBs and PPEs reveals distinct material behaviours, thermal degradation patterns, and process efficiencies. WTBs, made up of thermoset resins and reinforcing fibers, undergo degradation in several stages and necessitate elevated temperatures (~350°C), augmented oxidant levels (45%), and extended reaction times for efficient breakdown. However, their degradation process is hindered by a significant ash content (57.9%) and reduced volatile matter, leading to less effective outcomes. In contrast, PPEs composed of thermoplastics such as PP and PE exhibit rapid and efficient degradation at lower temperatures (approximately 200–250°C) and moderate oxidant levels (30%). This process results in a higher TPD rate (85–90%) while consuming significantly less energy (0.7–1.2 kWh compared to 1.3–4 kWh for WTBs). While WTBs are effective in producing OCCs at elevated temperatures, extended exposure tends to diminish yields. In contrast, PPEs excel in generating OCCs under more moderate conditions, which enhances their suitability for large-scale recycling. The waste-to-liquid ratio has a more pronounced effect on PPEs compared to WTBs, highlighting the necessity for process control tailored to specific materials. Ultimately, PPEs provide a more energy-efficient and commercially viable recycling pathway, whereas WTBs necessitate additional process optimization to achieve a balance between degradation efficiency and economic feasibility. This highlights the importance of customized recycling strategies to enhance sustainable waste management.

Introduction to the next section

The previous chapter was based upon the detailed discussion on comparative analysis of oxidative liquefaction potential to degrade complex WTBs and rather simpler PPEs, both polymeric in nature. The study offered an in-depth analysis of both waste composition, their thermal degradation patterns, calculating TPD and OCCs production, and optimizing the overall experimental plan. On other hand MSW due to its continuous escalation and intricate nature is also providing continuous challenges when it comes to effective waste management. Targeting this problem and to highlight the necessity of modern MSW waste management techniques the next chapter will provide short details about escalating MSW production both globally and specifically within Poland. In detail the chapter will analyse trends in waste generation, waste composition, and current disposal practices, thereby emphasizing the broader challenges in MSW management.

Chapter 6

6 An Overview of MSW Generation, Globally and in Poland

Paper v (Appendix E): A waste wet oxidation technique as a solution for chemical production and resource recovery in Poland – a review

6.1 Background

The generation of MSW has exceeded 1.2 billion tons per year and is anticipated to surpass 2 billion tons by the year 2025 [106]. The processes of rapid urbanization, population growth, and industrialization are significant factors leading to increased waste generation, which in turn intensifies environmental and health issues [107]. The composition of MSW exhibits considerable variation across different regions worldwide, with plastic waste constituting approximately 10–12% of the overall MSW and presents substantial environmental challenges [108]. Countries such as China (220 million tons/year), the USA (258 million tons/year), and India (169 million tons/year) produce substantial amounts of waste, highlighting the urgent need for effective waste management strategies [109,110]. At present, 20% of MSW undergoes recycling processes, while 12% is transformed into energy. The remaining portion is disposed of in landfills, resulting in environmental contamination and the loss of potential energy resources. MSW comprises hydrocarbons that, when subjected to pyrolysis, yield biofuels exhibiting calorific values ranging from 35 to 44 MJ/kg. This positions biofuels derived from MSW as a plausible substitute for fossil fuels [111,112]. Poland, similar to other EU nations, is witnessing an increase in waste generation (Figure 6.1), with landfilling (over 150 active sites), incineration (with Poznan as the largest facility), mechanical-biological treatment (MBT), composting, and recycling identified as the main waste management strategies [113]. Nonetheless, Poland demonstrates a deficiency in effective waste-to-energy (WTE) strategies, in contrast to more affluent OECD countries that employ sophisticated recycling and conversion technologies [114]. The implementation of chemical recycling methods, including pyrolysis, gasification, plasma gasification, and hydrothermal processing, has the potential to enhance resource recovery, improve waste management practices, and contribute to the advancement of sustainable waste management [115]. While advancements in WTE technologies have been extensively documented in countries such as Australia, Denmark, Japan, and the USA, Poland remains without a thorough investigation into its technological and economic challenges related to WTE processing [116]. It is essential to address these gaps through innovative conversion techniques and policy integration to achieve sustainable waste management in Poland.

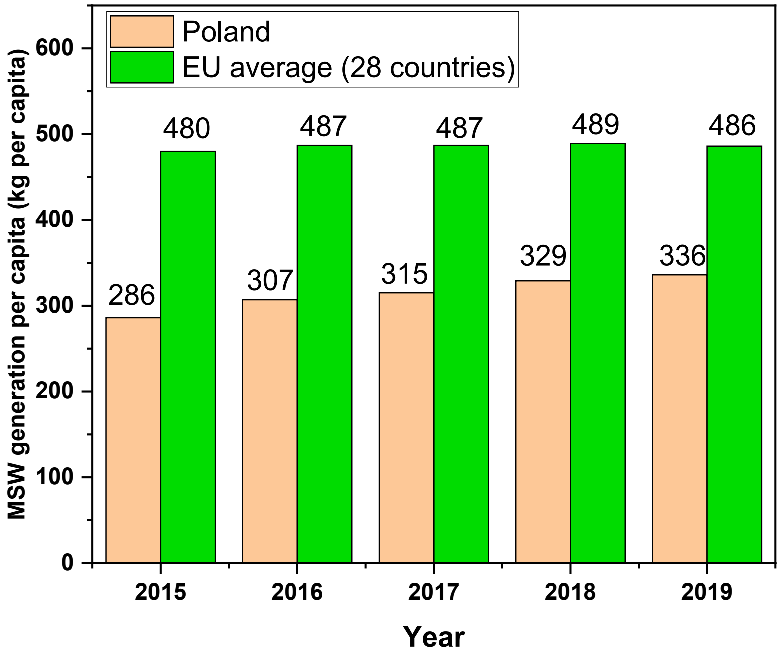


Figure 6.1 Comparison of MSW generation in Poland with EU

Alignment of the presented research with PhD thesis objectives

This chapter presents a thorough evaluation of MSW generation, composition, and management in Poland, laying the groundwork for waste valorisation. In addition, the chapter provides the composition of MSW, focusing on the organic, plastic, and biomass fractions, to demonstrate the technical feasibility of oxidative liquefaction as a method for converting waste into liquid fuels and chemicals. The discussion encompasses regulatory challenges, data reporting gaps, and the necessity for innovative recycling technologies, thereby underscoring the critical importance of sustainable waste conversion. This chapter effectively connects traditional waste-to-energy technologies with oxidative liquefaction, illustrating its ability to improve resource recovery, reduce reliance on landfills, and contribute to the objectives of a circular economy. This establishes a foundation for the subsequent experimental and analytical investigations within the thesis related to oxidative liquefaction of MSW.

6.2 MSW Quality Estimates in Poland

The waste management system in Poland is governed by the Waste Act, which establishes the legal framework for the processes of waste collection, treatment, and disposal. This system involves several key stakeholders, including municipalities, waste management companies, and the Polish Environmental Protection Agency [117]. The database on products and packaging (BDO) serves as a crucial element of this system, overseen by the Polish Minister of Climate and Environment. It is responsible for monitoring packaging waste and ensuring adherence to the Packaging and Packaging Waste Act, in accordance with EU directives [118]. The measurement of waste volume in Poland is conducted using surveys, waste transport registration, and data obtained from waste management companies. However, it is noteworthy that private enterprises frequently underreport the amount of waste collected, a phenomenon attributed to inadequate regulatory enforcement [119]. Between 2001 and 2010, a notable discrepancy was identified between the anticipated waste generation as outlined in the National Waste Management Plan (KPGO) and the actual waste collected as reported by the Central Statistical Office (GUS). This gap can be attributed to several factors, including ineffective waste management practices, the absence of waste collection services in rural areas, inaccuracies in waste generation estimates, and efforts to minimize landfill taxes. Poland faces challenges related to low collection efficiency, which can be attributed to factors such as inadequate funding, subpar infrastructure, and a shortage of personnel, as indicated in the report by the European Environment Agency. In rural regions, there is a notable deficiency in waste collection services, which contributes to the prevalence of illegal dumping and the presence of unaccounted waste. Furthermore, estimates of waste generation frequently exhibit inflation, leading to an overestimation of waste management capacity. It has been observed that certain businesses may engage in the practice of underreporting landfill waste as a strategy to mitigate landfill taxes, which are currently established at 100 PLN per 1 Mg of waste.

In light of the challenges faced, it is noteworthy that waste collection coverage in Poland has experienced a substantial enhancement, rising from 94.1% in 2010 to 98.2% in 2019. Concurrently, the collection of separate biowaste has escalated from 9.9% to 45.1% during this timeframe [120]. The observed improvements indicate a degree of advancement; however, waste management continues to present a multifaceted challenge. This necessitates additional policy adjustments, improved infrastructure, and more robust enforcement mechanisms to guarantee precise waste reporting, heightened recycling efforts, and diminished environmental repercussions.

6.3 MSW Compositional Analysis

The viability of MSW as a significant resource is predominantly influenced by its composition, which is subject to variation due to factors such as geography, demographics, socioeconomic status, consumption patterns, and industrial activity. The Central Statistical Office of Poland (GUS) systematically monitors the generation and composition of waste in various urban areas. The characteristics of waste are notably influenced by residential surroundings, as evidenced by data gathered from 2019 to [121]. As shown in Figure 6.2 single-family homes (S1) produce the highest amount of waste per capita, quantified at 344 kg annually or 0.94 kg daily.

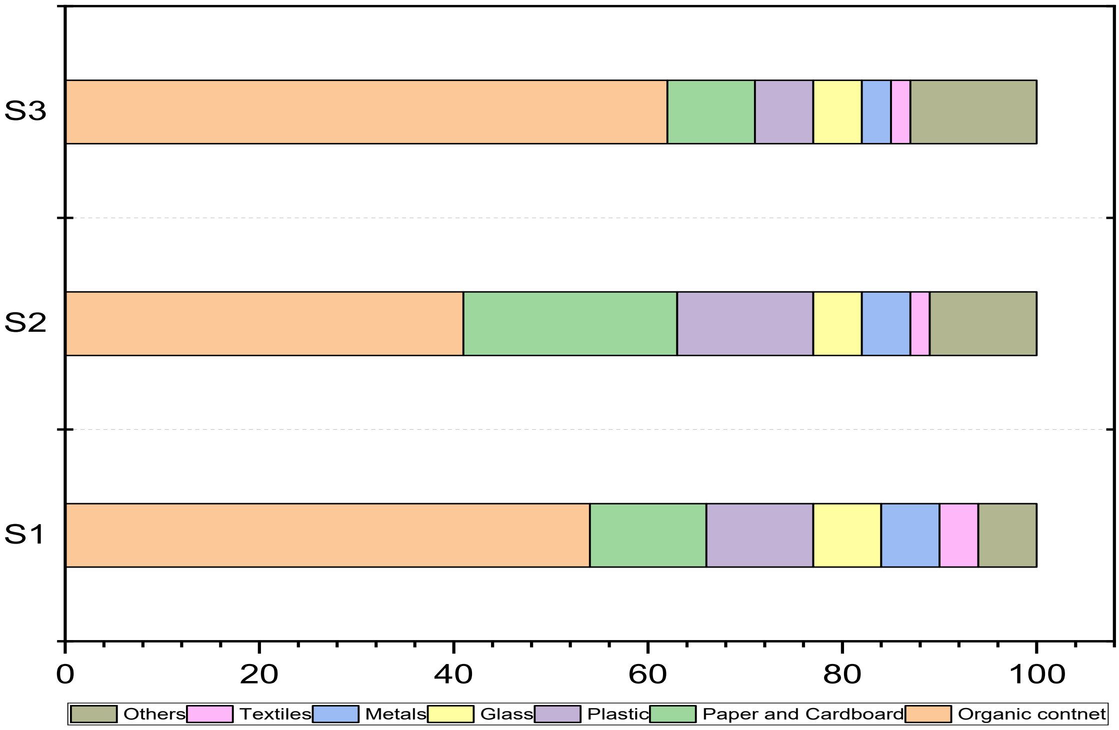


Figure 6.2 Poland average waste composition by environment, expressed as a mass percentage on a wet basis

The predominant component of this waste is organic material, constituting 54% of the total, followed by paper at 12%, plastics at 11%, and glass at 7%. Multi-unit residences (S2) generate an annual waste output of 218 kg, which translates to a daily production of 0.60 kg. The composition of this waste includes organic materials constituting 41%, a significant proportion of paper and cardboard at 22%, and plastics accounting for 14%. Rural households (S3) produce an annual waste of 296 kg, translating to a daily average of 0.81 kg. This waste exhibits a significant organic content of 62%, while the proportions of plastic and paper waste are comparatively lower, at 6% and 9%, respectively. Furthermore, the type of heating system employed influences the composition of waste, with wood and coal heating generating a greater amount of ash and combustion residues compared to gas or electricity-based systems [118].

The fuel viability of Polish MSW is determined by several factors, including the grain fraction, moisture content, percentage of organic matter. Detail proportion of major constituents making up MSW in two big cities of Poland has been provided in Table 6.1. Nevertheless, the available waste composition data for various Polish cities is predominantly outdated, with the most credible figures accessible only up to the year 2005. The examination of municipal waste in Wroclaw from 1992 to 2005 reveals notable seasonal fluctuations in both moisture and organic content. The analysis identifies that the 10–40 mm fraction is characterized by a higher concentration of biodegradable materials, whereas the 40–80 mm fraction is predominantly composed of combustibles, including paper and plastics. In a similar vein, the MODECOM technique was employed in 2001 in Poznan for the analysis of household waste composition, while the SWA tool, as part of the EU 5th Framework Program, evaluated waste generation in Krakow in 2003. The findings from these studies offer valuable insights into both packaging and non-packaging waste, which are critical for the development of effective waste-to-energy conversion strategies. In light of the absence of current data, it is imperative to conduct additional investigations to refresh the understanding of waste composition trends, refine waste recovery methodologies, and improve sustainable waste management strategies in Poland.

Table 6.1 Household municipal garbage in Wrocław and Krakow consists of packaging and non-packaging waste items [114]

Material	**Wrocław/inhabitant Per year**		**Krakow/inhabitant Per year**		**Average**	
	% mass in wet source	kg/inhabitant Per year	% mass in wet source	kg/inhabitant Per year	% mass in wet source	kg/inhabitant Per year
Waste material from packaging						
Paper	3.45	9.50	2.72	6.40	3.2	8.21
Plastic	5.80	16.30	4.96	11.89	5.2	14.12
Glass	10.15	28.15	9.48	22.55	9.7	25.39
Metals	0.80	1.65	1.51	3.55	1.14	2.81
Nonmetals	0.58	1.65	0.19	0.39	0.39	1.03
Composites	1.40	3.80	1.22	2.85	1.2	3.39
Waste material from non-packaging						
Paper	4.95	13.75	7.49	18.02	6.24	16.01
Plastic	4.97	13.85	7.08	16.97	6.12	15.39
Glass	1.77	4.98	0.58	1.45	1.18	3.19
Metals	0.48	1.35	0	0	0.20	0.71
Nonmetals	0.08	0.24	0.09	0.27	0.12	0.30
Composites	1.22	3.36	1.92	4.55	1.58	3.89

6.4 Overall MSW Management Scenario

The management of MSW has progressed through the implementation of diverse technologies for waste-to-energy and recycling. These technologies encompass pyrolysis, gasification, incineration, anaerobic digestion, and mechanical-biological treatment. The efficacy of these methods in decreasing reliance on landfills, recovering energy, and mitigating environmental impact has been substantiated through various studies (Table 6.2). Nonetheless, obstacles remain, especially in the management of diverse waste streams, non-recyclable plastics, and composite materials that traditional methods find difficult to process effectively. Poland, similar to numerous other countries, continues to depend significantly on landfilling and incineration methods. These practices, although prevalent, raise substantial environmental and economic issues related to emissions, ash production, and elevated operational expenses. In light of the escalating MSW crisis and the imperative for enhanced sustainable waste valorization techniques, oxidative liquefaction presents itself as a viable alternative. This method presents the opportunity to transform heterogeneous polymeric waste into useful liquid chemicals and fuels through regulated oxidative processes, offering a more energy-efficient and scalable alternative to traditional approaches. The integration of oxidative liquefaction within Poland's current waste management system presents a viable approach for the effective utilization of hard-to-recycle waste fractions.

This strategy not only mitigates environmental impacts but also promotes resource recovery and aligns with the objectives of a circular economy.

Table 6.2 Assessment of traditional and nontraditional waste-to-energy conversion techniques [122]

Criteria	**Traditional Techniques**				**Non-traditional techniques**		
	Composting	Anaerobic digestion	Landfilling	Incineration	Pyrolysis	Gasification	Plasma gasification
Plant total life and technical capabilities comparison							
Plant life (years)	10-15	15-20	30	30	20	30	20
Categorization of waste required	✓	✓	✓	✓	✓	✓	✓
Wet waste handling	Restricted	Restricted	Restricted	×	Restricted	Restricted	Restricted
Computerization level	↓	↓	↓	Modest	Modest	Modest	↑
Hazardous waste handling	↓	↓	↓	Modest	↑	↑	↑
Cost Analysis							
Typical capital cost ($M)	10	50	70	115	85	80	100
Compliance cost	Modest	↓	↓	↑	Modest	↑	↑
Operational cost ($M)	1	2	2	8	7	6.5	8.2
Total income ($M)	-0.1	+0.5	+0.5	+0.5	+0.5	+3.1	+3.2
Total energy							
Total energy produced (kg/ton of MSW)	-2.7-3.1	9-13	4-9	36-45	45-50	35-63	63-80
Willingness level comparison							
Society willingness level	Modest	Modest	↑	↓	↓	↓	↓
Customer willingness level	↑	↑	Modest	↑	Modest	Modest	Modest

Technology willingness level	↑	↑	↑	↑	Modest	Modest	↓

6.5 Summary of Key Findings

The analysis underscores the escalating difficulties associated with the management of MSW, as global waste generation is anticipated to surpass 2 billion tons per year by 2025. Poland encounters comparable challenges, as landfilling remains the primary method of waste disposal, notwithstanding the European Union's initiatives advocating for recycling and waste-to-energy approaches. The presence of inefficient waste collection systems, the underreporting of waste data, and the existence of gaps in rural collection services have led to notable discrepancies between the predicted and actual amounts of waste collected. The characteristics of MSW exhibit variability influenced by factors such as housing type, socioeconomic conditions, and geographic location. Single-family homes produce the greatest amount of waste per capita, quantified at 344 kg per year, with organic waste constituting 54% of this total. In contrast, multi-unit residences generate 218 kg per year, and rural homes account for 296 kg per year, each exhibiting distinct waste distribution patterns. Plastics represent a significant portion of MSW, comprising approximately 10–12%. This situation presents both an environmental concern and a potential avenue for energy recovery. At present, the predominant waste management strategies employed in Poland include landfilling, incineration—particularly notable is the Poznan facility, which is the largest of its kind—mechanical-biological treatment, composting, and recycling. However, the implementation of advanced waste-to-energy technologies is still relatively constrained. The data indicates a significant increase in recycling rates, rising from 9.9% in 2010 to 45.1% in 2019. However, it is important to note that inefficiencies in waste collection continue to be a challenge, especially in rural regions. Current waste-to-energy technologies, including pyrolysis and gasification, exhibit potential; however, they necessitate significant energy input and face challenges in processing mixed, non-recyclable, and composite waste materials. This highlights the necessity for a viable and scalable method for waste conversion. Oxidative liquefaction presents a viable approach for the transformation of MSW into liquid fuels and valuable chemicals, operating under moderate conditions and demonstrating a lower energy requirement in comparison to pyrolysis and incineration methods. The incorporation of oxidative liquefaction within Poland's waste management system has the potential to improve resource recovery, reduce reliance on landfills, and contribute to the objectives of a circular economy.

Introduction to the next chapter

This chapter has laid the groundwork for comprehending the composition of MSW, the challenges associated with its treatment, and the necessity for innovative technologies in waste conversion. The forthcoming chapter will broaden the scope of this investigation by performing a comparative analysis of oxidative liquefaction concerning MSW and PPEs. This analysis aims to assess their degradation potential, chemical composition, and process efficiency. This comparison is crucial due to the significant heterogeneity of MSW, in contrast to the predominantly synthetic polymer composition of plastic waste (PPE). This distinction facilitates an evaluation of the potential of oxidative liquefaction to treat distinct waste streams.

Chapter 7

7 Comparative Analysis of Oxidative Liquefaction Process for MSW and PPEs

Paper VI (Appendix F): Oxidative liquefaction: a method of valorisation of municipal solid waste and personal protective equipment used in the medical sector

7.1 Background

Oxidative liquefaction is a thermochemical process that decomposes complex organic compounds into liquid products by utilizing oxygen or an oxygen donor at elevated temperatures and pressures. Its efficacy in the treatment of WTBs wastes, the facilitation of glass fiber recovery, and the production of OCCs has been demonstrated in previous chapters. The successful application of oxidative liquefaction in the processing of composite materials has prompted its investigation into two additional significant waste streams: MSE and polymeric PPE refuse from the healthcare sector.

Rapid urbanization, increasing living standards, and population growth have all contributed to a significant increase in the global generation of MSW. The World Bank (2023) estimates that the average individual produces 0.74 kg of waste per day, which equates to approximately 2 billion kilograms of MSW annually of this total, 33% remains uncollected [123]. Furthermore, the imperative necessity for sustainable waste processing solutions is underscored by the fact that half of the global population lacks access to adequate waste management services [124].

The current waste management methods, such as mechanical recycling, incineration, and landfilling, are significantly constrained by their low material recovery efficacy, environmental contamination, and high energy consumption. In order to confront these obstacles, this chapter investigates the potential of oxidative liquefaction as a method for the processing of MSW and PPE refuse. There are two primary objectives: to decrease the volume of solid waste and to generate OCCs for waste-to-resource recovery.

In order to characterize waste materials and analyze decomposition behavior, this study implements ultimate and proximate analysis, FTIR, and GC-FID to identify liquid products. The oxidative liquefaction assays evaluate the impact of temperature, oxidant concentration, and waste-to-liquid ratio on the efficacy of the process. Additionally, in order to optimize experimental conditions for the most efficient waste reduction and chemical recovery with the least amount of energy consumption, the TSR and OCC yield are quantified. This research endeavors to establish oxidative liquefaction as a viable and scalable waste management approach by addressing these aspects, thereby bridging the divide between waste reduction and high-value chemical production.

Purpose of the experimental study

The objective of this experimentation demonstrated in chapter is to evaluate the oxidative liquefaction characteristics of PPEs and MSW in terms of TSR, OCCs yield, and energy consumption. The study endeavors to determine the disparities in thermal degradation efficiency and chemical recovery potential of these two waste streams by optimizing critical parameters, including temperature, oxidant concentration, and waste-to-liquid ratio. Decomposition pathways are assessed using modern analytical methods, such as FTIR, TGA, and inverse analysis of process heating, to guarantee a data-driven comparison of their potential for valorization.

Alignment of the presented research with PhD thesis objectives

This investigation broadens the scope of oxidative liquefaction beyond WTBs to evaluate its efficacy in the treatment of MSW and PPEs. This chapter further validates oxidative liquefaction as a versatile waste valorization technique by comparing the degradation efficacy, OCC recovery, and energy consumption of these waste streams, which builds on previous findings. The comparative analysis provides valuable insights that contribute to the overarching thesis objective of the development of a scalable and sustainable recycling approach for a variety of mixed waste streams. This reinforces the potential of the approach for large-scale waste-to-resource applications.

7.2 Materials and Methods

The oxidative liquefaction of PPE and MSW was conducted to transform the waste materials into OCCs through systematically structured experiments utilizing CCD. This process involved varying parameters such as temperature, oxidant concentration, and the waste-to-liquid ratio. An inverse analysis of process heating was performed to ascertain the temperature range associated with significant organic degradation, as well as to evaluate the exothermic or endothermic characteristics of the reaction. The evaluation of process performance was conducted through the measurement of TSR, OCC yield, and energy consumption, with ANOVA utilized to optimize the operational parameters. Comprehensive descriptions of the experimental protocols and analytical techniques are presented in Chapter 2.

7.3 Results and Discussion

7.3.1 Comparative FTIR analysis of MSW and PPE

The FTIR analysis of MSW and PPEs (Figure 7.1) waste revealed significant differences in their chemical compositions, which can directly influence the final yield and quality of liquid products obtained through oxidative liquefaction. The FTIR spectrum of MSW exhibited distinct peaks associated with the degradation of lipids, hydrocarbons, cellulose fibers, and organic matter. Notably, peaks at 2950, 2920, and 2850 cm^{-1} corresponded to C-H stretching vibrations, while the peak at 1710 cm^{-1} indicated the presence of C=O stretching vibrations. Additional peaks at 1460 cm^{-1} and 1380 cm^{-1} were linked to CH_3 and CH_2 group vibrations, suggesting a complex heterogeneous composition. The broad band between 1100–870 cm^{-1} confirmed the presence of silicates, aromatic ethers, and polysaccharides, reinforcing the diverse nature of MSW.

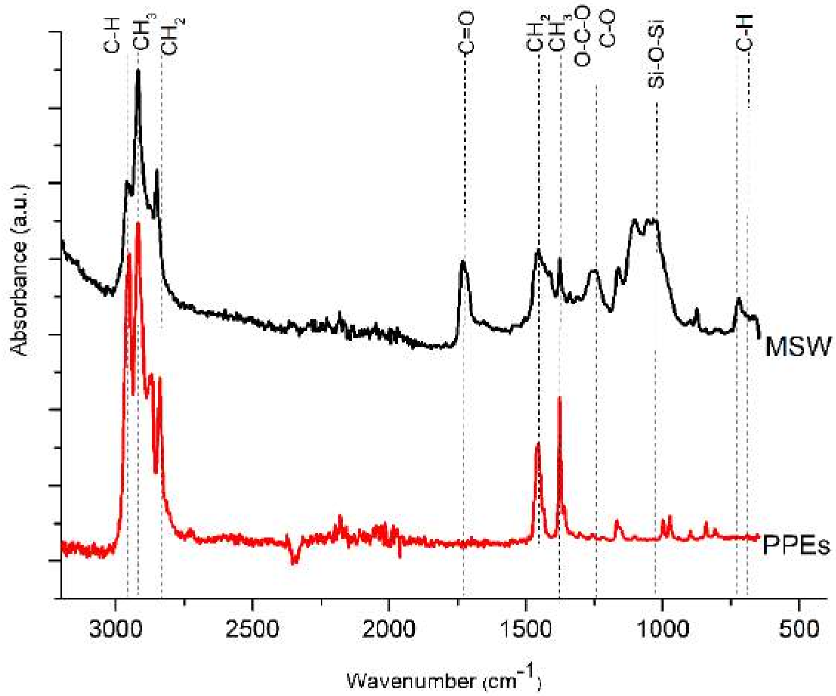


Figure 7.1 FTIR spectra of MSW and PPE samples

Conversely, the FTIR spectrum of PPEs exhibited characteristic peaks commonly associated with PP and related polymers. Prominent peaks at 2950 and 2920 cm^{-1} indicated antisymmetric stretching vibrations of CH_3 and CH_2 groups, while peaks at 2890 and 2850 cm^{-1} corresponded to symmetric stretching vibrations. The significant peak at 1460 cm^{-1} was linked to in-plane antisymmetric deformation vibrations of CH_2, whereas the 1380 cm^{-1} peak was attributed to in-plane symmetric deformation vibrations of CH_3. These findings highlight the distinct chemical structures of the two waste streams, which in turn affect their decomposition pathways and potential for liquid product formation during oxidative liquefaction.

7.3.2 Inverse analysis of process heating

The inverse analysis of process heating yielded significant insights into the thermal degradation dynamics of MSW and PPEs during the oxidative liquefaction process. The temperature profiles (Figure 7.2 (a)) obtained within the reactor indicated that the heating profiles for both waste types exhibited analogous patterns; however, they displayed notable deviations when compared to the dummy runs executed with water alone. It was observed that an intersection of heating profiles occurred after approximately 20 minutes, succeeded by a subsequent increase in temperature, which suggests the exothermic characteristics of the decomposition process. An analysis of heating rates (Figure 7.2 (b)) indicated notable variations between the two waste streams. The preliminary experiment utilizing water demonstrated consistent heating rates devoid of abrupt peaks. In contrast, the preliminary experiment involving the oxidant revealed a significant peak within the temperature range of 110–140°C, which can be attributed to the decomposition of the oxidant. In the analysis of MSW, two closely positioned peaks were identified within the temperature range of 90–120°C, with heating rates varying between 1 and 1.5 K/sec. In contrast, PPEs demonstrated a prominent singular peak within the temperature range of 130–150°C, accompanied by a notably elevated heating rate of 5 K/sec. The results indicate that PPEs exhibits a rapid decomposition process attributed to its polymeric composition, while MSW, due to its heterogeneous nature, undergoes a more gradual thermal degradation.

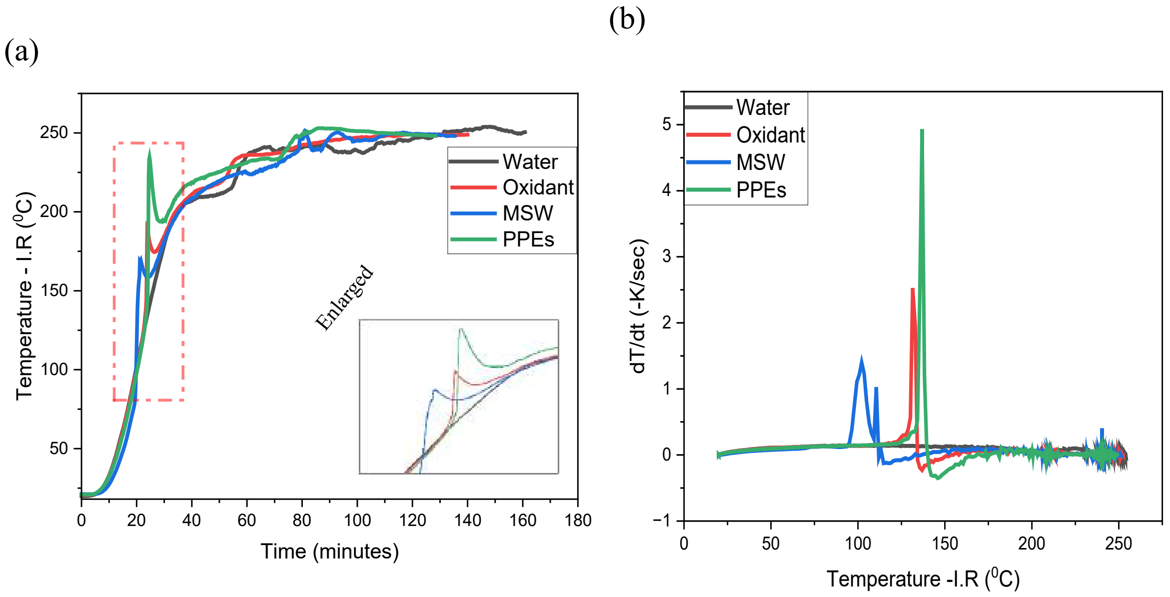


Figure 7.2 Comparison of (a)inside reactor temperature profiles (b) heating rates for MSW and PPEs

In order to enhance the quantification of energy contributions, the supplementary heat generated during the process of oxidative liquefaction was systematically calculated. The absorbed heating power for water served as a reference point, and the heat absorbed during the modeled runs involving MSW and PPEs was analysed for comparative purposes. The findings demonstrated that the oxidative liquefaction process for both categories of waste exhibited exothermic characteristics within defined temperature intervals, thereby augmenting the energy output of the system. Nevertheless, the process exhibited limitations in self-sustainability, necessitating the introduction of external heat input to facilitate the complete decomposition of the material. The observations presented are essential for enhancing process efficiency. A comprehensive understanding of the thermal behaviour associated with various waste types can inform reactor design and dictate energy input requirements for large-scale applications.

7.3.3 Comparison of TSR for MSW and PPEs *(RG-3)*

The TSR quantifies the degree of solid waste degradation that occurs during oxidative liquefaction, serving as a critical metric for evaluating process efficiency. The comparative thermal chemical stability results for MSW and PPEs exhibited notable trends that were affected by changes in process parameters (Figure 7.3). The maximum TSR for MSW was observed at 95%, attained under specific parameters of 300°C, 60% oxidant concentration, and a waste-to-liquid ratio of 3, accompanied by an energy consumption of 1.4 kWh. A comparable pattern was noted for PPEs, with the peak TSR attaining 96.67% under identical process parameters, although accompanied by a marginally lower energy requirement of 1.2 kWh. A crucial element affecting TSR is the composition of the waste material. The PPEs, primarily made up of synthetic polymers including PP, PE, and PVC, demonstrated a more consistent degradation pattern in contrast to the varied characteristics of MSW. The elevated volatile content in PPEs was associated with an increased reduction efficiency. In contrast, MSW comprises a heterogeneous mixture of organic and inorganic constituents, including cellulose-derived components such as paper and wood. These materials are more likely to yield residual char instead of completely converting into liquid or gaseous byproducts. Moreover, the presence of heteroatoms in MSW can function as impurities, which may impede oxidation efficiency and result in uneven reaction kinetics, wherein certain fractions exhibit resistance to complete degradation under the same reaction conditions.

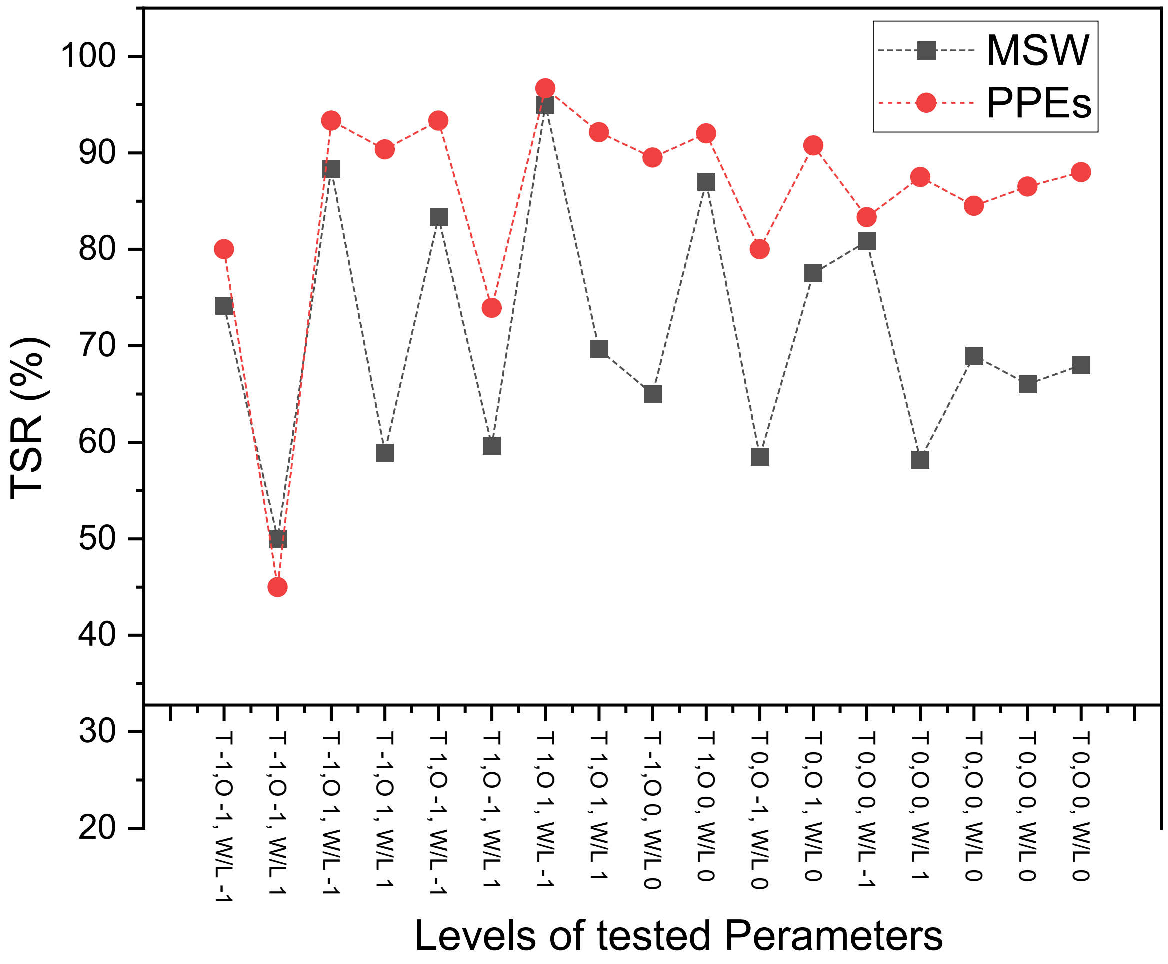


Figure 7.3 Extent of TSR achieved for MSW and PPEs under different combinations of experimental conditions

The impact of process parameters, including temperature, oxidant concentration, and waste-to-liquid ratio, was critical in determining the outcomes of TSR. The elevation of temperature, coupled with an augmented concentration of oxidants, significantly enhanced the decomposition of organic matter, thereby leading to a more pronounced decrease in solid residue. Nonetheless, a waste-to-liquid ratio of approximately 3 was determined to represent the most effective equilibrium between the availability of reactants and the efficiency of heat and mass transfer processes.

Despite these findings, the inherent complexity of MSW presents a challenge to achieving uniform degradation, in contrast to plastic PPEs, where a consistent polymer composition ensures predictable conversion rates. The findings underscore the importance of tailored process conditions that are optimized for specific waste compositions. This emphasizes the ongoing requirement for refinement in oxidative liquefaction methodologies to improve waste reduction efficiency and minimize energy consumption.

7.3.4 Comparison of OCCs yields for oxidative liquefaction of MSW and PPEs *(RG-3)*

The production of oxygenated OCCs through oxidative liquefaction exhibited notable variability when comparing MSW to PPEs (Figure 7.4). This discrepancy can be attributed to the inherent differences in their compositional characteristics and degradation mechanisms. The yield of OCC derived from MSW was observed to range from 13.04 to 51.51 g/kg. In contrast, the yields associated with polymeric PPEs were significantly elevated, spanning from 37.43 to 212.66 g/kg. This disparity suggests a superior conversion efficiency for polymeric PPE waste compared to MSW. The influence of temperature on the formation of OCC was significant, with PPEs demonstrating optimal yield at 200°C. However, an increase in temperature to 300°C led to a reduction in yield, attributed to excessive thermal degradation and the conversion of oxygenated intermediates into gaseous byproducts. A comparable pattern was noted for MSW; however, the overall organic OCCs yield was consistently lower. This discrepancy can be attributed to the heterogeneous composition of MSW, which encompasses non-degradable inorganic materials, including glass and metals, that do not facilitate chemical recovery processes.

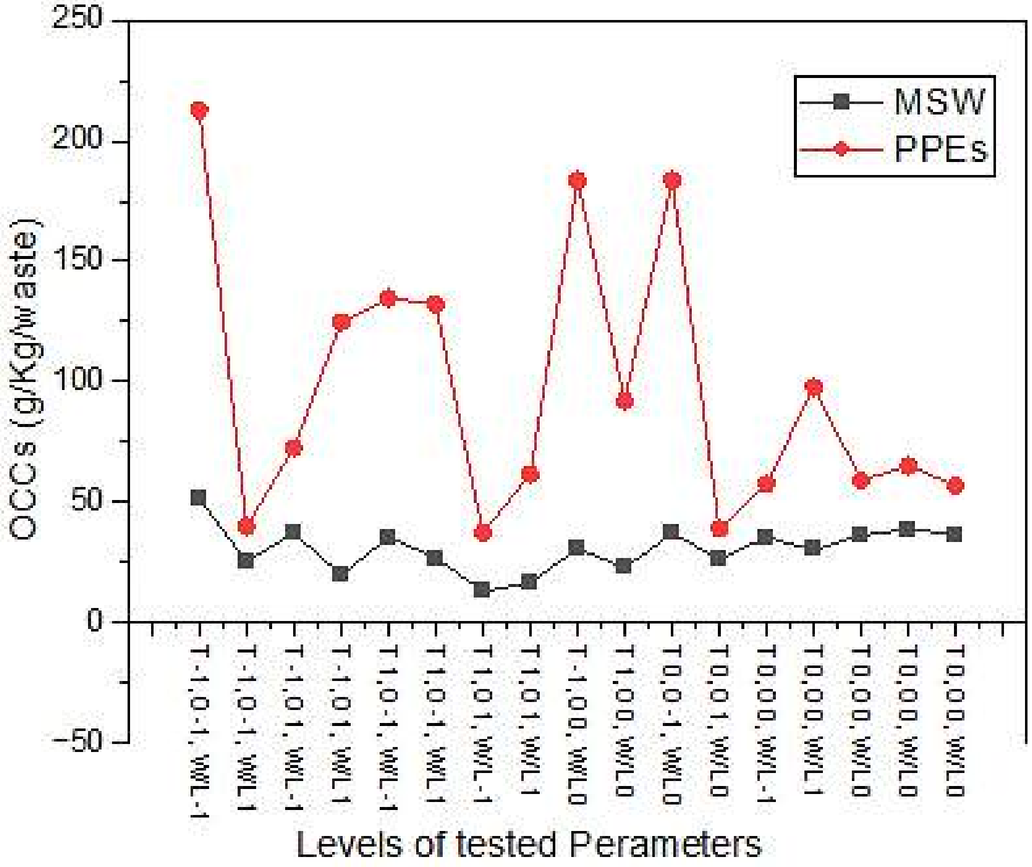


Figure 7.4 Yields of OCCs achieved for PPEs and MSW under various combination of reaction parameters

The concentration of oxidants exhibited a significant impact on the formation of OCC. Specifically, a reduced concentration of H_2O_2 at 30% was found to promote the production of OCC in PPEs, whereas an elevated oxidant level of 60% resulted in excessive oxidation, leading to the degradation of compounds into volatile gases. The behavior of MSW exhibited a similar pattern; however, its OCC yield demonstrated reduced sensitivity to variations in oxidant concentration. The waste-to-liquid ratio had a significant impact on OCC yield, as evidenced by the increase from 3:1 to 7:1, which corresponded with a reduction in OCC production for both types of waste. This phenomenon can be attributed to dilution effects, which subsequently diminished the efficiency of oxidative conversion. The introduction of excess water into the system resulted in a pronounced decrease in OCC yield at 200°C for PPEs, indicating that achieving an optimal equilibrium between waste and reaction medium is essential for maximizing chemical recovery.

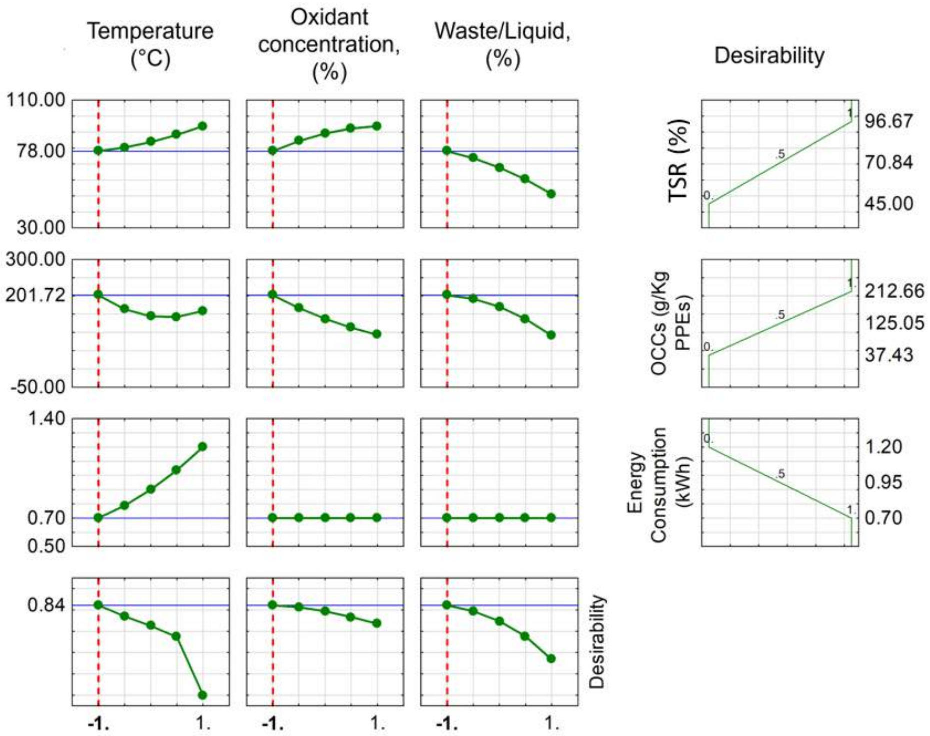
A comparative assessment indicated that PPEs consistently yielded higher OCC outputs compared to MSW, attributable to their uniform and polymer-dense composition, which enhances the efficiency of oxidative degradation. The heterogeneous and inorganic-laden characteristics of MSW resulted in a decrease in conversion efficiency and constrained the production of high-value oxygenated compounds. The findings underscore the significance of refining critical process parameters, such as temperature, oxidant concentration, and waste-to-liquid ratio, to improve OCC yields. The results indicate that PPE waste possesses significant potential for transformation into valuable chemical intermediates, thereby reinforcing its feasibility for sustainable waste-to-resource recovery methodologies.

7.3.5 Comparative analysis of optimal reaction conditions for oxidative liquefaction of MSW and PPEs *(RG-1,3&4)*

The study aimed to identify and compare the optimal reaction conditions for the oxidative liquefaction of MSW and PPEs, concentrating on three primary parameters: temperature, oxidant concentration, and waste-to-liquid ratio, while maintaining constant pressure and residence time. The findings (Figure 7.5 (a)) indicate that while elevated temperatures contribute to an enhancement in TSR, there is a concomitant minor decline in the yield of OCCs, alongside a linear escalation in energy consumption. A negative correlation was identified between energy consumption and temperature, indicating that reduced temperatures may enhance energy efficiency. Moreover, reduced oxidant concentrations were observed to facilitate the formation of OCC by inhibiting excessive oxidation, which would otherwise lead to the degradation of intermediate compounds. Furthermore, a diminished waste-to-liquid ratio promoted the occurrence of complete reactions while maintaining energy consumption at minimal levels. The decrease in waste volume per unit of liquid contributed to enhanced mass transfer and improved heat distribution.

In the case of MSW (Figure 7.5 (b)), a comparable trend was noted, indicating a preference for lower temperatures to optimize energy efficiency while minimizing OCC production. It was observed that an intermediate concentration of oxidant is optimal for MSW processing, as elevated concentrations resulted in overoxidation, adversely affecting the yields of OCCs. The findings suggest that maintaining an optimal waste-to-liquid ratio is critical, as an increased liquid volume may lead to heightened energy consumption per unit of waste processed. The findings underscored the critical need to optimize operational parameters in order to enhance TSR and OCCs, concurrently reducing energy consumption. The conclusive optimized reaction parameters for the oxidative liquefaction process of MSW and PPEs were established at a temperature of 200°C. The oxidant concentrations were identified as 30 wt.% for PPEs and 45 wt.% for MSW, with a waste-to-liquid ratio set at 3 wt.%. The results underscore the necessity for customized process parameters to enhance the efficiency of oxidative liquefaction across various waste streams.

(a)



(b)

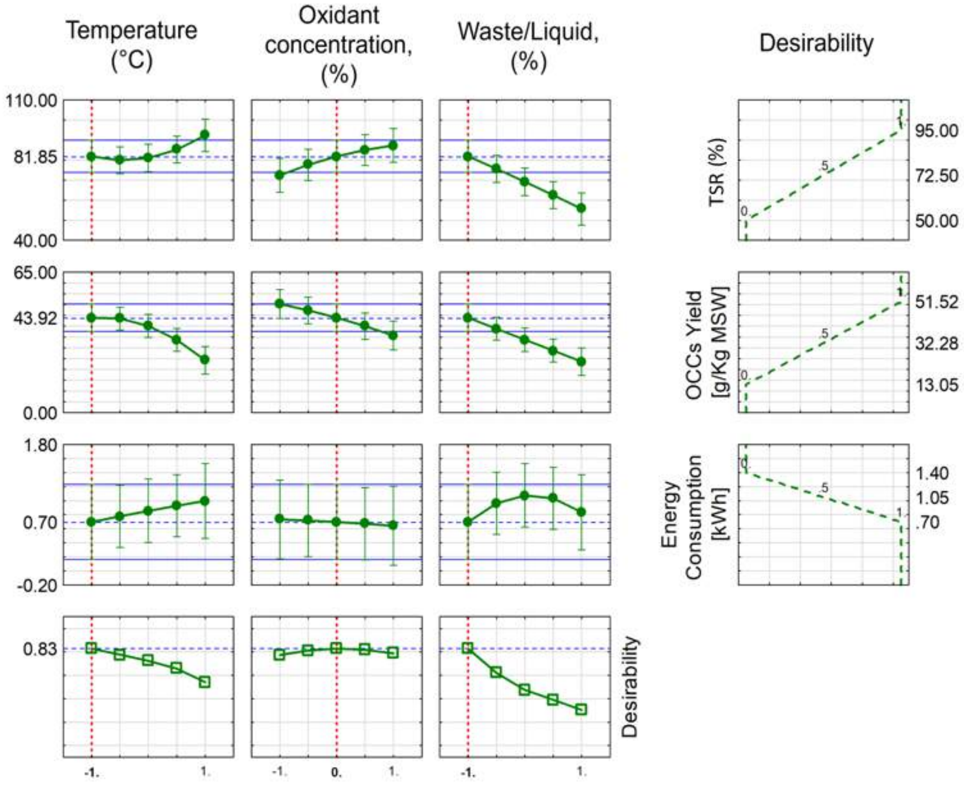


Figure 7.5 Comparative optimal reaction conditions for oxidative liquefaction of (a) PPEs, (b) MSW

7.4 Summary of Outcomes

In this chapter, the comparative analysis of oxidative liquefaction processes for MSW and PPEs revealed notable differences in degradation behaviours, which were significantly affected by the composition of the feedstock and the specific reaction conditions employed. The analysis of PPEs, which are predominantly made of synthetic polymers, demonstrated a greater TSR and yields of OCCs in comparison to MSW, characterized by its diverse array of organic and inorganic materials. The optimal reaction conditions were determined to be 200°C, with a 30 wt.% oxidant concentration and a 3:1 waste-to-liquid ratio for PPEs. In contrast, MSW necessitated a marginally elevated oxidant concentration of 45 wt.% to facilitate efficient conversion. The investigation further elucidated that an elevation in temperature augments TSR, concurrently diminishing OCC yields and escalating energy consumption. This underscores the necessity for process optimization aimed at targeted resource recovery. In summary, oxidative liquefaction represents a viable method for the valorization of polymeric waste into valuable chemical products. It necessitates the implementation of specific operational strategies tailored to various waste types to enhance both efficiency and sustainability.

Introduction to next chapter

The results presented in this chapter provide a robust basis for the application of oxidative liquefaction to PV panel waste, which introduces further complexities owing to its intricate multi-material structure, encompassing polymers, glass, and metals. The subsequent chapter will investigate the viability of this process concerning PV waste, concentrating on the optimization of reaction conditions to improve polymer degradation and evaluating the impact of inorganic constituents on process efficacy. The successful development of an efficient recycling method for PV waste is anticipated to enhance the sustainability of the renewable energy sector. This advancement will address challenges associated with end-of-life disposal and facilitate the recovery of materials for future energy technologies.

Chapter 8

8 End-Of-Life Disposal of Photovoltaic Panels, Outcomes, and Challenges

Paper VII (Appendix G): Innovative recycling of end-of-life photovoltaic panels with the aim of polymer degradation and valuable chemical production

8.1 Background

The rising utilization of PV technology as a renewable energy solution has sparked heightened awareness about the management of PV panels at the end of their life cycle. The contribution of solar panels to the reduction of greenhouse gas emissions is substantial; however, their disposal poses an environmental challenge. This is primarily due to their intricate multilayer structure, which includes polymers, glass, metals, and semiconductor materials [125,126]. With the growth of the global solar energy sector, the amount of decommissioned PV panels is projected to increase significantly, highlighting the urgent need for effective and sustainable recycling strategies [127].

Traditional disposal techniques, including landfilling and incineration, present significant challenges both environmentally and economically, resulting in the depletion of valuable resources and the risk of environmental pollution. Presently, recycling methodologies encompass mechanical processing, thermal decomposition, and chemical treatments; however, these techniques encounter constraints regarding efficiency, energy usage, and material recovery rates. For example, mechanical recycling frequently leads to downcycling, whereas pyrolysis necessitates significant energy consumption and has the potential to generate harmful emissions [128,129]. Consequently, it is essential to develop a recycling strategy that effectively balances material recovery, energy efficiency, and environmental sustainability.

This chapter examines the use of oxidative liquefaction as a novel approach for recycling PV panels, with a specific emphasis on the degradation of polymers and the generation of valuable oxygenated secondary compounds. Oxidative liquefaction utilizes hydrothermal treatment alongside an oxidizing agent, commonly H_2O_2, to decompose organic components found in PV waste. The research focuses on assessing the effectiveness of this process through the analysis of thermal degradation patterns, identification of optimal reaction conditions, and measurement of the yields of TPD and OCCs. Additionally, an inverse analysis of the process heating behavior is performed to evaluate the thermal characteristics and exothermic properties of polymer degradation, offering valuable insights into the energy demands of the process.

Purpose of experimental study

This study aims to assess the practicality of oxidative liquefaction as a progressive recycling technique for decommissioned PV panels. The study seeks to optimize the process for improved material recovery and energy efficiency through a systematic analysis of thermal degradation patterns, reaction conditions, and the production of OCCs. The study aims to identify the optimal combination of temperature, oxidant concentration, and waste-to-liquid ratio to enhance TPD while reducing energy consumption. Furthermore, the research examines the inverse heating behavior of the process to gain insights into the thermal characteristics associated with PV panel breakdown, which is essential for advancing the technique for industrial applications.

Alignment of the presented research with PhD thesis objectives

This chapter broadens the use of oxidative liquefaction to include PV panel waste, drawing from earlier studies on polymeric waste streams like WTBs, PPEs, and generic MSW. In contrast to earlier materials, PV panels introduce unique challenges stemming from their multi-material structure, necessitating a more nuanced strategy to enhance polymer degradation while effectively addressing the inorganic components. The results enhance the overarching goal of creating a scalable and energy-efficient approach to recycling intricate waste streams. This research highlights the practicality of oxidative liquefaction as an adaptable approach for waste valorization, connecting sustainable material recovery with the principles of circular economy integration.

8.2 Materials and Methods

The oxidative liquefaction of end-of-life PV panels was performed through systematically designed experiments aimed at assessing TPD and the yield of OCCs. TGA and an inverse analysis of process heating were conducted to elucidate the degradation profile, temperature range, and characteristics of the reaction. Additionally, ANOVA was employed to optimize conditions aimed at maximizing TPD and OCC yield while minimizing energy consumption. Comprehensive descriptions of the experimental protocols and analytical techniques are delineated in Chapter 2.

8.3 Results and Discussions

8.3.1 SEM and EDS analysis of raw PV sample

The analysis conducted using SEM and EDS on raw PV waste samples indicated that only a limited number of elements were present in substantial quantities, whereas the majority were detected in trace amounts, rendering their economic recovery less advantageous. The primary elements observed were carbon (53.7 at.%), oxygen (19.2 at.%), and silicon (16.3 at.%), which mainly derive from polymeric binders and glass materials. Additional elements identified include fluorine (2.6 at.%), aluminium (2.0 at.%), sodium (1.8 at.%), and calcium (1.2 at.%), which were found in significantly lower concentrations. Furthermore, various trace elements, including magnesium, titanium, phosphorus, bromine, chlorine, cerium, praseodymium, and neodymium were detected in concentrations lower than 0.2 at.%, which diminishes their feasibility for economical recovery. The significant inorganic composition, along with the sporadic occurrence of valuable elements, indicates that the economic viability of recovering materials from PV waste via oxidative liquefaction or alternative methods might be constrained. The results underscore the importance of recovery strategies that focus on selective polymer degradation, while also addressing the challenges linked to the extraction of valuable trace metals in economically feasible amounts.

8.3.2 Thermal degradation behaviour of raw PV waste

The analysis of TGA and DTG concerning PV panel waste (Figure 8.1) indicates the presence of two separate stages of thermal decomposition. At the outset, within the temperature range of 300-385°C, a gradual reduction in mass occurs as a result of the release of volatile organic compounds, and the liberation of acetic acid from the vinyl acetate monomer present in the EVA structure [130,131]. This phase reflects the breakdown of low molecular weight organic constituents. During the second stage, occurring between 385-500°C, more stable organic materials, including PE PP, polyvinyl butyral (PVB), polyester resins, and silicone-based polymers, especially EVA, experience additional decomposition [132]. This phase encompasses the disintegration of intricate organic molecules, resulting in the formation of volatile compounds and char residues. The TGA and DTG trends at heating rates of 4 and 16 K/min exhibit consistent decomposition behaviour, with minor variations in decomposition temperatures, thereby affirming the stability of the observed thermal transitions.

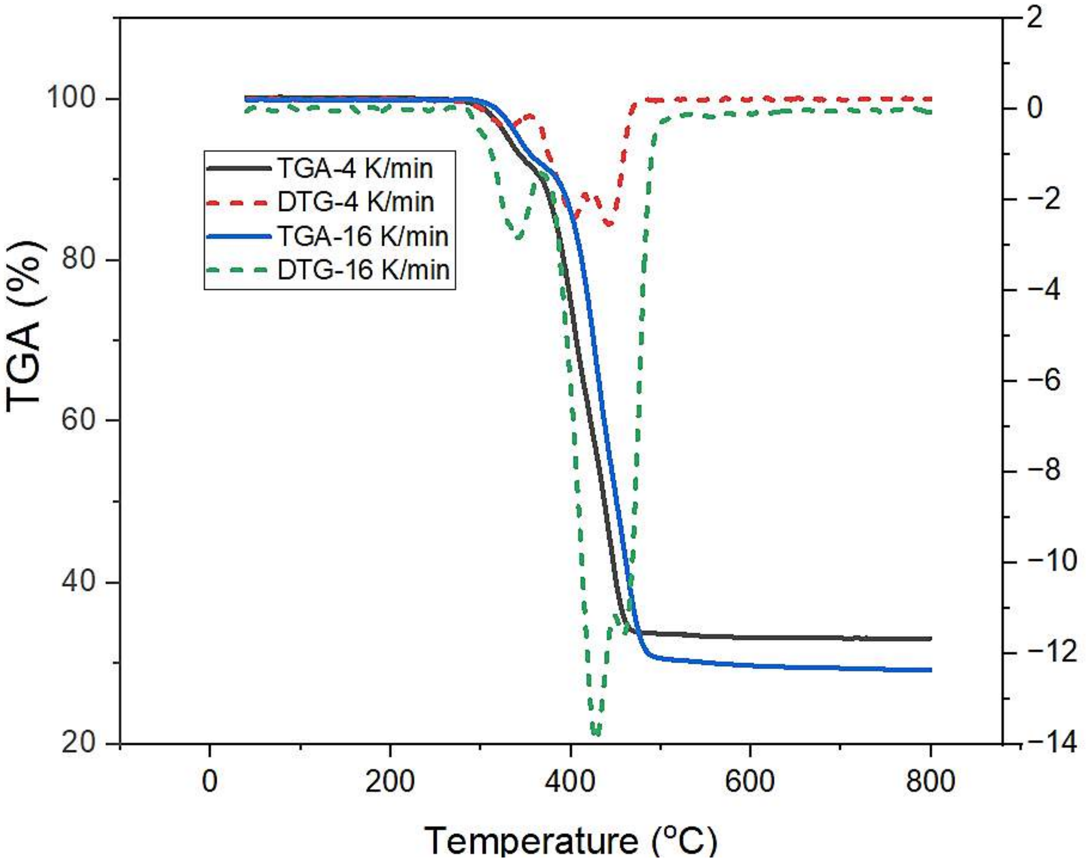


Figure 8.1 Thermal degradation patterns of PV waste at two different heating rates

8.3.3 Inverse analysis of process heating for oxidative liquefaction of PV waste

The temperature profiles observed during the oxidative liquefaction of PV waste exhibit (Figure 8.2 (a)) notable variations when contrasted with control runs utilizing only water. After 30 minutes, the heating profiles of PV waste with water and oxidant intersected, suggesting the introduction of heat, which was not observed during the water-only dummy runs. The findings were further corroborated by the heating rate profiles, which exhibited sharp peaks in the experiments involving water + oxidant and PV waste, indicating exothermic decomposition. The observed peaks manifested at marginally reduced temperatures for the PV waste in contrast to the dummy runs, with heating rates ranging from 9 to 12 K/min (Figure 8.2 (b)).

(a) (b)

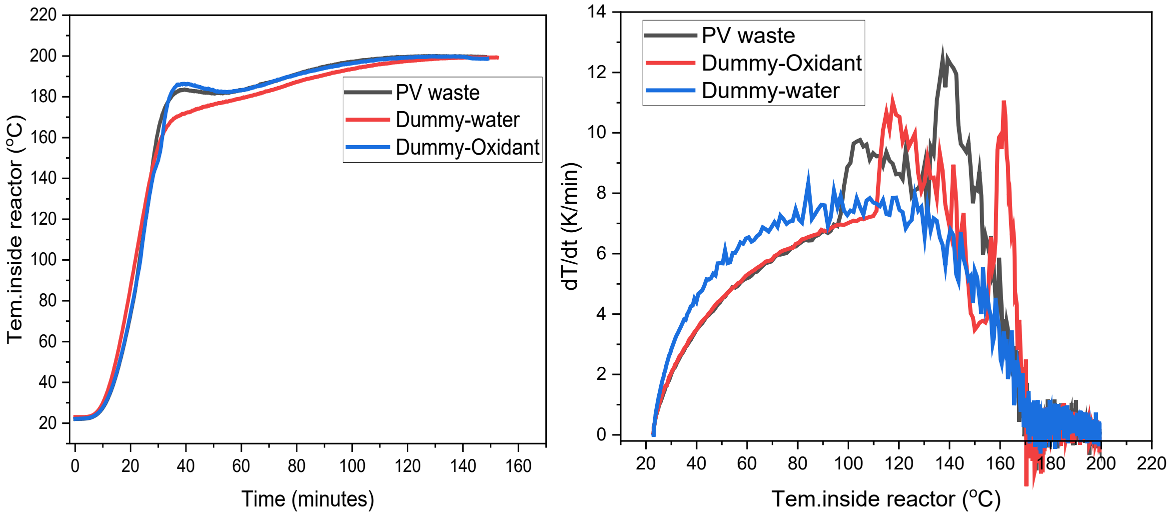


Figure 8.2 Comparison of (a) inside reactor temperature profiles (b) heating rates for PV waste and dummy runs

The breakdown of waste and oxidants in the oxidative liquefaction process generated extra heat, thereby accelerating the reaction. Notably, the reaction involving PV waste achieved 200°C 8-10 minutes sooner compared to the water-only dummy run. The supplementary heat was determined through an energy equation, utilizing the heat absorbed during the preliminary trials with water as the reference point. The total heat absorbed was 311 watts for the water-only run and 286 watts for the water + oxidant run, while the modelled PV waste run absorbed 288.73 watts. This indicates that the reaction itself contributed additional heat, with 25 watts for the water + oxidant and 22.27 watts for the PV waste. Nonetheless, the presence of PV waste somewhat impeded the decomposition of the oxidant, as there was a lower heat evolution in comparison to the water + oxidant run. The oxidative liquefaction of PV waste is characterized as exothermic within a defined temperature range; however, it does not maintain self-sustainability. The examination of the regions beneath the heating rate curves validated that the energy released adhered to the following sequence: dummy run with oxidant > modelled run with PV waste > dummy run with water.

8.3.4 TPD and OCCs production from oxidative liquefaction of PV waste *(RG-2,3)*

The oxidative liquefaction of PV waste uncovers significant patterns in polymer degradation (Figure 8.3 (a)) and the production of OCCs (Figure 8.3 (b)) under different conditions, such as temperature, oxidant concentration, and waste-to-liquid ratio.

At 200°C, the optimal TPD is attained with a waste-to-liquid ratio of 12.5% and an oxidant concentration of 60%. This suggests that achieving effective degradation at reduced temperatures necessitates a greater concentration of oxidant. The lowest TPD at 200°C is observed with a 30% oxidant concentration and a 37.5% waste-to-liquid ratio, indicating that an excess of waste or inadequate oxidant concentration may impede the degradation process. The optimal TPD is noted at 250°C with a 45% oxidant concentration, independent of the waste-to-liquid ratio. This underscores the critical function of oxidants in facilitating polymer degradation at moderate temperatures. The minimum TPD at 250°C is observed with a 30% oxidant concentration, suggesting that the oxidation process at this level is insufficient to effectively decompose polymers. At 300°C, the peak TPD is noted under complete degradation conditions with 60% oxidant and a 12.5% waste-to-liquid ratio, indicating that at elevated temperatures, even low levels of oxidant can significantly enhance polymer degradation. The minimum TPD at 300°C is observed with a 30% oxidant concentration and a 37.5% waste-to-liquid ratio, indicating that suboptimal conditions can still limit degradation efficiency, even at higher temperatures.

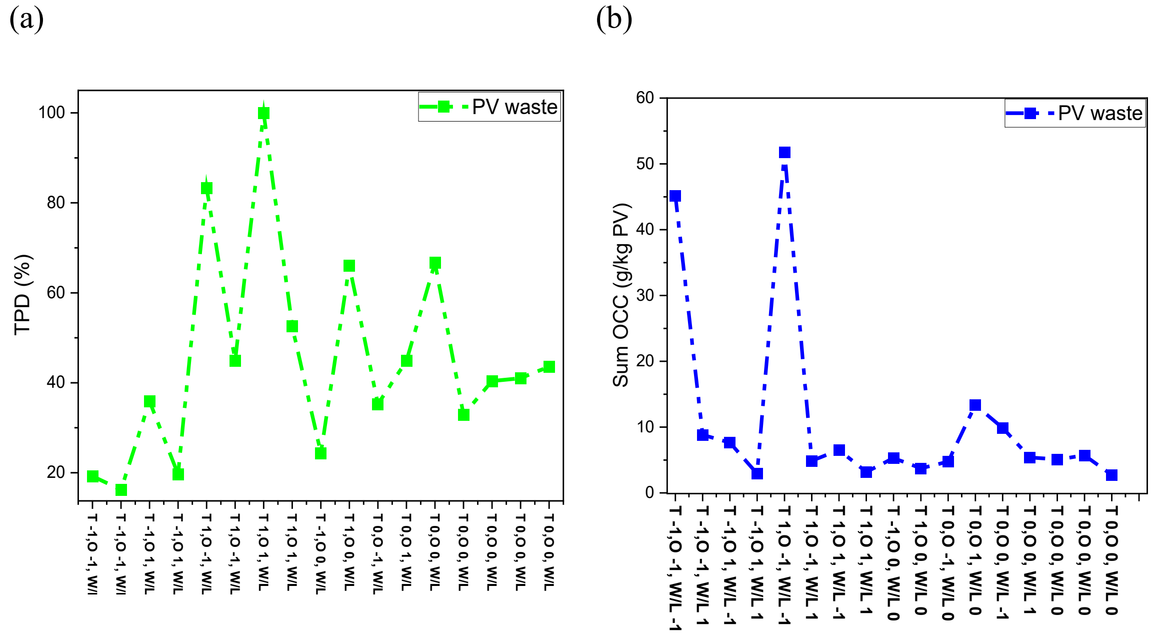


Figure 8.3 Yield of (a) TPD and (b) OCCs achieved through oxidative liquefaction of PV waste

In the context of producing OCCs, it is noted that at a temperature of 200°C, the highest yield of OCCs is achieved with a 30% concentration of oxidant and a waste-to-liquid ratio of 12.5%. The observed conditions seem conducive to the production of oxygenated compounds. Increased oxidant concentrations and waste-to-liquid ratios lead to a decrease in OCC yield, indicating that an abundance of oxidants and waste could hinder the production of OCCs. At 250°C, the peak OCC concentration is observed with a 60% oxidant concentration and a 25% waste-to-liquid ratio, suggesting that particular combinations of these parameters are most effective for enhancing OCC formation at this temperature. The minimum OCC arises under particular circumstances, even with a steady oxidant concentration, highlighting the intricate interactions that affect OCC generation. At 300°C, the peak OCC is observed with a 30% oxidant concentration and a 12.5% waste-to-liquid ratio, indicating that reduced levels of oxidant and waste are more advantageous for OCC development at elevated temperatures. Conversely, elevated levels of oxidants and waste impede the production of OCC.

8.3.5 Optimization of experimental conditions for maximizing TPD and OCCs production from oxidative liquefaction of PV waste *(RG-1,2)*

The careful adjustment of experimental parameters, including temperature, waste-to-liquid ratio, and oxidant concentration, is essential for enhancing the yields of OCCs and ensuring thorough polymer degradation. The trends illustrated in Figure 8.4 emphasize the ideal reaction conditions, indicated by red lines, whereas the blue lines depict the variations in yields of oxygenated compounds and polymer degradation in response to alterations in these parameters.

The role of temperature in polymer degradation is crucial, as lower temperatures lead to a decrease in the rate of degradation. On the other hand, elevating the temperature results in an increase in polymer degradation. Nevertheless, the temperature exerts a negligible influence on the synthesis of oxygenated compounds. It is important to observe that with an increase in temperature, there is a corresponding rise in energy consumption that aligns with the extent of polymer degradation attained. Under ideal circumstances, temperatures generally align with average values.

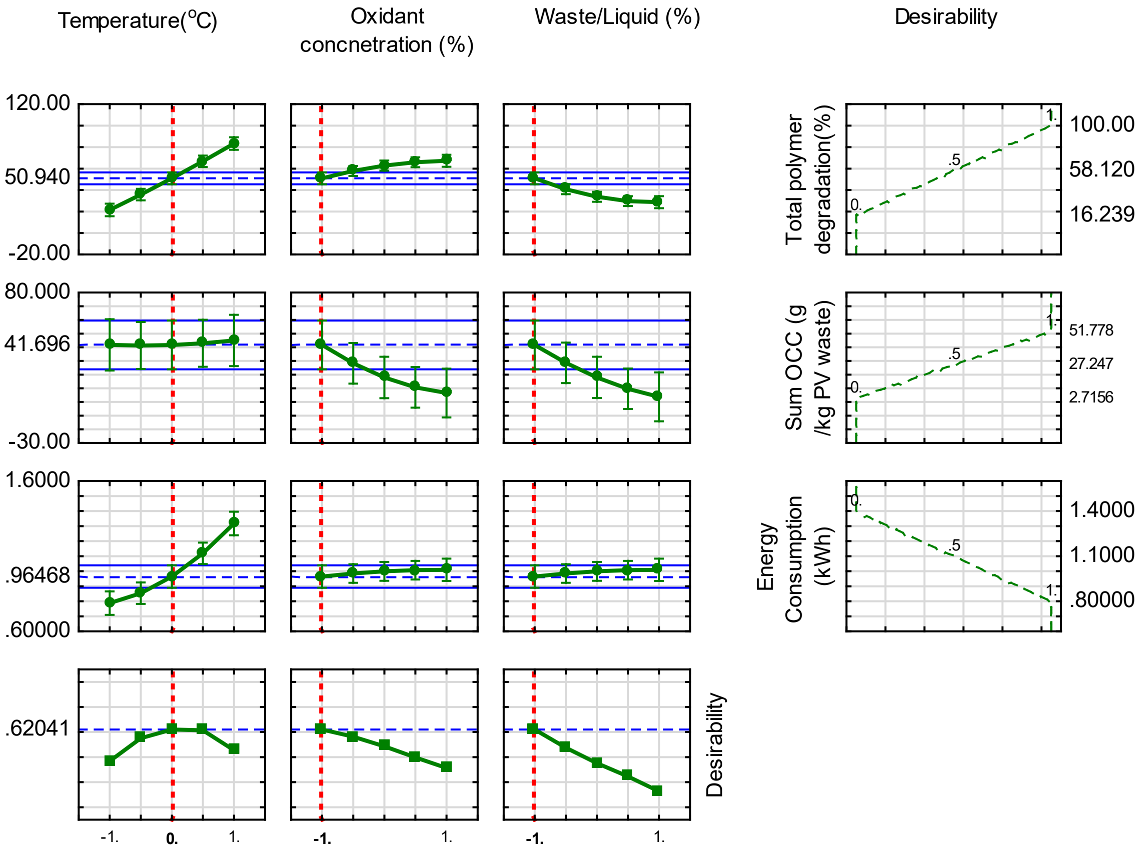


Figure 8.4 Identification of optimal reaction conditions for oxidative liquefaction of PV waste

The concentration of oxidants significantly influences polymer degradation, where elevated levels result in a modest enhancement of degradation rates. Excessive concentrations of oxidants can hinder the production of oxygenated compounds, as they may lead to the over-oxidation of intermediate compounds, resulting in the formation of unwanted gaseous byproducts. The concentration of oxidants does not have a significant impact on energy consumption, indicating that reduced levels of oxidants may be ideal for the process. The waste-to-liquid ratio represents a significant parameter, as elevated ratios result in reduced polymer degradation and lower OCC yields. Enhancing the waste-to-liquid ratio guarantees sufficient reaction media for the required reactions, ultimately leading to optimal outcomes. The meticulous choice of ideal parameters is crucial for enhancing yields, reducing energy usage, and increasing process efficiency. The analysis of current trends and discussions reveals the ideal reaction conditions for achieving maximum polymer degradation and OCC yield, all while reducing energy consumption.

8.4 Summary of Outcomes

The study's outcomes emphasize the practicality of oxidative liquefaction in breaking down polymeric materials from decommissioned PV panels into OCCs. The results indicate that oxidative liquefaction serves as a viable approach for polymer degradation; however, the presence of high inorganic content in PV waste introduces particular challenges that impact process efficiency. The investigation revealed the ideal reaction parameters, such as temperature, oxidant concentration, and waste-to-liquid ratios, that enhance polymer degradation while reducing energy usage. An increase in oxidant concentration was noted to enhance the degradation of polymeric structures; however, it adversely affects OCC yields. In a similar manner, temperature fluctuations revealed specific degradation pathways, where elevated temperatures resulted in secondary reactions that diminish OCC production. The study lays a crucial foundation for creating sustainable, industrially scalable approaches to PV waste management, highlighting the necessity for additional investigation to enhance degradation pathways and reactor design.

Summary and Conclusions of the Study

This thesis has conducted a systematic and thorough examination of the oxidative liquefaction process applied to various polymer-rich and composite waste materials, i.e., WTBs, PPEs, MSW, and end-of-life PV panels. The research targeted significant issues in sustainable waste management by enhancing the scientific understanding of the oxidative liquefaction process while advancing the scalable method for material recovery for effective waste valorization.

The research was planned in response to the rising global demand for efficient waste management practices for complex polymeric waste materials. Traditional waste management techniques, including landfilling and incineration, contribute to environmental challenges and lead to considerable losses in both materials and energy resources. In light of this context, oxidative liquefaction has been recognized as a viable thermochemical conversion method, proficient in decomposing polymer matrices into OCCs and facilitating the recovery of valuable secondary materials. This study prominently features the combination of advanced material characterization techniques with a methodical approach to experimental design. The application of proximate and ultimate analyses, TGA, FTIR, and SEM facilitated the establishment of comprehensive baselines regarding the chemical composition, thermal behavior, and structural characteristics of each waste stream. The characterizations conducted were pivotal in optimizing the process conditions for various waste types, consequently improving the efficiency and selectivity of oxidative liquefaction.

The experimental campaigns were conducted in a high-pressure batch reactor specifically engineered to endure the demanding operational conditions associated with oxidative liquefaction. The investigation involved the systematic variation of key process parameters, which included temperature, pressure, oxidant concentration, waste-to-liquid ratio, and residence time. The effects of these parameters were analyzed utilizing response surface methodology and ANOVA. The statistical framework facilitated a thorough identification of significant factors and interactions, while optimization tools, including Pareto analysis, offered practical insights into the equilibrium between yield maximization and energy efficiency. The application of inverse heating analysis has facilitated the investigation of the thermal and energetic dynamics associated with the degradation pathways, thereby confirming the presence of exothermic contributions that are advantageous for scaling up and industrial implementation.

The results obtained for each waste stream emphasize the inherent versatility and adaptability associated with oxidative liquefaction processes. The investigation into WTBs demonstrated that the process facilitated near-complete resin degradation when subjected to optimized conditions, concurrently maintaining the structural integrity of the glass fibers. This dual outcome not only illustrated the capacity of oxidative liquefaction to recover clean, reusable fibers but also underscored its potential significance in tackling one of the most critical composite waste challenges within the renewable energy sector. During the COVID-19 pandemic, PPEs emerged as a significant waste stream. The process of oxidative liquefaction resulted in the production of substantial amounts of short-chain VFAs and demonstrated high efficacy in polymer degradation. This positions the method as a viable and environmentally sustainable approach for addressing this new category of waste. The utilization of oxidative liquefaction in the context of MSW demonstrated a significant TSR and produced elevated yields of OCCs, notwithstanding the intrinsic heterogeneity associated with this feedstock. The results indicate the resilience of the process when utilized with mixed waste streams, thereby supporting its wider relevance for urban waste management approaches. The disposal of end-of-life photovoltaic panels poses distinct challenges, characterized by elevated ash fractions and diminished recoverable concentrations of essential elements, which restrict the efficacy of oxidative liquefaction in processing this material stream. Nonetheless, the research yielded significant insights regarding the limitations of oxidative liquefaction in the context of inorganic-rich waste materials. It underscored the critical role of eco-design in the advancement of future photovoltaic technologies, which is essential for facilitating more efficient recycling pathways. The overall conclusions of the research are presented below,

1. **Oxidative liquefaction as a versatile recycling technology:** This study showed that oxidative liquefaction has the potential to serve as a viable method for the treatment of diverse and complex waste streams, such as WTBs, PPEs, MSW, and PV panels, without any specific pretreatments *(RG-1,3)*. This process enables the breakdown of polymers, recovering the useful resources and generating valuable secondary compounds, making it a noteworthy option for waste valorisation.
2. **Material-specific degradation efficiency:** The effectiveness of oxidative liquefaction is significantly influenced by the composition of the waste material. Polymer-rich wastes, including PPEs, demonstrated greater TSR/TPD and OCCs yields, whereas PV panels, characterized by an exceptionally high inorganic content (93% ash), revealed restricted polymer degradation potential. The results highlight the necessity for customized reaction conditions based on the specific types of waste involved *(RG-2,3)*.
3. **Recycling of fiber-reinforced composites**: The research revealed that oxidative liquefaction is capable of efficiently recovering high-quality glass fibers from composite waste by selectively degrading the polymeric matrix while maintaining the integrity of the fibers. This approach facilitates the recovery of materials for reuse in composite manufacturing, thereby decreasing dependence on virgin fibers and lessening waste generation. The extraction of glass fibers from WTBs exemplifies the significant potential of this method for sustainable recycling in fiber-reinforced composites *(RG-1)*.
4. **Influence of reaction parameters on product yield:** Through experimental optimization, it was determined that temperature, oxidant concentration, and waste-to-liquid ratio are the key parameters significantly impacting polymer degradation and OCC formation during the oxidative liquefaction process. Reduced oxidant concentrations (30–45%) promoted OCC production by inhibiting overoxidation, while elevated temperatures (>250°C) encouraged increased polymer degradation but diminished OCC selectivity as a result of secondary reactions *(RG-1,4)*.
5. **Thermal behavior and process energy dynamics:** The inverse analysis of process heating has established that oxidative liquefaction exhibits partial exothermicity mainly because of the decomposition of peroxide, with the degradation of polymers providing supplementary heat in addition to the energy supplied externally. Nonetheless, the overall process is characterized by endothermic behavior, requiring an external heat source to maintain degradation, especially in the case of high-ash materials such as PV panels.
6. **Comparative waste stream analysis:** The investigation revealed that PPEs, made up of uniform polymers (PP, PE, PVC), demonstrated the highest OCC yields and lowest energy demand for each unit of degraded material. In contrast, WTBs and MSW necessitated optimized conditions to achieve a balance between polymer conversion and energy efficiency, whereas PV panels presented challenges owing to their elevated inorganic fraction and restricted organic degradability *(RG-3)*.
7. **TSR/TPD and OCCs yield as performance indicators:** The TSR/TPD and OCCs yield metrics functioned as essential performance indicators for assessing oxidative liquefaction efficiency. PPEs demonstrated a >96% TSR, with MSW following

closely at 95%, while PV panels showed minimal degradation potential. The yields of OCC exhibited considerable variation, with PPE-derived waste generating as much as 212.66 g/kg $_{\text{of waste}}$ of oxygenated products, underscoring its substantial valorization potential *(RG-2,3)*.

8. **Scalability and industrial feasibility considerations:** Although oxidative liquefaction has demonstrated effectiveness in laboratory settings, there are still obstacles to its large-scale application, especially concerning energy demands, the variability of waste materials, and the management of inorganic residues. Future investigations ought to concentrate on the integration of this process with catalytic upgrading and energy recovery strategies to improve its commercial viability (RG-5).
9. **Environmental and circular economy implications:** The results indicate that incorporating oxidative liquefaction into circular economy frameworks provides a viable approach for recovering resources, minimizing waste, and producing sustainable chemical feedstocks. Nevertheless, the existence of harmful substances (fluorine, chlorine, heavy metals) in PV and MSW waste requires additional evaluation of environmental risks and regulatory factors prior to widespread implementation.
10. **Future research directions:** This study emphasizes the necessity for additional exploration into catalyst-assisted oxidative liquefaction, process heat recovery, and hybrid waste processing strategies to enhance efficiency and economic viability. Furthermore, enhancing reactor designs to “continuous-flow systems” instead of batch processing can promote industrial-scale implementation (RG-5).

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Appendices

Table 3.1 A Recycling techniques applied for WTBs based on literature review in years 20xx-20xx [133]

No.	**Method**	**WTB input, pre-treatment needed**	**Recycling type**	**Reactor type and technology**	**Process conditions**	**Recovered fiber yield**	**Fiber quality**	**Liquid products**	**Gaseous products**	**Sustainability assessment**
1	Oxidative liquefaction	GF	Chemical	Batch 500 ml reactor, approx. 30 g feed	*n.a.*	72-100 %	89-100% purity	*n.a.*	n.d. (minimum acetone emissions to air from fibre cleaning)	*n.a.*
2	Pyrolysis	CF, unsaturated PS resin,	Thermal	*n.a.*	Inert, temperature 500 (up to 650 °C)	*n.a.*	*n.a.*	Styrene, phenol rich oil, 15.8 % mass yield	CO_2, CH_4, CO, H_2, C_2H_6 gas, 7 % mass yield	*n.a.*
3	Microwave-assisted pyrolysis	*n.a.*	Thermal	Batch 10 l, 3 kg feed	Inert, temperature 300 -600 °C, 90 min	Up to 75%	25% loss of initial t tenacity	*n.a.*	*n.a.*	*n.a.*
4	Mechanical recycling	Glass fiber reinforced plastics (GFRP)	Mechanical	Table saw with a diamond blade	*n.a.*	Up to 100 %	GFRPs in the form of needles (quality	*n.a.*	*n.a.*	*n.a.*

							not assessed)			
5	Mechanical Recycling	E- GFs	Mechanical + Thermal	Band saw + Hammer mil grinder	*n.a.*	Up to 100 %	48-50 % more tensile strength than obtained through pyrolysis	*n.a.*	*n.a.*	*n.a.*
6	Pyrolysis	GF recovery under H2O and CO2 Environment	Thermal	Fixed bed reactor	500°C, 20% of H_2O with N_2, and 20% of CO_2 with N_2	*n.a.*	5.97 and 16.0% reduction in tensile strength for H_2O and CO_2	Phenolic compounds, o-cresol, 4-isopropyl phenol, 4-isopropenyl phenol, and bisphenol A	CO_2, CH_4, and CO,	*n.a.*
7	Pyrolysis	CF	Thermal	Thermogravimetric analyzer	550-650 °C, 10 and 30 °C /min	64 to 72%	*n.a.*	*n.a.*	*n.a.*	Recovery cost Estimated
8	Pyrolysis	GF	Thermal	Fluidized bed reactor	500 °C, 150 mm and 1.5 m/s		85 % reduction in tensile strength before secondary treatments	*n.a.*	*n.a.*	*n.a.*

9	Pyrolysis	GF	Thermal	Tube Furnace	380 - 550°C	70-81%	24 - 54 reduction in tenacity	Phenolic Compounds (10.49 -13.58 % mass yield	CH_4, C_2H_4, C_3H_6, CO_2	*n.a.*
10	Pyrolysis	GF	Thermal	Fixed bed reactor	500 °C for 30 min, with a heating rate of 10 ◦C/min	78%	57 – 68 % Tensile strength	Phenolic Compounds with a 14.88 % mass yield	CO_2, CH_4, and CO	*n.a.*
11	Pyrolysis	GF	Thermal	Pyrolysis furnace	500 ◦C for 45 min	*n.a.*	52-58 % less tensile strength than ground fibers	*n.a.*	*n.a.*	*n.a.*
12	Microwave-assisted chemical recycling	GF	Thermochemical	Glass beaker	Microwave irradiation (700 W), (220 s, 360 s, and 450 s)	Up to 97%	1547-3032 MPa of Tensile strength	*n.a.*	*n.a.*	*n.a.*
13	Solvolysis	GF	Chemical	*n.a.*	*n.a.*	100%	58% Tensile strength	*n.a.*	*n.a.*	Cost comparison of different recycling techniques for WTBs

14	HTL/Solvolysis	GF	Chemical	Sealed high-pressure vessels (stainless steal)	250-370 °C and 100-170 bar	Up to 100%	*n.a.*	< 1% monomeric organic compounds, larger oligomeric fragments or hydrophilic compounds	*n.a.*	*n.a.*
15	Oxidative Liquefaction	GF	Chemical	Batch 500 ml reactor, approx 30 g feed	250-350 °C, 20-40 bar initial pressure	Up to 100%	*n.a.*	Oxyginted chemical compounds	*n.a.*	*n.a.*

Appendix A

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Hydrothermal treatment of plastic waste within a circular economy perspective

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ABSTRACT

Concentration of plastic waste is increasing rapidly in the environment posing serious threats to the lives of all species and emerging ecological instability. Increased consumption of plastic goods, the ability to generate high revenue, and less availability of recycling methods shift the focus on the plastic economy. Various strategies have been employed to mitigate this problem but the conversion of plastic waste to energy-rich fuels is more promising and can be more supportive in the future. Mechanical recycling, incineration, pyrolysis, and hydrothermal treatment are the conversion technologies that have been adopted over the passage of time for energy production applications. For the success of all these waste to energy technologies, they need to reduce their capital costs and generate some additional revenues may be in form of fuels or other by-products. Thus the circular economy approach can be used to solve the increasing waste problem and to moderate the increasing energy demand by the conversation of waste into energy. In this article details, discussion has been carried out on all the waste to energy conversion technologies in the context of circular economy perspective by highlighting the important research gaps to solidify the new directions for future studies.

1. Plastic waste generation and efforts to mitigate plastic pollution

Nowadays the environmental pollution is the is major threat to human communities. The most challenging situation is the large amount of plastic waste that is continuously increasing and resulting to the nature contamination (Ilyas et al., 2018). Minimal costs, satisfactory mechanical properties, low density and superior stability are the properties that encourage its use for various applications such as packaging purposes, film formations, for wrapping covers, making containers and bags, in construction and in electrical and electronic applications (Jamshidian et al., 2010). The word plastic is derived from a Greek term "plastikos" which means fit for modeling (Vered and Shenkar, 2021). Plastics are high molecular weight, long chain synthetic or semisynthetic polymers with high malleability and considered to be the derivative of petrochemical industry. Plastics mostly have long chain structure with some side molecular groups attached to main backbone having the influence on overall properties, some blends added as additives, cheap inert fillers that make the product comparatively economical; some plasticizers are also blended to improve the rheology (Galiano et al., 2018). On the base of responses attained after the thermal treatments, plastics can be divided in two main categories: thermosets and thermoplastics. Polystyrene (PS), polypropylene (PP), Polyvinyl chloride (PVC), high and low density polyethylene (HDPE and LDPE) do

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not exhibit a chemical change on heating and can be molded every time, on the other hand the thermosets on heating will tend to irreversible change in bond structure so once shaped they can not be retreated, common examples are Bakelite and Melamine (Effect of multi, 1234). Different types of linking of distinct type of side chains with backbone results in another type of classification, i.e. acrylics, polyesters, polyurethanes, silicones, halogenated plastics and some others (Chattopadhyay and Raju, 2007). Plastics are also classified on the base of process of synthesis like addition, condensation and cross-linking polymers (Goto, 2009).

While targeting the recycling of plastic the most important identification criteria is type of resin. The Society of Plastic Industry in 1988 gave a unique resin identification code to each type of plastic for its easy recognition to improve sorting, recycling ability and excellence of recycled product (Amici et al., 2021). For instance, PET has a resin code of 1, HDPE has the resin code of 2, similarly 3,4,5,6 and 7 are the codes for PVC, LDPE, PP, PS and other type of plastics respectively (Dogu et al., 2021a).

Polymers are getting widespread around the world because of their special properties such as less weight, high durability, economic and technological effectiveness (Amici et al., 2021). On the other hand almost 1.5 million people are directly employed in plastic industry contributing 30 billion EUR to economy of Europe (Dogu et al., 2021a). According to survey the worldwide production of plastic was more than 320 million tonnes in 2015 and 335 million tonnes in 2016 and more than 8 percent of crude oil is used for this purpose. According to PlasticsEurope report for the year 2017 the different type of plastics is produced in mentioned order PP (19.3 wt%) > LDPE (17.5 wt%) > HDPE (12.3 wt%) > PVC (10 wt%) > PET (7.4 wt%) > PS (6.7 wt%) (Hassan et al., 2019).

Global plastic demand and plastic waste generated by various industries is shown in Fig. 1 which shows the largest plastic consumption 36% in packaging field. This segment includes consumer packaging like bottles made of PET and packaging used in business-to-business transections in industry. Second largest demand is estimated in construction industry with PVC as main component of windows and door frames, water pipes because of high durability. Synthetic fibers including ropes, carpets and clothing in textile industries demands for 3rd largest plastic intake of 15 percent by weight (Lebreton and Andrady, 2019).

From the data shown in the graphs its obvious that extensive use of these plastic products in various fields is resulting in serious increment of plastic waste around the globe, adversely effecting the environment.

1.1. Serious threats to the environment

Increasing production and use of plastic products results in continuous boost in plastic waste that is threatening the lives on globe. Plastics is high molecular weight, long chain polymer with stable structure, that is not degradable by microorganism (Balla et al., 2021). As a complex solid waste, the plastic has proposed the serious threats to environment in following ways.

(1) Affecting the soil function and agricultural production. Incineration of plastic waste on land reduces the amount of dissolved nitrogen and phosphorus that adversely affect the soil nutrition. The mixing of plastic waste with the soil, blocks the pores of root cell walls that results in less intake of water and other nutrients to the plants so decrease in its output (Vanapalli et al., 2021);
(2) While eating the food the waste plastic products on the land or in water can easily be taken up by animals resulting in their death (Li et al., 2016a);
(3) The toxic effect of plastic waste is biological. Adverse reactions caused by plastic, attacks on organisms. Microplastics can inhibit the expression of genetic material involved in oxidative stress in the body of plant and transport of transmembrane, therefore, affects its development (Shen et al., 2019). On the other hand, micro plastics are categorized as plastics with the size less than 5 mm so owing the fact that they possess high surface area because of which they can adsorb other pollutants to initiate the combined injuriousness (Godswill and Gospel, 2019);
(4) Can cause the white pollution by effecting the cityscape and posing visual tremor to people.
(5) While reaching in oceans the hydrophilicity of plastic increases with increase in charge, that is now more favourable for conversions in microplastics by attack of microorganisms present in the form of colonies on surface causing the serious damage to other organisms in oceans (Jeyavani et al., 2021). Also consumption of microplastics by fishes stimulates the fall sense of

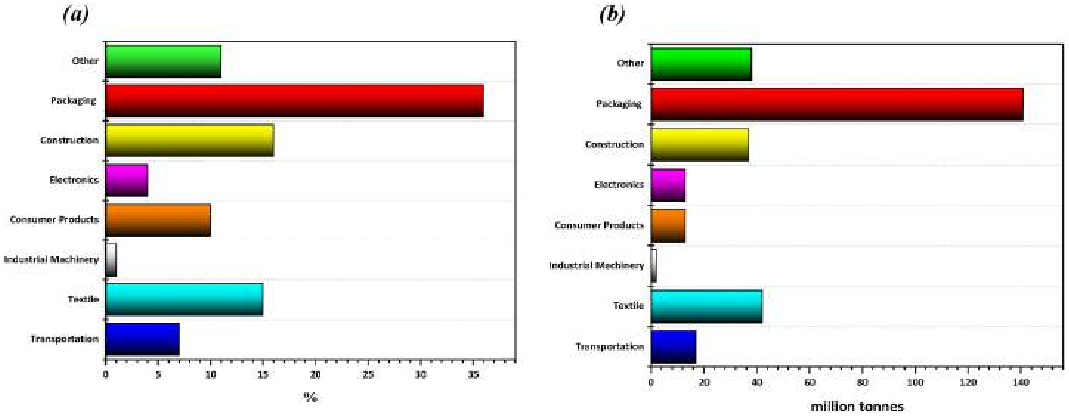

Fig. 1. (a) Plastic Demand and (b) Plastic waste, generated by different sectors.

satiety, resulting in decrease of food intake thus fish size and quality get reduced due to lack of growth energy (Mallik et al., 2021). Furthermore the microplastics in soil are taken by plants and when people feed on these pants the microplastics are transferred to their body causing the intestinal infections reducing the human growth and development (Jaiswal et al., 2022).

According to Al-Salem et al. the plastic waste mainly consists of Polyethylene's, PP, PS, PVC and PET. The composition of plastic waste reported by Adrados et al., Sing et al. and Kaminsky et al. for different geographical regions have been shown in Fig. 2 (Dogu et al., 2021b). Hence it is very clear from these studies the composition of solid plastic waste is highly variant and depends upon geographical region and directly related to production of different types of plastics and product life cycle. So it is important to perform a detail characterization of feed stock in introducing the optimal process design for various heat treatments of waste plastics. After performing the detail characterization, the consecutive step is to develop comprehensive model for simulation of heat treatment process.

2. Plastic waste management

According to an estimation total 27 million tonnes of waste plastic was collected through out of Europe in year 2016.31% of this total amount was recycled successfully, 42% was subjected to energy recovery purpose and remaining 28% was landfilled (Dahlbo et al., 2018). Fig. 3 exhibits the trends for different types of waste management techniques employed from 2006 to 2016 (Ravindran and Jaiswal, 2016). In addition, the European Union claimed that in 2018, 29.1 million metric tons of plastic waste was collected in Europe alone, of which 32% was recycled and the other 7.2 million metric tons was disposed of in landfills (Nandy et al., 2022). According to the report in 2020, top 5 leading countries in EU generating plastic waste were Germany, France, Italy, Spain and Poland which produced 11 thousand metric tonnes of plastic waste and 38% percent of it was recycled (EU-27: plastic packaging waste generation, 2010). In last two years COVID-19 waste generated from the use of personal protective equipments is one of the major reasons of plastic waste accumulation in environment. Yeming et al. presented that 8.4 ± 1.4 million tons of pandemic-associated plastic waste have been generated from 193 countries as of August 23, 2021, with 25.9 ± 3.8 thousand tons released into the global ocean (Peng et al., 2021).

Although the total amount of waste subjected to recycling and energy utilization is gradually increasing but still a large amount of waste is i.e. 7.4 million tonnes of plastic was landfilled in Europe in 2016 that is substantial because as it always have high potential to be used as feedstock for energy production applications (Lausselet et al., 2016). Low price of fossil fuel-based plastics is an important economic factor impeding the enhanced recycling and which depends upon crude oil prices (Dogu et al., 2021c). This worth noticing that the 130 billion Joules of energy can be saved by recycling one ton of plastic and it's the same amount that will be used to

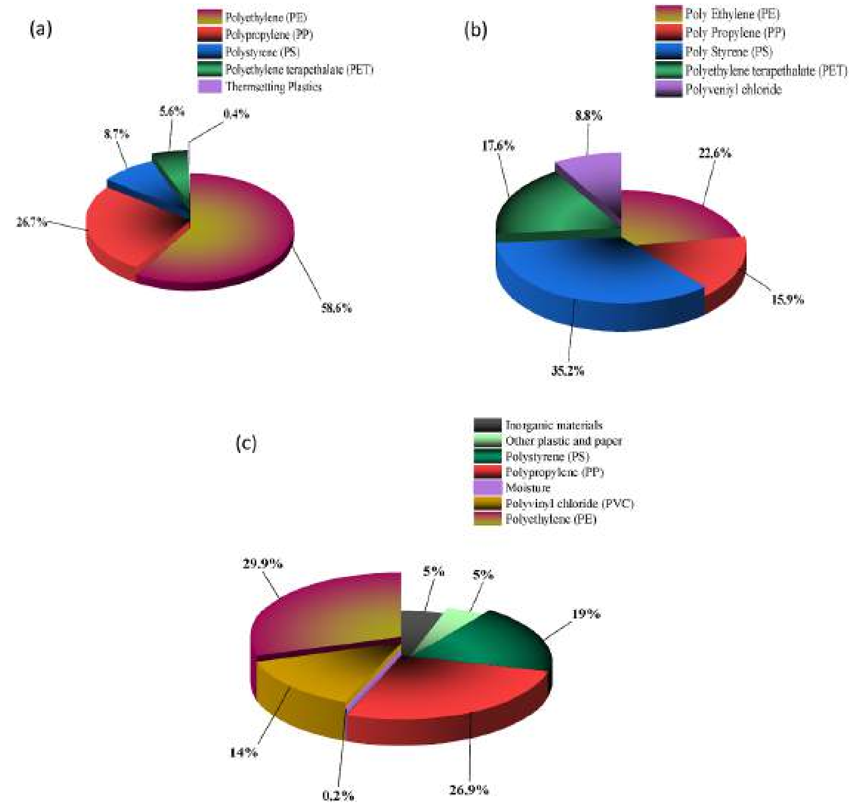

Fig. 2. Composition of waste in (a) India, (b) Spain, (c) China.

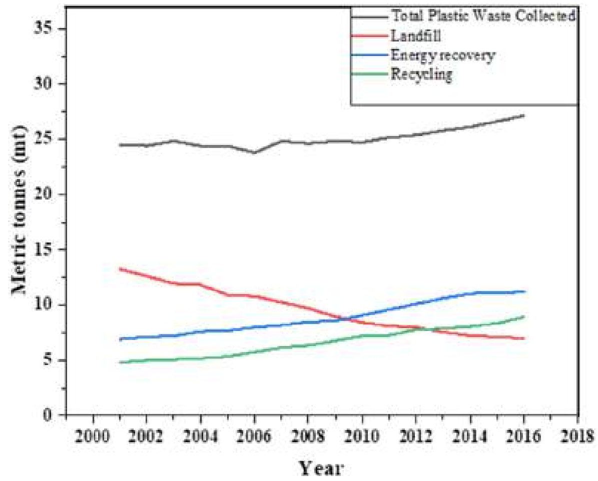

Fig. 3. Different types of waste management techniques employed from 2001 to 2016.

convert one ton of waste plastic into virgin plastic (Ferdous et al., 2021). Although these values are highly optimistic but these figures dictate the potential involvement of plastic waste to recycling.

Thus relative plastic waste management processes should be modeled to reduce the process pollution through improve process efficacy and achieving energy conversion. Plastic waste management have been divided in four major categories named as mechanical recycling, feedstock recycling, energy recovery and land filling (Chen et al., 2019).

2.1. Mechanical recycling

Waste or scrap plastic commodities are converted into the products with the similar properties of original product without disturbing the original molecular structure of the base material. All the types of thermoplastics including PP, PS, PVC, PP, PET, HDPE and LDPE can be subjected to mechanical recycling with small or no quality diminishing, but this technique is popular for some kind of plastics while not economically and technically feasible for others (Yin et al., 2015). So before the recycling, the mandatory step is sorting of waste to identify the plastic types based on the resins code mentioned in starting sections to improve the quality of product (Clark et al., Serrano). Identification of plastic polymers is manual or may be mechanized including cutting and shredding, separating the contaminants and flakes, sieving to the required particle size by using specific density with suitable medium, magnetic separation (Vanapalli et al., 2019a). Some techniques also involve colour separation before recycling then undergo removal of impurities like paper labels (Gundupalli et al., 2017). After the glue removal by washing through the caustic soda the material is melted and turned into even size pellets. Some additional treatment like additives and pigments addition they are sold in market for producing similar products (Welle, 2011).

Compared to the recycling of glass and metallic materials the mentioned process is quite challenging for plastics because its low density and value of material (Ignatyev et al., 2014). Plastics are long chain molecules with side by side attachments of other molecules defining its major properties. Thermal treatment alone is not considered to be the best for treating such stoichiometrically different molecules so the mixed plastic recycling is demands for plastics with almost same compositions, labors with expertise (Meereboer et al., 2020). When different types are plastics are melted together they settled down in different layers phase wise that effects the structural strengths in resulting product reducing the overall quality (Vanapalli et al., 2019b). Major problem that has been faced while recycling the plastic is removal of dies, pigments and fillers that is not economically feasible and original polymer will get damaged after the successive tries. Most commonly recycled plastics are type 1, 2 and 3. The type 4 and 5 are also recycled while type 6 and 7 are not considered for recycling because of techno economic issue (Singh et al., 2003). Adoption of unconventional ways without following the proper standards and norms, recycling of plastic is becoming cause for several respiratory and dermatological problems because of inhalation of toxic fumes mostly the hydrocarbons and exposure to dangerous residues (Vanapalli et al., 2019c).

2.2. Energy recovery/Incineration

Thermal degradation of waste materials by burning in presence of excess amount of oxygen is termed as Incineration. Incineration is the technique that is mostly adopted in cities to treat the municipal solid waste, for waste to energy production applications and reducing the excessive amount of waste (Li et al., 2016b). In this chemical process the elements like hydrogen and carbon are mixed with oxygen is combustion zone to generate the large amount of heat (Nunes et al., 2014). Carbon dioxide, carbon monoxide, oxides of nitrogen some vapours are major components that are produced through incineration processes. For the proper combustion of waste and removal of odor the temperature of heating chamber is maintained in the range of 900 °C–1100 °C (Nunes et al., 2014). Three T's turbulence, temperature, time and air flow rate are key parameters that are critically managed to reduce the emissions of gasses (Wiinikka and Gebart, 2004). At the end of incineration process produced inert solid residue with the weight only 10% of initial solid waste and comparatively less volume is discarded in landfills (Vanapalli et al., 2019d).

Thermal decomposition of solid waste at elevated temperatures produces the carbon base molecules including CO_2 and CH_4 and energy can be recaptured for use in power or heating applications (Boretti, 2021). In addition to providing alternate of burning the fossil fuels for energy production applications the best method to eliminate the CH_4 from solid waste is incineration (Reza et al., 2013a). Various plastic polymers including HDPE, PP, and LDPE have total energy content of 40 MJ/kg comparable with the calorific value of heating oil i.e., 44.5 MJ/kg. Similarly the PS has the calorific value less than 40 MJ/kg while the PET and PVC have the least calorific values of 30 MJ/kg, so all these types of plastics are favourable for energy production applications (Sannita et al., 2012).

Incineration technology mainly relies on pre-treatment, combustions system, and energy recovery flue gas cleaning steps. Metals and glasses trapped in plastic structure that are known as non carbonaceous materials are mostly removed during pre-treatment process to generate refused derived fuels (Quina et al., 2008). In addition, the characterization of ash is highly dependent upon physical and chemical properties. In physical properties the particle size distribution, moisture content, bulk density, compressive strength, and porosity are important, while discussing the chemical behaviour, loss if ignition, heavy metals and leachability, organic constituents, chloride content and chemical structure are main concern (Bhatt et al., 2019). Waste composition, operational circumstances, type of incineration and design of air pollution control system will have an impact on chemical and physical properties of ash. After implication of process treatment method, the ash can be used in cement and concrete production, road pavement, glasses, ceramics, and as a stabilizing agent and adsorbent (Lam et al., 2010).

Adoption of this technology offers the benefits of energy efficiency and furnace size reduction but demand for separation of non homogenous plastics and high costs associated with it makes it less feasible (Plastics Waste). Production of NOx and other harmful emissions must be controlled by installation of proper combustion systems. Generation of fuel upon cooling the flue gasses produced during the burning of waste materials is aspect of energy recovery (Sharma et al., 1998). The flue gasses before entering into environment are cooled down in condenser. Fuel obtained after the required post treatment can be use for cofiring in processes like pyrolysis (Evangelopoulos et al., 2020). But the major problem that encounters during the incineration process is the control of emissions to meat the environment safety measures that re highly regulated by “European Hazardous Waste Incineration Detectives” to avoid the air pollution. Based on complex composition the incineration of plastics results in emissions of organic compounds that are highly volatile such as furans, polychlorinated dibenzofurans (PCDFs), dioxins, cyano compounds and halogenated compounds (Buekens and Zhou, 2014). In general, the energy recovery method is less feasible in economic and environmental point of views so European Waste Framework Directive (EWFD) suggested the preference of recycling option on energy recovery option.

3. Feedstock recycling/Chemical recycling

It governs all the methods that are employed to convert end-of-life plastics into the low molecular weight compounds that have high potential to being employed as feedstock materials for production of petrochemicals and new plastics. These processes are gathered under the umbrella of chemical recycling as they involve the change in chemical structure of raw material to generate new products.

3.1. Pyrolysis

The process of heating the plastic waste at 300 °C–600 °C in an anaerobic environment to change its molecular structure by providing the activation energy necessary for cracking of polymers to convert it in fuel, is termed as pyrolysis (Dharmaraj et al., 2021). Pyrolysis of long chain polymers results in the formation of solid product called char that is rich in carbon with some liquid or gaseous by-products depending upon the process conditions so the process can be tailor made (Giudicianni et al., 2013). To achieve the goal of producing intense carbon rich char the pyrolysis can be subjected to pressurized pyrolysis that is a customized technique. Adoption of this technique to generate the required fuel either by thermal or chemical cracking is feasible as it does not require the washing and sorting the different types of plastics, which will reduce the cost of pre-treatment, however compromise will be needed on the quality (Khosravanipour Mostafazadeh et al., 2018). The oil produces in this way can be used as fuel for the energy production applications in boilers and various furnaces because of high calorific values.

Pyrolysis of plastic either slow or fast depending upon the properties of product can generate the hydro-carbonaceous liquid like oil that can be used as fuel for further pyrolysis processes (Panda et al., 2010). Attempts have been made to increase the yield and quality of such oils for some special applications. Solid char produced form pyrolysis of plastic have various applications after activation such as adsorbent material for oxides of nitrogen and carbon, heavy metals removal, wastewater treatment and also a successive fuel source for coal by making pieces from char (Saleem et al., 2019). In addition, the synthetic gas commonly known us syn gas produced from pyrolysis of plastics can serve as good energy carrier with high calorific value having the potential to serve as ignition source (Demirbaş, 2001). Calorific values of oils obtained from pyrolysis of PP, PS and PVC are 44, 40.6 and 40 MJ/kg respectively with PS resulting the liquid gasoline hydrocarbons (C_5-C_{12}) up to the yield of 83% that confirms the existence of large amount of gasoline and diesel fractions in these oils (Zhou, 2021). However low octane value of gasoline, high carbon distribution, and existence of large number of olefins hinders the use of these oils directly as fuels and demand some special treatments. Some important operating conditions for production of chlorinated oils have been mentioned in Table 1 for single as well as some mixed kind of plastics (Li et al., 2022a). Obtained oils are subjected to special refining treatments to convert them in alkanes and aromatics. So the less chlorinated and high calorific value oil produced from the pyrolysis of plastic waste can be used as mitigate the energy deficiencies.

Important factors that will govern the process of conversion of plastics into fuels are heating rate, heating temperature, catalyst used and composition of feedstocks. For LDPE when the heating rate is increased from 6 to 14 the yield of nonaromatic product decreased from 80% to 71% (Onwudili et al., 2009). From some other examples it is very obvious that slow pyrolysis is always favourable for conversion of plastic into suitable fuels with high calorific values (Kasar et al., 2020). Optimization of all these chal-

Table 1
Operating conditions for various types of plastics under pyrolysis process (Li et al., 2022a; Zhou et al., 2021; Hall and Williams, 2007; Miandad et al., 2019; Bagri and Williams, 2002).

Plastic type	Operating conditions	Product type	Yield, %
HDPE	T = 575 °C, Plastic/biomass = 1/4	Liquid oil	57.6
PS	T = 500 °C, Filling ratio of heat carrier = 15%	C_5-C_{12} Liquid oil	82.5
PE	T = 400 °C	Liquid oil	92.2
PP	T = 300 °C	C_6-C_{16} naphtha	50.0
PP/PE/PS	T = 500 °C, Heating rate = 20 °C/min	C_5-C_{19} liquid oil	92.0
LDPE/PP mixture	T = 275 °C, Time = 80 min	C_5-C_{12} gasoline fraction	48.6
PE/PP/PS/PET/PVC mixture	T = 500 °C, Time = 30 min	C_5-C_{16} Liquid oil	87.0
Plastic waste from electronic components	T = 600 °C, Time = N/A	Liquid oil	83.0
HDPE	T = 620 °C, with ZSM-5 catalysts	Hydrocarbons rich in aromatic and isomerized aliphatic content	48.9
PE	T = 500 °C, Time = 20 min	Liquid oil	95
PS, PE, PP, and PET	T = 550 °C, with natural zeolite, Time = 75 min	Liquid oil	50.8

lenges that effect the yield and quality of product is a major challenge. Addition of catalyst can reduce the temperature for thermal cracking hence saving energy but it also effects the yield and quality. So, choosing the catalyst is an important scenario. Copyrolysis of plastics with coals results in improved crude oil quality with viscosity reduction. Other pyrolysis techniques are microwave assisted and fluid based catalytic cracking (Fan et al., 2017).

Copyrolysis of plastic with some biomass is an important mostly practiced technique in the recent past to introduce the required properties in the copyrolysate. For example, the pyrolysis of polystyrene (PS) alone results the diesel fractions yields slightly higher than 20 percent but this yield is increased to almost 28 percent during the copyrolysis PS with RH (Li et al., 2022b). The addition of red oak in pyrolysis process with HDPE produced the oil with the calorific value of 35 MJ/kg which is much higher that pyrolysis of HDPE alone (Uzoejinwa et al., 2018a). The pyrolysis of mix plastic and pin improves the overall efficiency as compared to slow pyrolysis of pine alone. There for compared to slow pyrolysis of biomass it was possible to achieve the higher liquid products yield (Paradela et al., 2009). Increase in the liquid yield has also been observed during the copyrolysis of palm shell and PS. This increase was almost 15% and calorific values of the product also increased from 15.50 to 38.01 MJ/kg (Dorado et al., 2015). In addition to less microwave and thermal energy demand, the loss of thermal conductivity is low so the copyrolysis of plastic waste with some special biomass can be tested to get the oil of required properties.

Plastic waste is mainly of two types post-industrial and post-consumer, the later one has high contamination, unsorted composition, addition of metallic, glass and wood pieces so not suitable for mechanical recycling until it is completely washed and thoroughly separated, this type of waste can easily be treated through pyrolysis process (Horodytska et al., 2018). This process also gives the freedom to change the properties of output product by changing the reactor type and modifying the operating conditions so the process can be used to produce the different compounds like wax, important monomers, aromatics or some chemicals with or without the catalytic treatment (Chen et al., 2014a). These products can be used feasibly as energy source. Since the oil and waxes obtained by the process of pyrolysis are rich in hydrocarbons content so they can be used as primary fuel in refineries (Buah et al., 2007). This type of integration of pyrolysis process have been practised in ReOil pilot plant named OMV oil refinery situated in Austria (Lechleitner et al., 2020). Pyrolysis is the mature and well stable technology based on which different plants are working for plastics and other fuels as well for commercial purposes. The process have the flexibility to treat the various kind of plastics from simple one to complex like rubber and one contaminated with hazardous materials i.e. waste from hospitals (Faussone, 2018).

Pyrolysis process is widely dependent upon the availability of required feedstock. Unavailability of this feedstock in previous time is main reason of failure of most of pyrolysis plants (Ippolito et al., 2020). A continuous and steady flow supply of consistent feedstock is required to accomplish the economically feasible process. Plastic waste collected from different areas greatly varies in composition and highly heterogenous (Arafat and Jijakli, 2013). A major portion of plastics in made up of polyolefins while PET and PVC are also found in different proportions. Polyolefins are favourable for pyrolysis process and converted into the valuable hydrocar while PET and PVC are less favourable for high temperature degradation prove to be problematic so their concentration is kept less than 5% in mixture (Mohanraj et al., 2017). No doubt the pyrolysis has tendency to treat contaminated plastic but in order to maintain the technoeconomic feasibility of plastic to fuel (PTF) the waste must be pretreated and pre-sorted. Some sort of plastic waste products also need crushing and grinding treatments before subjected to pyrolysis (Eke et al., 2020). The choice of reactor is also very important in defining the pyrolysis product spectrum. No doubt the quality of pyrolysis product is widely dependent upon feedstock, but the type and size of reactor is also an important factor to define the yield and heat content of final pyrolysis product (Uzoejinwa et al., 2018b). So special care must be adopted for selecting the type and design of reactor. Oils generated from the pyrolysis of plastic are not considered to be standardized so the standard methods for testing are not existent. At the end the oils produced through pyrolysis process are chemically unstable and tend to repolymerize so post treatment of these oils are always required our extended periods of times (Diebold and Czernik, 1997).

In comparison with all the mentioned techniques, the hydrothermal treatment is the most promising process in which the waste materials are heated with water at certain proportion in the presence of an inert gas at high temperatures. This process has an advantage of neglecting the pre-drying process that is highly energy intensive in case of pyrolysis to produce the wide verity of prodects. The water used itself acts as medium to carry the hydrolysis reaction so the less activation energy requirements and flexibility in producing the fuels in required phases are the main characteristics of this process (Marzbali et al., 2021). When the both pyrolysis and hydrothermal process are compared to produce the liquid fuels from wet biomass, the composition of resulting fuels was almost same but the hydrothermal treatment method was found to be more energetically favourable and less energy demanding almost half of the energy required for pyrolysis process. In addition the hydrothermal treatment also provides the benefit of elimination of waste associated biological risks like pathogens existence due to autoclaving at temperature above 120 °C (Wang et al., 2018a). Finally, the products from hydrothermal treatment of waste have less moisture content with supress oxygen amount, but higher heating values that can make handling and storage processes economically feasible rendering the process competitive for waste plastic treatment.

There are several reviews published on hydrothermal treatment of waste plastic materials in which the focus was on the effect of operating conditions on product distributions, various types of output products, characterization techniques and overall reaction mechanism but with no or little focus on concept of using hydrothermal treatment of plastic as circular economy idea. The contribution of this treatment to the circular economy perspective is established by reducing the plastic waste and using it to produce the raw materials from which this plastic is originally made. This favours the use of same product and materials thus supporting the regeneration of natural systems. So state of art review is required to highlight this aspect in addition with discussing the materials and conditions of the hydrothermal treatment of plastic. So previous section of review was targeting the plastic waste composition, its effect on environment and life of living organisms, and pros and cons of different waste management technologies. Details on the hydrothermal treatment of plastic waste and concept of circular economy are coming in the next sections.

3.2. Hydrothermal treatment (HT)- State of art review

In this process the waste material is converted into useful product for energy production applications by heating it at elevated temperatures in the presence of water in high pressure sealed container. Water at the high temperature and pressure is subjected to ionization resulting the H_3O^+ and OH^- ions, serving as hydrolysis medium for conversion of complex compounds in subunits like glucose, so role of water in HT process is of key importance (Hydrothermal catalytic liquefaction and deoxygenation, 1717). Density of water is slowly decreased with the increase in temperature while the viscosity experience a sharp decrease. On the basis of dielectric constant (ε) the solvents are characterized as polar ($\varepsilon > 50$), semi polar ($20 < \varepsilon < 50$) and non-polar ($\varepsilon < 20$) so the decrease in the dielectric constant of water at elevated temperatures shift its characterization to words non polar solvents (Collins and Washabaugh, 1985). Now the water has this capability to dissolve the organic compounds having repulsion for water under normal conditions like free fatty acids. Water with these change parameters like high ionization constant and decreased viscosity, density and dielectric constant is most suitable solvent for HT process (Biller and Ross, 2014). But there is almost a thrush hold temperature to start the decomposition of waste biomass as hydrogen bonds resist this type of breakage. With the increase of temperature number of hydrogen bonds are going to reduce to form glucose that may be converted to some acids later (Greenwich Academic Literature Archive, 2357). At lower temperature the output product is mostly in solid form and mostly known as char, and the process is known as hydrothermal carbonization, as temperature increase the output products may be liquid or gaseous and the processes are known has Hydrothermal liquification and gasification.

The overall reaction mechanism of hydrothermal liquefaction is comparable to that of traditional pyrolysis. When PE and PP are taken as example, for instance, depolymerization is carried out through free radical reactions. Hydrogen abstraction reaction converted the highly reactive long-chain free radicals into saturated aliphatics while in parallel the beta-scission reaction produced the saturated compounds. Notably, additional cracking could convert paraffin produced by saturated aliphatics into C_2-C_4 combustible gases. Moreover, unsaturated aliphatics underwent cyclization and aromatization, resulting in the formation of C_6–C_9 aromatic hydrocarbons and C_8–C_{18} cycloalkanes, respectively. So the hydrothermal liquefaction of plastic waste is supposed to undergo through these steps: Depolymerization, degradation of the monomers through fracture, dehydration, decarboxylation, and deamidation, and fragment repolymerization.

$$\text{Plastic waste} + H^{\cdot} \rightarrow -R - (R_n) - R^{\cdot}$$

Hydrogen abstraction reaction

$$-R - (R_n) - R^{\cdot} + H_2O \rightarrow \text{Saturated aliphatics} + OH^-$$

In parallel the Beta-scission reaction

$$-R - (R_n) - R^{\cdot} + H_2O \rightarrow \text{Unsaturated aliphatics} + R^{\cdot}$$

Saturated aliphatics	→ (Isomerization)	Paraffin
Paraffin	→ (Gasification)	C_2-C_4 (Gas)

(continued on next page)

Unsaturated aliphatics	→ (Cyclization)	C_8-C_{18} (Cycloalkanes)
Unsaturated aliphatics	→ Aromatization	C_6-C_9 (Cycloalkanes)

3.2.1. Hydrothermal carbonization (HTC) process

HTC process may be known as wet torrefaction process can be used to produces the energy rich solid products from waste materials. In this process the material is heated in confined vessel at temperature above 180 °C–260 °C at pressure of 2–6 MPa for 5–240 min (Kambo and Dutta, 2015a). Corresponding to the rise in temperature the pressure is autogenerated with saturation vapour pressure of subcritical water. Dehydration of organic matter, polymerization and finally carbonization are major steps that govern the process of HTC (Funke and Ziegler, 2010; Paini et al., 2021). As the result of these reactions besides, solid-solid interaction the process is categorized for liquid and solid products like coke and char respectively.

HTC process can be prolonged in two pathways i.e. Polymerization process resulting the dissolution of intermediate compounds and decomposition very similar to pyrolysis process depending upon the severity of process conditions (Wang et al., 2018b). As amorphous cellulose is easy to collapse under subcritical water conditions so forts pathway is always dissolved part of cellulose and lignin (Satari et al., 2018). The second pathway is very similar to pyrolysis process for undissolved biomass. The char obtained from later mentioned process has high aromatic structure based on lignin. So the whole process will result in two various types of products, phenolic char and polyaromatic char (Cheng and Brewer, 2017). Lignin start to decompose at low temperatures with the breakage of weaker bonds like bond of carbon with hydroxide ions, and rupture of stronger bonds at high temperatures. Initial decomposition of lignin results in small molecules like aldehydes, styrenes and secondary decomposition at higher temperature results in formation of phenols, and catechols (Li et al., 2015). The radicals will continue to form the products until two radicals collide to form a stable compound like polyaromatic biochar via random polymerization.

Fracture of waste material is somehow different to the decomposition of single entity due to presence of strong covalent and hydrogen bonds between the components (Grochala and Edwards, 2004). The original lignocellulose always require a high amount of activation energy to destroy the base components. So this can be concluded that the severity of production of high energy char will depend upon both, the lignocellulosic composition and hydrothermal conditions (White, 2009). For same hydrothermal conditions the order of degradation of lignocellulosic material is reported as follows lignin < cellulose < hemicellulose (Reza et al., 2013b).

HTC of biomass: HTC process can convert the waste biomass into value added energy products at comparatively low temperature less than 250 °C and at saturated pressure of 10 MPa (Jamari and Howse, 2012). The final product has carbon content very close to that of lignite within range of 35–60% dissolved in aqueous phase with small amount of gas (Hoekman et al., 2011). Yield and heat content of the product is widely dependent upon type of biomass and operating conditions. No doubt with the increase of temperature energy densification is increased but most of benefits are related with moderate temperatures. Also the high temperatures are always related with high pressure so in such cases more safe, complex and costly reactor is required that makes the process less economical commercially (Newman and Jensen, 2013). The reported optimal conditions for the production of hydrochar with maximum yield, high energy density and coal like properties 255 °C and 5 MPa (Kambo and Dutta, 2015b). Carbonization process thus enhances the heating value and dehydrating capability, and process efficiency can be further increased by improving the solid yield and by recycling. Table 2, highlights the important parameters including temperature and residence time for different biomass materials that are widely available and utilized in daily life and can be used as feedstock materials to obtained energy dense products (Shen, 2020a).

Table 2
Operating conditions for various waste materials treated under HTC process (Shen, 2020a, 2020b; Iñiguez et al., 2019, 2019liz et al., 2022a).

Type of feedstock	Operating conditions	Reactor	Applications
Lignocellulose Cellulose	T = 200 °C, p = 16 bar, Time = 8–48 h	Stainless Steel autoclave	Solid fuel
Holocellulose	T = 220 °C, Time = 4–20 h	Stainless Steel autoclave	Solid fuel
Eucalyptus Bark	T = 220–300 °C, Time = 2–10 h	Stainless Steel autoclave	Solid fuel
Loblooy pine	T = 180–240 °C, Time = 2–6 h	Parr reactor	Solid fuel
Empty fruit Bunch	T = 150–350 °C, Time = 20 min	Parr reactor	Solid fuel
Rice husk	T = 230 °C, Time = 48.0 h;	Teflon autoclave	Porous carbon/battery material
Tobacco stalk	T = 180–260 °C, Time = 1–12 h	Teflon autoclave	Solid fuel
Human excreta	T = 180–240 °C, Time = 0.5–2 h	Stainless steel reactor	Fertilizer/solid fuel
Sweet potato Waste	T = 180–300 °C, Time = 0–4 h	Autoclave reactor	Solid fuel
Biomass and plastic waste	T = 180–250 °C, Time = 0–4 h	N/A	Solid fuel
E-Waste plastics	T = 250–350 °C, Time = 0–1 h	Autoclave reactor	Monomers of plastic production/chemical feedstock
Marine plastic debris	T = 200–300 °C, Time = 0–3 h	Batch type reactor	Solid fuel
Wet fraction from mixed municipal solid waste	T = 200–220 °C, Time = 1,4,8 h	Stirred reactor	Solid fuel

Analyzing the data shown in the table, its very obvious that the minimal temperature for HTC of biomass is 180 °C except for empty fruit bunches i.e.150 °C and maximum temperature is 300 °C for food waste but for most of other materials its nearer 220 °C–280 °C. With the increase of temperature the solid product yield is always reduced and product formation shifts towards the liquid phase but heat content of the solid product will increases. Residence time is an important parameter here that varies from few minutes to several hours and have direct relation with characteristics of product output, so it is necessary to find the optimal conditions of temperature and residence time for best process efficiency. Selection of suitable reactor type is also an important scenario.Its found that two types of reactor one is Parr reactor and other autoclave (Teflon-lined and Stainless steel) are widely used in these applications in batch or semi-continuous modes. So far, commercial application of HTC process is has been hampered by operational requirements.

HTC of waste plastics: Plastic waste with comparatively less amount of moisture is mostly treated on elevated temperatures (liquification and Gasification) for recovery of oil and gas fuels with high heating values (Nanda and Berruti, 2021). Some literature has been found on HTC of municipal solid waste consisting of paper and plastic for conversion in solid fuels (Lin et al., 2017; Lucian et al., 2018; Alves et al., 2021). Direct burning of plastic waste will result the formation of hazard gaseous compounds because existence of high content of chlorine (Li et al., 2019). HTC can be performed for dehalogenation that is debromination and dichlorination of waste from plastic, this will improve the energy density and will facilitate the effective combustion, the resulting oil can be used as chemical feedstock and char is used as solid fuel (Zhan et al., 2020).

HTC of polybutadiene and polystyrene copolymer consists of zip depolymerization and random chain breaking. The first step is the depolymerization of complex compound in simple polymers (Shen, 2020c). Polystyrene is converted to styrene through zip depolymerization. In addition to the double bond removal the hydrothermal energy breaks the C-C bond to form the radicals phenyls and alkyls (Zhu et al., 2016). Meanwhile the energy provided by subcritical water can be used to break the C-C bond of polybutadiene through random chain breakage to form linear alkyl radicals (Ma and Webster, 2018). So the decomposition of polymers generally included three steps chain initiation, free radical reaction and chain termination.

Co-HTC is another concept of interest where two polymers or materials are subjected to chemical treatment together. A common example is Co-HTC of PVC with biomass where reaction starts from the generation of free radicals (Shen et al., 2017). A subsequent elimination of HCL results in formation polyene. In case of aqueous suspension, decomposition of PVC is concluded by ionic chain reaction and chain cracking (Shen et al., 2017). Presence of lignin always prohibit the accumulation of particles of hydrochar during HTC so a lignin rich biomass can be used for the purpose of dichlorination of PVC. Literature also reports the co-HTC of PVC with wood chips bearing the fact that these wood chips also have high amount lignin (Huang et al., 2019). The condensed liquid product at end of the process and after dehydration always needs to be treated further. It has one significant use as a solvent to remove the soluble chlorine from solid products through washing process (Zhao et al., 2014). Obtained products are thoroughly washed with distilled water for specific period with some suitable speed. After completing the washing process the water is filtered to get the HTC solid product and can be recycled for next washing cycle (Hoekman et al., 2017).

Researchers in this area have been searching for simple, inexpensive, ecologically friendly, and nontoxic ways to make novel functional materials that can be commercialized soon due to the lack of energy, the environmental crisis, and growing customer demands. Among other methods, a viable contender for the synthesis of novel carbon-based polymers with a wide range of possible applications is the hydrothermal carbonization (HTC) process of biomass, whether it be made up of isolated sugars or unprocessed plants. A efficient technique for producing multi-walled carbon nanotubes (MWNTs) that are well-crystallized is the HTC process at high temperatures. For the synthesis of MWNTs, certain new methods have been reported (Lee et al., 2004; Manafi et al., 2008, Sliz et al., 2022b). At a temperature of 800 °C and a pressure of 100 MPa, Yoshimura's coworkers reported using a hydrothermal technique to create high-quality MWNTs from amorphous carbon without the need of a metal catalyst (Moreno and Yoshimura, 2001). Carbon films and materials with exceptional flexibility could be created using the HTC process at high temperatures. The development of carbon films on carbides under hydrothermal conditions at 300–800 °C was a good example of this process. This straightforward method made it possible to apply carbon films with adjustable thicknesses ranging from nanometers to micrometers to the surface of SiC fibers, powders, platelets, and single crystals (Gogotsi and Yoshimura, 1994). The monodispersed colloidal carbonaceous spheres produced by the HTC method at low temperature are made from carbohydrate sources like sugar, glucose, cyclodextrins, fructose, sucrose, cellulose, and starch. These materials are created through a variety of chemical reactions, such as dehydration, condensation, polymerization, and aromatization (Sevilla and Fuertes, 2009). In addition hydrochar with low chlorine content, acceptable particle size and higher heating value can be used as clean fuel for energy production applications.

3.2.2. Hydrothermal liquefaction (HTL)

The process of conversion of solid carbonaceous waste into liquid fuels at subcritical or supercritical water conditions 280–450 °C and at pressure range of 7–30 MPa, by knowing this fact that at this high temperature and pressure the water contain the sufficient amount of energy to break the carbon-carbon bonds in organic compounds (Kumar, 2013). During this process of conversion of solid waste into liquid a complex series of following reaction take places: initial cracking, hydrolysis in presence of water, free radical reactions, nucleophilic attacks, and cyclization reactions (Singh and Sharma, 2008). Water at temperature and pressure above its critical point is considered to be in super critical state, serves as catalyst or reagent, as in this state at temperature above 350 and pressure above 20 MPa the water behaviour is dramatically different as compared to ambient conditions (Kruse, 2008a). Low dielectric constant, higher density and ionic nature strongly supports the solvation process, and faster mass transfer is dependent at higher diffusivity and low viscosity as the reactant can permeate in solid waste structure more easily (Dogu et al., 2021d). In HTL the diffusivity is an important aspect as it believes that the rate of reaction is highly dependent on rate of diffusion. The process when carried out at suitable low temperatures the resulting product is liquid mostly the bio-oils but higher temperature shift the equilibrium towards the gaseous products (Zacher et al., 2019). As opposite to pyrolysis process the heating rate has no significant effect on product yield and other characteristics but the residence time is an important parameter of consideration while maintain the balance between heavy oils and light oils to minimize the gaseous product formation. So at the end of HTL process it is important to calculate the yield of various obtained products for example, Aqueous fraction (AQ), acetone-soluble fraction (AS), and content of residues (RS).The following equations can be adopted for these calculations (Dimitriadis and Bezergianni, 2017a).

$$Percentage\ HTL\ Yield = 100 - \left(\frac{mass\ of\ residues}{mass\ of\ feedstock}\right) \times 100 \tag{1}$$

$$Percentaeg\ of\ Aqueos\ mass\ fraction = 100 - \left(\frac{mass\ of\ AQ}{mass\ of\ AQ + mass\ of\ AS}\right) \times 100 \tag{2}$$

$$Percentage\ of\ Acetone\ Soluable\ fractions = 100 - \left(\frac{mass\ of\ AQ}{mass\ of\ AQ + Mass\ of\ AS}\right) \times 100 \tag{3}$$

Success of HTL Process is widely dependent upon the yield of liquid oils so accurate measurement of yield is important. When various biomasses are subjected to HTL process the generally predicted range from literature is 10–60 wt% which increases to more than 75% in some cases (Demirbas, 2011).

HTL of biomass, various wastes and microalgae: An important renewable energy source and representor of all types of non-conventional energies in Europe is wood (Hall et al., 2014). Biomass with high percentage of lignocellulosic content commonly known as woody biomass mostly comes from forests or wood processing industries, is strong candidates for being employed in fuel production applications because of easy and economical availability (Tribot et al., 2019). Some common examples of woody biomass that have been considered as HTL feedstock in previous years are wheat straws (Seehar et al., 2020), rice husk (Syamsul et al., 2014), date seeds (Al-Ansari et al., 2020), sawdust (Yang et al., 2022), corn stoves (Liu et al., 2021), sorghum (Stamenković et al., 2020), switch grass (Midgett et al., 2012), bamboo shells (Zhou et al., 2016), pine wood (Obeid et al., 2022) and others. This type of biomass has composition of cellulose, hemicellulose and lignin 30–50%, 15–35%, and 20–35% deliberations respectively and yield of HTL product from 17 to 68% by wight depending upon the operating conditions and parameters (Lee et al., 2019).

Apart from woody biomass waste coming from industrial sectors, agricultural waste and municipal waste have been extensively studied as the feedstock materials for HTL process to produce the bio-crude oils with encouraging yields and heating values. The produced bio-crude oil has the complex compositions of nitrogen-based species, (mainly pyridines, amines, indoles, amides and nitriles), non nitrogen based species mainly phenol and phenolic based compounds, easters, alcohols and hydrocarbons (Lee et al., 2020).

Solid waste consist of swine manure was also treated under the HTL process the resulting oil has the heating values above 35 MJ/kg with viscosity of 843 cP at 50 °C (Xiu et al., 2010). When the paper sludge from the paper industry was studied under this process the output products has the compositions of 20–45 percent oils soluble in water, up to 25 weigh percentage of heavy oils, with the heating values more than 400 MJ/kg (Zhang et al., 2011). Bio-crude oil extracted from the HTL treatment of agricultural waste has the yield of 36%wt on organic bases, with the composition on weight basses as 70% of carbon, 7% hydrogen, nitrogen with less than 1% weight (Cao et al., 2017). Increasing human population is the direct cause of rapid increase in unmanageable waste with problematic disposal. This waste is not only from household application but form food processing industries. Use of waste from food processing industries as feedstock for HTL process has also been studied.

From recent past years algae is introduced as important source for energy production applications for some reasons i.e. high production rate per acer, rapid growth, ability to survive against various environmental conditions, availability of byproducts. Algae has very high moisture content so HTL method is best appropriate as it does not require the pre-drying process make the process economical (Chernova et al., 2017). HTL of algae results in production of biocrude oil, solid char, gas and some water-soluble products (Chen et al., 2014b). Another benefit of algae feedstock is availability of chances for extraction and collection of nutrients, as the water at end of HTL process is rich in nitrogen, phosphorus and other important elements such as calcium, magnesium, and potassium so special treatments can be performed to obtain these value-added products (Guo et al., 2015).

HTL of Plastic: As compared to pyrolysis and HTL of biomass, the plastics that are long chain polymers are less investigated in past but now increasing concentration of various types of plastics and plastic products and their special compositions are making them favourite among the materials selected for use as feedstock in HTL. Table 3 summarizes the operating conditions for treating various kind of plastics (Li et al., 2022c).

It was concluded that with the temperature rise from 380 °C to 450 °C the concentration of aliphatic hydrocarbons decreases with the subsequent increment in concentration of aromatic hydrocarbons. While treating the PET the benzoic acid changed its significance from minor to major product with the rise of temperature above 400 °C so it appears the high temperature results HTL of plastic wastes in aromatic compounds. In case of LDPE the concentration of cycloalkanes increased from 17 to 86% when temperature increased by 50 °C from 250 °C and it again decreases to almost 76% with the further rise in temperature to 325 °C. Giving importance to residence time of reaction when HDPE was subjected to HTL process, the cycloalkanes and n-alkanes experienced the rise in concentration in 40–60 min and reached 43% at 120 °C. Similarly, when PS was subjected to HTL process with processing conditions of 400 °C, 30 MPa, and reaction time of 20 min the main products developed were styrene and propane while increasing the time to 1hr the considerable products were toluene and benzene. Thus, HTL can be adopted as suitable product for fuel production from waste plastics but prolonged reaction time is not supportive for gasoline product formation.

While working with HTL of plastic waste the water is mostly used as solvent but there are or some other options. PS yield in presence of water as reaction medium was almost 74% which was increased 84% with ethanol as reaction medium (Huang and Yuan,

Table 3
Operating conditions for HTL of various types of plastics (Li et al., 2022c; Seshasayee and Savage, 2020, 2021; Wang et al., 2014; Jin et al., 2020).

Plastic type	Catalyst	Operating conditions	Products	Maximum Yield (%)
LDPE	Sugarcane bagasse	T = 280°C, Time = 75 min, S = Ethanol	Bio-oil	32.3
PS	–	T = 350°C, Time = 30 min, p = 25 MPa, S = Pure water	Liquid oil	85.4
LDPE	Pt-promoted SZ	T = 250°C, Pt ratio = 1.5%	Olefins	55.6
PE	Sugarcane bagasse	T = 280°C, Time = 60 min, RCP = 17:3	Bio-oil	31.5
LDPE	Cu_2TiO_2	T = 300°C, Time = 30 min, RCP = 1:19	C_{13}-C_{19} liquid oil 86.4	86.4
PE/PP/PS (Mixture)	Commercial equilibrium	T = 400°C, Time = 30 min, N_2 flow rate = 600 mL/min,	C_5-C_9 gasoline	56.5
PE/PP/PS (Mixture)	Ni/Si-Al	T = 410°C, Time = 60 min, Ratio of Si to Al = 1: 1	C_5-C_{12} gasoline	78.5
PP, PS, PC, and PET	–	T = 350–450°C, Time = 30–60 mints.	Liquid oil	86
Mixture of plastics	Biomolecules	T = 300, 350, 400, 425°C, Time = 30 mints.	Liquid oil	78 with energy recovery of 45%
PC	–	T = 300–500°C, Time = 0–60 mints.	Phenol	58
Plastic waste	Jingou lignite, wheat straws	T = 260–300°C, Plastic waste/biomass = 5:4:1	Liquid oil	75

2015). Ethanol has potential to serve as reaction medium for HTL but more details investigations are missing in this scenario. In addition, the co-HTL of plastics has been reported in various studies for obtained the required results for example, when PE was subjected to co-liquification with bagasse the percentage of bio-oil was more than 30% with the calorific value of 34.9 MJ/kg (Baloch et al., 2020). In general the co-liquification of plastic with biomass can result high-values fuels but the yield need to improved.

Operating parameters: From all above-mentioned details its very obvious that HTL is process that is widely influenced by its operating parameters, some of these are off worth importance to discuss here. Reaction temperature, reaction/residence time, the use and type of catalyst, solvent type either water or ethanol, and final waste to water ratio.

Temperature is the most important parameter while performing the HTL process because it has a noticeable effect on the yield and quality of products. While referring the literature the temperature range for the process is 200 ˚C–450 ˚C but its very important to choose the exact value of temperature that varies depending upon the type of waste and its composition (Zhao et al., 2018). In predicting the overall trend, the yield of product is increased with the increase in temperature but this increment is limited to the certain temperature value, above this temperature value the yield of required product will start decreasing because of the competition between two processes hydrolysis and polymerization (Song et al., 2014). High temperature degradation of hemi-cellulose and lignin, that is endothermic at low temperatures but becomes exothermic at higher temperatures can be considered as another reason of decrease in yields at high temperatures (Xu and Etcheverry, 2008). Infect there is no certain values of temperature for HTL of waste but in generally it can be predicted that with the increase of temperature the yield increase up to a certain point after that point the product yield levels off or decreases.

In some cases that have been reported in literature use of suitable catalyst effects the product yield and characteristics in supportive way. The catalysts that are commonly used with different types of biomass materials are Na_2CO_3, H_2SO_4, FeS, HCl, $FeSO_4$, K_2CO_3 and solid alkalis (Hydrothermal processing of biomass). Main purpose of using these catalysts is reducing the yield of char and enhancing the liquid product formation that are mostly oils. Technically catalysts supress the repolymerization and some condensation reactions happening between the intermediary compounds formed by the continuous disintegration of lignin at high temperatures (Shrotri et al., 2017). In case of microalgae use of homogenous catalysts were found to be supportive for increasing the yield but heterogenous catalysts have adverse effects because of sintering, dissolution of products and limits in diffusion process (Xue et al., 2016). So selection of suitable catalysts is of great importance to achieve the targeted outcomes, the details research is still needed in determining the parameters that can help in selecting the proper catalyst to narrow down the product distribution to support the commercialization of HTL.

The time period for which the maximum temperature is maintained during HTL process excluding the heating time to reach the desired maximum value or cooling time at end of reaction during the HTL process is known as residence time. Residence time variation effect the process outputs comparatively in similar way of temperature. With the increase of residence time the yield of product is increased but up to a limit, further enhancement of this residence can effect he outcomes in adverse way (Patil et al., 2020). Increasing the residence time limits the solid product formation but high residence time will support the repolymerization reaction resulting the increase char formation (Jayathilake et al., 2021).

As the water is almost the part of every type of biomass in less or more proportions, so it is very important to evaluate the overall ratio of solid reactant to water. High biomass to water ratio when employed in HTL process the reduces the yield of heavy oils while increasing the water content results higher yield of heavy oils but the operation need more sever conditions that need more energy (Caporgno et al., 2016).

HTL process is not only limited to water as liquid medium. During the HTL process the success of achieving the required outcomes is dependent upon the selection of suitable liquid medium. Most commonly used solvent during the HTL process is water because its easy availability and low cost, however literature report some other solvents that can be employed to accomplish the HTL process goals. Water has to play triple role, as a solvent, reactant, and to support the reaction by working as catalyst (Casanova et al., 2009). Its fact that at normal temperature and pressure conditions most of biomass-based products are not soluble with water but high temperature make the water suitable solvent. Some other liquids like use of ethanol and methanol is also supported through already existing literature, because these two have parameters like, critical points, dielectric constants, boiling points less than that of water, making them suitable liquids for HTL process (Singh et al., 2015). While employing the ethanol and methanol as solvents, due to less critical points the HTL reaction can successfully carried at less sever conditions as compared to water as reaction medium (Xiu and Shahbazi, 2012). Finally due to comparatively low dielectric constants methanol and ethanol has possibility to dissolve very high molecular weight products. Concept of co-solvent HTL process is also existing in literature. When co-solvent system consisting of equal ratios of alcohol to water applied to pine sawdust the bio-crude yield was high as 65% (Yerrayya et al., 2022). Effectiveness of co-solvent HTL has also proved for Tertiolecta liquefaction with ethanol to water ratio of 40/60 by volume and overall product yield of 64% (Dimitriadis and Bezergianni, 2017b).

Hence the choice of proper solvent, alcohol or water or combination of both depends upon the type of biomass. Researchers can further investigate the technoeconomic aspects of using the alcohol as solvent during the HTL by owing the fact that use of ethanol or methanol require milder operating conditions that can save the energy cost at higher scale but buying the alcohol is maybe expensive. So a detail cost analysis is required for using the organic liquid as solvent in HTL process. Further details studies are still needed about the co-solvent HTL of various types of materials, proper ratios of liquids and resulting outcomes.

3.2.3. Hydrothermal gasification (HTG)

Employment of comparatively elevated temperature and pressure to various types of feed stocks for production of sin gas rich in hydrogen content, is commonly known as HTG (Lu et al., 2008). In super critical state water does not exhibit distinct liquid and gaseous phases and have the dissolution properties compared to that of liquids and diffusion characteristics of gasses. At super critical state the water is highly sensitive towards any change in its pressure and temperature but there is no existence of surface tensions because of absence of boundary layer between two phases that are already merged (Dahms and Oefelein, 2013). Under super critical conditions i.e. 22.1 MPa of pressure and 374 °C of temperature water has some interestingly changed properties for example high diffusivity, viscosity, low dielectric constant, that support high mass transfer and solvation properties (Okolie et al., 2019).

As compared to conventional gasification processes, the HTG is proved to be preferable because of its ability to deal with feed stock having high moisture content. During the conventional process the heat to evaporate the moisture content dominates the heat of combustion of feedstock. So required step is predrying of feedstock that makes the process less economical. In addition the reaction rate is higher in case HTG than other gasification techniques (Barneto et al., 2008). Water in super critical state is mostly used for the production of hydrogen gas from waste biomass and other organics (Azadi and Farnood, 2011). Similar to HTL in HTG the product characteristics and products distribution is widely dependent upon the reaction temperature, residence time, pressure, biomass to water ratio, and use of catalysts (Das et al., 2021). These parameters are suspectable to effect the product yield, efficiency of gasification and carbon conversion process, hydrogen selectivity and other attributes.

Fluidized bed technology is frequently employed in production of hydrogen-rich synthesis gas because of its many benefits, which include high heat transmission, uniform and adjustable temperature, favourable gas-solid interactions, etc. Mansaray et al. (Śliz et al., 2022b) investigated a fluidized bed system with a dual distributor design for rice husk gasification. On the performance of the gasifier, the impact of altering fluidizing velocity (0.22–0.33 m/s) and equivalence ratio (0.25–0.35) was discussed. A maximum C (carbon) post conversion of 70% was attained in the biomass gasification study conducted by Miccio et al. (1999). Numerous publications (Li et al., 2004; An experimental study on biomass; Turn et al., 1998) have researched the sawdust gasification performance for production of hydrogen-rich synthesis gas. On the composition and heating value of the produced gas, the impacts of the gasification temperature, equivalency ratio, O/C ratio, and steam-to-biomass ratio were investigated. Over the range of experimental conditions investigated, Turn et al. found the hydrogen yield potential to be the most sensitive with equivalency ratio (Li et al., 2004). Li et al. (An experimental study on biomass) have noted that the O/C ratio has a significant impact on the gas composition and heating value. Lim et al. (Turn et al., 1998) air gasification of wood chips in a bubbling fluidized bed gasifier also involved studying the performance in terms of heat output. At a bed temperature of 733 °C and an equivalency ratio of 0.23, they demonstrated that the gas produced has an energy content of 4.75 MJ/m^3. The final thermal output was 355.55 kWth, with a thermal efficiency of 61.32%.

Effect of HTG process on lignocellulosic biomass and various residues: Lignocellulosic material has cellulose, hemicellulose and lignin as major structural constituents. While discussing the detail composition, cellulose is the 2nd major component with more than 25 wt%, hemicellulose with 33 wt% and lignin as more then10 wt% (Carrier et al., 2011). Hydrolysis of cellulose mostly results in glucose, which is completely homogenous, providing the ease to study the reaction kinetics, this property makes cellulose favourite as model compound to study the HTG process (Kruse, 2008b). When the HTG of cellulose was performed in glass reactor at super critical water conditions the yield of gas product was 8.2 mmolg^{-1} that is comparatively less than reported for steel reactor under same conditions (Castello et al., 2013). The predicted reason for the high yield, in case of steel reactor is heterogenous catalyst effect coming from walls of reactor. Contribution of cellulose towards H_2 gas production is always higher than that of cellulose and lignin (Kang et al., 2016).

Hemicellulose is the mixture of sugars as well as sugar acids mainly mannose, glucose, and xylose and more abundant after the cellulose as the constituent of biomass feedstock (Saha, 2003). High content of moisture existing with hemicellulose makes it most suitable type for HTG, while less suitable for other gasification processes (McKendry, 2002). Timothy grass that is widely found in Europe is considered as high energy source because its ability to produce the high percentages of gaseous products. For example under super critical water conditions the Timothy grass produced total gas yield more than 17 mol kg^{-1} with hydrogen content more than

5 mol kg^{-1} in absence of any catalyst. Addition of KOH as catalyst increased the overall percentage of gas in much supportive way (Nanda et al., 2016).

Lignin is considered as essential component of most of the biomass materials having higher percentages of lignocellulosic materials. HTG under super critical water conditions is used for both, mainly for production of H_2 gas and recycling process to treat the biomass base residues after specific process. Coconut shells with the comparatively high content of lignin, when subjected to HTG at 600 °C the results were more enthusiastic as compared to HTG of other food residues with numbers of more than 7 mmolg^{-1} for overall production of gas while, 2.15 mmolg^{-1} for production of hydrogen gas with out the implication of catalytic conditions (Shan et al., 2020). When lignin is treated under subcritical water conditions, the initial and very basic step is hydrolysis of branches into phenolic compounds and aldehydes. These intermediate compounds can undergo repolymerization process to form aromatic solid products like chars at elevated time periods. However supercritical treatment of lignin can convert it into liquid state prolonged to gaseous phase and yields of gaseous products cane be increased by catalytic or other suitable methods (Pavlovič et al., 2013).

4. HT and concept of circular economy

The present waste management directives of European Union (EU) seek to encourage the waste avoidance and implementation of waste hierarchy principle i.e., reduce the waste by reusing, recycling, recovering the valuable part (including the energy recovery) before landfilling or disposal. In order to achieve the best overall environmental outcome and to reintroduce the valuable materials into economy, waste management based on waste hierarchy was defined in 2015 by circular economy strategy from EU (Geissdoerfer et al., 2017). Concentrations of solid waste and energy deficit, difference between energy produced and energy demand are increasing in both developed and developing countries. So conversion of waste into value added products or in energy rich fuels by adoption of various waste-to-energy techniques can solve the problem of increased waste and energy deficiency (Kothari et al., 2010). Incineration, pyrolysis, gasification, and HT are the major techniques that can be employed for mentioned purpose, but each technique has different potential to convert waste to energy with some limitations, so selecting best technology for management of waste in terms of energy conversions can underpins the concept of circular economy. But this concept is highly reliable on multidisciplinary approaches and intangible framework. One of such framework is shown in Fig. 4 (Munir et al., 2021). Circular economy always plans to recycle the waste by adoption of conventional and non-conventional technologies to minimize the landfilling of that waste. Segregation of organic and inorganic species is also a secondary purpose (Awasthi et al., 2022).

Organic materials that have higher ability of being recycle can still treated through conventional technologies but non recyclable materials are mostly subjected to HT processes (Zhang et al., 2010). Obtained energy and useful products can again subjected to homes and various industries in this way product remains in cycle for a long time. The HT of waste biomass need the cooperation of farm owners, entrepreneurs, local government entities, research institutes, suppliers, and industrial sections. Successful commercialization of HT for bioenergy production from waste materials, assures the most successful use of waste, and ensures the job opportunities for locals. Energy production through HT of waste materials also provides the energy security to all those countries where the fossil fuel resources are depleting and import of oils and coal is burden on economy (Jaber et al., 2004).

In general the HT treatment has high potential to efficiently dispose the waste materials as an alternative to other wase management techniques like incineration and landfilling in addition with renewable energy production. By providing the alternative solution of conventional waste management technologies, the concentration of toxic contaminants in the environment can be reduced so reducing the health threats and negative impacts of global warming. Selling of HT products will generate the revenue and the process can be made more economically feasible by asking for the fee from large industrials sectors to manage their waste (Chen et al., 2010). Lot of work has been done on HT treatment of various type of materials, but detail studies are still needed for commercialization of this technology and on economic and life cycle assessment of HTC, HTL and HTG processes.

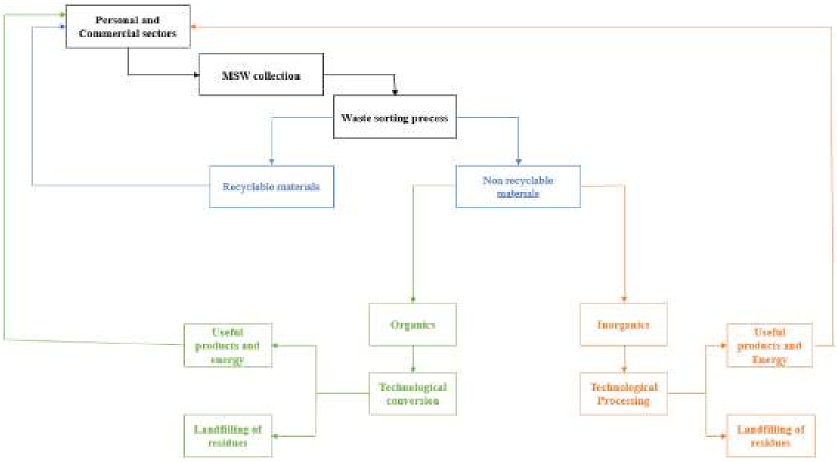

Fig. 4. Circular economy framework.

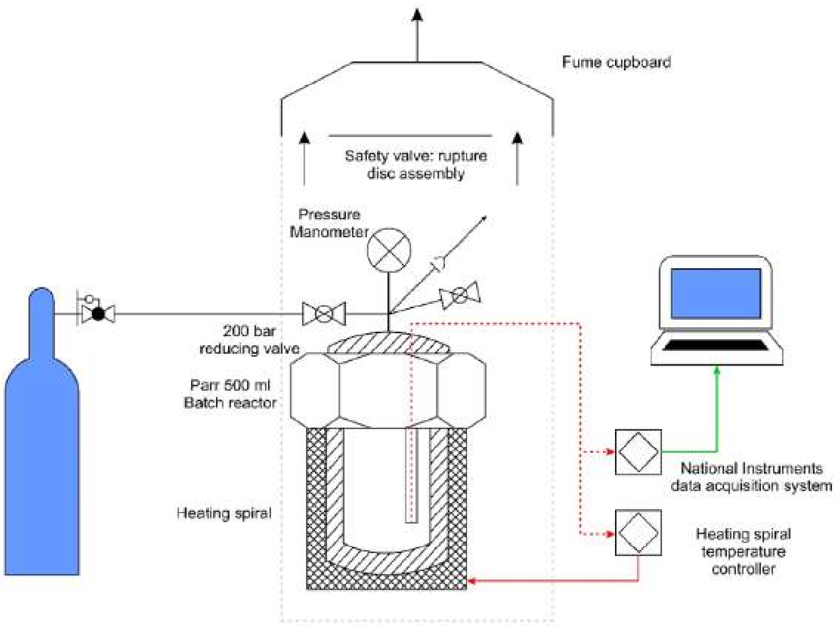

Fig. 5. Heating spiral, Parr reactor, parr reactor controller.

5. Details of setup for HT process

An example for batch HT process setup (Fig. 5) is the installation setup available in Departmental of Thermal Technology, Silesian University of Technology, Poland. HT experiments including HTC, HTL, and HTG are performed in Parr reactor (series 4650, II, USA) having the volume of 250 ml coupled with bench top high temperature spiral used for heating the parr reactor and heating temperature, pressure are controlled by Parr 4838 temperature controller.

Upper part of the Parr reactor that is called head has a pressure gauge on the top that can be used to measure the pressure in Bar and Psi with the maximum range of 344 Bar and 5000 Psi. Two straight walls one is used to connect the reactor to some pressure source to fill some inert gas may be nitrogen and other valve is used remove the unwanted gasses or collect the useful one after the process finishes. Head has a hole making the way to the thermowell in which thermocouple is placed to measure the inside reactor temperature. Lower part is just a cylinder like chamber for keeping the reactants. Both parts are connected together by drop banned W screws.

Temperature during the process is controlled by the Parr controller based on PID groups and each group with certain temperature value. Ports are provided on the back of controller for connecting power supply and pressure and temperature measuring sensors. J-type thermocouple is used to measure the temperature. There is another port with name Comm connector and its for communication purpose. On the front side of the controller there is a switch whose position determines either the heater is off, working at maximum or half capacity while the other switch is to turn the controller on or off. High limit indicator light will glow in red colour to give the signal either temperature or pressure have reached high limit and high limit reset switch has opened. There is also small display that exhibits the set value for the temperature inside the reactor and current value of value of the temperature. And these values can be changed by using the keys with display.

6. Conclusion

Use of various kinds of plastics is increasing in industrial sectors that results in large amount of plastic waste with the problem of waste management and recycling. These plastics are not only dangerous for human beings but also reducing agricultural production, causing health problems for animals and putting the aqua lives on high risks. Landfilling, mechanical recycling, incineration, pyrolysis are previously used technologies to convert this plastic waste into energy but to overcome the drawbacks associated with these technologies like, less product yield, air pollution, high operating cost, HT is proved to be as better solution. HT including HTC, HTL and HTG are widely dependent upon operating temperature, residence time of the reaction, type of catalyst and water to waste ratios. But details studies are still needed upon the parameters to select the most suitable catalyst having the dominant effect on product distributions. One can investigate the use of methanol and ethanol for various kind of plastics with detail technoeconomic analysis. Various efforts are still needed to commercialize the HT process to convert waste to energy. Waste to energy conversion also brings the idea of circular economy where the products are recycled to keep them the part of working cycle for a long time hence reducing the concentration of waste. But high process cost, limited understanding of process, partial commercialization, meeting the technology readiness levels are various challenges that still needed to overcome.

Authorship statement

Conception and design of the study: H.Mumtaz.
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Analysis and/or interpretation of data: H.Mumtaz Roksana Muzyka.
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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Plastics Waste: Feedstock Recycling, Chemical Recycling and Incineration - A. Tukker - Google Books, https://books.google.pl/books?hl = en&lr = &id = 16-QHqe03foC&oi = fnd&pg = PA20&dq = Incineration + technology + mainly + relies + on + pre-treatment, + combustions + system, + energy + recovery + flue + gas + cleaning + steps. + Metals + and + glasses + trapped + in + plastic + structure + that + are + known + as + non + carbonaceous + materials + are + mostly + removed + during + pre-treatment + proces&ots = kWycr1OZgf&sig = QYNEwN2FP_d8b9t6plyQeO4SLT8&redir_esc = y#v = onepage&q&f = false.

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Appendix B

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An experimental investigation and process optimization of the oxidative liquefaction process as the recycling method of the end-of-life wind turbine blades

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ABSTRACT

The article contextualizes and expands upon research related to oxidative liquefaction of wind turbine blades for resin degradation and glass fiber recovery, presented at the 17th SDEWES conference series on Sustainable Development of Energy, Water and Environmental Systems 2022. The effect of five different parameters, including reaction temperature, residence time, pressure, waste-to-liquid ratio, and oxidant concentration, on resin degradation, has been studied in detail. Experiments were performed in the temperature range of 250 °C–350 °C with a residence time of 30–90 min, at a pressure of 20–40 bar, a waste-to-liquid ratio of 5–25%, and oxidant concentrations of 15–45% by weight. The maximum resin degradation yield achieved was in the range of 95–100% against the different combinations of tested parameters, and its minimum value was 43%, but detailed analysis revealed that the waste-to-liquid ratio is the key parameter affecting resin degradation yield. In addition, energy consumption is one of the important parameters determining the economic feasibility of the process, so a detailed optimization of the experimental plan based on maximum resin degradation and energy consumption has also been performed to identify the most suitable conditions that support the implication of the process at a larger scale.

1. Introduction

Considering the role of wind energy in renewable energy sector [1–4] this special issue from the 2022 conference on Sustainable Development of Energy, Water, and Environmental Systems (SDEWES) presents an advancement in hydrothermal treatment technique presented in previously reported special issues [5–9] for effective recycling of wind turbine blades.

The wind energy sector is playing a crucial role in achieving the goals of the climate change agreement, improving energy security and diversity, as well as reducing the impacts of fossil fuel consumption [10]. In 2021, the total amount of wind power installed globally reached approximately a total of 837.5 GW, which is mainly distributed among five countries China, the USA, Germany, the UK, and India [11]. Contrary to other turbine components, and assuming a lifetime of 20–25 years for a wind turbine, it is predicted that around 42 Mt of waste wind turbine blades (WTB) will need to be recycled annually worldwide by 2050 [12]. According to the EU Waste Framework Directive hierarchy, the disposal of waste without recovery of any form of energetic or material potential should be avoided [13,14]. The recycling of the WTB should be aimed to recover and reverse as much of the materials and substances back to the loop to not deepen the already environmentally intense cost of its manufacturing.

Effective recycling of the WTB represents a challenge due to the materials used and their complex composition. The WTB consists of various materials with different properties. Although specific compositions may vary depending on the blade types and manufacturers, final blades are generally composed of [15]:

- Main reinforcement: glass, carbon, aramid, or basalt fibers;
- Polymer matrix: epoxy, polyester, vinyl ester, thermoplastic, or polyurethane (PUR);
- Core: light wood e.g., balsa and foams e.g. polyethylene terephthalate (PET);
- Coatings and small metal parts.

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Symbols

M – moisture content, wt.%
A – ash content, wt.%
VM – volatile matter, wt.%
C – carbon, wt.%
O – oxygen, wt.%
H – hydrogen, wt.%
N – nitrogen, wt.%
S – sulfur, wt.%
IR infrared
PTFE polytetrafluoroethylene
TC – thermal conductivity

Superscripts
^{a} – analytical state
^{d} – dry state
$^{diff.}$ – calculated as difference

The combination of fibers and polymers represents the majority of the WTB's material composition (60–70% reinforcing fibers and 30–40% resin by weight).

Wind energy is often perceived as clean RES, not generating any emissions during the wind farm operation, however, a detailed ecological study may indicate otherwise even for this stage [16]. The manufacturing stage of the wind farm is energy and resource-intensive and is associated with a range of non-renewable chemical usage [17]. Landfilling of the decommissioned and dismantled WTB parts poses a significant environmental threat, as well as enormous losses of the primary energy and materials used for its construction. The necessity of recycling WTB components is crucial not only from the environmental point of view but allows the recovery of energy and valuable materials e.g., glass fibers and resin monomers from waste composites, otherwise directed to the landfills. Most of the decommissioned wind turbine parts and components e.g., the tower, steel parts, magnets, and batteries can be recycled, however, problems arise when the end-of-life blades are taken into consideration.

Due to the WTB's extraordinary mechanical strength and additions of complex chemical compounds, the WTB is considered a challenging material considering conventional thermal recycling methods, with low calorific value and high pollutants and particulate emissions [18]. Mechanical recycling of the WTB on the other hand allows to process and segregation of specific fractions of the original structure with relatively low energy consumption, however, at the cost of the loss of high–aspect ratio fibers that can contribute to greater modulus, strength, and toughness during grinding [19,20]. The last of the recycling methods for the WTB is the chemical solvolysis and oxidation methods allowing apart from the virgin fibers also recovery of the epoxy resin monomers or the production of other chemicals. In most of the literature findings, the chemical recycling methods are perceived as the least mature methods that need further research for recognition of the optimal technologies, process parameters, energy consumption, and recovered product quality [21]. Having that in mind, an efficient and sustainable strategy for dealing with WTBs from withdrawal from the exploitation of wind turbines is announced as one of the major environmental issues in the coming years.

1.1. *Recycling methods of the large composite wastes*

Currently, methods for WTB recycling are co-processing in cement kilns, pyrolysis, or solvolysis, however, very little legislation for the disposal of end-of-life blades is available [22]. In general, the recycling methods of composite wastes can be divided into three main categories: (1) thermal, (2) mechanical, and (3) chemical. According to Jensen et al. [15], the energy input required to produce 1 kg of composite material is estimated to be 111.88 MJ/kg, including fiber production, fabric production, resin production, and the extrusion process, whereas the recycled material will have an energy demand only one-tenth that of the original composite, justifying the need to further develop the WTB recycling methods in the future. Numerous review papers already presented and discussed the comparison between specific recycling methods concerning energy consumption, fiber quality, and secondary products, so in this paper only a summary will be presented with emphasis on state-of-the-art experimental achievements and the latest reports in the field [23–26].

Pyrolysis of the WTB is aimed at thermally degrading the polymer matrix at high temperatures in the absence of oxygen [27,28]. The recovered fibers are covered in char and mixed with a liquid product of the process. What must be added is that the glass fibers' mechanical strength suffers from processing at temperatures above 450 °C, and additional removal of char creates the necessity of secondary processing to decontaminate the fibers from pyrolysis char at temperatures as high as 1300 °C. In the case of carbon fibers, which are more resistant to high temperatures, pyrolysis forms a char-like layer on the fibers' surface, decreasing their capacity to bond with new resins [29]. Fonte et al. [25] presented a study on composite matrix pyrolysis using static and concluded that polyester completely decomposes at a temperature of 450 °C while other polymers *i.e.*, phenolic resin, epoxy, polypropylene, polyethylene, and vinyl ester, required higher temperatures 500–550 °C.

When recycling is done mechanically, the mechanical treatment and separation processes have the ability to create new raw materials. Mechanical recycling is an efficient way to recycle wind turbine blades. This solution is usually used to recycle carbon fiber-reinforced composite blades. By substituting conventional fossil fuels and employing the GF composite leftovers within the cement matrix, the waste composite panels (WCPs) are crushed and blended with components that might be used as a great solid combustible for the cement industry. In a different investigation, Palmer et al. [30] recycled GFRPCs, or sheet molding compounds, mechanically by grinding and reincorporating (SMCs). SMCs and DMCs are ground into a fine powder to reduce their size, or granulate, in order to be used again. The next step was to sort the fiber size using a cascade air classification system, which is mostly used in industry to dedust goods. For the creation of composites, it is typically advised to replace 5–30% by weight of virgin fibers (VFs) with recycled fibers (RFs) in order to obtain the best mechanical qualities [30,31]. The impact of mechanically processed GFRPCs on the wind turbine blade shell was studied by Yazdanbakhsh et al. [32]. The addition/replacement of recycled thin elements called needles (5% and 10% by volume) in the concrete mixture was noted. The results showed that there was no adverse impact on the new concrete's stability, workability, tensile, compressive, or flexural strength.

A recent study presented by Nagle et al. [33] on end-of-life turbine blade recycling presented a hypothetical assessment of WTB co-processing in the cement industry in Ireland and Germany. Co-processing in a cement kiln requires that blade material be shredded into smaller parts, thus mechanically processed, and then blended with Solid Recovered Fuel (SRF) as an alternative fuel made from mixed dry recyclables that are too difficult to separate and that would otherwise be directed for landfilling. The study concluded that the co-processing of Irish blade waste at a 10% material substitution rate in a German cement kiln was found to be six times better environmentally than depositing waste in an Irish landfill. Nevertheless, the authors stated that future research is needed to compare the costs of co-processing to other repurposing ideas and to develop a policy that requires farm owners to set aside bonds to pay for more sustainable second-life options for blade waste.

Reduced reaction times, improved performance, ease of examination, parity with green chemistry methods, and an increase in the reaction's stereoselectivity are all common benefits of microwave irradiation. The efficiency of multiple/numerous organic modifications and synthesis has been strengthened by the effectiveness of microwave-assisted synthesis. To recover CFs from carbon fiber epoxy composites, Lester et al. [34] used a microwave-assisted pyrolysis recycling process (multimode microwave applicator with power 3 kW and heating time 8 s). Small changes in the surface topology of CFs were noted, including relatively clean surfaces, improved tensile strength, and a greater modulus. Using a microwave pyrolysis technique, Akesson et al. [35] retrieved RGFs from used wind turbine blades. The decision was made that the fibers could be used to make new composites. Fiber mats with changed VGFs and RGFs were used to create laminates. Mechanical testing revealed that composites with up to 35 wt% RFs may be produced without the mechanical characteristics degrading. Jiang et al. [36] reported recovering CFs from CFRPCs by irradiating them with an energy-efficient microwave.

The chemical recycling of the WTB is based on the solvolysis process, where the solvent breaks down the thermosets resins epoxy and polyester sometimes with the additional of organic catalysts. The process can be performed at different temperatures and through the use of various solvents, usually at lower temperatures than pyrolysis and at higher pressures [37]. The term solvolysis implies a technique to use a reactive solvent to break the covalent bonds of a polymer matrix [38]. As a result, the polymer matrix monomers and decomposition products, whose ratios are dependent on the process conditions, are mixed with the solvent to form a liquid product, while the fibers are separated and freed from the matrix structure.

Comparing the energy consumption of all of the reported methods, the specific energy demand for mechanical processes is minimal 0.27–3.03 $MJ/kg_{composite}$, followed by the pyrolysis 1.0 $MJ/kg_{composite}$, whereas the same for chemical processes is the highest (63–91 $MJ/kg_{composite}$) [38]. However, despite the high energy consumption of the solvolysis, it is the only method that allows recovering the high-energy-dense polymer matrix from the blade in the form of useable matrix monomers, which are otherwise destroyed during the pyrolysis or mechanical grinding, justifying the effort to further develop and optimize the chemical recycling methods of the WTB.

Thermochemical methods are the particular perspective of sustainable techniques for valorization of organic waste and can be divided in conventional one dry route (pyrolysis and gasification) and wet route (hydrothermal treatment) [39]. Hydrothermal treatment is the process of chemical conversion of waste materials at intermediate temperature and high pressure in aqueous environment. This process is also supportive for treating the organic fractions with high moisture content as it omits the pre-drying step [40]. When water is maintained at its subcritical conditions its dissociation constants increase drastically and it acts as universal solvent to dissolve different types organic compounds as in this phase the hydrolysis and ionic reactions are very dominant [41]. As the results of these reactions and depending upon operation conditions the obtained products can be divided in four major types i.e. (I) solid fraction called bio char and process is known as hydrothermal carbonization at temperature less than 250 °C, (II) organic liquid products as crudes, (III) polar liquid products dissolved in water, process is known as hydrothermal liquefaction and subcritical or near critical conditions of water favors the rection, (IV) gaseous products that are obtained as the result of hydrothermal gasification [42]. Tendency of resulting the wide verity of products the process has been used to treat the various waste materials i.e. chicken meat and bone meal [43], cherry pomace [39], general plant waste [44], domestic sludge in high-rate ponds [45], sludge dewatering [46], Ammi visnaga plant [47], duckweed [48], but its potential to treat the complex composite waste like WTBs is still hidden.

1.2. Aim of the paper

This paper proposes a new method for the chemical recycling of end-of-life composite blades, namely oxidative liquefaction. The process combines the hydrothermal treatment of the composite waste in subcritical water with the addition of the oxidizing agent, in this case, the hydrogen peroxide H_2O_2 in moderate concentrations. The study aims to experimentally investigate the WTB polymer matrix degradation during the oxidative liquefaction process in a batch reactor at variable temperatures, processing times, waste-to-liquid ratios, and oxidizer concentrations to measure the total solid reduction, resin degradation, glass fiber yield, and quality. Analysis of variance has been used to identify the most important parameters affecting the resin degradation yield total solid reduction, and process optimization have also been carried out to identify the most suitable conditions for oxidative liquefication of WTBs.

2. Materials and methods

2.1. End-of-life wind turbine blades

Pieces of wind turbine blades were provided by the ANMET, Poland, company working in the WTB recycling field. At the Silesian University of Technology, the samples were cut with an angle grinder and milled into 1–2 cm pieces with shredder mills (Fig. 1). The obtained parts of the WTB were most probably the high-end tips of the blades, consisting only of the polymer matrix and glass fiber structures, without any metal or wooden parts.

2.2. Ultimate and proximate analysis

The ultimate analysis of the WTB sample was carried out using a Leco 828 Combustion Series analyzer. The proximate analysis was performed using the thermogravimetric and weight methods. The investigated parameters were determined according to the standards presented in Table 1.

2.3. Oxidative liquefaction process

2.3.1. Batch reactor

In this study, a Parr 4650 (Parr Instr., ILL, USA) 500 ml batch reactor

Fig. 1. Wind turbine blade samples use for experiments.

Table 1
Standards and methods used for the ultimate and proximate analysis of the investigated WTB sample.

Parameter	Standard	Method
Moisture, M^{a}	PN-G-04560:1998	Thermogravimetric
Ash, A^{a}	EN ISO 21656:2021–06	Weight method
Volatile matter, *VM*	EN 15402:2011	Weight method
Carbon, C^{a}	EN ISO 21663:2021–06	HT combustion with IR detection
Nitrogen, N^{a}	EN ISO 21663:2021–06	HT combustion with IR detection
Hydrogen, H^{d}	EN ISO 21663:2021–06	HT combustion with IR detection
Sulfur, S^{a}	EN ISO 21663:2021–06	HT combustion with TC detection
Oxygen, $O^{a.d.}$	EN ISO 16993:2016–09	Calculated as a difference

was used to carry out the oxidative liquefaction process (Fig. 2). The reactor is equipped with a Parr 4838 temperature controller and an additional data acquisition system based on the cDAQ controller and temperature recording module NI-9212 (National Instruments, USA). Before the experiments, the reactor and reactor controller were calibrated for specific temperatures, to optimize the heating power of the spiral in order to maintain the constant temperature of the sample at given residence times.

2.3.2. Design of experiment (DoE) plan

As an experimental design technique, the central composite design (CCF) was employed to discover the wet oxidation conditions. The CCF required $2{\cdot}k + 2^{(k-1)} + n_{centre}$ trials, where k is the number of variables that changed during the experiment. The design is made up of three types of points: the $2{\cdot}k$ axial points are generated by a screening analysis, the $2^{(k-1)}$ cube points are generated by a fractional factorial design, and the centre (n_{centre}) point is generated by a nominal design. Each variable in these circumstances has three tree levels, denoted by the symbols 1, 0, and +1. In this strategy, variables might be either quantitative or qualitative. The full terms and conditions of the trials are listed in Table 2. Five variables were examined during this experiment: the temperature of the wet oxidation process, the residence time, the pressure, the amount of oxygenated reagent (hydrogen peroxide solution), and the waste-to-oxygen solution ratio. to minimize the number of tests required As a result, the number of feasible tests was severely limited, and it was decided to use a 29 for CCF, requiring a total of nineteen trials (for k = 5; 10 from $2{\cdot}k$, 16 from $2^{(k-1)}$ and additional 2 in the center). The CCF is a valuable tool for estimating interactions between variables. It can estimate a constant term, five linear terms, ten two-term interactions, and five quadratic term interactions.

Table 2
The coded values of the central composite face-centered (CCF) $2^{(5\text{-}1)}$ experimental plan were used for the investigation of the oxidative liquefaction process.

No.	Variable	−1 *(minimum)*	0 *(center)*	1 *(maximum)*
1.	Temperature, °C	250	300	350
2.	Initial pressure, bar	20	30	40
3.	H_2O_2 addition, wt.%	15	30	45
4.	Process time, min	30	60	90
5.	Waste-Liquid ratio, wt.%	5	15	25

2.3.3. Sample preparation

Before the experiments, the WTB samples were milled with a blade grinder to obtain WTB chips of 1.5–2 cm in length. Next, a specific amount of the raw WTB was placed in the Parr glass liners, and the liquid reaction medium consisting of the mixture H_2O/H_2O_2 at specific ratios (Table 2) was added.

2.3.4. Experimental procedure

Before each of the experiments, the 4838 reactor temperature controller was calibrated to the desired temperature level following the Parr calibration procedure. After feeding the reactor with a glass liner (Parr Inst., Ill., USA) containing the prepared sample, the reactor was sealed and pressurized with nitrogen to the desired pressure for the tightness test. Next, the reactor was placed in the Parr heating spiral, and the pressure readout was checked for 30 min. After the tightness test was completed, the reactor was heated up to the desired temperature and kept there for a specific time according to the experimental matrix. After the process, the reactor was removed from the heating spiral and cooled on air. After the cooling, the reactor was opened, and the glass liner.

The energy consumption during the process is directly measured by using Primera-Line energy meter PM 231 E from Brennenstuhl company. The meter has the capability to directly measure the energy consumption of the device with which it has been connected with a protection

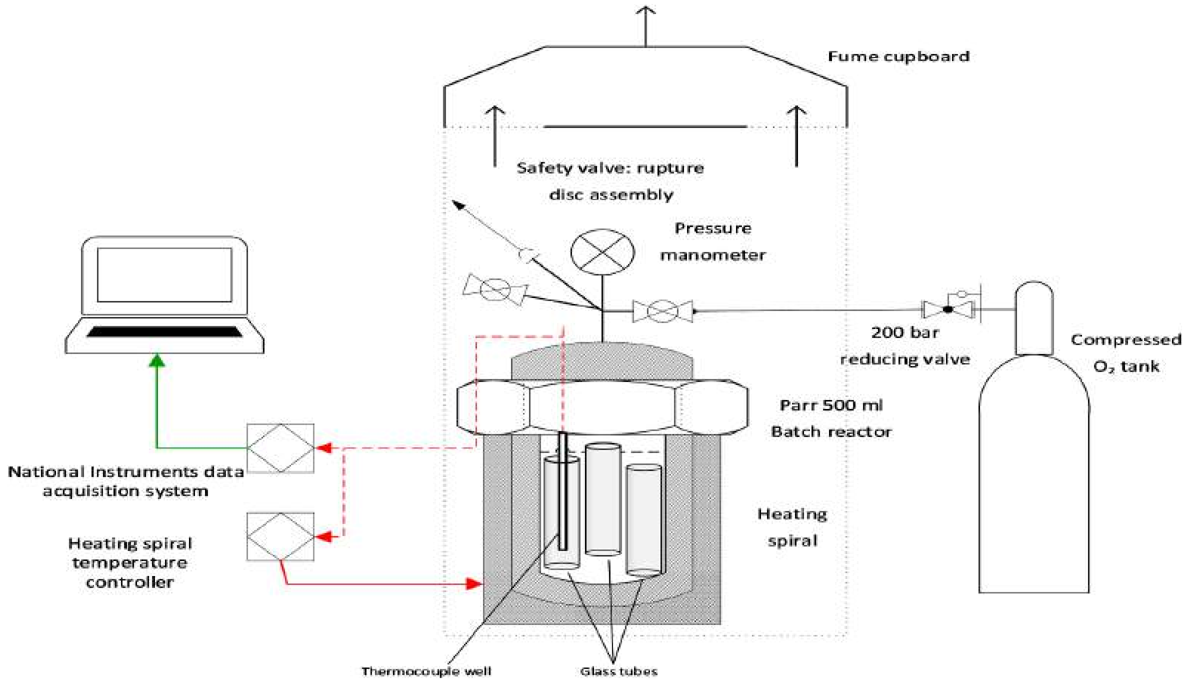

Fig. 2. Experimental setup used for oxidative liquefaction of wind turbine blades.

class of IP20, maximum load capacity of 3600 W, and measuring accuracy of ±1%. To measure the energy consumption during the process the device is directly plugged into an electrical socket and connected to the heating spiral. Set the reading mode to energy consumption and press and hold the reset button to erase any previously recorded values before starting the experiment. Periodically recorded the energy consumption values until the process is complete.

2.4. Products analysis

2.4.1. Recycled glass fiber collection, separation, and calculation of total solid reduction (TSR) and resin degradation yield (RDY)

After the process, the batch reactor content was filtrated through filter paper to separate the liquid product from the solid product which mostly contains glass fibers (Fig. 3). After the separation, the solid product was dried in a laboratory dryer in a forced air drying oven WGL-30B 105 (Adverti, Poland) at 105 °C for 8 h and weighed. The liquid product was stored in a glass flask, sealed and stabilized, and stored in a freezer for analysis. The Total Solid reduction (TSR), was calculated according to Equation (1):

$$TSR = \frac{m_0 - m_s}{m_0 \cdot} \cdot 100\% \tag{1}$$

where, m_s represents the mass of the solid product after drying, and m_0 initial mass of the WTB. The Resin Degradation Yield was calculated on the base of TSR and then this RDY value is justified by relating it to the ash content in each sample after the process by using Equation (2):

$$RDY = \frac{m_0 - m_s}{m_0 \cdot (1 - A)} = TSR \cdot (1 - A)^{-1} \tag{2}$$

In Eq. 2, A is the ash content in each sample after the process has been completed. In these calculations, the *RDY* is that the mass of the solid product after the process is expressed as the degraded epoxy resin related to the initial mass of the epoxy assumed as the difference balancing the ash content (glass fiber) of the sample.

Fig. 3. Recovered glass fibers after the process.

2.4.2. Analysis of variance (ANOVA) and process optimization

During the optimization process, the Pareto chart of standardized effects, profiles for predicted values, and desirability and response surface contours have been drawn to find out and compare the effect of temperature, pressure, residence time, the concentration of oxygen, and the waste-to-liquid ratio on RDY and energy consumption. P-values, which represent the likelihood of obtaining a result that is equal to or greater than the experimental result, were calculated during the analysis. Each tested parameter change has a substantial impact on the product output when the p-value is less than 0.05. On the other hand, a p-value higher than 0.05 denotes that the parameter being tested has no significant impact on the RDY. To study all variable effects that may have an influence on the analyzed sample parameters, multivariate analysis of variance, or more precisely two-way ANOVA, was performed. As a null hypothesis, this technique posits that all values of the independent variable have the same influence on the characteristic being evaluated (the dependent variable). The alternate hypothesis stated that at least one variable influenced the other more than the other. The null hypothesis is based on the assumption that all levels of the independent variable have the same influence on the measured characteristic (dependent variable). Individual hypotheses are offered for each independent variable. Furthermore, the interaction between the independent variables can be thought of as the combined influence (not decomposable into individual component effects) of the two independent variables on the dependent variable (continuous) under investigation.

Using data from the specified trial plan, the approach is optimised by identifying a local or global maximum for the parameter under assessment. When the required product or process attributes are inversely proportional, the desirable feature is the parameter x_1 with the lowest value and the parameter x_2 with the highest value. Using the so-called desirability function is a wise decision in this scenario. Desirability functions, such as linear desirability functions, voiceover-IP desirability functions, threshold desire functions, real-time, rate-adaptive, and stepwise desirability functions, can be employed in a variety of ways [49]. This study, on the other hand, focuses on the usage of a linear desirability function, which can be represented by Equation (3) below [50].

$$f(d(g)) = \frac{\sum_{i=1}^{M} w_i d_i}{\sum_{i=1}^{M} w_i} \tag{3}$$

The overall desirability function *f(d(g))* is an average of the d individual desirability functions, balanced by user-specified weights, w, where M is the number of response variables and w is the user-specified weight used to determine the significance and sign of a given parameter, during optimization, i.e. whether we will minimize or maximise its value.

3. Results

3.1. Characterization of the investigated WTBs

Results obtained from the ultimate analysis: weight percentages of different elements such as carbon, nitrogen, hydrogen, sulfur, and oxygen, and those from the proximate analysis, such as the content of moisture, ash, and volatile matter, can be found in Table 3. High ash content is an indication of the existence of inorganic residues that are

Table 3
Ultimate and proximate analysis results of the WTB sample.

Parameter, wt.%	M^a	A^a	VM	C^a	H^d	N^a	S^a	$O^{a.d.}$
Value	1.3	57.9	40.7	28.4	2.9	1.3	<0.1	8.1
U(X)	0.8	2.9	2.0	0.82	0.23	0.1	–	–

mostly the glass fibers and fillers used in WTBs and their recovery is economically beneficial, and the rest is actually resins of different kinds represented as volatile content. These resins have a prolonged lifetime and they are not environmentally friendly but on the other hand with the implication of proper chemical treatment, they can be degraded to low or intermediate-molecular-weight organic compounds, that can be used for different applications. Fatih et al. [51] reported the results of proximate analysis of one hundred different types of biomass materials for which the total ash content was in the range of 0.60–15.80 wt% and the volatile matter was 45–87 wt%. WTBs is a rather unusual feedstock for the determination of the fuel properties but the appearance of high ash content in our case is an indication of the possibility of glass fibers recovery and comparable volatile content is directed towards the production of useful chemical compounds.

Expanded uncertainty U(X) was calculated based on the confidence level of 95%, and converge factor k = 2.

3.2. *Oxidative liquefaction results*

3.2.1. *Total solid reduction, resin degradation yields, recovered glass fibers*

According to the DoE, various combinations of temperature, pressure, residence time, waste-to-liquid ratio, and oxidizer content have been tried to get the maximum TSR that is directly related to resin degradation and amount of recovered glass fibers. It was found that the maximal value of TSR i.e., 49% and 100% RDY is achieved at a temperature of 350 °C, with a starting pressure of 40 bar, a residence time of 30 min, a 45% oxidant concentration, and a waste-to-liquid ratio of 5%. But very similar values of TSR i.e., 48 and 47% and RDY i.e., 97.96 and 95.92% were obtained at 250 and 300 °C respectively, with the residence time 30 and 60 min. The only parameter that was not changed during the maximum TSR and RDY was waste-to-liquid, which remained at its least level of 5%. While referring to the minimum values of TSR and RDY, these were 21% and 42.86% at 250 °C, 31% and 63.27% at 300 °C, and 35% and 71.43% at 350 °C respectively against the maximum residence time of 90 min and the maximum waste-to-liquid ratio of 25%. These results highlight the waste-to-liquid ratio as a parameter of key importance in the process and glass fibers recovered after maximum resin degradation can be seen in Fig. 3. During the study the sample size was kept 1–2 cm to obtain the required waste-to-liquid ratio, depending upon the size of the reactor but analysing the effect of sample size on process output could be an interesting future aspect of the study as larger sample size may require a longer reaction time and higher oxidant concentrations. A possible reason is, a larger sample size will typically have more surface area that needs to be oxidized, and it may take longer for the oxidizing agent to penetrate the interior of the material (less availability of exposed surfaces), and reaction kinetics may be different. But the size of the sample will be highly dependent upon the waste-to-liquid ratio and volume of the reactor.

During these experiments, energy consumption was also an important factor that highlighted the economic feasibility of the process. At higher temperature of 350 and 300 °C the average TSR values were comparatively higher than at 250 °C even though the minimum values were closed to the average value 34–37%, but at these temperatures, the average energy consumption was 2.8 kWh which is almost double the average energy consumption at 250 °C *i.e.*, 1.5 kWh. So it was important to identify the optimum reaction conditions that result in the maximum TSR to enhance the RDY and recovery of glass fibers and have minimum energy consumption to make the process commercially feasible. Some experiments were repeated randomly to estimate the percentage standard deviation in RDY, and its average value is 2.9% which indicates the repeatability of experiments is reasonable. Table 4 provides the data for the repeated experiments about mass loss, TSR, and RDY calculated on the base of ash content in the sample and values for standard deviations. These deviations in RDY values are in the range of 1.44–4.33%, very similar to that reported in various studies [52–54], are because of sample inhomogeneity used in repeated experiments, oxidative liquefaction is a complex process having a number of reactions happening in parallel so slight changes in the reaction mechanism or appearance of any unpredicted chemical reaction can change the resin degradation yield.

Table 4
standard deviation for repeated experiments.

Initial mass of sample, m_0 (Grams)	Final mass of the sample, m_s (Grams)	Total solid reduction, TSR (%)	Resin degradation yield, RDY (%)	Standard deviation estimate of RDY (%)
10	7.8	22	44.89	2.60
2	1.19	40.50	82.65	2.89
2	1.14	43	87.75	3.61
2	1.07	46.50	94.89	1.44
2	1.1	45	91.83	2.89
6	3.94	34.33	70.08	2.87
2	1.06	47	95.91	2.89
6	3.9	35	71.42	4.33

3.2.2. *Analysis of variance (ANOVA) and process optimization*

The desired experimental design resulted in 29 WTB wet oxidation tests (with an additional three repeats conducted at the midway point, for a total of five) under various process conditions. Under the investigated process conditions, which included a temperature range of 250–350 °C, a pressure range of 20–60 bar, a hydroxy peroxide solution amount of 6–18%, a residence time range of 30–90 min, and a waste to oxygenated solution ratio of 5–25%.

Using the method of planning experiments and analysis of variance, it was possible to determine the statistically significant variables that affect the wet oxidation process studied, as well as whether there were interactions between the selected variables and whether they had a statistically significant effect on the degree of resin removal from WTB. The p = 0.05 was used for the significance analysis.

Fig. 4 illustrates the outcomes of the ANOVA analysis as a Pareto diagram, which represents the study's outcome. The statistically significant variables for the standard confidence interval size of 0.05 include the waste-to-oxygenated solution ratio, temperature, amount of oxidant, and two interactions between temperature and waste to oxygenated solution ratio and temperature and amount of oxidant. The first has a negative influence on total solid reduction efficiency because an increase in waste relative to the oxidising solution utilised leads in a loss in wet oxidation process efficiency. The combination between temperature and amount of oxidant had the same detrimental effect, but it was smaller. Temperature and interactions between temperature and the waste-to-oxygenated solution ratio were found to have a statistically significant and favorable effect.

Based on this knowledge, the wet oxidation process was optimised (see Table 5). In addition to productivity: the resin degradation yield (RDY), another measure against which optimization was performed was the process's energy consumption (EC). During this investigation, it was discovered that the ideal parameters for boosting the resin removal rate from WTB composite samples while reducing the process's energy intensity are:

Under these conditions, a resin degradation yield value of 100.00% (with a standard deviation around ±2.9%) on average is achieved, as can be seen in Fig. 5. According to the data obtained from the ANOVA analysis, process pressure has no significant effect on the RDY value. An increase from 20 to 40 bars results in an insignificant decrease in mean RDY values from 100 to 96.5%, respectively. As in the case of pressure, no statistically significant effect is observed for residence time; however, it can be seen from the ANOVA that residence time is very close to the p = 0.05 value as a quartic function (Res. Tim (Q)), showing that although this variable alone has no statistically significant effect on RDY, its small effect is not linear but quadratic. A change in this parameter results first in a slight increase in RDY from 94.4 to 100 at 30 and 60 min,

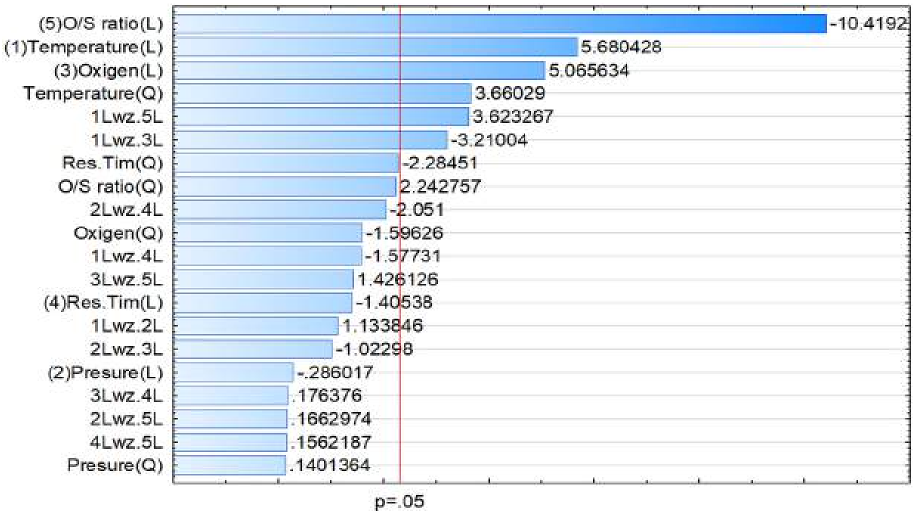

Fig. 4. Pareto graph showing the effects of process conditions on the RDY.

Table 5
Optimal reaction conditions for Maximum TSR and boosted resin removal.

Temperature, (°C)	Initial pressure, (bar)	H_2O_2 addition, (wt. %)	Process time, (min)	Waste-Liquid ratio, (wt.%)
250	30	18	45	5

respectively, followed by a decrease in RDY to 93.3 at 90 min with a further increase in holding time. The two statistically significant variables identified by the ANOVA analysis are the waste to oxygenated solution ratios, an increase in which results in a decrease in RDY values from 100.0 to 71.0% for the 5 and 25% waste to oxygenated solution ratios, respectively. The second variable is, amount of oxidant range, which causes an increase in RDY values from 94.0 to 100.0% at 6 and 18% H_2O_2 concentrations, respectively.

Fig. 6 illustrates the response surface profile with the same desirability functions (maximising RDY while minimising EC) to further demonstrate the impact of the independent variables on the wet oxidation process under investigation. The plot's axes correspond to the code values in Table 1, and the intensity depicts how the process's attractiveness evolves. The use of a response surface analysis-based optimization approach provides not only for the determination of optimal values for the optimised quantity, but also, as in the given case, for the determination of whether the maximum attained during optimization is a local or global maximum. The graphs are drawn with the points that define the previously specified optimised process conditions. To facilitate the examination of the response surface plots, just three factors with the largest impact on the process were chosen for Fig. 5. The additional material contains response surface plots for the other cases. The relationships between the provided independent variables are non-linear, as can be seen, and the response surfaces have a single global

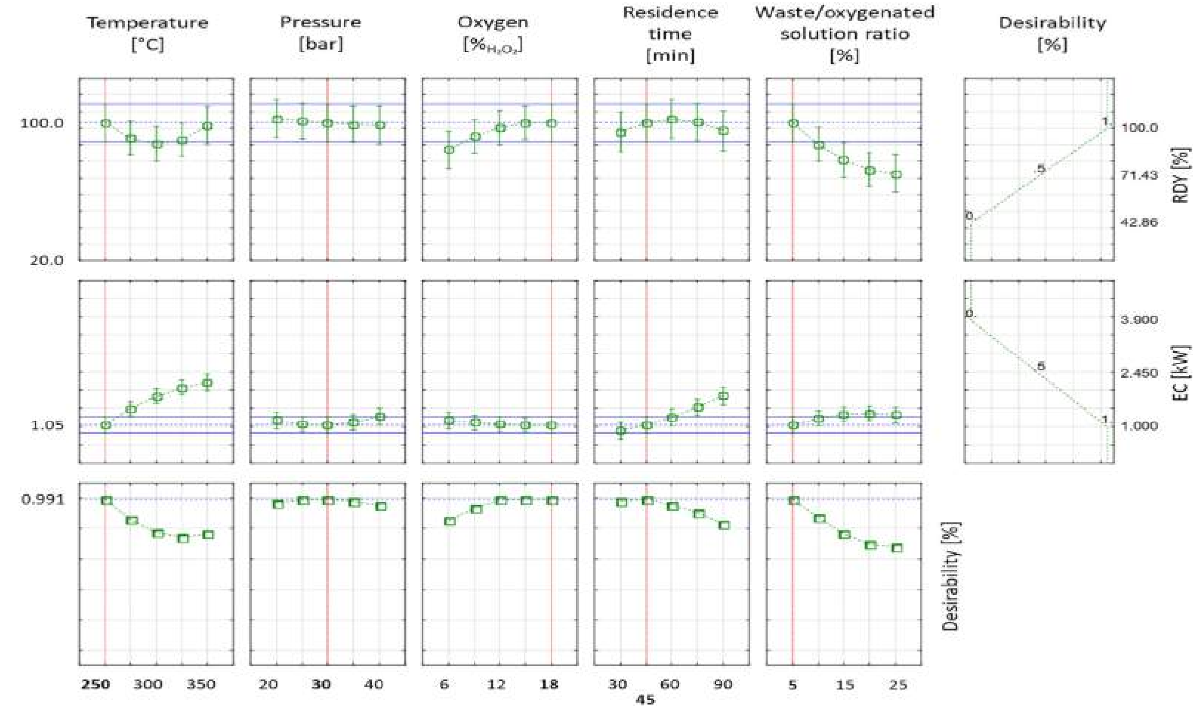

Fig. 5. Profile of predicted values and desirability for optimum conditions.

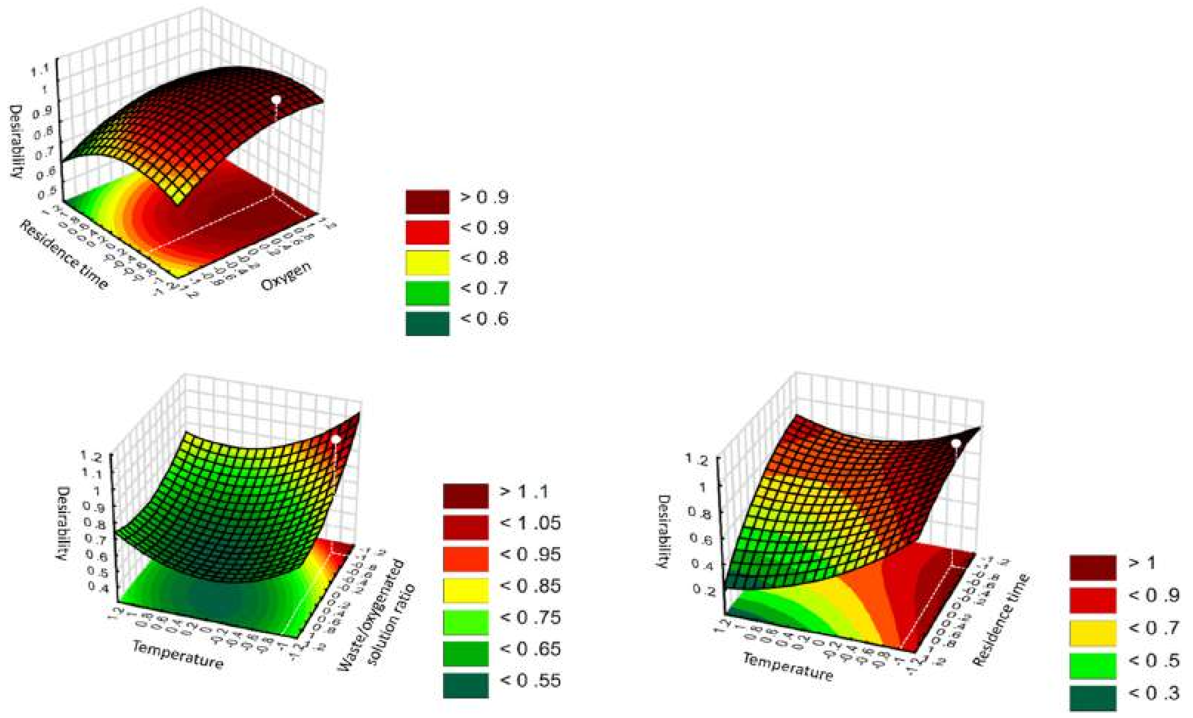

Fig. 6. Response surface against the desirability function assuming a maximization of RDY.

maximum.

4. Discussion

As it has already been described in section 2.4.1 that RDY is calculated based on TSR values so all the factors affecting the TSR have a substantial effect on RDY. Increasing temperature appears to have an effect on the TSR hence on RDY of WTBs in two halves. During the first half, there is a decrease in TSR when the temperature is increased from 250 °C to 300 °C so the RDY is decreasing accordingly, and it is caused by the competitive effect between important reactions hydrolysis/oxidation and the repolymerization process. Chumbaos et al. [55] while discussing this type of behavior, proposed that enhanced char formation due to condensation and cyclization reactions of products can be one of the reasons for this decrease in TSR. Similar kinds of studies have also been provided by Sun et al. [56] and Zhong and Wei [57].

During the second half, there is an increase in TSR with further increase in temperature from 300 °C may be caused by the fact that the Non-organic compounds that have been solubilized, oxidize at a faster rate because of the exponential temperature influence on the Arrhenius kinetics of the reaction and that results in increased RDY values [58]. This overall tendency of solids decreases with rising temperature was anticipated since solubility, reaction kinetics, and the rate of gas-liquid mass transfer are all positively influenced by increasing temperature.

The materials often break down in oxidation processes and are also dissolved in water, resulting in higher solid reduction at elevated temperatures. This increasing solid reduction with temperature has already been reported in the literature [59,60]. All the WTB samples experience weight deterioration at the lowest treatment temperature of 250 °C and degradation is increased as the treatment temperature increases from 300 °C to 350 °C. These results are consistent with the observations reported by Dhanya et al. [61] while studying the effects of temperature on the degradation of municipal solid waste and these observations were reported to follow the Arrhenius reaction kinetics. The Arrhenius reaction kinetics' response to temperature demonstrates that the rate of solubilization increases with the temperature. As a result, at higher temperatures, the proportion of suspended solids in the treated sample decreases, and the amount of resin degradation increases.

An increase in residence time increases the TSR hence RDY, but it is true for a certain period of time, more prolonged periods have adverse effects on the degradation process. This threshold is dependent upon the feed of the waste and the type of oxidant or catalyst [62]. One reason for less RDY on the base of TSR at elevated temperatures is the dilution of aqueous extractives present in solid waste [63]. The second possible reason presented is the formation of char at prolonged time periods through condensation, polymerization, and crystallization of liquid products [64]. In addition, the effect of residence time is strongly related to the reaction temperature.

The role of water is versatile during liquefaction reactions, as it acts as a solvent, catalyst, and medium to carry out important reactions [65–67]. A lower waste-to-liquid ratio, *i.e.*, a higher concentration of water, is suitable as it supports hydrolysis, ionic condensation, and cleavage reactions. Consequently, as the waste-to-liquid ratio decreases, the reactions happening in the overall process get intensified and reach equilibrium more quickly, encouraging more degradation and high TSR values and subsequently improved RDY. A higher amount of water will also result in a higher concentration of H^+ and OH^- ions, which are also favorable for initiation and propagation reactions. Higher TSR values with a lower waste-to-liquid ratio is in agreement with the trends provided during the various studies [68–70]. But higher water content is not suitable because it makes the liquefaction process less energy efficient as more water needs to be heated per unit of waste.

A stoichiometric amount of oxygen is also needed to achieve the required degree of oxidation, less of this oxygen than the stoichiometric value will reduce its availability for the complete oxidation of reactants, will support the char formation and TSR hence RDY will decrease. But on the other hand, the excess amount of oxygen has no effect on TSR, and RDY, maybe because the required degree of oxidation has already been achieved and waste material is acting as a limiting reagent.

5. Conclusions

Oxidative liquefaction appears to a promising technique for recovering glass fibers from end-of-life WTBs and achieve higher RDY. In this study, pressure had no significant effect on RDY, but all other tested parameters, *i.e.*, temperature, residence time, oxidant concentrations, and waste-to-liquid ratio, have a substantial effect on the process. While discussing the temperature the lower value 250 °C is favorable due to the fact that at 300 °C unwanted charring governs the process that reduces the RDY, as well as vastly increases the final energy demand. Prolonged time periods of more than 45 min are also not beneficial as they support the crystallization and polymerization reactions, and energy consumption during the process also increases. Lower waste-to-liquid values are suitable for getting the maximum RDY, but high content of water will demand more energy as more water is needed to be heated for a unit mass of WTBs. Oxidizer concentration should match the stoichiometric demand as the limited concentration will suppress the oxidation reactions and decreases the RDY on the other hand, excess oxygen has no effect on the degradation process of WTBs. The satisfactory results are obtained in real environment on the lab scale and through detailed optimization of process conditions and considering energy consumption, oxidative liquefaction can be applied on industrial scale for the glass fiber recovery and resin of degradation of WTBs. Furthermore, the liquid product obtained during the liquefaction can be chemically analyzed to find the existence of useful chemical compounds that will also make the process commercially suitable.

CRediT authorship contribution statement

Hamza Mumtaz: Conceptualization, Conception and design of the study, Acquisition of data, Formal analysis, Analysis and/or interpretation of data, Writing – original draft, Drafting the manuscript. **Szymon Sobek:** Conceptualization, Conception and design of the study, Writing – original draft, Drafting the manuscript, Revising the manuscript critically for important intellectual content. **Marcin Sajdak:** Acquisition of data, Analysis and/or interpretation of data, Writing – original draft, Drafting the manuscript. **Roksana Muzyka:** Formal analysis, Analysis and/or interpretation of data, Revising the manuscript critically for important intellectual content. **Sebastian Werle:** Conceptualization, Conception and design of the study, Revising the manuscript critically for important intellectual content.

Declaration of competing interest

I on the behalf of all authors, declare that there is no conflict of interest and all the elements of the submission are also in compliance with the journal publishing ethics. By submitting this manuscript, the authors agreed that the copyright for their article should be transferred to this journal if the article is accepted for publication. The work contained within the research paper is our original contribution and has not been published anywhere.

Data availability

Data will be made available on request.

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Appendix C

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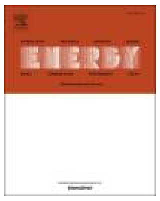

Oxidative liquefaction as an alternative method of recycling and the pyrolysis kinetics of wind turbine blades

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ABSTRACT

Oxidative liquefaction of wind turbine blades (WTBs) is carried out in a controlled environment having temperature ranges of 250–300 °C, pressure 20–40 bar, oxidant concentration of 15–45%, a reaction time of 30–90 min, and a waste-to-liquid ratio of 5–25 %wt. Fourier transform infrared spectroscopy (FTIR) in the wavenumber range from 650 to 3200 cm^{-1}, analytical pyrolysis at 500 °C was performed. Thermogravimetric analysis (TGA) was employed at a temperature range of 30–800 °C at heating rates of 2, 4, 8, and 16 K/min. The kinetics of WTBs pyrolysis were analyzed using the Fraser-Suzuki (FS) deconvolution method and a model-based kinetic modeling procedure. Oxidative liquefaction resulted in higher resin degradation of WTBs and the production of liquid chemical compounds. Gas chromatography with flame ionization detection (GC-FID) was used to investigate the insight into these chemical compounds which were mostly fatty acids. The resin degradation yield was found to be in the range of 55–100% while volatile fatty acid (VFA) concentrations were from 28.90 to 210.59 g/kg-WTBs. In addition, analysis of variance (ANOVA) have been performed to provide the optimal reaction conditions to maximize the process outputs and minimize the energy consumption to make the process economically feasible.

1. Introduction

Energy demand is on the rise worldwide, with a growth rate of 2.3% in 2019 and an expected annual increase of 1.3% until 2040 [1]. Wind energy has emerged as a leading player in the renewable energy sector, with its immense potential to provide clean, reliable, and cost-effective power [2]. Projections suggest that wind power's contribution to global electricity generation will increase to 30% by 2050 from its 2022 figure of 5% [3]. According to the report of the International Energy Agency (IEA), wind energy production is expected to exceed 3317 TW h (TWhs) in the coming five to seven years [4]. Wind energy is currently dominating the European renewable energy sector, followed by hydro and solar energy [5]. In fact, wind energy is projected to fulfill 30% of the European Union's (EU) energy demand by 2030 [6]. This expected increase in wind energy generation will contribute significantly to meeting the EU's energy targets and meeting the requirements of the European Green Deal and its goals for 2050. In its use phase, wind energy has low carbon emissions, potential cost-effectiveness, and is adaptable due to its ability to be installed onshore and offshore, making it a promising alternative to traditional energy sources and a crucial component of sustainable energy portfolios [7]. However, the end-of-life phase of wind energy sets a challenge for waste management and the environment, with the biggest impacts caused by the management of decommissioned WTBs.

The WTB consists of materials including a polymer matrix made from thermoplastics or thermosetting plastics, reinforcement such as glass, carbon, or aramid fibers, and a lightweight core material such as balsa wood or foam, and polymer coatings that serve to protect the blade from environmental damage and improve its strength to weight performance [8]. The majority of the blade material composition is made up of a combination of fibers and polymers, known as glass fiber-reinforced polymer composites (GFRPs), which typically make up 60–70% of the weight of the blade (reinforcing fibers) and 30–40% of the weight of the blade (resin) [9]. The core materials are typically packed in layers of GFs

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and epoxy resin, adding stiffness, and reducing the weight of the blade. Wind turbines have an average lifespan of about 20–25 years, although, with proper maintenance, upgrades, and newer technologies, this lifespan can be extended up to 30 years or more [10].

Management of decommissioned and end-of-life WTBs is already considered one of the biggest environmental problems of the 2nd decade of the XXI century. Starting in 2021, the United States has initiated the process of removing from exploitation approximately 8000 WTBs annually, and this practice will continue until 2025. On the other hand, the European Union removes around 3800 WTBs per year [11]. According to estimates from the International Renewable Energy Agency (IRENA), the wind energy sector could produce more than 40 million metric tonnes of waste annually by 2050, which is an alarming situation in the context of waste management [12]. As per the hierarchy established by the EU Waste Framework Directive, it is recommended to avoid the disposal of waste materials in a manner that does not allow for the recovery of any potential energy or material value [13]. The production of wind farms is resource-intensive and requires the use of non-renewable chemicals, which can have a significant environmental impact. Therefore, it is crucial to recycle wind turbine components, not only to mitigate their environmental impact but also to recover energy and valuable materials such as GFs and resin monomers from waste composites, which would otherwise end up in landfills and are the least preferable option.

1.1. Recycling methods of the end-of-life WTBs

1.1.1. Mechanical recycling

The large size and complex composition of WTBs make their recycling a technically challenging process. At the current stage, various recycling techniques are tested for decommissioned WTBs, including mechanical recycling, chemical recycling, pyrolysis, and oxidation in fluidized bed reactors [14]. Mechanical recycling is a method that involves reducing the size of composite materials using crushing, grinding, milling, or shredding techniques to obtain fibrous and powdered fractions [15]. Mechanical recycling is an option to treat WTBs due to its high treatment capacity and ability to recover fibers and resins. However, mechanical recycling often results in downcycling, as the stiffness and strength of the material are reduced due to the loss of reinforcing fibers [16,17]. Shredding and grinding can damage the fibers and matrix of the composite material leading to a loss of mechanical strength and durability. Separating and sorting the resulting shredded material can also be challenging, making the remanufacturing process difficult. Furthermore, mechanical recycling can produce impurities and contaminants that reduce the quality and suitability of the recycled material for high-performance applications [18].

Material recycling and thermal recovery are two common methods, pyrolysis offers a middle ground by allowing for partial material recycling [19,20].

1.1.2. High-temperature recycling methods

Pyrolysis is a thermochemical process in which materials are decomposed at high temperatures in the absence of oxygen. During the pyrolysis of WTBs, the complex matrix is broken down and produces useful chemical compounds that can be recovered, but the fibers in WTBs lose their mechanical properties during the process. Carbon fibers (CFs) may experience a reduction in tensile strength from 4% to 85%, while GFs may see a reduction of 52%–64% [21,22]. Pyrolysis of end-of-life WTBs, results in gaseous fractions containing CO_2, CH_4, and CO, pyrolysis oil with phenolic concentrations, and solid products which are mostly the GFs covered with residual char [23]. Certain catalysts can aid in reducing the required processing temperature for the recycling process [24]. Catalytic pyrolysis of GFRP using ZSM-5 zeolite catalyst revealed that the process effectively converted epoxy into volatile components with high yield and recovery. The addition of a catalyst had a significant impact on the composition and yield of the volatile components produced, while kinetic modeling showed high predictability [25]. The thermal degradation of CL-20 was analyzed using TG-FTIR-MS and kinetic models were presented using the chemical reaction neural network framework. Kinetic models and a one-step model with different substances effectively replicated the data, leading to the proposal of a skeleton mechanism [26]. A study explored the impact of carbon black fillers on the pyrolysis of GFRP and kinetic analysis using different models revealed that the presence of CB increased the production of flammable compounds by 146%. Factors such as heating rate and duration of heating, and pyrolysis temperature play a crucial role in the decomposition of the polymer resin and recovery of GFs [27]. Despite the maturity of the pyrolysis process of plastic and composite, reliable kinetic models of WTB pyrolysis are still needed.

1.1.3. Chemical recycling methods

Chemical recycling is an advanced and efficient method of recycling composite waste by decomposing or modifying the composite matrix in chemical solvents [28]. The frequently used solvents, in descending order of prevalence, are water, ethanol, methanol, propanol, and acetone, in addition to their mixtures [29,30]. Solvolysis can be used to recover composite materials, particularly those that contain CFs as they are not affected by the process, but GFs tend to degrade [31,32]. During the recycling of CFs-reinforced epoxy composites in water under supercritical or near-critical conditions temperature, time, oxidant, and catalyst concentration were identified as the most important reaction parameters and a second-order kinetic equation was used to model the reactive extraction process. The reclaimed fibers showed a resin removal efficiency of up to 95.3 wt% and a tensile strength of 90–98% compared to virgin fibers [33]. Other studies that also reported in the literature mostly focus on recovery CFs because of their high market value than GFs. The literature on chemical recycling composite materials by solvolysis suggests that optimizing reaction time and temperature for retaining high glass fiber strength results in longer times and higher energy consumption. High-temperature water can damage the fibers, while solvolysis with organic solvents has less damage and increased solvent diffusion [34]. Solvolysis, while a useful process for CFs recovery, suffers from a number of limitations. The high cost of equipment required, particularly for reactors capable of withstanding extreme temperatures and pressures, can be a significant barrier to implementation. Additionally, the use of sub- and supercritical conditions may result in corrosion, and acidic solutions pose safety and environmental hazards [35,36].

The recycling of composite materials, particularly those employed in WTBs manufacturing, poses a significant challenge owing to their intricate composition and heterogeneous nature. The cited literature highlighted that the mechanical recycling and pyrolysis of composite materials lead to the recovery of GFs with reduced mechanical properties and contamination with residual matrix material and involve a high cost of recovery that may not be economically favorable. Chemical recycling is mostly used to recover the CFs from composite materials than GFs so for the materials like WTBs exploring alternative recycling methods that can recover additional chemical compounds alongside GFs from waste composite materials would be a promising solution to address the challenges of the long-term sustainability of wind energy.

1.2. Aim of the paper

This study in the first half presents a detailed reaction kinetics model for the pyrolysis of WTBs in an inert environment (without H_2O_2 and water) while in the second half, it presents a novel approach to the material and chemical recycling of the end-of-life WTB using the oxidative liquefaction method, as a new method in the regime of chemical recycling. Oxidative liquefaction comprises hydrothermal treatment of composite waste with the addition of a liquid oxidizer mostly H_2O_2, recently used by the same authors for GFs recovery from WTBs, where energy consumption was highlighted to be an important factor determining the economic feasibility of the process [37]. H_2O_2 plays an important role during the process as it decomposes to provide the required oxygen for the oxidation of waste materials, and it also reacts with water to form hydronium ions (H_3O^+) and per hydroxyl ions (HO^{2-}) that increase the overall rate of reaction. The novelty of the method lies in the simultaneous recovery of fibers from the composite matrix and VFAs from the oxidative decomposition of the epoxy resin. The effect of different combinations of assessed parameters i.e., temperature, pressure, residence time, oxidant concentrations, and waste-to-liquid ratio on the process yield have been studied. An in-depth statistical analysis of obtained results has been carried out to identify the most influential reaction parameters and to provide the optimal process conditions for maximizing VFAs yields in liquid products. Additionally, presented WTB samples were fully characterized in terms of ultimate and proximate analysis, FTIR spectra, and pyrolysis behavior with the calculation of process kinetics, answering the need for kinetic models of WTB pyrolysis from the literature.

2. Material and methods

2.1. End-of-life WTBs

The WTB pieces were provided by ANMET company working in the field of WTB recycling since 2015. Originally the WTB samples for this study were stipulated in 25 × 30 cm segments. The samples were first cut into smaller 0.5 cm wide using an angle grinder before being milled into fine chips 0.5–1.5 cm in length using a shredder mill. Obtained WTB samples were consisting mainly of glass fiber and polymer matrix structures and lacked any large metal, wooden or foam filling parts.

2.2. Elemental analysis of WTBs

Ultimate and proximate analysis with ash composition has been determined using a plasma spectrometer, the Thermo iCAP 6500 Duo ICP. Determining moisture (M^a), volatile matter (VM), ash content (A^a), carbon (C^a), oxygen ($O^{a.d.}$) hydrogen (H^d), nitrogen (N^a), and sulfur (S^a) contents. All analyses were conducted using standards and procedures, including the following: the thermogravimetric method was done M^a according to PN-G-04560:1998; the gravimetric determination of VM and A^a was done according to EN 15402:2011 and EN ISO 21656:2021–06; and ultimate analyses were done according to EN ISO 21663:2021–06 and high-temperature combustion with IR detection. As required by EN ISO 16993:2016–09, the $O^{a.d.}$ Was determined as a difference.

2.3. Thermogravimetric analysis, FTIR and py-GC-MS analysis of the WTBs setup

2.3.1. Chemical composition analysis – FTIR and Py-GC-MS

FTIR studies were carried out with a Nicolet iS50-TRACE 1300 ISQ 7000 spectrometer (Thermo Scientific, USA) with a wavenumber range from 650 to 3200 cm^{-1}. Measurements were performed at room temperature, and 15 measurements were taken for the sample under study. Data were obtained using the attenuated total reflectance technique. Each sample was imprinted on a diamond crystal with a single reflection.

Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) analysis of the WTB waste was achieved using a Pyrolyser EGA/PY-3030D Multi-Shot Pyrolyser (Frontire Laboratories Ltd, Fukishima, Japan). The sample of around 1.00 mg was put in a quartz tube at the start of each test, and the ends were sealed with quartz wool. A Shimadzu QP-2010 Ultra Plus (Japan) gas chromatograph with a temperature-programmed capillary column and a Shimadzu MS-QP2010SE mass spectrometer at 70 eV was used. The generated sample vapours from the tube were fed into the column at a rate of 1.9 mL/min and 27.3 kPa pressure. A 30 m × 0.25 mm × 0.25 μm Zebron™ ZB-5MS capillary column (Phenomenex, USA) was used to separate the sample components, and its stationary phase was composed of 5% diphenyl and 95% dimethylpolysiloxane. The GC oven temperature was adjusted from 45 to 275 °C at a rate of 5 °C/min, while the pyrolysis temperature was set at 500 °C. The mass spectrometer was set at the following conditions: 10^{-5} Pa vacuum, 45–300 *m/z* range, 250 °C ion source heater, 300 °C interface heater, and 1428 scan speed. The chromatograms and spectra were analyzed using postrun LabSolutions software from Shimadzu (NIST17.0).

2.3.2. Thermogravimetric analysis setup

The tests were carried out using a Netzsch TG 409 LUXX thermogravimetric analyzer. The WTB analytical pyrolysis conditions were: temperature range of 30–800 °C, heating rates of 2, 4, 8, and 16 K/min, inert atmosphere - argon flow 35 cm^3/min, using open alumina Al_2O_3 crucibles.

2.3.3. Kinetic analysis of the WTB thermal degradation

Kinetic analysis of the WTB pyrolysis was based on Fraser-Suzuki (FS) deconvolution and model-based kinetic modeling procedure presented and discussed in detail by Sobek et al. [38], presented in this paper in Supplementary Materials A. In summary, the experimental conversion rate profile of the WTB pyrolysis was first: (1) modeled with the FS functions, optimized with the least square method (LSM) to fit the experimental data, and (2) Arrhenius parameters were inversely decrypted from the fitting of the canonic rata equation to the FS signal.

2.4. Oxidative liquefaction of WTB details

2.4.1. High-temperature, high-pressure reactor for the oxidative liquefaction of WTB

The experimental setup used in oxidative liquefaction of WTBs is already presented by Mumtaz et al. [39] while discussing the different types of hydrothermal treatments of waste. The Parr reactor series 4650 (Parr Instr., ILL, USA), with a total capacity of 500 mL, heated by high temperature spiral is used in this study. Parr 4838 reactor controller with an operating range of 0–800 °C, readout and setpoint resolution of 1 °C, and system accuracy of ± 2 °C is used to control reactor temperature. The pressure gauge mounted in the reactor head can measure pressure with an extreme range of 350 Bar. Two straight valves are available, one of these valves serves as a means for connecting the reactor to a pressure source, allowing it to be filled with an inert gas such as nitrogen. The other valve is employed for either removing flue gases or collecting useful gases after the process. The reactor head comprises a hole that provides access to the thermowell, which houses a J-type thermocouple to measure the reactor's temperature during the process. Temperature regulation during the process is carried out by the Parr controller, utilizing PID groups, each with a specific temperature value (Fig. 1).

2.4.2. Design of experimental (DOE) plan

To study how multiple variables (Temperature, pressure, resident time, oxidant concentrations, and waste-to-liquid ratio) impact the overall process and to optimize the process conditions on the basis of response variables (VFA concentration, RDY, and Energy consumption) a Central Composite Design (CCF) was utilized to plan the experiments in software STATISCA 13.1. The total number of trials was calculated using Equation 1

$$2 \cdot \mathrm{k} + 2^{(\mathrm{k}-1)} + \mathrm{n}_{\mathrm{centre}} \tag{1}$$

Where k is the number of tested variables. The CCF design involved three types of experimental runs - factorial points, axial points, and center points - factorial points are used to estimate the main effects of the variables and the two-way interactions, while axial points explore the curvature of the response surface by estimating the quadratic effects

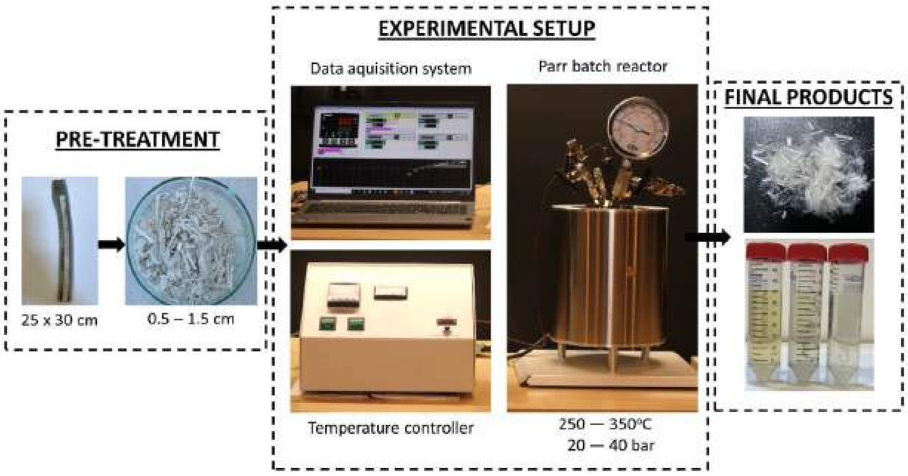

Fig. 1. Sample Processing of WTBs through oxidative liquefaction process.

and the interactions between the linear and quadratic effects. Center points are used to estimate the experimental error and to check for the lack of fit of the model. They allow for the estimation of the intercept and the curvature of the response surface. The response surface, which is a mathematical function, was used to describe the relationship between the input variables and the output or response of the process or system. The CCF design required a total of 29 trials for five variables - the temperature of the oxidative liquefaction process, residence time, pressure, amount of oxidant, and the waste-to-liquid solution ratio. Each variable had three levels denoted by -1, 0, and $+1$, which enabled the estimation of interactions between variables, such as constant term, linear terms, two-term interactions, and quadratic term interactions. Using this experimental design technique, the researchers were able to discover the wet oxidation conditions while minimizing the number of tests required.

2.4.3. Sample preparation and processing

A specific amount of the milled WTB was filed into glass liners and liners were afterwards charged with a liquid reaction medium consisting of a mixture of H_2O and H_2O_2 at specific ratios, as detailed in Table 1. Calibration of the temperature controller of the 4838 reactors was carried out in accordance with the Parr calibration procedure prior to each experiment to ensure the attainment of the desired temperature level. The prepared sample in the glass liner was then loaded into the reactor, which was subsequently sealed and pressurized with nitrogen for tightness testing. The pressure readout was monitored for a period of 30 min to ensure that the reactor remained tight. The heat is supplied to the reactor through ha eating spiral until it reaches the desired temperature and then maintained at that temperature for a specified duration as outlined in the experimental matrix. Following the completion of the process, the heating was turned off in the reactor is allowed to cool in ambient air. The glass liner was then opened to retrieve the reaction product.

2.5. Analysis of oxidative liquefaction products

2.5.1. Characterization of the structural raw WTBs before and after the oxidative liquefaction process

The morphology of the surface of raw WTBs and after the oxidative liquefaction process were investigated by means of scanning electron microscopy (SEM). For measurements, SEM was used: FEI/INSPECT S50 (Hillsboro, Oregon, USA). The acceleration voltages of the incident electron in basic SEM operation were 5 kV and 15 kV. The pressure in the chamber was about 10^{-7} mbar.

2.5.2. Calculation of resin degradation yield

After the batch reactor process, the resulting mixture was separated into liquid and solid fractions using 85–87 gsm filter paper. The solid product was then dried in an oven for at 105 °C and weighed, while the liquid product was stored in a sealed flask for analysis. The RDY is a measure of the amount of degraded epoxy resin in the solid product. RDY is calculated using Equation (2), very similar to one used by Ozkan et al. [40]. For calculation of liquefaction yield during the study of burnt pine heartwood acid-catalysed liquefaction.

$$\mathrm{RDY} = \frac{\mathrm{m_0} - \mathrm{m_s}}{\mathrm{m_0}}(1 - \mathrm{A})^{-1} \qquad (2)$$

where "m_0" represents the initial mass of the starting material (WTBs), "m_s" represents the mass of the solid product after drying, and "A" represents the ash content in the sample. This equation adjusts for the ash content in the sample by expressing the mass of the solid product as a difference between the initial weight of the epoxy and the ash content of the sample.

2.5.3. Liquid product analysis

DB-FAT WAX UI (Agilent Technologies, USA) capillary columns measuring 30 m × 0.25 mm x 0.25 μm were used in the PerkinElmer (USA) model Clarus 500 gas chromatograph equipped with a flame ionization detector (FID). The flow rate of the carrier gas, i.e., helium, was 1.0 cm^3/min. After 4 min of preheating at 40 °C, the temperature

Table 1
Levels of process parameters against the coded values based on central composite face-centered design (CCF).

Level of tested variable	Tested variable				
	Temperature (°C)	Initial pressure (bar)	H_2O_2 concentration (wt.%)	Residence time (min)	Waste/Liquid (wt.%)
Minimum (-1)	250	20	15	30	5
Average (0)	300	30	30	60	15
Maximum (1)	350	40	45	90	25

was then increased by 5 °C per minute until it reached 240 °C, after which it was held constant for 15 min. A split/splitless dispensing system was used. Calibration curves (correlation coefficients >0.99) were made for selected VFAs and aromatic hydrocarbons (AHs), and these were used to conduct quantitative analysis. The obtained values were in μg/mL of liquid media that were converted into g/kg-WTBs by using equation (3).

$$\sum \mathrm{VFA} = \frac{\mathrm{VFA} \bullet \mathrm{V}_{\mathrm{liq\_samp}}}{\mathrm{m}_{\mathrm{sample}} \bullet 1000}\left[\frac{\mathrm{g}}{\mathrm{kg}_{\mathrm{WTB}}}\right] \tag{3}$$

$\sum$VFA - sum of VFA [g/$\mathrm{kg}_{\mathrm{WTB}}$].

VFA- VFA in the liquid sample from oxidative liquefaction [μg/mL].

$\mathrm{V}_{\mathrm{liq\_samp}}$ – the volume of the liquid sample from oxidative liquefaction in [mL].

$\mathrm{m}_{\mathrm{sample}}$ – mas of WTB used to oxidative liquefaction [g].

2.5.4. Process optimization for maximum of volatile fatty acid production

The study aimed to investigate the effects of five independent variables, including temperature, pressure, residence time, waste-to-liquid ratio, and oxidant concentrations on the production of VFA improving RDY, while minimizing energy consumption. ANOVA was used as a statistical tool to analyse the data, while Pareto charts, profiles for predicted values, and desirability and response surface contours were employed to compare the effects of different variables on the process output. The p-value determines the overall probability of obtaining the desired results or results if the null hypothesis is true. If the p-value is below a pre-specified significance level, usually 0.05, it is considered statistically significant, and the null hypothesis is rejected. Conversely, if the p-value is above the significance level, the null hypothesis cannot be rejected. The ANOVA analysis was used to examine the relationships among multiple variables simultaneously. The null hypothesis of ANOVA assumes that all levels of the independent variable have the same effect on the dependent variable. The alternative hypothesis states that at least one variable has a greater effect than the others. The interaction between independent variables refers to their combined effect on the dependent variable. To optimize the process, a desirability function was employed. In this case, the parameter ×1 (Energy) with the lowest value and the parameter ×2 (RDY) and ×3 (VFAs concentration) with the highest value were considered desirable as the required product or process attributes are inversely proportional. A linear desirability function was used, which calculates the overall desirability function by taking the sum of individual desirability functions, each multiplied by a user-specified weight, and dividing by the sum of the weights. Significant factors that influence the process output were identified using the desirability function, and strategies for process improvement were developed.

3. Results

3.1. Elemental composition of WTBs

WTBs are typically made of composite materials that consist of a mixture of several different elements. Table 2 provides weight percentages of various elements such as carbon, nitrogen, hydrogen, sulfur, and oxygen on a dry-ash-free basis as well as moisture, ash, and volatile matter contents obtained from proximate and ultimate analyses of WTBs. The higher percentage of fixed carbon i.e., 69.7% is an indication that through proper treatment the material can be converted to carbon-rich secondary compounds. The high ash content of 41.2% as compared to 40 other materials (0.1–17.2%) reported by Jigisha et al. [41] indicates the presence of a higher amount of GFs used in the blades, and their recovery can be economically beneficial and is the point of key attention in various research works [42–44]. Ash content identified by proximate analysis of WTBs is slightly different that by TGA in later sections and a possible reason for this deviation is the inhomogeneity of the tested sample. WTBs has composite nature, and the size of the tested sample is 0.5 cm so there are strong chances of variation in the composition of the tested sample by Ultimate analysis and TGA. Resins used in the manufacturing of WTBs are responsible for a volatile portion of blades during proximate analysis. Epoxy resins and other types of resins can be converted into useful liquid compounds through the oxidative liquefaction process, providing a pathway for the recovery and reuse of these materials while minimizing their environmental impact.

Table 2
Ultimate and proximate analysis results of the WTB.

Ultimate analysis, wt.%[daf]	*U*(*X*)
C	69.7 ± 8.0
H	7.3 ± 1.1
N	3.0 ± 0.5
O [diff.]	19.8 ± 1.7
S	<0.5
Proximate analysis, wt.%	
Moisture	1.3 ± 0.7
Volatile matter[d]	58.7 ± 0.3
Ash[d]	41.2 ± 0.2
Fixed Carbon[diff.]	<0.5

[diff] Calculated as a difference.
[d] Dry state.
[daf] Dry ash free.

3.2. Results of the FTIR measurements, and WTB pyrolysis kinetics

3.2.1. FTIR spectra of the WTBs pyrolysis volatiles

Fig. 2 shows the FTIR spectra of WTB waste for all 15 measurements and the average of those measurements. The 3020 cm^{-1} band corresponds to C–H stretching vibrations in the epoxy group. The 2950 and 2860 cm^{-1} bands present correspond to C–H stretching vibrations in the CH_2 and CH_3 groups of the aromatic and aliphatic chains, respectively. The intense band at 1720 cm^{-1} was attributed to C=O bond stretching vibrations. Weak bands at 1630 cm^{-1} are attributed to C=C stretching vibrations of the aromatic ring. The bands at 1500 cm^{-1} are attributed to N–H bending vibrations of the primary amines. In contrast, the bands at 1450 and 1340 cm^{-1} are attributed to C–N stretching vibrations of the amine bonds. The 1220, 1120 and 1050 cm^{-1} bands are attributed to stretching vibrations in the ether group. The bands 750 and 660 cm^{-1} correspond to C–H vibrations outside the plane of the aromatic rings.

In this study, the analytical pyrolysis was conducted at 500 °C to examine waste WTB, and the obtained pyrograms revealed detailed information regarding on the resin's structure. The pyrogram of the waste

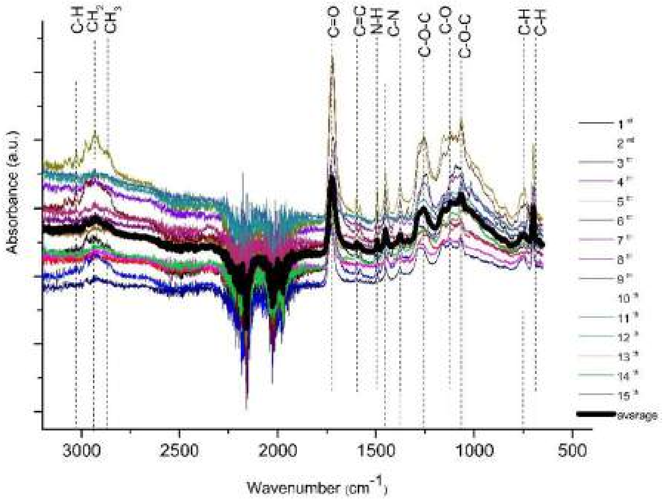

Fig. 2. FTIR spectra of the sample WTB subjected to the oxidative liquefaction process.

WTB showed that its primary components were styrene (3.05 min), 1,2-benzenedicarboxylic acid (12.79 min), heptacosane (49.44 min), 1-docosene (46.45 min), 3-(2-phenylethyl)benzonitrile (35.07 min), 2-(2-hydroxypropoxy)-1-propanol (6.07 min), cyclopropyl phenylmethane (21.97 min), toluene (1.83 min), α-methylstyrene (4.50 min) and a few other products which may be formed of thermal plastic conversion or from thermal degradation epoxy resin and unsaturated polyester resin [45–47].

3.2.2. *analysis results*

The mass loss and conversion rate of the virgin WTB during TGA pyrolysis at heating rates of 4, 8, and 16 K/min is presented in Fig. 3. The pyrolysis decomposition in all measurements can be divided into two stages. The first stage in the decomposition profile results in a very small mass change (<1–2%) due to the moisture evaporation followed by the decomposition of residual PE foam filling, and balsa wood dust, being a typical filling material of GF epoxy-based WTB [48]. Next, the major mass drop occurs, denoted for the complete decomposition of the epoxy resin in the sample, between the temperatures of 280 and 450 °C [49]. When composite-bounding resin is decomposed, the residual mass consisting of the recovered glass fiber is a main subject of interest in the recycling of end-of-life blades. The final mass loss of the WTB is strongly correlated to the GFs content in the composite sample prepared for the TGA. The presented results show certain deviations of the final residual mass reported during the TGA 71.58–74.42%, listed in Table 3. WTB is a highly heterogenic material when prepared for analytical purposes, posing a challenge to provide a homogenous sample at 5 mg. Nevertheless, the results are repeatable, and suitable for the determination of process kinetics, as similar observations were reported and confirmed in the literature by Yousef et al. [25,50]. Conversion rate profiles dα/dt, of the WTB pyrolysis, present a small and inconsistent across the heating rates peak at 181.5–198.2 °C, followed by a dominant peak contributing to the majority of the final mass loss with peak temperatures 342.4–359.9 °C. Based on observations of the TGA profiles, the suitable kinetic model for WTB pyrolysis is proposed as 2 stages independent pseudo-component model, where each stage represents a single peak observed in Fig. 3. Stage 1 of the model will represent moisture and organic solvents evaporation from resin matrix, and Stage 2 models main epoxy resin pyrolysis. Of course, epoxy-resin composite contains many pseudo-components, and the assumption of single-rate kinetics for its pyrolysis modeling is a simplification. However, the obtained DTG profile presents one dominant decomposition stage at main pyrolysis temperatures, thus approximation of epoxy resin with single-stage kinetics is justified, which was also highlighted by Yousef et al. [50].

Table 3
Results of the TGA measurements.

β, K/min	Residual mass, %	*Stage 1*		*Stage 2*	
		Mass loss, %	Peak temperature, °C	Mass loss, %	Peak temperature, °C
4	74.42	−1.58	181.5	−22.47	342.4
8	74.52	−1.5	187.4	−23.41	354.9
16	71.58	−1.79	198.2	−26.64	359.9

3.2.3. *WTB pyrolysis kinetics*

Results of the kinetic modeling using a 2-stage independent pyrolysis model are presented in Fig. 4. Kinetic modeling results provided very high fit quality (R^2>0.97) to the experimental TGA data, with minor deviations at the first stage of decomposition, where the highest differences in the experimental signal occurred, associated with different moisture and organic solvents contained in the composite were present. Kinetic modeling was based on the Fraser-Suzuki deconvolution, which results were inversely fitted with the traditional Arrhenius rate equation, presented in the Supplementary Materials. The final results of the model are 2 sets of kinetic triplets *i.e.*, activation energy E (kJ/mol), the logarithm of pre-exponential factor log(A) (min-1), and dimensionless reaction order, n, with an additional parameter – the contribution factor, c, representing the integrated percentage of the conversion rate contributing on the final mass loss of the sample during the process, listed in Table 4. In this study, the kinetic parameters of Stage 1 assigned for moisture and solvent evaporation were 101.4 ± 2.4 kJ/mol, 10.8 ± 0.7 log (min^{-1}), 2.37 for E, log(A), and n respectively. It must be stated, that Stage 1 of the WTB pyrolysis contributed to 9.7% of the final mass loss of the WTB pyrolysis, thus kinetic parameters of Stage 2, responsible for 90.3% of the mass loss of the process can be probably adapted for practical single-step kinetic modeling for the purpose of e.g., numerical modeling or process engineering, with kinetic parameters of 134.4 ± 2.4 kJ/mol, 10.7 ± 0.25 log (min^{-1}), 1.45 for E, log(A), and n respectively. During the second stage of pyrolysis at temperatures of 300–400 °C, where the majority of the resin's volatile compounds is released numerous and simultaneous reactions take place leading to the formation of various products, mainly 2-Butenoic acid, methyl ester, as well as Phenol and it's derivatives, e.g., Phenol, 4-(1-methylethyl)-, *p*-Isopropenylphenol [51]. However, based on the similarities TGA and DTG data presented here and results of FTIR-GC-MS reported by Yousef et al. modeling the main WTB pyrolysis stage with a single-step reaction model is justified [52].

Only a few literature studies investigated the kinetics of the WTB pyrolysis process. Qiao et [53]. studied the pyrolysis of epoxy glass-reinforced composite using the TGA-FTIR technique at heating rates of 5, 10, 15, and 20 K/min. Similar observations of mass loss behavior and DTG profiles were reported. The kinetic modeling was based on two approaches: model-free and model-fitting, and two sets of results were reported. WTB samples presented in this study were also assessed with model-free, isoconversional kinetics during study preparation, however, discrepancies in the final residual mass caused high

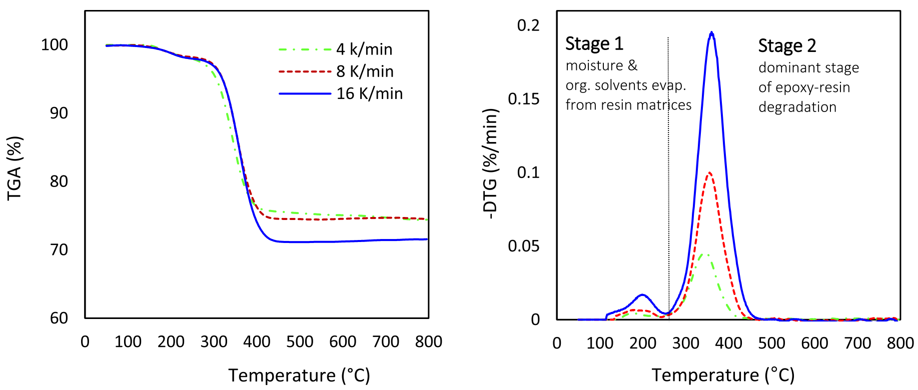

Fig. 3. TGA and DTG profiles of the WTB pyrolysis obtained at dynamic heating runs at 4, 8, and 16 K/min.

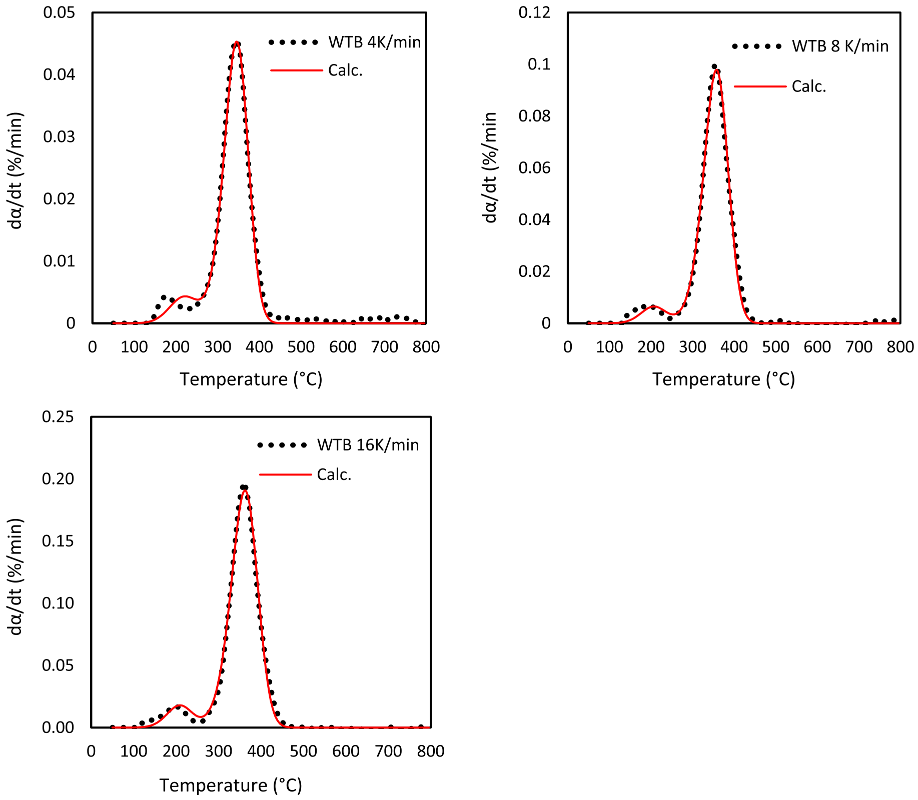

Fig. 4. 2-Stage pyrolysis kinetic model results plotted against experimental WTB pyrolysis conversion rate.

Table 4
Kinetic parameters of the 2 independent stage WTB pyrolysis model ($R^2 > 0.97$).

Parameter	Stage 1	Stage 2
E, kJ/mol	101.4 ± 2.4	134.4 ± 4.1
log(A), log (min^{-1})	10.8 ± 0.7	10.7 ± 0.25
n	2.37	1.45
c	0.097	0.903

deviations in the results, which made the whole analysis faulty and inaccurate. Nevertheless, the authors concluded that epoxy glass composite single-stage model-fitting kinetics provided the best fit to experimental data with the assumption of 1st reaction order model (F1), with ln(A) varying across the heating rates from 9.94 to 12.78, and E in the range of 126.61–139.90 kJ/mol, yielding very similar results to the ones reported in this study (Table 4.). Regarding the model-free kinetics results, several studies reported highly dependent values of the apparent activation energies $E\alpha$ across the pyrolysis conversion extent assigning it to the decomposition of numerous resin and epoxy compounds present in the composites. Yousef et al. studied catalytic pyrolysis of the epoxy-glass composite over ZSM-5 zeolite catalyst, with reported values of the $E\alpha$ varying as high as 120–500 kJ/mol across the conversion range for the isoconversional Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) or Vyazovkin methods [25]. However, due to the high heterogeneity of the samples, resulting in variable residual mass, model-free kinetics results, mathematically prone to such issues, should always be presented along with regression errors of the isoconversional lines, as presented in Ref. [54], where apparent $E\alpha$ were matching results of the model-fitting kinetics presented in this study, with obtained average values of 165 kJ/mol for KAS, 193 kJ/mol for FWO, and 177 kJ/mol for Vyazovkin methods with R^2>0.98. In another paper, Yousef et al. presented a TG-FTIR and Py-GC/MS study of epoxy-glass composite pyrolysis, with kinetic modeling based on linear and nonlinear isoconversional methods [55]. The model-fitting kinetics was based on the 2-stage Distributed Activation Energy Model (DEAM), and Independent Parallel Kinetic Model (IPR), with activation parameters yielding E, and A for both approaches as 200.4 kJ/mol, 3.33 E+20 min^{-1} for Stage 1, and 248.5 kJ/mol, 3.55 E+20 min^{-1} for Stage 2a for DEAM, and 10.9 kJ/mol, 5.55 E+14 min^{-1}, for Stage 1, and 234.57 kJ/mol, 1.40 E+17 min^{-1} for the IPR model respectively. The IPR approach, presented also in this study presented a similar pattern: the 2-stage WTB pyrolysis with the first stage activation parameter much lower than the primary pyrolysis stage. However, regarding the average isoconversional activation energies presented in the same study by Yousef et al. e.g., for KAS 143.29 kJ/mol, Vyazovkin 157.03 kJ/mol, and Cai 152.90 kJ/mol, presented values of E for the 2 stage model presented in Table 4 are in a very good agreement.

3.3. Results from oxidative liquefaction of WTBs

3.3.1. Microstructure of the raw WTBs before and after oxidative liquefaction

Fig. 5a Depicts the surface morphology of GFs in a polymer resin matrix. The results of the observation show that the preparation applied on-site by the manufacturer of the glass fiber-based composite has a uniform thickness and completely covers the surface of the individual fibers reinforced with the polymeric material.

Fig. 5b Shows the morphology of the GFs obtained for the sample with maximum resin degradation after the oxidative liquefaction process, i.e., the removal of the polymer matrix from the fiber surface. Single and well-separated GFs can be seen. The morphology of the glass fiber surface confirms that it is smooth and free of obvious discontinuities, indicating that the SiO_2 layer produced is of high quality. Locally, a few irregularities and minor impurities, which are products of resin decomposition, are observed.

3.3.2. Resin degradation as a base for volatile fatty acid production

RDY against the different combinations of tested parameters have

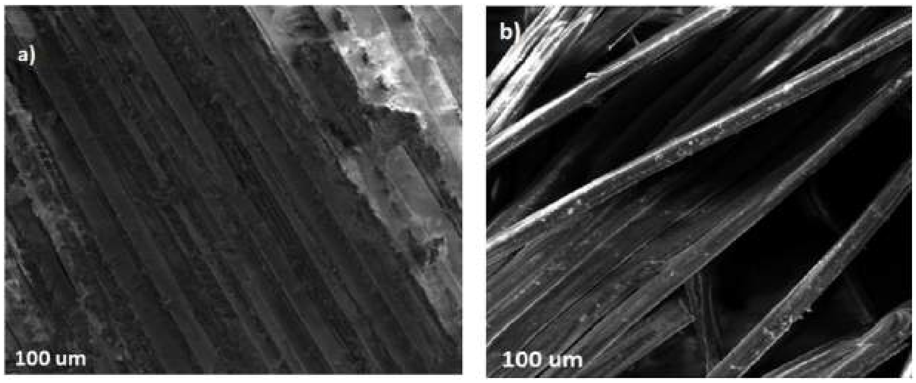

Fig. 5. SEM images - surface morphology of glass fibers: a) resin matrix fibers; b) fibers after the oxidative liquefaction process.

been shown in Fig. 6, by following the colors and type of lines, one can see the reaction condition against particular RDY values. For sake of simplicity, 2 samples with maximum and minimum RDY values from each tested temperature have been presented. The maximum value of RDY i.e. 100 % represented by a green dashed line was achieved for the sample prepared at the highest tested levels of temperature, pressure, oxidant concentration, and lowest values of residence time and waste-to-liquid ratio. During the highest tested temperature, 350 °C the average RDY was almost 86% with a range of 76–100%. While the 300 °C average value of RDY dropped to 72% with values lying in the range of 56–96%, for these values of RDY combination of tested parameters can be seen by following red and purple lines. At the lowest tested temperature of 250 °C the average value of RDY was 73% very close to that achieved at the intermediate temperature level. To ensure the accuracy and reliability of experimental results, the experiments were repeated randomly multiple times, and the standard deviation of the results was calculated. The standard deviation was found to be in the range of 2.5–4.5% which suggests that the results are sufficiently repeatable. However, it should be noted that the variation in the results may be influenced by factors such as the inhomogeneity of the sample or the existence of multiple reaction roots because of the complex composition of WTBs.

The results revealed that the highest temperature of 350 °C is favorable to attain the higher RDY by keeping all the combinations the same. But during the detailed analysis of obtained results, it was very interesting to note that all the samples that resulted with maximum RDY values were prepared strictly with a minimum waste-to-liquid ratio i.e., 5%, and residence time of 30 or 60 min. During these experiments, targeting the maximum RDY the magnitude of oxidant concentrations and pressure was continuously changing (the same results of RDY can be achieved at all tested levels) suggesting their minimal effect on RDY. But in the reaction process while choosing the pressure it is important to keep it high enough to keep the reactants in the liquid state and oxidant concentration should not be less than stoichiometric values. High-temperature values can result in maximum degradation, but the higher temperature is related to high energy consumption. The waste-to-liquid ratio is the most important factor in resulting in the required RDY, and by using its lowest values the same results achieved at higher temperatures could be achieved at lower ones. Increased RDY at elevated temperatures is because of decreased Hildebrand parameter, increasing the temperature decreases the Hildebrand parameter of water, making it more similar to that of different resins, which enhances its solubility in near-critical water and increases the solvation power of the water towards the polymer [56]. Lowering the waste-to-liquid ratio increases the concentration of liquid media, which enhances hydrolysis, ionic condensation, and cleavage reactions, leading to the attainment of

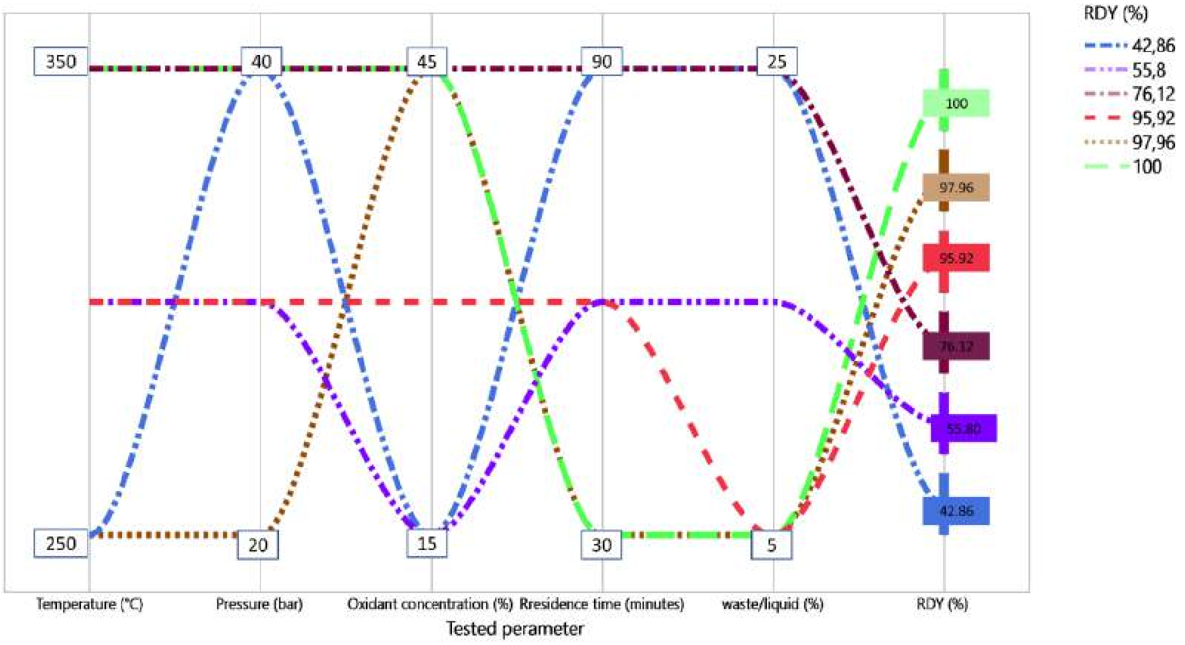

Fig. 6. Various combinations of tested variables against RDY.

higher degradation, and improved RDY values. A higher concentration of water also leads to an increase in H^+ and OH^- ions, favoring the initiation and propagation of reactions.

3.3.3. Volatile fatty acids concentrations in liquid products

Oxidative liquefaction offers a promising approach for converting solid waste into valuable resources, including VFAs, presenting a significant opportunity for sustainable waste management.

Various combinations of tested parameters were checked but only minimum and maximum values of VFAs concentrations have been presented in Fig. 7 for all three temperature levels. During the oxidative liquefaction of WTBs the maximum concentration of VFAs achieved at 250 °C was 210.59 g/kg-WTBs, the combination of tested parameters has been highlighted by green colour line, oxygen concentration, waste-to-liquid ratios residence time were at their minimum levels but the pressure was higher. VFAs yield at 250 °C was at its minimum value of 28.90 g/kg-WTBs when the residence time and oxygen concentrations and pressure were maximum while the oxidant concentrations was minimum (highlighted by blue line). At an intermediate temperature of 300 °C, the best yield of VFAs achieved was 158.54 g/kg-WTBs and the tested parameters have the average values except for the waste-to-liquid ratio which was at its minimum. At this average temperature with a combination of minimum oxidant concentrations, pressure, residence time, and oxidant concentration on average, the minimum concentration of VFAs was 60.92 g/kg-WTBs. At 350 °C the maximum yield of VFAs was 163.50 g/kg-WTBs, during this experiment the pressure, residence time, waste-to-liquid ratio, and oxidant concentration were at the least tested level, while the temperature was at its maximum. The minimum value of VFAs achieved at the highest temperature of 350 °C was 36.31 g/kg-WTBs, when reaction temperature, pressure, and waste-to-liquid ratio were reaching their maximum levels, oxidant concentration, and residence time were the minimum.

In the conducted experiments, the energy consumption was measured and it was observed that the average energy consumed for experiments performed at 350 °C was 2.9 kWh, which is almost double the average energy consumed for the experiments performed at 250 °C, which was 1.6 kWh. Additionally, the average energy consumption for the experiments performed at 300 °C was recorded as 2.41 kWh. Energy consumption plays a vital role in determining the commercial feasibility of the process. Moreover, the effects of different tested parameters on the VFAs production were not clearly understood. To overcome this, a detailed optimization of the experimental plan has been performed in the following section to provide optimal conditions for the process with minimum energy conversion, maximum RDY, and VFAs concentration.

3.3.4. Optimal conditions for maximizing oxidative liquefaction yield

The present study aimed to investigate the oxidative liquefaction of WTBs under various process conditions. A total of 29 experiments were conducted to assess the impact of temperature (ranging from 250 to 350 °C), pressure (ranging from 20 to 40 bar), H_2O_2 solution concentration (6–18%), residence time (ranging from 30 to 90 min), and waste to oxygenated solution ratio (5–25%) on the production of VFAs from WTBs. The planning experiments and ANOVA methods was utilized to determine the significant variables affecting the wet oxidation process, assess interactions between the variables, and evaluate their statistical significance. The significance analysis was performed using a p-value of 0.05. The findings of this study have significant implications for optimizing the wet oxidation process for improved efficiency in the treatment of WTBs.

Fig. 8 displays a Pareto chart illustrating the results from ANOVA of oxidative liquefaction of WTBs. The chart plots standardized effects on the x-axis and process variables on the y-axis in descending order on the base of their overall effect on process output. A red vertical reference line in the chart represents the cut-off point for the statistical significance of tested parameters, the variables having higher values than the cut-off point have a more dominant effect on process output and vice versa. The letter (L) and (Q) shows that tested parameters have both linear and quadratic behavior but, in most cases, the linear behavior is more dominant. The numbers (1), (2), (3), (4), (5) are randomly assigned to the tested variables and the term 3Lby5L represents the interaction of the 3rd variable i.e. Oxygen(L) with the 5th variable i.e. wate-to-liquid ratio(L). Standardized effects or variables, denoted with

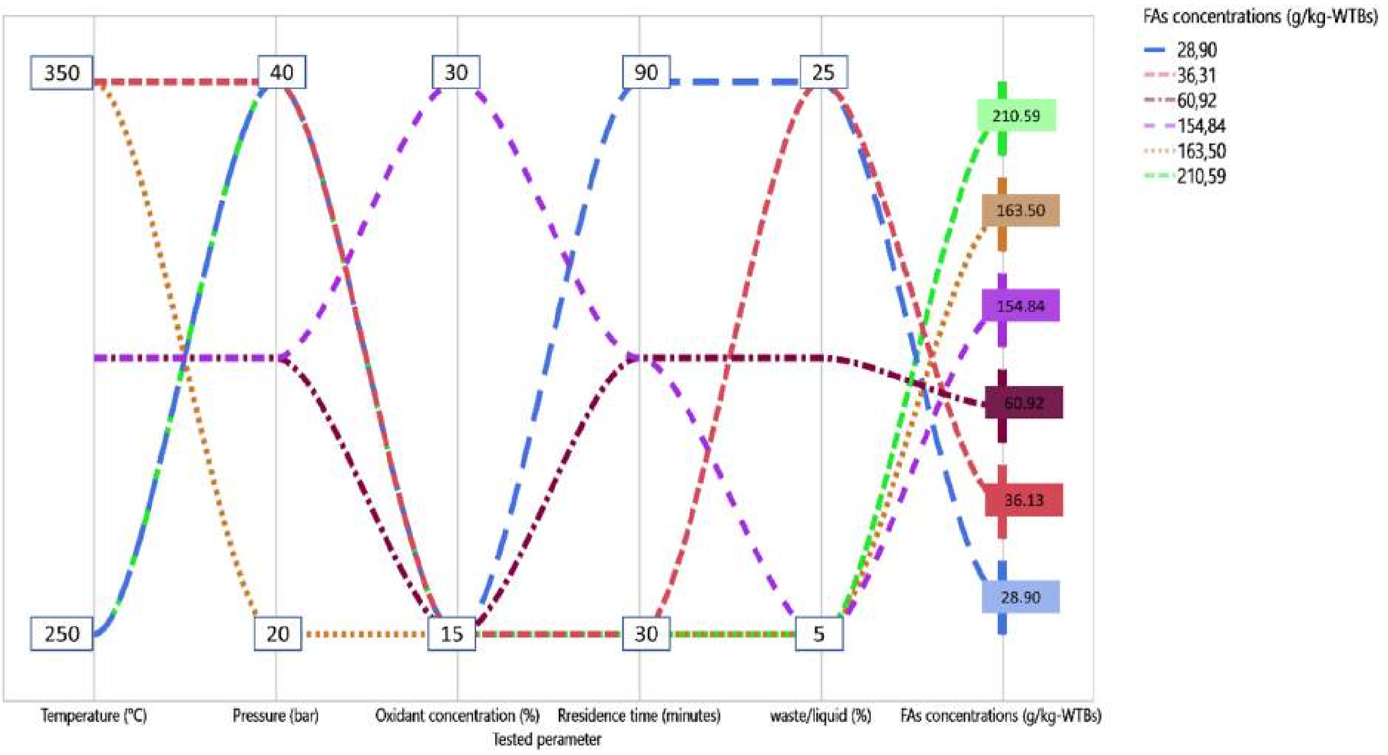

Fig. 7. Various combinations of tested parameters for minimum and maximum VFAs yield.

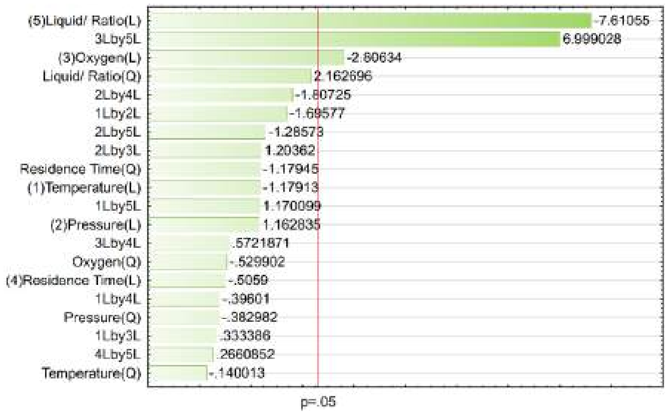

Fig. 8. Statistical significance and interactive effects of tested parameters on volatile fatty acids yield.

positive or negative signs, are used to represent the size and direction of the effect of a factor relative to the overall variability in the process e.g., a negative sign with waste-to-liquid ratio shows that it will negatively affect the process output. While referring Fig. 8, it was found that the waste-to-liquid ratio is the most dominant parameter in affecting the VFAs yield from oxidative liquefaction of WTBs but its effect on the process yield is negative, which means higher waste-to-liquid ratio will result in less concentration of VFAs. Oxygen alone has a weak negative effect on the process but when interacting with the waste-to-liquid ratio its effect is very strong, and positive indicating that less concentration of oxygen interacting with less waste-to-liquid ratio results in higher VFAs yield. All other factors examined in the study have both linear and quadratic effects on the process but their impact is lower than the statistical significance range, indicating that their contribution to the process outcome is negligible. Fig. 9 presents an optimization plan based on the effects of the tested parameters, including energy consumption during the process, to enhance the economic feasibility of the oxidative liquefaction process. The optimization plan seeks to achieve a balance between the production of VFAs, maximizing the RDY, and the energy consumed during the process.

From the observed trends in profiles of predicted values, temperature, pressure, and residence time are the factors that have an almost negligible effect on process output in the case of both RDY and VFAs production from WTBs. In the case of RDY the quadratic behavior of temperature suggests that at higher temperatures, slightly increased values of RDY can be achieved but at the lowest tested temperature of 250 °C, 95% of RDY has already been achieved but applying the higher temperature to the process will increase energy consumption drastically meanwhile the gain in RDY could not very higher. Reaction pressure has almost no effect on the process in the case of both VFAs and RDY as its lowest value is still giving results close to the maximum possible outcomes of the process, but the increased pressure has no concern with energy, so the best choice of the pressure is the one resulting the maximum values of RDY and VFAs. The behavior of the residence time during the whole reaction is quadratic, but less affects the process, so the best choice of residence time is related to the least energy consumption.

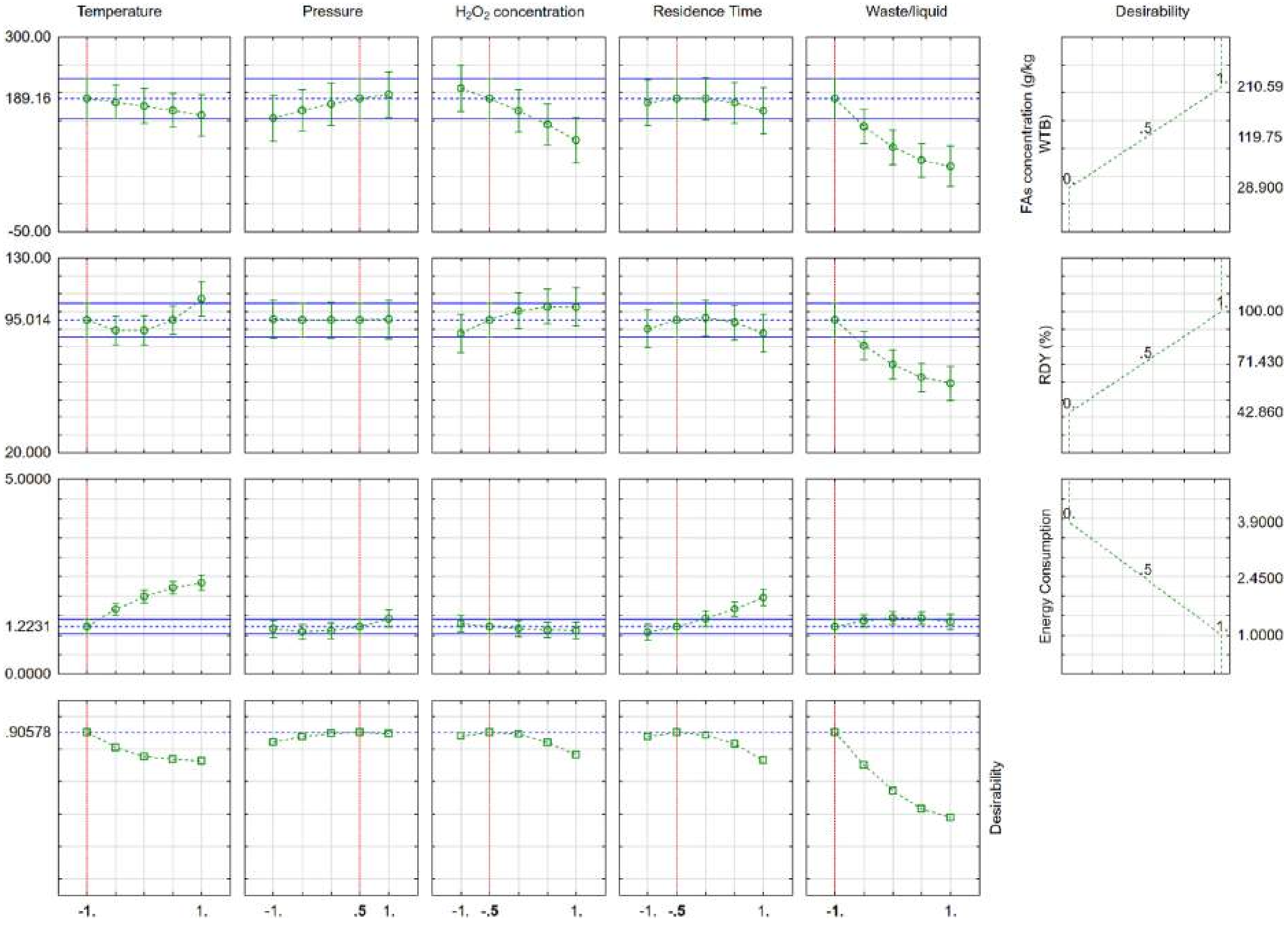

Fig. 9. Profiles of predicted values for best process performance.

Oxidant concentrations and waste-to-liquid ratios are identified as the most influential reaction parameters. A higher concentration of oxygen in reactants can slightly increase the RDY but on the other hand, this increase in oxidant concentration will linearly decrease the VFAs production from WTBs blades which is a major goal of the study. So, a balanced value of oxidant concentration is suggested for which both the RDY and VFAs production will be maximum. During the reaction process, the least waste-to-reaction ratio is the best choice as its higher levels affect both VFAs concentration and RDY in the same negative trend. Based on this discussion optimal reaction conditions have been shown in Fig. 9 indicated by red lines and summarized in Table 5 recalling the fact that -1 represents the lowest level of the tested parameters while 1 is the highest level.

Fig. 10 displays response surface profiles that depict the collective desirability of two functions with the aim of maximizing the process output. The coded values used in the profiles represent the highest and lowest levels of the parameters that were tested during the process. The desirability of each parameter was evaluated on a scale ranging from 1 to 10. These response surface profiles provide valuable insight into whether the process has reached a local or global maximum, with the latter being the sole global maximum in this case. By analyzing these response surface profiles, it was possible to gain a deeper understanding of the underlying relationships between the input parameters and the process output. This helped to identify critical process parameters that have the greatest impact on the desired response and facilitate the development of strategies for optimizing the process. For example, while discussing the collective desirability of pressure and temperature the curvature of the response surface suggests that low-pressure values are less desirable, while the desirability of higher-pressure values is more. The curvature of the surface along the temperature axis suggests that the desirability of low-temperature values is very higher, and this desirability decreases for higher temperatures, later the desirability for higher-temperature values slightly increases again but this desirability is still less than the desirability for low-temperature values, this discussion corresponds to the selection of 35 bar and 250 °C as the optimal reaction conditions. Prolonging the discussion to the collective desirability of H_2O_2 concentration and residence time the response surface has the curvature in the middle along both axes suggesting that the average values of both these factors are most desirable during the process. The same approach can be used to see the collective desirability of waste-to-liquid ratio and H_2O_2 concentration.

4. Discussion

Elemental and compositional analysis of WTBs suggested that there is a sufficiently large proportion of organic fraction in form of different resins that can be degraded to obtain valuable liquid products, while recovery of the inorganic fraction is beneficial as these are mostly the GFs. The morphological study of obtained solid products was the first indication of the success of the oxidative liquefaction process. The process effectively removed the resinous surface of the virgin WTBs, leaving behind separated GFs. This observation is indicative of the process's ability to achieve its intended objectives. During the optimization of the overall process, the oxidant concentrations and waste-to-liquid ratio are found to be the most important parameters governing the process outcomes. But the increase in RDY with the temperature can be attributed to unique properties of the near-critical environment inside the reactor, such as higher diffusivity, lower dielectric constant, lower density, and water expansion, allowing for higher degradation of the resins [57]. Another important consideration is the Hildebrand parameter of water at ambient conditions which is 48 $MPa^{0.5}$, epoxy resins for instance, has an estimated Hildebrand value of 20 $MPa^{0.5}$, which indicates that epoxy is barely soluble in water under ambient conditions [58,59]. This Hildebrand parameter of water tend to decrease as the temperature rises to higher levels and this reduction is due to the diminished extent of hydrogen bonding in near-critical water that results in higher degradation yields. The effect of temperature on VFAs production is almost negligible but still little decrease in VFAs concentration can be observed with the increase in temperature and this decrease is attributed to the oxidation of intermediates. During the liquefaction of various materials, it has been observed that there is a plateau in the yield of liquid products obtained after reaching a certain temperature [60,61]. Moreover cracking processes of liquid products can produce gases like CO_2 as well as condensation, cyclization reactions of liquid products cause a rise in the growth of char at higher temperatures. The effects of residence time are similar for both RDY and VFAs concentrations, and they are quadratic in nature means first a slight increase in process output and then a point of diminishing returns where further increases in reaction time do not result in significant improvements in liquid yield. The effect of residence time is strongly related to the temperature as extended exposure to high temperatures can promote cracking and condensation reactions [62]. High temperatures and prolonged reaction periods are responsible for higher energy consumption so a balanced trade-off of operating conditions is required. Pressure has no direct connection with the energy consumption during the process and its effect on the process yield is minimum but comparatively high pressure assures a single-phase reaction media, which avoids the need for large amounts of heat to maintain a two-phase system. High pressure in oxidative liquefaction can increases solvent density, which will enhance penetration into waste components for better decomposition and extraction of desired products [63]. Waste-to-liquid ratio and oxidant concentration are also closely related to each other while determining the process efficiency, lower waste-to-liquid ratios are most suitable for getting the maximum RDY and VFAs concentration from WTBs. The role of water in the process is very versatile it severs as the solvent as well as the reaction medium for carrying out the required chemical reactions hydrolysis, oxidation, and bond scission. A decreased waste-to-liquid ratio in oxidative liquefaction promotes faster attainment of equilibrium, leading to higher RDY and VFAs concentration. Higher water content can provide more H^+ and OH^- ions, which can act as catalysts for the initiation and propagation of reactions in the process. During the oxidative liquefaction of WTBs a stoichiometric amount of oxygen was also needed to carry out the complete oxidation of complex resins, RDY values can be enhanced by using the higher oxidant content but on the other hand, the excess oxygen content was reducing the yield of liquid products as an excess of oxygen can lead to over-oxidation of intermediate products, resulting in the breakdown of these compounds into smaller and less stable molecules [64]. These reactive species can further undergo reactions to form undesired by-products such as carbon dioxide and water. Additionally, an excessive concentration of oxidants can increase the reaction temperature unpredictably, leading to the thermal degradation of the obtained liquid products so optimal oxidant concentration selection is important.

Table 5
Optimal conditions for maximizing the RDY and VFAs concentration from oxidative liquefaction of WTBs.

Process parameter	Optimal value
Reaction temperature (°C)	250
Initial pressure (bar)	35
Reaction time (minutes)	45
Oxidant concentration (H_2O_2) (%)	22.5
Waste-to-liquid ratio (%)	5

5. Conclusion

In the current study, oxidative liquefaction has been proven to be an effective method for recycling WTBs to ensure the long-term sustainability of wind energy. Compositional analysis showed WTBs contain a large proportion of different types of resins that were degraded to produce the VFAs which is the core purpose of the study and GFs were

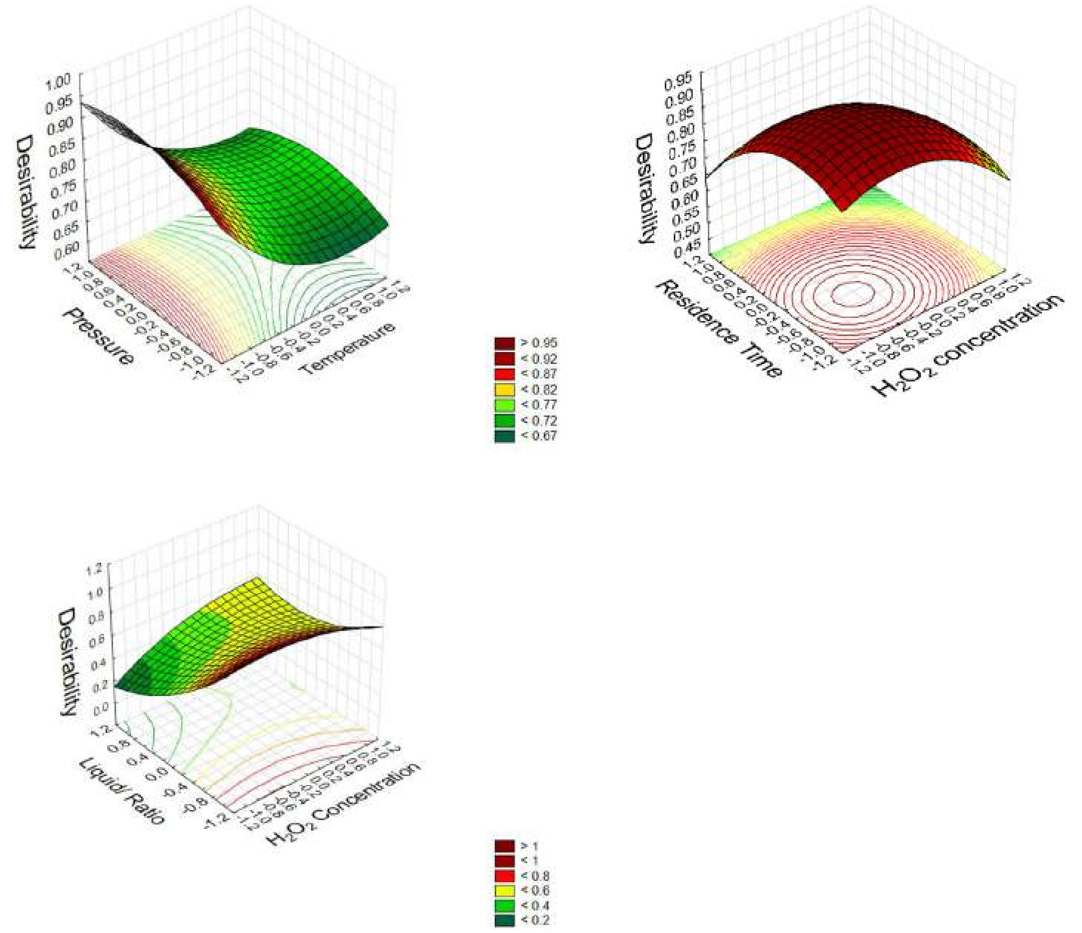

Fig. 10. Response surface profiling of the combined desirability of tested parameters in optimizing the process output.

recovered as secondary products. During TGA pyrolysis of WTBs at different heating rates, mass loss is mainly due to the decomposition of epoxy resins and residual filling materials. Pyrolysis shows two stages with a small peak at 181.5–198.2 °C and a dominant peak at 342.4–359.9 °C. Two-stage independent pyrolysis model was the best for the experimental data. During the oxidative liquefaction, the maximum RDY obtained was 100% and the waste-to-liquid ratio is found to be the most important parameter affecting the extant resin degradation. While all the tested parameters pressure, temperature, reaction time, and oxidant concentration have the minimum impact on RDY. VFAs production slightly decreases with increasing temperature and prolonged residence times as the obtained products undergo decomposition that results in gaseous fractions. Higher oxidant concentrations also negatively impact the VFAs yield, as an excess of oxygen in combination with higher temperatures results in the overoxidation of intermediate products and the generation of less stable molecules that can react further to produce CO_2 and H_2O. Less waste-to-liquid ratios are preferable as a higher content of liquid media will provide sufficient ionic species to carry out the initiation and propagation reaction. ANOVA identified the optimal reaction conditions as a temperature of 250 °C, a pressure of 35 bar, a reaction time of 45 min, an oxidant concentration of 22.5%, and a waste-to-liquid ratio of 5% that will result in the maximum RDY and VFAs yield against the minimum energy consumption.

Authorship statement

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in data collection, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar material has not been and will not be submitted to or published in any other publication before its appearance in the "Energy journal".

Authorship contributions

Hamza Mumtaz: Conception and design of the study: Acquisition of data, Analysis and/or interpretation of data, Drafting the manuscript. Szymon Sobek: Conception and design of the study, Drafting the manuscript, Revising the manuscript critically for important intellectual content. Marcin Sajdak: Conception and design of the study, Analysis and/or interpretation of data, Drafting the manuscript. Roksana Muzyka: Conception and design of the study, Analysis and/or interpretation of data, Drafting the manuscript. Sabina Drewniak: Analysis, Sebastian Werle: Conception and design of the study, Revising the manuscript critically for important intellectual content, Funding acquisition.

Declaration of competing interest

I on the behalf of all authors, declare that there is no conflict of interest and all the elements of the submission are also in compliance with the journal publishing ethics. By submitting this manuscript, the authors agreed that the copyright for their article should be transferred to this journal if the article is accepted for publication. The work contained within the research paper is our original contribution and has not been published anywhere.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.energy.2023.127950.

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Appendix D

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Research article

An in-depth study of the oxidative liquefaction process for polymeric waste reduction and chemical production from wind turbine blades and personal protective equipment used in the medical field

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ABSTRACT

An in-depth study of the oxidative liquefaction process has been provided to degrade the polymeric waste from personal protective equipment (PPEs) and wind turbine blades (WTBs). Thermogravimetric investigations demonstrate that WTBs have three prominent peaks throughout the degradation, whereas PPEs display solitary peak features. Experiments are carried out employing specific experimental design approaches, namely the Central Composite Face-Centered Plan (CCF) for WTBs and the Central Composition Design with Fractional Factorial Design for PPEs in a batch-type reactor at temperature ranges of 250–350 °C, pressures of 20–40 bar, residence times of 30–90 min, H2O2 concentrations of 15–45 %, and waste/liquid ratios of 5–25 % for WTBs. These values were 200–300 °C, 30 bar, 45 min, 30–60 % and 5–7 % for PPE. A detailed comparison has been provided in the context of total polymer degradation (TPD) for PPE and WTBs. Liquid products from both types of wastes after the oxidative liquefaction process are subjected to gas chromatography with flame ionization detection (GC-FID) to identify the existence of oxygenated chemical compounds (OCCs). For WTBs, TPD was 20–49 % and this value was 55–96 % for PPE while the OCC yield for WTBs (36.31 g/kg - 210.59 g/kg) and PPEs (39.93 g/kg - 212.66 g/kg) was also calculated. Detailed optimization of experimental plans was carried out by performing the analysis of variance (ANOVA) and optimization goals were maximum TPD and OCCs yields against the minimum energy consumption, though a considerable amount of complex polymer waste can be reduced and high concentrations of OCC can be achieved, which could be applied for commercial and environmental benefits.

1. Introduction

1.1. Outbreak of COVID-19 and increased personal protective equipment (PPE) waste in the environment

The rapid development in the renewable energy sector especially wind energy resulting the higher number of aging wind turbine blades (WTBs) and adoption of personal protective equipment (PPE) in the healthcare industry has certainly led to a rise in the generation of plastic waste. The severity of this issue has been amplified by the epidemic when disposability of PPEs, although was essential for the purpose of infection prevention but the increase in the utilization of single-use PPEs to ensure the safety of healthcare staff and patients has significantly contributed to the existing environmental challenge presented by plastic waste. The onset of the COVID-19 epidemic occurred in late 2019 and rapidly disseminated worldwide, ultimately evolving into a global pandemic. Various precautionary measures were adopted to reduce its transmission, including as the utilization of PPEs, adherence to physical distance, regular hand hygiene, and promotion of vaccination (Jiang et al., 2023). These PPEs include N95 masks, surgical masks, face shields, gowns, and gloves. A research from Politecnico di Torino in Italy forecasts that during the second phase of resuming public activities, the monthly demand for masks and gloves was increased to 1 billion and 500 million, respectively ("Nello smaltimento di mascherine e guanti serve responsabilità | WWF Italia," n. d.). The database of a website dedicated to giving information on various aspects of the Corona virus

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reveals that Asia utilized a staggering 3716.20 million masks every day throughout the epidemic, weighing a total of 1486.48 tonnes. Following closely behind, Africa used 922.22 million masks, weighing a total of 368.89 tonnes. The data indicates that Europe received a total of 884.71 million masks, weighing an average of 353.88 tons ("COVID - Coronavirus Statistics - Worldometer," n. d.). During the peak of the pandemic in Wuhan, China, the city produced over 247 tons of medical waste per day, a roughly six-fold increase compared to the pre-pandemic period (Singh et al., 2020).

Plastic is a predominant component of the medical waste produced during the COVID-19 pandemic. Typically, face masks are made from polypropylene (PP) and textile cotton however, PP plays a more significant part in the conception of respirator masks (Fadare et al. n.d.) while face shields are made up of polycarbonate (PC), polyethylene terephthalate (PET), or polyvinyl chloride (PVC) (Sangkham, 2022). Protective gowns are made from basic plastic materials such as PP, polyester (PEs), or polyethylene (PE), whereas coveralls are developed using high-density polyethylene (HDPE) (Al-Omran et al., 2021). Protective gloves are available in several varieties, including latex, vinyl, nitrile, natural rubber, PVC, and acrylonitrile/butadiene, which serve as their basic materials (Manhart et al., 2020). The plastic waste generated from PPEs can persist for several decades before it decomposes. Improper disposal of this waste can have detrimental effects on the environment, animals, and human health (Wang et al., 2022).

Thus the heightened generation of waste from PPEs has impaired the plastic waste crisis, putting strain on the global waste management system (Mumtaz et al., 2023c; Skrzyniarz et al., 2022). In order to minimize the ecological footprint of PPEs it is crucial to adhere to appropriate waste disposal methods and use reusable and biodegradable alternatives. Medical waste is frequently treated via high-temperature incineration. Nevertheless, it is linked to significant environmental issues and needs extra fuel to achieve elevated temperatures. Flue gas treatment is necessary; however, the only valuable output is heat. Medical waste carbonization results in the formation of uniform, solid carbonized products that possess increased energy density and enhanced stability (Ma et al., 2020). Specifically, the process of liquefaction of PPEs presents various challenges that are contingent upon the specific technique employed. Thermal cracking, a process known for its efficiency, necessitates a substantial amount of energy to achieve elevated temperatures and also demands the use of costly equipment. The release of harmful gases during the heating process is a cause for concern (Rasul et al., 2021; Sadrameli, 2015). The process of chemical liquefaction involves the use of strong chemicals, which can potentially lead to environmental and health hazards if not handled properly. Moreover, it is worth noting that these reactions have the potential to generate hazardous byproducts (Joseph et al., 2021). The utilization of solvothermal methods in the production process results in the presence of residual solvent within the final product, thereby requiring additional treatment procedures to be implemented. Furthermore, it is important to note that these solvents elicit safety concerns as a result of their inherent flammability and potential toxicity (Ghalandari et al., 2022; Saha et al., 2022). Supercritical fluid liquefaction, could be an alternative option but it is associated with significant costs due to the requirement for specialized equipment and the need to operate under extreme pressures. Under the conditions employed in this method, there is a potential for the formation of undesired byproducts or the deterioration of the target material (Preetam et al., 2023). The process of pyrolysis applied to medical waste yields a combination of solid, liquid, and gaseous products, exhibiting significantly lower CO_2 emission levels compared to combustion (Dharmaraj et al., 2021). Gasification is an alternative choice for treating medical waste, as it generates syngas that can be used for energy production and heating applications, and the generation of secondary chemical compounds but it offers process complexity, feedstock pretreatment, and environmental concerns (Molino et al., 2016).

1.2. Wind energy as a backbone of the renewable energy sector and the recycling of wind turbine blades (WTBs)

Wind energy is gaining significance in the field of renewable energy, reducing the price of electricity but proper repurposing is required to make it a reliable supply of environmentally friendly energy (Nagle et al., 2022). The increasing advancements in technology are revealing the growing potential of wind energy to emerge as a significant electricity source. Wind turbines are employed for electricity generation in several countries globally, including the United States, China, and Europe (Chen et al., 2023). As of 2020, the global wind turbine count exceeds 600,000, spread across more than 100 nations, and together generating a total installed capacity of 603 GW (GW) (Adlong, 2012). China leads the world in installed wind power capacity with 211 GW, followed by the United States with 96 GW, Germany with 68 GW, and India with 37 GW ("Wind energy program in India on JSTOR," n. d.). The Gansu Wind Farm in China holds the title for being the biggest wind farm globally, boasting an impressive installed capacity of 7965 MW (Nazir et al., 2022; Boretti and Castelletto, 2019; Deurs et al., 2017; Nieradzinska et al., 2016).

WTBs generally comprise three primary elements: the airfoil, the spar, and the shell. The airfoil and spar are often constructed from composite materials, such as fiberglass or carbon fiber, together with epoxy resins. These materials are specifically engineered to possess both low weight and high durability (Fonte and Xydis, 2021). The shell is often fabricated from resilient polymers such as polyurethane or polypropylene. The sandwich layer consists of balsa wood. Moreover, several WTBs are enveloped with a safeguarding layer of paint or alternative coating substance in order to shield the blade from corrosion and deterioration (Saraswati et al., 2020). Therefore, the lack of a specific recycling procedure poses a significant environmental hazard when it comes to the growing number of waste blades with increased polymer content. The European Union Directive on landfill waste has led to strict regulations for the disposal of big, composite items like WTBs as this not only signifies an ecological problem but also a waste of potentially retrievable resources. Several recycling procedures have been documented in the literature, categorized into three main types: thermal, mechanical, and chemical.

Pyrolysis is a thermal degradation technique commonly used in the recycling of carbon fiber-reinforced composite blades (Fonte and Xydis, 2021). This technique efficiently breaks down the polymer matrix at high temperatures without oxygen, leading to the formation of carbon fibers or glass fibers that are covered with a subsequent amount of char (Hadigheh et al., 2021). To ensure their structural integrity, these fibers need to undergo a cleaning process so that they may be utilized in various secondary applications. The bio-oil, a liquid byproduct generated, has a potential to be used as fuel or chemical feedstocks. Although pyrolysis offers benefits for carbon composite recycling, it is crucial to recognize that this process demands a significant amount of energy due to the high temperatures involved. Furthermore, the release of flue gases during pyrolysis requires efforts to enhance overall efficiency and reduce the resulting environmental impacts (Meier and Faix, 1999). Glass fibre-reinforced polymer composites (GFRPCs) and sheet molding compounds (SMCs) are recycled through the utilization of mechanical processing techniques. This technique entails pulverizing the fibers into a fine powder and subsequently categorizing the fiber size by a cascade air classification system (Psomopoulos et al., 2019). Co-processing in a cement kiln necessitates the fragmentation of blade material into smaller fragments, which are then mixed with solid recovered fuel (SRF) to serve as a substitute fuel. The recovery of carbon fibers (CFs) from GFRP is achieved by the utilization of microwave-assisted and hybrid processing techniques. This procedure entails subjecting the blades to irradiation using a microwave that is highly efficient in terms of energy consumption. Chemical recycling is the sole technique that enables the retrieval of the high-energy-dense polymer matrix from the blade in the form of useable matrix monomers. This technique entails utilizing a solvent to disrupt the covalent bonds within a polymer matrix. Nevertheless, it is worth noting that this process exhibits the most elevated energy consumption among all the documented approaches (Rani et al., 2021).

The presented drawbacks in current recycling methodologies discussed earlier need a cohesive approach to effectively manage the varied waste compositions integrated into wastes like WTBs and PPEs. In order to fill this notable research void, it is crucial to develop an innovative approach that can efficiently handle the intricate composition of WTBs while also managing the relatively simpler structure of PPEs. This methodology aims to enhance processing efficiency and achieve significant reductions in energy consumption to establish a comprehensive and sustainable recycling approach. This approach can effectively address the challenges posed by both complex WTBs and relatively simple PPEs, using a unified and ecologically responsible recycling approach.

1.3. Aim of the paper

The principal objective of this investigation was to evaluate the feasibility of utilizing oxidative liquefaction as an innovative method for the efficient recycling of polymer waste obtained from WTBs and PPEs. The goal of the study was to gain a thorough knowledge of the characteristics these materials displayed during thermal degradation. The study attempted to identify the supreme conditions supporting maximal Total Polymer Degradation (TPD) from both PPEs and WTBs by carefully comparing several reaction parameters, including temperature, pressure, residence duration, waste-to-liquid ratio, and oxidant concentrations. The study also examined how these different reaction parameters affected the amount of Oxygenated Chemical Compounds (OCCs) that were produced through degradation of polymers. In order to provide a sustainable and effective recycling process for both PPEs and WTBs, the ultimate aim was to determine and identify the optimal reaction conditions that would maximize the combined yield of TPDs and OCCs within the liquid products while reducing energy consumption during the process.

2. Materials and methods

2.1. Materials used in study

The ANMET company played a significant role in the procurement of end-of-life WTBs. The materials underwent fragmentation and milling processes, leading to the production of chips within a size range of 1–2 cm. As depicted in Fig. 1(a), the WTB samples had a polymer matrix including a substantial proportion of glass fibers. To ensure the maintenance of security measures and minimize the risk of virus transmission, a local medical company supplied the new PPEs used in the medical industry. The inventory of these PPEs encompassed various items such as single-use face masks, gloves, N-95 face masks, protective gowns, and bedsheets. Subsequently, the PPEs components underwent precise segmentation into similar sizes of WTBs simple i.e. 1 and 2 cm, as depicted in Fig. 1 (b). The objective of this strategic approach was to safeguard individuals involved in material processing from potential risks associated with viral exposure and transmission.

2.1.1. Elemental analysis of WTBs and PPEs

Ultimate and proximate analysis were performed in detail for both WTBs and PPEs. The LECO TruSpec CHN analyzer, with the SC 632 instrument, was crucial in performing a thorough analysis of WTBs and PPEs. The utilization of this analytical methodology facilitated the accurate assessment of the elemental composition, encompassing carbon, oxygen, hydrogen, nitrogen, and sulfur concentrations, in both the WTBs and PPEs samples.

The standards followed during the analysis can be found in already published research (Mumtaz et al., 2023a, 2023b). The analysis of samples total moisture, volatile matter, and ash levels were performed using a meticulous weight method, following PN-G-04560:1998, PN-EN 15402:2011, and PN-EN ISO 21656:2021–08 standards respectively.

2.1.2. Time -temperature-dependent degradation of WTBs and PPEs

The study focused on examining the thermal degradation of WTBs and PPEs, taking into consideration the influence of different heating rates. To conduct the analysis, a Netzsch thermogravimetric analyzer, TG 409 LUXX, was utilized in combination with a QMS 403D Aëolos quadrovule mass spectrometer. Systematic analytical processes were implemented under well-defined conditions, with a temperature range spanning from 30 to 800 °C. Different rates of temperature increase, specifically 2, 4, 8, and 16 K/min, were methodically implemented while ensuring an inert environment by regulating the flow of argon at a rate of 35 cm^3/min. Argon gas helps to identify the degradation potential of waste materials by preventing oxidation reactions during TGA and by allowing the isolation of the intrinsic thermal degradation behaviors. The application of this comprehensive methodology enabled an inclusive examination of the thermal degradation properties, so augmenting a mature understanding of the materials' effectiveness throughout a spectrum of temperature fluctuations.

2.2. Details of the experimental section

2.2.1. Reactor design for oxidative liquefaction of WTBs and PPEs

The experimental configuration employed the Parr reactor series

Fig. 1. WTBs and PPEs samples used for *oxidative* liquefaction.

4650, which is a 500 ml batch reactor manufactured by Parr Instruments (Parr Instr., ILL, USA). The reactor was equipped with a high-temperature spiral for heating purposes and accompanied by a Parr 4838 reactor controller, which has operating limit of 800 °C. The controller is precise up to 1 °C for a readout and setpoints, ensuring precise temperature control. Additionally, the system accuracy of the controller was within ± 2 °C. The gauge located at top of reactor exhibited a substantial range of 350 Bar of pressure. The system consisted of two straight valves, one designed for connecting to a pressure source to fill the system with suitable gas, and the 2nd valve is employed for gas removal or collection that were beneficial after undergoing a specific operation. The reactor head was equipped with an aperture for thermowell, that contained a J or K- type thermocouple used for monitoring the reaction temperature through whole course of the operation. The temperature regulation during the trials was performed using a Parr controller equipped with PID groups, with each group being allocated a distinct temperature value. Furthermore, before conducting the experiments, the reactor and its controller were subjected to thorough calibration processes to maintain the desired temperature for preset residence time. Nitrogen gas served a dual function, serving as both an inert environment and pressurizing the reactor to the necessary levels. The implemented comprehensive configuration enabled the execution of controlled and exact oxidative liquefaction procedures within the reactor system. The complete setup of apparatus, together with the overall sample processing approach can be seen in Fig. 3 in subsection *2.2.3*.

2.2.2. Details of experimental design framework

The present study systematically conducted an experimental investigation on the oxidative liquefaction of WTBs and PPEs, by employing two distinct design methodologies, namely the Central Composite Face-Centered Plan (CCF) for WTBs (Fig. 2(a)) and a combination of Central Composition Design (CCD) and Fractional Factorial Design (FFD) for PPEs (Fig. 2(b)). The selection of CCF for WTBs and CCD-FFD for PPE studies considered feedstock heterogeneity and optimizing resource allocation for effective liquefaction. These design approaches thoroughly investigated the impact of five distinct independent variables, including reaction temperature, starting pressure, reaction time, percentage of waste-to-liquid ratio, and concentrations of oxidants for WTBs, and in the case of PPEs, the pressure and residence time were kept constant while remaining parameters were the point of interests.

In the context of WTBs, the CCF design was employed, which encompassed a total of 29 experimental runs. This design was carefully devised to include factorial points, axial points, and center points. The factorial points yielded valuable insights into the primary effects and interactions of the variables, whereas the axial points gave additional information regarding the curvature of the response surface. The utilization of center points was crucial in the estimation of error variance and the assessment of lack of fit. The experimental matrix was designed in accordance with the principles of 2 k + 2(k-1) + n_{center}, where k represents the number of variables and n_{center} designates the three central runs. Each variable was subjected to testing at three levels (−1, 0, 1), resulting in a robust experimental matrix. A dual approach was developed for PPEs as the experimental matrix was constructed by employing a Central Composition Design for three variables, each having three levels, and a Fractional Factorial Design for three variables with two levels (minimum and maximum). The fractional factorial design entailed the deliberate selection of a subset of factors from a larger set, resulting in a reduction in the total number of experimental runs to the 17 needed for the investigation. This technique was deemed relevant due to the delicate physical characteristics of PPEs, ensuring that the chosen experimental conditions were not overly stringent for these specific sample types. These design approaches not only offer a thorough understanding of the primary impacts and interactions of the variables being examined, but they also exhibit a practical regard for the distinct attributes of the materials being studied.

2.2.3. Sample preparatory approach for oxidative liquefaction of WTBs and PPEs

Glass liners were meticulously filled with a predetermined quantity of milled WTBs or PPEs and subsequently charged with liquid media comprising a specified ratio of H_2O and H_2O_2, presented in Table 1. Before starting the set of experiments at a fixed temperature, the temperature controller was thoroughly calibrated using the Parr calibration technique to ensure that the targeted temperature levels would be accurately attained.

The prepared sample was subjected to the reactor, sealed and pressurized with inert gas i.e. nitrogen to go through a rigorous monitoring process for 30 min to make sure its airtightness. A heating spiral was used to heat the reactor until the target temperature was attained and rection time is carefully observed to follow the experimental matrix. After the designated reaction time had elapsed, the heating spiral was deactivated, so enabling the reactor's temperature to gradually decrease in accordance with the prevailing ambient circumstances. The reactor was then opened, and the products were filtered to separate the solid and liquid content. Liquid products were stored in air sealed bottles for further analysis while solid products were dried in oven to evaporate any moisture content. The utilization of this systematic and regulated approach in oxidative liquefaction process ensured the attainment of accurate and replicable results when applied to both WTBs and PPEs. The sample processing approach for oxidative liquefaction of WTBs and PPEs has shown in Fig. 3.

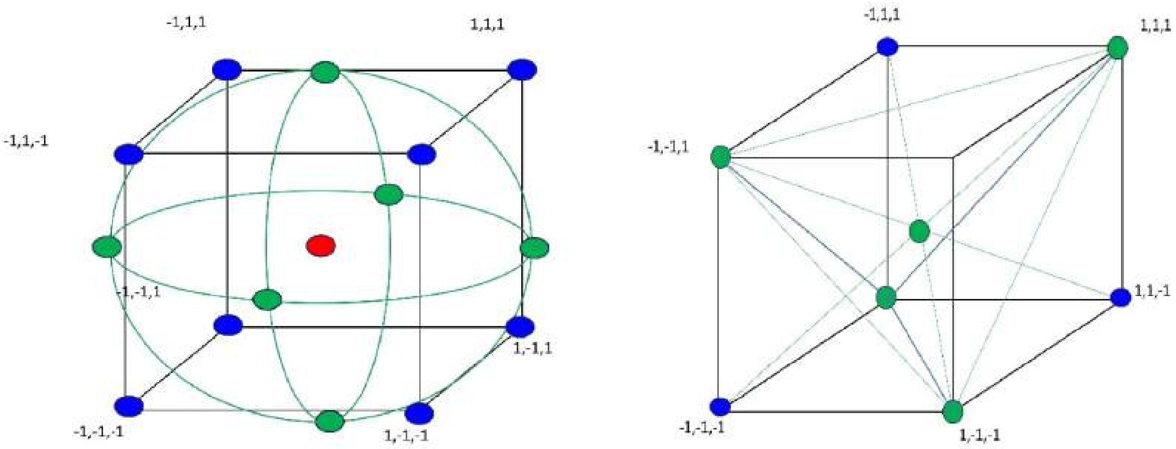

Fig. 2. Design approaches used during oxidative Liquefaction of (a) WTBs & (b) PPEs.

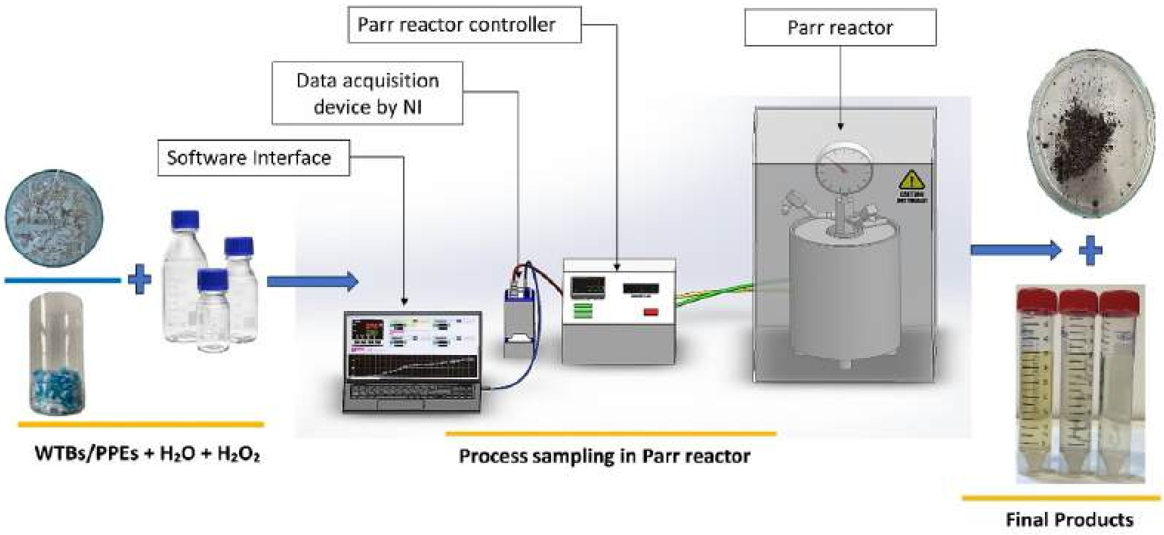

Fig. 3. Sample processing approach for oxidative liquefaction of WTBs and PPEs.

Table 1
Details of tested perameter levels for wind turbine blades and personal protective equipments.

	Wind Turbine blades Lowest (−1), Average (0), Highest (1)	Personal Protective Equipments Lowest (−1), Average (0), Highest (1)
Temperature (°C)	250, 300, 350	200, 250, 300
Pressure (Bar)	20, 30, 40	30
Wast-to-liquid ratio (%)	5, 15, 25	3, 5, 7
Reaction time (minutes)	30, 60, 90	45
Oxidant concentration (%)	15, 30, 45	30, 45, 60

2.3. Oxidative liquefaction products quantification and analysis

2.3.1. Total polymer degradation (TPD)

After the completion of the oxidative liquefaction process, the resulting mixture from the batch reactor was subjected to separation of its liquid and solid phases through filtration using filter paper with a grammage of 85–87 gsm. The solid content underwent a drying procedure in a laboratory dryer for a period of 8 h at a temperature of 105 °C. This was accomplished using a forced air-drying oven (WGL-30 B 105, Adverti, Poland). After the process of drying, the mass of the solid product was precisely measured. Simultaneously, the liquid product was carefully enclosed in a glass flask, stabilized, and later stored in a freezer for further comprehensive analysis.

The quantitative evaluation of polymer degradation, referred to as TPD, was conducted using Equation (1).

$$TPD = \frac{m_i - m_f}{m_i \cdot} \cdot 100\% \tag{1}$$

equation (1) represents the calculation of the percentage change in a variable, denoted as TPD. The variable m_f denotes the solid product mass subsequent to the drying procedure, whereas m_i indicates the original mass of the waste material being studied, the reduction is weight is subjected to the polymer degradation. The aforementioned methodology was continuously employed to compute the TPD for both WTBs and PPEs.

2.3.2. Liquid product analysis of WTBs and PPEs for quantification of OCCs

The resulting OCCs, including volatile fatty acids (VFAs) from C2 to C16 and aromatic carboxylic acids (ACAs), aromatic hydrocarbons (AHs), fatty acid methylene esters (FAMEs) from C2 to C16, and aromatic carboxylic acid esters (ACAEs), were determined using a GC instrument, the Clarus 500 GC manufactured by PerkinElmer in the USA. The capillary column used was DB-FAT WAX UI from Agilent Technologies in the USA, with dimensions of 30 m × 0.25 mm x 0.25 μm. The furnace temperature program was set at 40 °C for 4 min, then increased to 240 °C at a rate of 5 °C/min. We performed quantitative analysis by utilizing calibration curves prepared for selected chemical compounds.

2.3.3. Process optimization for maximizing the TPD and OCCs yield against the minimum energy consumption through analysis of variance (ANOVA)

This study employs Analysis of Variance (ANOVA) method to investigate the impact of five separate independent factors: reaction temperature, initial pressure, reaction duration, waste-to-liquid ratio, and oxidant concentrations for WTBs, and temperature, oxidant concentration, and waste-to-liquid ratio for PPEs, on process outcomes. An analytical framework involves the application of Pareto charts, predicted values profiling, and desirability and response surface contours. Graphical representations provide a comprehensive analysis of the influence of parameters on the process output. In addition, the study utilizes P-values and applies a two-way ANOVA to investigate the intricate connections between several independent and the dependent variables. The null hypothesis proposes that there is an equal effect of the independent variable across all levels, whereas the alternative hypothesis argues that there are varying effects, with at least one level of the variable having a bigger impact than others.

In the quest for optimization, the process entails the identification of either local or global maxima for the parameter being evaluated. In the present context, the desired characteristics, namely the highest levels of OCCs and TPDs for both WTBs and PPEs exhibit an inverse relationship with the minimum energy consumption. In order to address this trade-off, the utilization of the desirability function is applied, providing a method to effectively balance various characteristics. The desire function utilized in this study is linear in nature, signifying the aggregation of individual desirability functions with consideration of user-defined priorities. The utilization of methodological trials in the context of the oxidative liquefaction of WTBs and PPEs ensures a complete and scientifically sound approach to process optimization.

3. Results and discussions

3.1. Elemental makeup of WTBs and PPEs

Detailed composition of both pivotal materials, WTBs and PPEs has been provided in Fig. 4. The elemental composition of PPEs and WTBs exhibits notable differences, as evidenced by the comparative study of their ultimate and proximate analytical findings. The composition of PPEs has a low moisture content of 0.1%, an ash content of 8.7%, a high volatile matter content of 97.0%, a carbon content of 80.1%, a hydrogen content of 12.8%, a nitrogen content of 0.2%, a chlorine level of 0.04%, and a sulfur content of 0.03%. The present composition implies a mostly organic and flammable characteristic, which signifies the possibility for harnessing energy and generating value added chemical compounds. On the other hand, WTBs samples demonstrate a comparatively higher moisture content of 1.3%, a considerably increased ash content of 57.9%, volatile matter content of 40.7%, carbon content of 28.2%, hydrogen content of 2.7%, nitrogen content of 1.2%, oxygen content of 8.0%, and sulfur content of 0.1%. The elevated levels of ash and oxygen content seen in WTBs indicate a greater degree of inorganic composition and oxidation as compared to PPEs.

The disparities in elemental composition between PPEs and WTBs might have a substantial impact on their capacity for generating OCCs and overall polymer breakdown when subjected to oxidative processes.

3.2. Time -temperature-dependent degradation of WTBs and PPEs

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) provide significant insights into the thermal degradation behavior of WTBs and PPEs. Upon analysis of the TGA and DTG data in Fig. 5 and Table 2, it is observed that the presence of separate peaks for WTBs signifies different stages of thermal degradation. When subjected to a heating rate of 4 K/min, the initial peak seen at a temperature of 181 °C indicates the occurrence of a primary stage of mass reduction, that occurs within the temperature range of 150 °C–250 °C and has a minor alteration in mass which might potentially be attributed to the evaporation of moisture or the release of volatile substances originating from organic constituents. The succeeding peaks seen at temperatures of 226 °C and 324 °C correspond to distinct phases of deterioration. The occurrence of the second peak might potentially be associated with the degradation of polymeric components such as polyethylene or silicone acrylic resins, in addition the thermal degradation of PVC is also reported to start from this temperature range (Yu et al., 2016). The peak observed at a temperature of 324 °C is highly notable as it signifies a substantial reduction in mass spanning from 275 °C to 420 °C, this phenomenon may be attributed to the deterioration of the reinforcing materials or the breakdown of intricate polymers such as epoxy resins that are found inside the blades. The concluding stage, which extends from 450 °C to 800 °C, exhibits a gradual decline in mass, indicating the existence of thermally stable constituents or inorganic residues mostly glass fibers that undergo slight or least decomposition at elevated temperatures, as Ge et al. reported the maximum loss of glass fibers in the range of 2.0–4.3% when tested in different environments. The higher mass loss rates during the second step are because of the higher mass loss rates of epoxy that are 1.0 and 4.8 %/min for heating rate of 4 and 16 K/min, similar kind of decomposition rate in range of 2.4–4.1 %/min are also reported for epoxy in the literature (Ge et al., 2023a). Decomposition of WTBs at higher heating rates of 16 K/min showed the same pattern as discussed above but the peaks appeared at higher temperature and decomposition rates were also high.

PPEs used in the medical industry, such as aprons, gloves, face masks, and plastic bed sheets, exhibits unique thermal degradation behavior due to their complex compositions. These materials often consist of a mixture of several thermoplastic components and synthetic polymers including polyethylene, polypropylene, and polyvinyl chloride (PVC). DTG analysis revealed a single peak at 429.3 °C, corresponding to a significant mass change rate of 10.3 %/min at a regulated heating rate of 4 K/min. The DTG curve showed an elevated peak at 453.3 °C when the heating rate was increased to 16 K/min, indicating an accelerated mass change rate of −42.8 %/min. This abrupt mass loss indicates a fast degradation process, implying the disintegration of important polymer constituents present in these materials. This rapid mass loss is mostly attributable to existing polymers PP, PE and PVC, which breaks down quickly at high temperatures (Das and Tiwari, 2017). At both heating rates TGA analyses highlighted significant mass changes within two temperature ranges: 350 °C to 480°Cat 4 K/min and 380 °C–480 °C at 16 K/min. These temperature ranges correspond closely to the distinctive characteristics of breakdown of a number of polymers frequently used in PPEs (Yu et al. n.d.).

The observed breakdown tendencies in TGA and DTG analysis of WTBs and PPEs can be attributed to their respective material compositions. WTBs due to their complex composition consisting of a combination of polymers, fillers, and additives, display different peaks in DTG curves. These peaks signify the presence of different constituents within WTBs that undergo decomposition at distinct temperatures. On the other hand, PPEs which is made up of PVC, PP, PE, PET, and PS, has a distinct peak in its DTG analysis. This can be attributed to the narrower or more

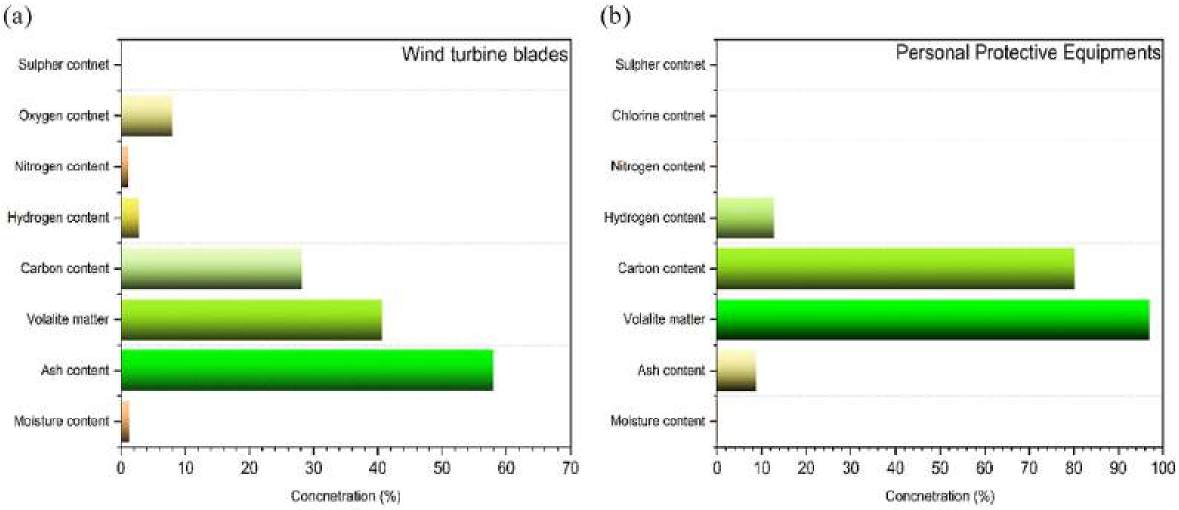

Fig. 4. Elemental composition of (a) WTBs & (b) PPEs.

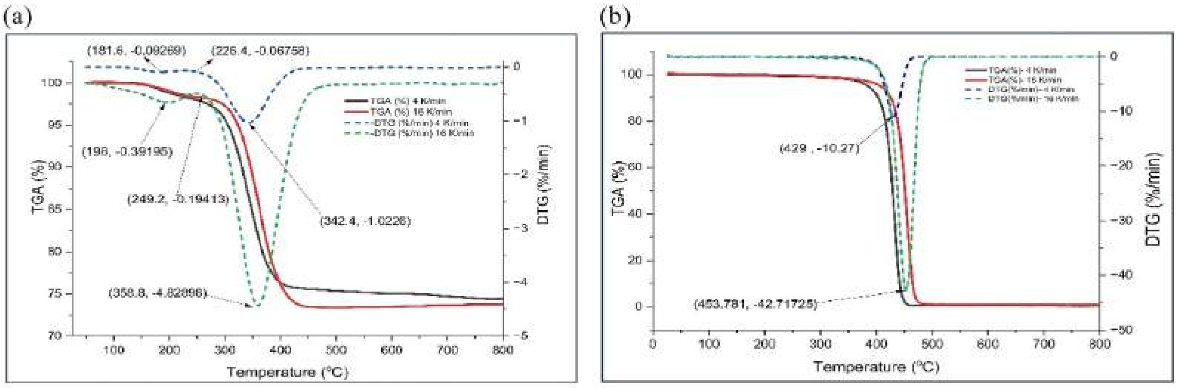

Fig. 5. Thermal decomposition patterns of (a) WTBs and (b) PPEs at heating rates of 4 and 16 K/min.

Table 2
Detail parameters of TG-DTG analysis of WTBs and PPEs.

	β, (K/min)	R_m (%)	*Stage 1*			*Stage 2*			*Stage 3*		
			r_m (%/min)	Δm_L (%)	T_{peak} (°C)	r_m (%/min)	Δm_L (%)	T_{peak} (°C)	r_m (%/min)	Δm_L (%)	ΔT (°C)
WTBs	4	74.4	−0.1	−1.7	181.5	−1.0	−22.5	342.4	N/A	−1.4	420–800
	16	71.6	−0.	−1.8	198.2	−4.8	−26.7	359.9	N/A	0.4	460–800
PPEs	4	0.	−10.3	N/A	429.3	N/A					
	16	0.8	−42.8	N/A	453.3						

R_m = Residual mass, %.
r_m = Mass loss rate, %/min.
Δm_L = Total Mass loss, %.
T_{peak} = Peak Temperature, °C.
ΔT = Gradual change in Temperature, °C.

closely matched temperature ranges at which these individual polymers undergo breakdown. The observed disparity can be attributed to the distinct thermal degradation properties and overlapping breakdown areas of the component materials present in WTBs, as opposed to the more closely matched degradation profiles found in PPE.

3.3. Comparison of total polymer degradation for WTBs and PPEs

The collective findings from the 29 trials done on WTBs revealed a range of polymer breakdown spanning from 21.1% to 49.0% (Fig. 6(a)). Experiment 15 had the most significant TPD, with a recorded value of 49.0%. The experimental conditions encompassed a notable temperature of 350 °C, highest pressure level, enhanced oxygen levels of 45 wt%, residence duration of 30 min, and waste-to-liquid to the minimum. The observed environment emphasized the significant propensity of the material to undergo severe degradation under well-regulated circumstances. Throughout the conducted trials, WTBs had an average deterioration rate of around 37.0–38.0%. The trials exhibited substantial variations in parameters, demonstrating modest degrees of deterioration across a wide range of combinations including all the tested parameters.

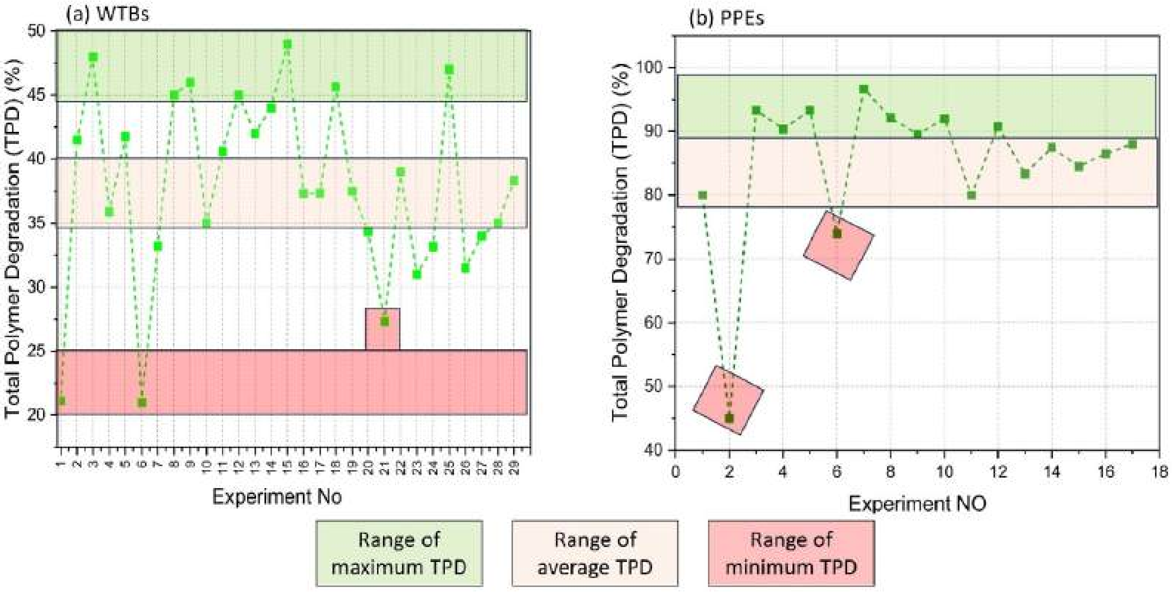

Fig. 6. Minimum, average, and maximum ranges of TPD for (a) WTBs & (b) PPEs.

Experiment 1 recorded the minimum observable TPD, which amounted to around 21.1%. The experimental conditions encompassed a moderate temperature of 250 °C, a lower pressure of 20 bar, a mid-level oxygen concentration of 15 wt% H_2O_2, a short residence period of 30 min, and waste-to-liquid mass ratio of 25%. These factors imply constraints on the ability to achieve optimal TPD under less sever experimental conditions.

In the context of PPEs it was observed that the extent of polymer degradation exhibited considerable variation throughout a total of 17 experimental trials, ranging from 45.0% to 96.7%. The experimental conditions encompassed a range of temperature settings (200–300 °C), oxygen levels (30–60), and waste-to-liquid ratios (3–7). The results of Experiment 7 demonstrated the most significant level of TPD, with a recorded value of 96.7%. The experimental conditions encompassed a higher temperature of 300 °C, a raised oxygen concentration of 60 wt% H_2O_2, and a reduced waste-to-liquid ratio of 3%. The aforementioned settings exhibited the remarkable efficacy of the material in attaining significant degradation.

PPEs consistently exhibited higher average levels of deterioration, with an average range of around 85.0–90.0%. The trials demonstrated the efficacy of several combinations, with a particular focus on lower temperatures, varying oxygen levels, and increasing waste-to-liquid ratios, consistently resulting in significant degradation of the polymer.

The minimum level of TPD reported for PPEs was roughly 45.0%. The aforementioned conditions were observed in Experiment 2, which entailed a lower temperature of 200 °C, a mid-level oxygen concentration of 30 wt% H_2O_2, and a greater waste-t-liquid ratio of 7. Even in circumstances that were not as favorable, the material demonstrated a pretty effective process of deterioration.

The observed standard deviation ranges for WTBs from 1.5% to 4.3% and for PPEs from 0.5% to 3.5% suggest variations in the consistency of TPD results between the two. WTBs demonstrate a greater range of variability, which may be attributed to their intricate composition. Conversely, PPEs displays more consistent patterns of deterioration, mostly due to their less complex and standardized composition. The observed discrepancies indicate that WTBs are responsive to changes in parameters, whereas PPEs demonstrate resistance to fluctuations. This suggests that WTBs and PPEs possess unique material reactivities and different structural complexity.

3.4. Quantification of OCCs

The range of maximum, average, and minimum values for OCCs from the oxidative liquefaction of WTBs and PPEs has been presented in Fig. 7. Experiments that resulted in the largest observed OCC values for WTBs exhibited some similar characteristics. Notably, these experiments frequently included higher temperatures, namely around 350 °C, suggesting a link between raised thermal energy and enhanced OCC generation. Moreover, these occurrences commonly exhibited an increased level of oxidant concentration, typically around 45%, indicating a more robust oxidation mechanism that leads to a more widespread degradation of the WTB materials. In numerous instances, it was observed that the length of the reaction was significantly extended, spanning a range of 60–90 min. Nevertheless, it should be noted that there was no consistent correlation seen between the waste-to-liquid ratio and the highest levels of OOCs. This implies that the impact of the waste-to-liquid ratio on OCC may be less straightforward or more intricate in nature. Instances that resulted in the greatest OCCs values for PPEs were often found to be associated with certain experimental settings. The aforementioned situations were commonly seen at a temperature of 200 °C, accompanied by a moderate concentration of oxidant, notably at 30%. The prevailing circumstances were favorable for the significant production of OCC. It is noteworthy that different waste-to-liquid ratios were seen in these high-yield situations, indicating a less direct influence on the generation of or OCCs. The tests conducted in this study (experiments 1, 9, and 11) for PPEs demonstrated the prominence of lower waste-to-liquid ratios in generating better OCC yield. Additionally, the results highlighted the impact of temperature and oxidant concentration on OCC peak values.

The trials conducted to determine the minimal OCCs values for WTBs were often seen at lower temperatures, namely around 250 °C, suggesting that reduced thermal energy levels may impede the formation of optimum OCCs. The aforementioned situations exhibited a high frequency of correlation with reduced levels of oxidants, often falling within the range of 15–30%. This indicates a less efficient oxidation process and a restricted capacity for the decomposition of WTB materials. Certain occurrences also showed reduced response times, often averaging around 30 min. The shorter periods may not offer the time for the comprehensive breakdown required to achieve greater overall process yields. Interestingly, there was no consistent correlation seen between the waste-to-liquid ratio and decreased OCCs indicating that the

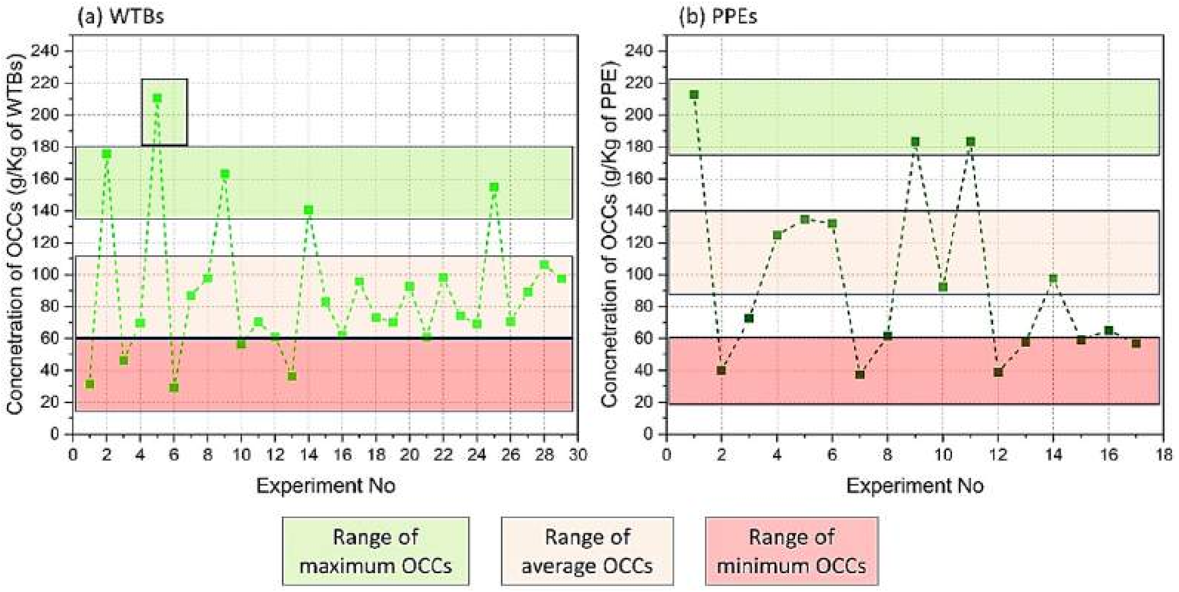

Fig. 7. Minimum, average, and maximum ranges of OCCs for (a) WTBs & (b) PPEs.

influence of this ratio on OCC may not be as significant as that of other parameters. On the other hand, experiments conducted on PPEs exhibited the lowest OCCs values when subjected to a 60% oxidant concentration and a temperature of 200 °C (as shown in experiment 3). The aforementioned factors posed a considerable limitation to the manufacture of OCC.

When conducting studies to determine the average yields of WTBs, a more diverse and multifaceted outcome was seen. The temperature range observed in this study varied between 250 °C and 350 °C, suggesting a combination of influences on the formation of OCCs with a moderate overall effect. The concentrations of oxidants exhibited variability within the mid-range values of 30–45%, indicating a modest level of efficacy in the degradation of the WTB materials. The observed reaction durations exhibited a range of 45–60 min, indicating a symmetrical impact on the production of OCC. The conducted experiments yielded average OCC values for PPEs in a variety of situations. The prevailing condition was seen at a temperature of 250 °C, accompanied by an oxidant content of 45%. The conducted studies provided evidence of a moderate level of OCC formation, indicating that the specified parameters may present a favorable equilibrium between oxidant concentration and temperature, resulting in an intermediate degree of OCC creation.

During each experiment with WTBs and PPEs, the energy consumption was also calculated that lies in the range of 1.3–4 kWh for WTBs and 0.7 to 1.2 kWh for PPEs. This different energy consumption during the experimentation and the complex relation between the sets of tested parameters suggest there is a crucial need of design optimization to provide the optimal values for oxidative liquefaction of WTBs and PPEs.

3.5. *Process optimization for maximizing the OCCs yield with minimum energy consumption*

The planning experiments and analysis of variance method were used to determine the significant variables affecting the oxidative liquefaction process, assess interactions between the variables, and their statistical significance on TPD and the production of OCCs from WTBs and PPEs. The significance analysis employed a p-value of 0.05. The optimization of the process was of paramount importance in ensuring its economic feasibility, as the reduction in energy usage would enhance the prospects of widespread commercial acceptance.

During the process of thorough optimization, the study examined five reaction parameters for WTBs. However, for PPEs, the number of factors was decreased to three by maintaining constant pressure and reaction time. The optimal values for these reaction parameters are indicated by the red lines in Fig. 8.

In terms of temperature, there are notable distinctions in the performance characteristics exhibited by WTBs and PPEs. The TPD in WTBs exhibits an initial drop, followed by a subsequent increase, as temperatures rise. On the other hand, when it comes to PPEs, the degradation of polymers shows an almost linear rise in correlation with temperature. Nevertheless, there is a negative correlation between rising temperatures and the levels of OCCs in both cases, which is not the intended result. Based on the aforementioned findings, it can be deduced that the minimal temperatures are considered to be appropriate in order to achieve maximal TPD and the production of OCCs, while simultaneously limiting energy consumption.

In experimental studies pertaining to PPEs, the pressure is maintained at a constant level as alterations in pressure levels do not have a substantial impact on the overall degradation of polymers in WTBs. An optimal pressure threshold, as shown by the red line, is present to attain the highest possible yields of OCCs.

The observed pressure variation does not result in any energy change, as it does not involve the utilization of mechanical or electrical sources.

The extent of polymer breakdown and the generation of OCCs are greatly influenced by the concentration of oxidants present in the reactants. Increased levels of oxidants have been found to significantly accelerate the overall breakdown of polymers in both materials. Nevertheless, it has been shown that the concentrations of OCCs in PPEs and WTBs decrease in a linear manner as the oxidant concentration increases. Therefore, it is preferable to have lower levels of oxidants for PPEs, although WTBs are regarded to have optimal values slightly greater than the lowest limits that were evaluated.

The energy usage throughout the experimental process is significantly influenced by the duration of the reaction. Fig. 8 (a) for WTBs illustrates an initial upward trend in the breakdown of the polymer as well as the presence of OCCs as reaction time increases. However, this trend is subsequently followed by a notable decline at longer reaction periods. Prolonged reaction periods have detrimental effects on both the complete breakdown of polymers and the production of OCCs, resulting in increased energy consumption.

The waste-to-liquid ratio has an equivalent influence on the overall breakdown of polymers and the production of OCCs for both materials. The drop in both metrics is considerable when waste concentrations are higher and liquid volumes are lower. Therefore, it is advantageous to maintain the lowest waste-to-liquid ratio in order to get the required outcomes from the oxidative liquefaction of WTBs and PPEs. The optimized values of all tested parameters for WTBs and PPEs are summarized in Table 3.

In order to maximize the overall process, yield through assessing the combined desirability, the response surface profiles are shown in Fig. 9. Values that are encoded represent the extremes of the parameters that are examined and are ranked from 1 to 10 to indicate their desirability throughout the process. These profiles, insight into achievement of local or global maximum which in our situation, is single global maximum for both WTBs and PPEs. The color coding in Fig. 9 indicates a higher level of desirability represented by the color red, and a lower level of desirability, represented by the color green, with respect to the parameters being examined.

Fig. 9(a), part 1, exhibits a clear and discernible pattern pertaining to the evaluation of the collective desirability of waste-to-liquid ratio and oxidant concentrations in the process of oxidative liquefaction of WTBs. Significantly higher desirability is demonstrated by lower values of the waste-to-liquid ratio and oxidant concentrations. The incremental gain in desirability, however, decreases as these parameters rise, indicating an ideal balance that promotes process efficiency.

A similar tendency may be seen when looking at the combined desirability of temperature and waste-to-liquid ratio for WTBs in Fig. 9 (a) part 2. The temperature and waste-to-liquid ratio at their lowest levels show increased desirability, suggesting an ideal range critical to improving process efficiency. The degree of desirability decreases as one or both values surpass specific thresholds, highlighting the need to keep these parameters within an ideal range for a productive oxidative liquefaction process. In a similar, way the combined desirability of tested parameters can be accessed for the oxidative liquefaction of PPEs by referring to Fig. 9(b).

4. Discussion

The compositional analysis revealed that there is a large proportion of organic matter, mostly the polymers in WTBs and PPEs, that can be degraded to produce the valuable secondary compounds. The presence of high levels of carbon and hydrogen in PPEs and WTBs are pertinent to the synthesis of OCCs using the oxidative liquefaction process. Distinct degradation tendencies were observed in the thermal degradation of WTBs and PPEs. The WTBs demonstrated intricate thermal profiles characterized by the presence of several peaks, suggesting the occurrence of distinct disintegration processes at different temperature intervals. On the other hand, PPEs had a distinct peak, indicating a more consistent pattern of deterioration.

The observed disparities are presumably attributable to the diverse

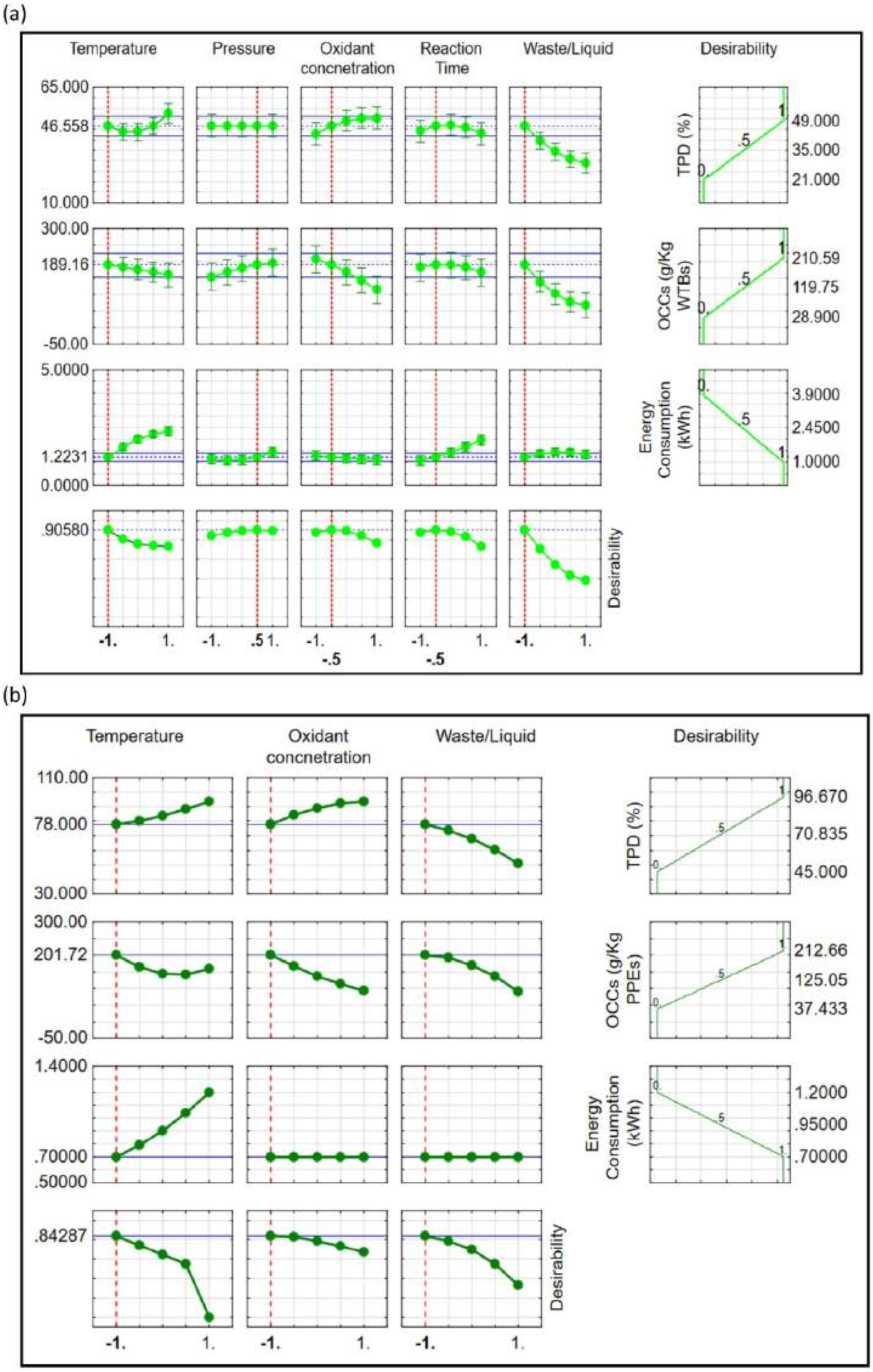

Fig. 8. Process optimization for (a) WTBs and (B) PPEs through profiles of predicted values.

Table 3
Optimal reaction conditions for maximum TPD and OCC production from the oxidative liquefaction of WTBs and PPEs.

	Temperature, (°C)	Initial pressure, (bar)	H_2O_2 Concentration (wt.%)	Residence time (min)	Waste-to-Liquid ratio (wt.%)
WTBs	250	35	22.5	45	5
PPEs	200	30	30	45	3

compositions of the materials. WTBs which are engineered to possess enhanced durability and are constructed using several layers incorporating various additives, exhibited a distinct multi-peak behavior (Ge et al., 2023b). In contrast, PPEs designed for specific uses with a focus on both comfort and human protection, demonstrated the use of materials with a homogenous response against thermal stresses, as evidenced by a singular peak observed in thermal analysis (Qin et al., 2018). The importance of material composition and structural complexity in shaping degradation behaviors is underscored by the thermal degradation characteristics. A comprehensive comprehension of these characteristics was of utmost importance in order to develop an efficient waste treatment procedure that is specifically adapted to various categories of polymer-based products.

The analysis of TPD and the generation of OCCs were conducted in a thorough manner, which allowed for the identification of noticeable effects caused by the variables under investigation. These variables include temperature, oxidant concentration, waste-to-liquid ratio, pressure, and reaction time, all of which were shown to have some influence on the outcomes of the process. Within this set of parameters, it was seen that pressure and response time had a relatively limited impact on the overall performance of the system for WTBs, so for PPEs these parameters were held constant. The correlation between elevated temperatures and the heightened TPD of WTBs and PPEs may be ascribed to the distinctive attributes of the near-critical environment present within the reactor. The characteristics of this particular environment, including increased diffusivity, decreased dielectric constant, lower density, and enlarged water properties, contribute to the improved degradation of the resinous materials (Akiya and Savage, 2002). A crucial factor to be taken into account is to the Hildebrand parameter of water under standard atmospheric conditions, which is measured at 48 $MPa^{0.5}$. On the other hand, epoxy resins used in WTBs have a calculated Hildebrand value of 20 $MPa^{0.5}$ and PE, PS, PET polymers frequently used in PPEs have Hildebrand parameter value in range of 16–22 $MPa^{0.5}$ suggesting a restricted ability to dissolve in water under normal circumstances (Fink, 2013; Li et al., 2021; Mirmohammad Sadeghi et al., 2020). Nevertheless, when temperatures increase, the Hildebrand parameter of water drops. The Hildebrand parameter of water exhibits a tendency to drop as the temperature increases to elevated levels. This decline can be attributed to the decreased strength of hydrogen bonding in near-critical water, leading to increased levels of degradation yields. The decrease in OCC yield observed in PPEs as temperature increases can be ascribed to the enhanced oxidation of intermediate that are generated during the liquefaction process. The increase in temperature might potentially enhance the rate of oxidation processes, resulting in a decrease in the total production of desirable OCCs. Conversely, in the context of WTBs, this decline may be attributed to the distinctive characteristics of the materials utilized. The intricate structure of WTBs, which consists of a combination of different polymers and composite materials, may experience reworked breakdown mechanisms when exposed to elevated temperatures. The aforementioned processes have the potential to provide various intermediates or facilitate their accelerated oxidation, hence playing a role in the observed decrease in OCC yield with increasing temperature. In the realm of oxidative liquefaction, the efficacy and output of the process for WTBs is weakly impacted by influence of prolonged reaction time and high pressure yet the pressure has no direct connection with energy rise but its function in enabling a single-phase reaction system is advantageous. The density of the solvent is increased in this single-phase condition because to the higher pressure, which facilitates better penetration into the waste components (Kleinert et al., 2009). As a result, this process facilitates the effective breakdown and retrieval of needed substances, which is particularly significant when dealing with complex materials such as WTBs but as the nature of constituents for PPEs is much delicate so elevated pressure

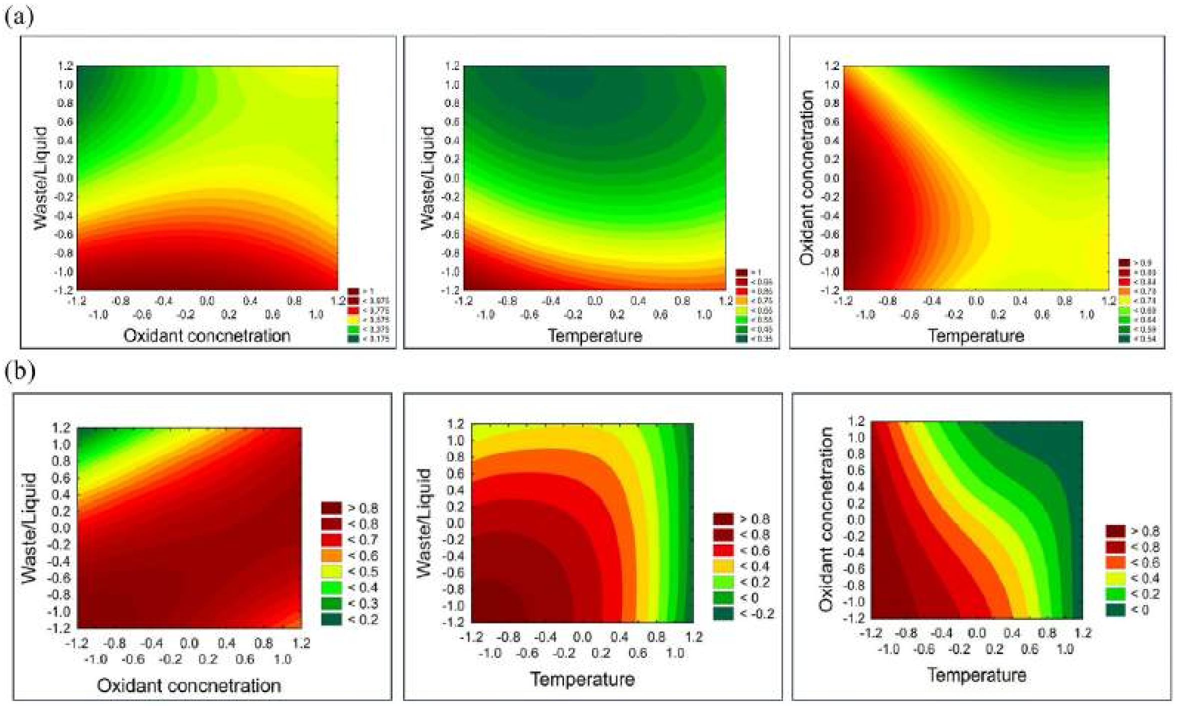

Fig. 9. Response surface profiles showing the combined desirability of tested parameters for (a) WTBs and (b) PPEs.

are not required.

The efficiency of WTBs and PPEs processing is strongly influenced by the complex interaction between the ratio of waste-to-liquid and the concentration of oxidant. There is a positive correlation between lower waste-to-liquid ratios and greater yields of TPD and OCCs. The observed impact is characterized by many facets. Subjecting to higher waste-to-liquid ratio i.e. higher amount of water in reactants, the increased water content within this framework provides a dual function, functioning as both a solvent and a catalytic agent. The presence of a higher concentration of water adds to an increased abundance of H^+ and OH^- ions, which serve as crucial species for the beginning and development of several chemical processes involved in oxidative liquefaction (Mumtaz et al., 2023d; Wu et al., 2022). Oxidant concentration in reactants is very crucial in determining the effectiveness and getting the required process outcomes such as high yields of OCCs from liquefaction of WTBs and PPEs. An increase in oxidant content has the potential to raise TPD levels as higher oxygen content support less char formation; however, too high concentrations result in unfavorable consequences. The excessive presence of oxygen leads to over-oxidation, which poses a threat to the production of liquid OCCs since it causes the degradation of intermediate products into smaller, less stable molecules (Kolaczkowski et al., 1999). The present circumstances give rise to the production of undesirable by-products, such as carbon dioxide and water, so undermining the intended goal of acquiring beneficial OCCs. In addition, the presence of an excessive amount of oxidants leads to unpredictable increases in temperature, hence increasing the likelihood of thermal deterioration of the liquid products that are produced as a result. Therefore, it is crucial to exercise careful control and optimization of oxidant concentrations in order to attain the intended outcome while avoiding any detrimental reactions or deterioration of the products. Based on this study it is evident that this preliminary investigation offers significant insights that warrant further investigation. Future studies should focus on examining the variations and commonalities in the degradation pathways through this particular process.

5. Conclusions and future perspectives

To decompose the polymeric content of WTBs and PPEs into useful OCCs, this research examined the feasibility of the oxidative liquefaction process. The findings highlight that complex polymeric waste materials such as WTBs and PPEs can be efficiently degraded by oxidative liquefaction; however, the two feedstocks have different breakdown routes and product yields. WTBs blades have different constituents with different responses against the temperature and high content of inorganic residues while PPEs are made up of polymers with comparably analogous responses against temperature and with very low concentrations of inorganic residues. TPD was in the range of (20–49% and 55–96%) for WTBs and PPEs respectfully while (36.31–210.59 g/kg, and 39.93–212.66 g/kg) yields of OCCs were also obtained. The results of the temperature manipulations demonstrated distinct patterns: WTBs exhibited non-linear relationships between temperature and the extent of polymer degradation, in contrast to PPEs which showed a more linear increase in degradation. The significance of oxidant concentration has been identified as a crucial factor. Increased concentrations of the oxidants resulted in enhanced breakdown of the overall polymer content. However, this had a negative impact on the production of oxygenated compounds for both materials. The study found that reaction time and waste-to-liquid ratio were significant aspects in the experiment. Prolonged reaction durations resulted in higher energy consumption without corresponding benefits. On the other hand, smaller waste-to-liquid ratios were crucial for achieving positive outcomes for both materials. So the optimal conditions of reaction parameters i.e., temperature, pressure, waste-to-liquid ratio, oxidant concentration, and reaction time for WTBs and PPEs are 250 and 200 °C, 35 and 30 bar, 5 and 3%, 22.5 and 30%, 45% each respectively were found. These findings provide a fundamental basis for developing environmentally friendly industrial methods, in line with efforts to reduce waste and recover resource use in the treatment of polymer waste, while detailed research is still needed to identify degradation pathways and reactor design.

CRediT authorship contribution statement

Hamza Mumtaz: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sebastian Werle:** Writing – review & editing, Project administration, Funding acquisition. **Szymon Sobek:** Writing – review & editing, Supervision, Conceptualization. **Marcin Sajdak:** Writing – review & editing, Software, Formal analysis. **Roksana Muzyka:** Writing – review & editing, Formal analysis.

Declaration of competing interest

I on the behalf of all authors, declare that there is no conflict of interest and all the elements of the submission are also in compliance with the journal publishing ethics. By submitting this manuscript, the authors agreed that the copyright for their article should be transferred to this journal if the article is accepted for publication. The work contained within the research paper is our original contribution and has not been published anywhere.

Data availability

Data will be made available on request.

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Appendix E

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REVIEW

A waste wet oxidation technique as a solution for chemical production and resource recovery in Poland

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Abstract

Effective municipal solid waste (MSW) management and waste-to-resource recovery has a key potential to play a vital role in economic growth of a country. MSW contains the different items of daily use that makes its composition mix in nature. Different waste-to-energy techniques are already available to treat this waste but these techniques always require some pre-treatments such pre-separation and pre-drying of mix MSW that makes these processes less techno-economic to apply on large scales. To provide an effective solution to this problem, potential wet oxidation technique has been reviewed in this study. In the first section, the statistics for MSW generation and composition for different cities in Poland have been presented to show the existence of maximum organic content which can be converted to useful organic compounds. In the later section, the wet oxidation technique and its various aspects have been reviewed in detail to justify the potential of this technique to treat mix MSW at larger scales to produce different valuable products in the context of waste-to-resource recovery.

Graphical abstract

Keywords Municipal solid waste · Waste composition analysis · Waste-to-resource recovery · Wet oxidation technique · Wet oxidation reaction kinetics

Introduction

Current MSW generation is more than 1.2 billion tons per year, that is increasing at exponential rates, and will reach more than 2 billion tons per year in 2025 (Ghosh et al. 2018). Thousands of individuals have relocated from the countryside to major cities worldwide in recent years, and currently,

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Extended author information available on the last page of the article fifty percent of the world's population resides in municipal cities (Marandi and Main 2021). Furthermore, according to a United Nations (UN) prediction, the total world's inhabitants will expand to 6.4 billion by 2040 (Helin and Weikard 2019). Numerous health and environmental issues are related to continuous population expansion. The increased rate of population growth is an important factor directly targeting the environmental problems in big cities as it affects people's life, industrial development, business and exchange, the number of automobiles, energy and water consumption, and waste generation.

Over the past decades, the literature has reported serious threats to communities related to the adverse health effects associated with increased environmental pollution because of weak waste management systems (Jansson and Voog 1989; Lloyd et al. 1988). Every year, around 1.92 billion tons of mixed MSW is generated worldwide, equating to about 220 kg per person (Sharma and Dubey 2020). According to Zhang et al. (2017), China's MSW production has reached 220 million metric tons, and this rate is steadily increasing at a rate of 10% each year. In the USA and India, MSW generation was recorded to be 258 million metric tons and 169 million metric tons, respectively, for 2020 (Arya and Kumar 2020). According to statistics, before the notion of recycling, the annual growth rate of MSW rose with the passage of time due to increasing population and urbanization (Knickmeyer 2020). In 2013, a survey was conducted in Sweden, which revealed that 4.5 million tons of MSW were generated in a single year (Hailu and Kumsa 2021). This MSW is made up of approximately 32% recycled material, 16% medical waste, and 52% energy-related materials (Lazzarino et al. 2021). Waste production is increasing both in Europe and globally with Poland also experiencing a notable rise in municipal waste generation per capita. In 2018, the amount of municipal waste generated per capita in Poland was among the lowest in the EU, totaling 329 kg per capita, as opposed to the EU average of 489 kg per capita (Bilska et al. 2020). Figure 1 illustrates the changes in municipal waste generation levels in Poland and the EU average between 2014 and 2019.

MSW attracts the attention of many academics and researchers due to its unique composition, which includes some form of energy. MSW contains a variety of hydrocarbons bound together by various bonds; when these bonds disintegrate into gases or liquids, they release tremendous amounts of energy (Naik et al. 2010). Liquid fuel obtained from the pyrolysis of MSW has a calorific value between 35 and 44 MJ/kg, having the potential to replace traditional fossil fuels like a diesel with a calorific value of 45.5 MJ/kg in internal combustion engines, power generation systems, and industries. As a result, MSW has a significant potential for producing biofuels (Velghe et al. 2011; Zaman et al. 2021). Biomass-based fuels have a significant potential to replace traditional fuels that's why it has attracted the attention of many scientists and researchers (Khoo et al. 2020). Biofuels have the ability to cut CO_2 emissions. Food waste, wood, leaves, crops, waste plastic, wastepaper, and municipal solid waste (MSW) have all been used to produce biofuels (Chum and Overend 2001). MSW is commonly associated with waste or litter, but it actually consists of everyday items that are used and then thrown away, such as packing materials, mowed grass, wood, broken furniture, ripped clothing, plastic bottles, food leftovers, newspapers, home appliances, paints, rubbers, and, last but not least, batteries. These are some of the most common materials found in every home, hospital, and school (Mumtaz et al. 2023). A fraction of MSW can serve as a source of biomass, and it mostly includes mixed commercial and residential waste materials such as paper and paperboard, yard trimmings, plastics, leather, rubber, textiles, and food wastes (Chen 2016). Plastic is a large component of MSW, as plastic is widely used around the world for its numerous attributes such as toughness, light weight, and cost-effectiveness. According to the World Bank, waste plastic is mainly responsible for the manufacture of MSW, which plays 10–12% part in total MSW generation (Nguyen et al. 2020). In 2012, the entire amount of plastic produced in the world was projected to be at 290 MT, with estimates that this number will rise to 25% by 2030 (Ghayebzadeh et al. 2020). Furthermore, it is expected that by 2025, waste plastic concentrations will increase to 10–13% (Camilleri 2021). Plastic will be consumed in various ways around the world. For example, in Europe, serious policies have been ensured to collect at least half of the plastic waste generated, with the remainder being disposed of in landfills (Silva et al. 2021). A substantial amount of MSW is generated in Finland, with PVC plastic being the

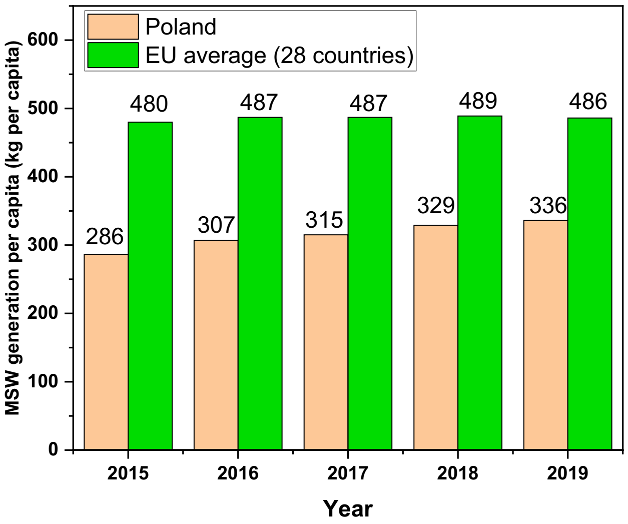

Fig. 1 Comparison of MSW generation in Poland with the EU

most important contributor in MSW production, which is used in household appliances. PVC contains 90% chlorine, which is known to be the most hazardous to human health and the environment. In the Middle East, a similar trend has been observed; the Kingdom of Saudi Arabia (KSA) has been acknowledged as the world's second largest producer of MSW, producing roughly 7 million metric tons of plastic each year (Alagha et al. 2018). China has used 82% flammable plastic and 18% non-combustible plastic in comparison with other Asian countries (Ghimire and Ariya 2020).

Adoption of proper waste management techniques is one of the key challenges for environmental policy making at the international level, including the European Union (EU), where the policy framework to save the environment and ensure public health against the effects of various health hazards associated with MSW has been constantly implemented in past (Mazzucco et al. 2020). But at the current moment, the MSW management strategies are integrated in nature and based on a hierarchical attitude: reduction, recycling, and reuse (Allwood 2014). According to studies, around 20% of MSW collected is recycled, 12% is used for energy recovery, and the remainder is disposed of in landfills (Gutierrez-Gomez et al. 2021). In this context, landfilling must be considered as the least preferable method as it demands wide space and comes with a high risk of soil and water contamination. The landfill dumping system has several challenges, including worker health, machinery maintenance, and transportation costs, and in fact, it provides no chance to use the energy content of MSW. Energy security in addition to continuous economic growth and subsequent environmental protection is the national energy policy goal of any country of the world. As the world population is growing at higher rates so the energy demand is increasing proportionally. Therefore, states in the EU are asked to promote proper waste management techniques based on the 3-R approach, i.e., reuse, recycle, and recover to reduce the total municipal solid waste by 10%, so any idea of converting MSW to valuable products is worth important in this context (Malinauskaite et al. 2017). The technologies adopted to convert the waste into energy by any country are largely determined by its energy demands and economic status (Afrane et al. 2021). According to the World Bank division, the world's economy can be divided into four major categories including rich income, upper–middle income, lower–middle income, and, last but not least, the poor income. Rich-income countries, the majority of which are part of the Organization for Economic Cooperation and Development (OECD) are not limited to a single waste-to-energy technology and instead utilize a combination of them. Furthermore, in high-income economies, MSW management systems are stable enough to collect a considerable amount of waste to recycle and ensure material reuse (Boer et al. 2010). But in contrast, low- and middle-income economies do not have effective MSW management systems and have fewer chances of material recycling, a high portion of openly dump waste, all of which have negative environmental consequences. In Poland, the use of proper waste-to-energy conversion technology with the potential of resource recovery could aid in the management of MSW and the maintenance of an approximately steady energy deficit rate. Currently, the most common MSW disposal system in Poland is landfilling. In 2020, there were over 150 active landfills in the country. Incineration is another MSW disposal system used in Poland. There are several incineration plants in the country, with the largest one located in Poznan (Jakubus and Stejskal 2020). According to Eurostat data, in 2019, Poland incinerated around 3.3 million tons of municipal waste, which was an increase of 13% compared to the previous year. Mechanical–biological treatment (MBT) plants are becoming increasingly popular in Poland to treat MSW before disposal. These plants use mechanical and biological processes to sort, separate, and treat waste, with the goal of reducing the amount of waste that goes to landfills. According to a report from the European Environment Agency, there were 31 MBT plants in Poland in 2018, with a total capacity of around 2.9 million tons per year. Composting is another waste management system used in Poland. Composting facilities process organic waste (e.g., food waste and garden waste) into compost, which can be used as a soil conditioner. Recycling is also an important waste management system in Poland. The country has a well-developed recycling infrastructure, with separate collection systems for paper, plastic, glass, and metal. There are also recycling plants that process these materials into new products through mechanical and chemical recycling. Poland could benefit from a better understanding of chemical recycling techniques pyrolysis, gasification, plasma gasification, and hydrothermal processing, each with its own set of technological capabilities, optimal process parameters, prices, total energy potential, and ecological consequences. Discovering more about conversion techniques and their various aspects, promises, current state, and technical barriers could help in improving available waste management techniques in Poland, which will also support the concept of the circular economy. Numerous literature reviews on waste-to-energy conversion techniques in India and in developed countries, for example, Australia, Denmark, Japan, and the USA are already existing (Mukherjee et al. 2020). Nevertheless, there appears to be no recent research into waste-to-energy processing and the accompanying critical hurdles for successful implementation in Poland (the current study's originality).

Household waste quality estimates in Poland

The waste management system in Poland is regulated by several laws and regulations, including the Waste Act, which establishes the framework for waste management activities in the country. The Polish waste management system is composed of a number of actors, including municipalities, waste management companies, and the Polish Environmental Protection Agency (Uliasz-Misiak et al. 2014). One important aspect of waste management in Poland is the database on products and packaging (BDO), which is a central register of producers and importers of packaged products. The BDO is managed by the Polish Minister of Climate and Environment and is intended to provide information about the types and amounts of packaging materials placed on the market in Poland. The BDO was established in accordance with the Packaging and Packaging Waste Act, which transposes the European Union's Packaging and Packaging Waste Directive into Polish law. The database contains information about producers and importers of packaged products, as well as information about the types and amounts of packaging materials used. The BDO is used to monitor compliance with legal requirements for packaging waste management in Poland, including the obligation for producers and importers to finance the collection and recovery of packaging waste (Haładyj 2020). It is also used to calculate the contributions that producers and importers must pay to the national packaging waste management fund, which is used to finance the collection and recovery of packaging waste. The most common ways used to measure the volume of waste in Poland are through the use of surveys, registration of waste transport, and data from waste management companies. Surveys are used to obtain data on the types and amounts of waste generated and disposed of, while registration of waste transport provides information on the amount of waste transported between different locations (Przydatek and Wota 2020). Data from waste management companies are used to track the amount of waste collected, treated, and recycled. Additionally vehicles transporting waste to landfilling areas or waste sortation and composting capabilities are mostly used to measure the volume of waste. Private waste collection businesses in Poland also frequently collect and transport municipal waste from large cities for eventual disposal at a variety of facilities. Because of a lack of proper waste management practices, the amount of waste that is collected and disposed of is intentionally undercounted by involved business entities. Thus, due to negligence or failure to meet reporting requirements, the amount of waste collected and disposed of is sometimes undercounted.

Comparison of predicted waste generation with actual amount of waste collected in Poland from 2001 to 2010 is shown in Fig. 2. This comparison is between the amounts provided by Central statistical office (Główny Urząd Statystyczny, GUS), and National Waste Management Plan predicts (KPGO). The amount of waste collected is significantly lower than predicted by the KPGO for years 2001–2010, and this can be attributable to the fact that:

- *Inefficient waste management systems*: According to a report by the European Environment Agency, Poland has a relatively low level of waste collection efficiency compared to other EU countries. The report cites factors such as insufficient funding, inadequate infrastructure, and a lack of skilled personnel as reasons for this inefficiency.
- *Limited waste collection services in rural areas*: Poland has a significant rural population, and waste collection services in these areas may be limited or non-existent. Waste collection programers are only available to a small percentage of the population (about 90%). This can lead to illegal dumping or burning of waste, which is not accounted for in official waste collection statistics.
- *Inaccurate waste generation estimates*: Predicted values of waste generation may be based on incomplete or inaccurate data, which can lead to overestimations of the amount of waste that will be generated. This can result in waste management systems being designed with a higher capacity than is actually required.
- *Minimizing the landfilling tax*: The reported amounts of waste being sent to landfills are being deliberately underestimated in order to minimize the landfill tax, which is currently set at 100 PLN per 1 Mg of waste.

Figure 2 also presents the amount of waste collected in Poland till 2019, these values are provided by GUS, but unfortunately, the predicted values by KPGO could not be attained. But in terms of waste collection systems improvements, the percentage of the population covered by municipal waste collection has increased from 94.1% in 2010 to

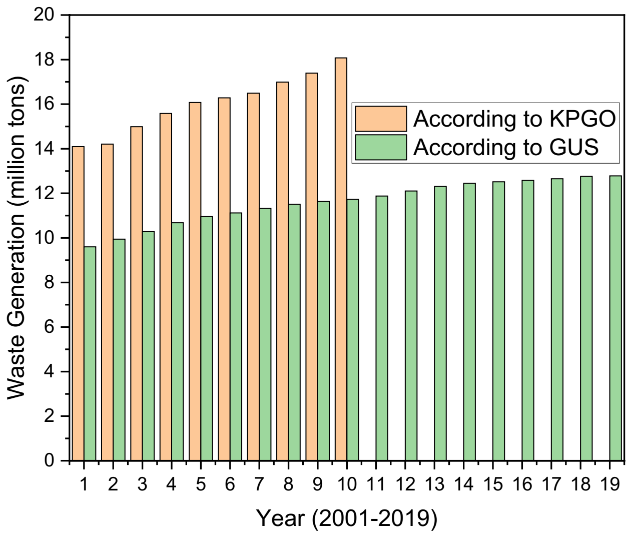

Fig. 2 Comparison of household garbage collected in Poland

98.2% in 2019, according to Eurostat. The percentage of households served by separate collection of biowaste has also increased from 9.9% in 2010 to 45.1% in 2019. Based on these statistics, it appears that waste collection systems in Poland have improved since 2010, with increased coverage of the population and increased recycling rates. However, it is important to note that waste management is a complex issue, and there may be other factors at play that affects the overall effectiveness of the waste collection system.

Waste composition analysis

Potential of any type of waste material to be converted into valuable products is highly dependent upon its composition. The total production of the waste and percentage existence of various materials in this waste has been provided for different cities in Poland. The Central Statistical Office of Poland (GUS) carries out regular surveys and data collection activities to gather information about various aspects of Polish society, including waste generation and management. Waste composition is influenced by various factors, including geography, population and demographics, socioeconomic status, consumption patterns, and industrial activity. These factors interact in complex ways to determine the types and amounts of waste generated in a given context. As a result, waste composition can vary widely depending on the location, population characteristics, and other local factors.

Figure 3 illustrates how the houses with three different types of surroundings S1, S2, and S3 have different effects on the composition of the waste (based on the average samples collected from each individual's environment during the course of four separate measurement series carried out between 2019 and 2020).

Surrounding I (S1) Single-family homes: These homes are typically heated using furnaces or boilers that burn natural gas, oil, or propane. The waste generated includes food waste, paper products, plastics, glass, and metals, as well as yard waste such as grass clippings and tree trimmings. In addition, these homes may generate hazardous waste such as used oil, batteries, and cleaning products.

Surrounding II (S2) Multi-unit housing: These types of housing, such as apartments and condominiums, often have central heating systems that use natural gas, oil, or electricity. The waste generated may include more paper and plastic waste from packaging and mail, as well as electronic waste from outdated devices.

Surrounding III (S3) Rural homes: Homes located in rural areas may use a variety of heating systems, including wood stoves, pellet stoves, or electric heaters. In addition to the waste generated by single-family homes, rural homes may generate more agricultural waste such as manure and crop debris. They may also generate more hazardous waste such as pesticides and chemicals due to the use of these substances in farming and other rural activities.

The composition of municipal waste generated by different types of housing in Poland (data provided by GUS) varies based on a variety of factors, including lifestyle, location, and household size. Single-family homes in Poland generate the most municipal waste per person, with an average of 344 kg per year, or about 0.94 kg per day. The largest proportion of waste generated by single-family homes is organic waste, which includes food waste and garden waste,

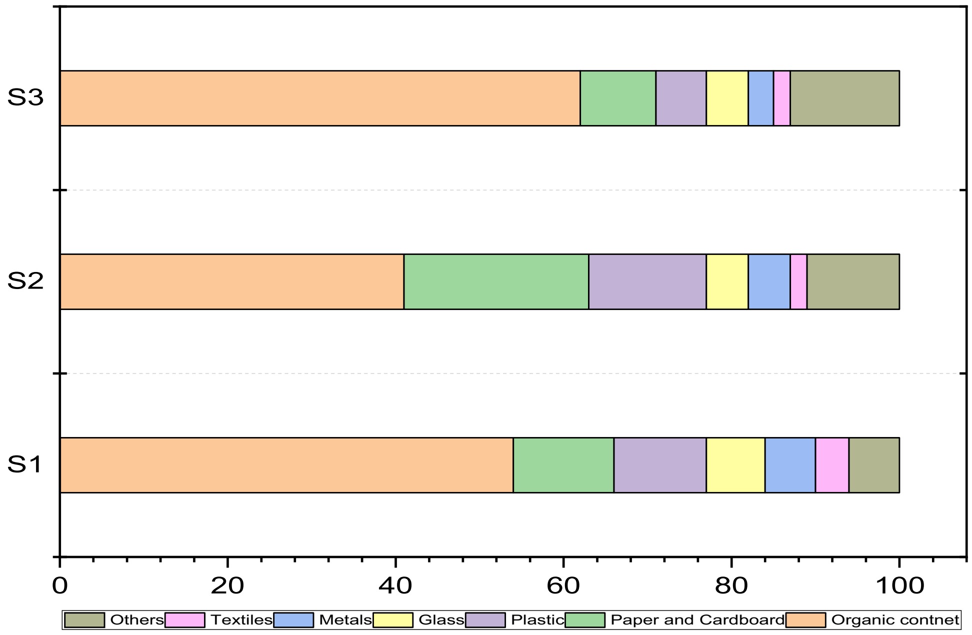

Fig. 3 Poland average waste composition by environment, expressed as a mass percentage on a wet basis

accounting for 54% of the total waste generated. Paper and cardboard account for 12%, plastics account for 11%, and glass accounts for 7%. Metals, textiles, and other types of waste make up the remaining 17%. Multi-unit residential buildings in Poland generate less waste per person than single-family homes, with an average of 218 kg per year, or about 0.60 kg per day. The largest proportion of waste generated by multi-unit residential buildings is also organic waste, accounting for 41% of the total waste generated. Paper and cardboard account for 22%, plastics account for 14%, and glass accounts for 5%. Metals, textiles, and other types of waste make up the remaining 18%. Rural households in Poland generate an average of 296 kg of municipal waste per person per year, or about 0.81 kg per day. The largest proportion of waste generated by rural households is also organic waste, accounting for 62% of the total waste generated. Paper and cardboard account for 9%, plastics account for 6%, and glass accounts for 5%. Metals, textiles, and other types of waste make up the remaining 18%. It's important to note that the type of heating system used can also impact the amount and type of waste generated. For example, households that use wood or coal for heating may generate more ash and other types of waste related to heating than households that use natural gas or electricity.

The evaluation of the qualities of the waste from Poland municipal operations includes, among other factors, the following parameters, which characterize the waste viability as a fuel source:

- Grain fraction and selected component moisture content in percent.
- To determine the total amount of organic matter [% dry mass], we must look at all fractions and individual components.
- Specific components heat value (in MJ/kg in dry conditions)

Detailed waste composition analysis for different cities of Poland has been presented in the coming sections, but unfortunately, these numbers are only limited to 2005 as authentic sources could not be found in the literature that provide the most recent detailed data for different cities. Figure 4a represents the total moisture content, and Fig. 4b represents the percentage organic content on a wet basis of Wroclaw's municipal garbage composition from 1992 to 2005. For all four seasons, spring, summer, autumn, and winter, the size of waste samples has been divided into three fractions, 10, 10–40, and 40–80 mm.

Moisture and organic matter concentration in the fine fraction (less than 10 mm) fluctuates the most during the year. However, the lowest levels of moisture and organic materials can be found in this portion. The 10–40-mm fraction, which contains the most biodegradable materials, has the highest moisture content. The 40–80-mm fraction had the largest concentration of organic material. Combustible materials make up the majority of this portion (paper and plastics).

Sogreah France used MODECOM technique to identify the composition of mixed household garbage in Poznan in May 2001. Eight waste samples were analyzed, two each from four different municipal settings. The 5th EU Framework Program's Solid Waste Analysis (SWA) Tool experimented in Krakow, Poland, in 2003 with the composition and quantity of household waste (Tables 1, 2, and 3 Solid Waste Analysis Data). By using SWA tool, the detailed composition of household waste is presented in Table 3. These data were used to compute the amount of packaging

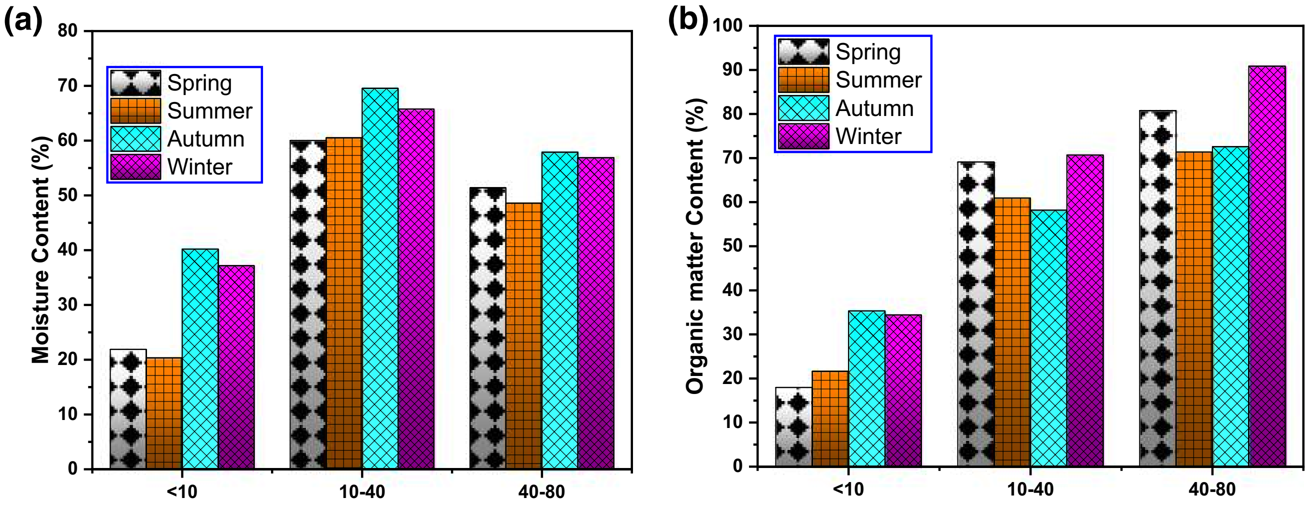

Fig. 4 **a** Moisture content and **b** organic content (as a percentage of dry mass) in Wroclaw's household waste (Boer et al. 2010)

Table 1 Composition of waste generated in Poznan based on a Sogreah survey's findings (Boer et al. 2010)

Waste material	Mass percentage	Waste material	Mass percentage
Oragnic waste	23.6	Waste glass	9.3
Wastepaper	9.8	Metals	2.1
Cardboard	4.5	Waste plastic	10.8
Waste composite	1.6	Sanitary products	2.8
Fabric	2.8	Food packages	0.7

Table 2 Krakow's residential make-up in its entirety (Boer et al. 2010)

Waste material	Mass percentage	Waste material	Mass percentage
Organic matter	40.51	Waste plastic	12.11
Wood	0.89	Glass	10.9
Wastepaper	10.19	Textile	2.71
Metals	4.1	Hazardous waste	0.19
Composite waste	3.9	Inert waste	5.61
Other waste	4.11	Fine fraction	8.49

and non-packaging waste generated by each home (refer to Table 1) based on the results.

From the data presented in all the figures and tables, it's obvious that MSW waste in Poland has the major concentration of organic compounds, more or less same for other European countries, and that can be converted into carbon-rich chemical products through suitable waste-to-energy conversion technique that also provides the chance of waste-to-resource recovery.

Waste-to-energy conversion techniques and role of oxi-liquefaction/wet oxidation

Biodegradation, anaerobic digestion, pyrolysis, gasification, and plasma gasification are some of the processes that can be used to transform municipal solid waste into energy directly or in a more indirect manner. Table 4 compares various traditional and nontraditional techniques to convert waste into valuable products in terms of plant life, waste handling capabilities, cost-effectiveness, energy production potential, and society readiness level.

It is important to note that composting and putting waste in landfills are usually thought of as ways to get rid of it, not as ways to turn waste into useful products, but in composting, it is possible to get some energy as the heat given off when carbohydrates are broken down. Still, compared to other ways to turn waste into energy, the amount of energy made is not that great.

However, it is clear from more recent research such as that conducted by (Munir et al. 2021) that modern techniques, including pyrolysis, hydrothermal treatment, and gasification, are much more preferable to conventional waste-to-energy conversion techniques. However, due to numerous constraints in the areas of technology, economy, environment, and society, there is currently no technique reported that can be considered universally applicable for converting various waste types in MSW regime to

Table 3 Household municipal garbage in Wrocław and Krakow consists of packaging and non-packaging waste items (Boer et al. 2010)

Material	Wrocław/inhabitant per year		Krakow/inhabitant per year		Average	
	% mass in wet source	kg/inhabitant per year	% mass in wet source	kg/inhabitant per year	% mass in wet source	kg/inhabitant per year
Waste material from packaging						
Paper	3.45	9.50	2.72	6.40	3.2	8.21
Plastic	5.80	16.30	4.96	11.89	5.2	14.12
Glass	10.15	28.15	9.48	22.55	9.7	25.39
Metals	0.80	1.65	1.51	3.55	1.14	2.81
Nonmetals	0.58	1.65	0.19	0.39	0.39	1.03
Composites	1.40	3.80	1.22	2.85	1.2	3.39
Waste material from non-packaging						
Paper	4.95	13.75	7.49	18.02	6.24	16.01
Plastic	4.97	13.85	7.08	16.97	6.12	15.39
Glass	1.77	4.98	0.58	1.45	1.18	3.19
Metals	0.48	1.35	0	0	0.20	0.71
Nonmetals	0.08	0.24	0.09	0.27	0.12	0.30
Composites	1.22	3.36	1.92	4.55	1.58	3.89

Table 4 Assessment of traditional and nontraditional waste-to-energy conversion techniques (Munir et al. 2021)

Criteria	Traditional techniques					Non-traditional techniques		
	Composting	Anaerobic digestion	Landfilling	Incineration	Pyrolysis	Gasification	Plasma gasification	Wet oxidation
Plant total life and technical capabilities comparison								
Plant life (years)	10–15	15–20	30	30	20	30	20	20
Categorization of waste required	✓	✓	✓	✓	✓	✓	✓	×
Wet waste handling	Restricted	Restricted	Restricted	×	Restricted	Restricted	Restricted	✓
Computerization level	↓	↓	↓	Modest	Modest	Modest	↑	↑
Hazardous waste handling	↓	↓	↓	Modest	↑	↑	↑	↑
Cost analysis								
Typical capital cost ($M)	10	50	70	115	85	80	100	80
Compliance cost	Modest	↓	↓	↑	Modest	↑	↑	↑
Operational cost ($M)	1	2	2	8	7	6.5	8.2	8
Total income ($M)	-0.1	+0.5	+0.5	+0.5	+0.5	+3.1	+3.2	+2
Total energy								
Total energy produced (kg/ton of MSW)	-2.7–3.1	9–13	4–9	36–45	45–50	35–63	63–80	Not applicable
Willingness level comparison								
Society willingness level	Modest	Modest	↑	↓	↓	↓	↓	↓
Customer willingness level	↑	↑	Modest	↑	Modest	Modest	Modest	Modest
Technology willingness level	↑	↑	↑	↑	Modest	Modest	↓	↓

value-added products without any separation and another pretreatment processes. For this reason, it is often recommended to use different combinations of waste-to-energy techniques, both conventional and non-conventional, to achieve the optimum outcomes that are economically and technologically favorable. To provide an effective solution to this problem and introduce the single technique that can treat various types of waste materials in MSW, in the current study, various aspects of oxi-liquefaction/wet oxidation technique including reaction conditions, stages, types, and involved chemistry have been reviewed; in addition, few works have also been reported in which the current technique has been already used to treat the various waste materials that are also the major part of MSW that justifies the potential of this method to treat complex MSW in context of energy production and waste-to-resource recovery. It is important to note that this technique will be applicable to handle the organic fraction of waste because only the organic compounds have the essential carbon available to be converted into the required chemical compounds.

As shown in Table 4, wet oxidation technique outperforms other available approaches in terms of waste handling, total income, and competing with conventional and other thermochemical processes in technological skills, net energy output, and the repercussions on the environment. Thermochemical procedures are superior to biological or landfilling methods regarding plant service life and technological capabilities. Net or total income generated by oxi-liquefaction processes is higher than by biological or landfilling processes and comparable to other thermochemical processes. In comparison with thermochemical and oxi-liquefaction processes, biological and landfilling technologies recover less value, but they are less expensive, deep-rooted, and their technological and social readiness levels are higher.

Wet oxidation process

The wet oxidation (WO) process is carried out comparatively at higher pressures ranging from 5 to 20 MPa and at critical water temperature in the range of 150–350 °C to oxidize the organic and inorganic materials in the aqueous phase by pure oxygen or any chemical oxidant to mainly produces the volatile acids. Strong hydrolysis reactions and solubility of oxygen in an aqueous solution at higher temperatures support the better oxidation process (Yang et al. 2022). MSW can be decomposed into oxidative products having hydroxyl, carbonyl, and carboxyl functional groups mainly acetic acid and some other organic acids through a controlled oxidation process, which are the product of key importance in the studies, while the complete oxidation will result in carbon dioxide (CO_2), water (H_2O), and ash production. This process is also known as "wet oxidation," and its name comes from the use of water.

$$C_xH_y(\text{MSW}) + O_2 + N_2 + \text{Heat} + H_2O \rightarrow \text{Aldehydes}$$

$$\text{Aldehydes} \rightarrow \text{Alcohols} + \text{Ketones} + \text{Carboxylicacids}$$

$$\text{Alcohols} \rightarrow \text{Ketones} \rightarrow \text{Carboxyacids}$$

$$\text{Alcohols} \rightarrow N_2 + CO_2 + H_2O + \text{Ash}$$

$$\text{Carboxylicacids} \rightarrow N_2 + CO_2 + H_2O + \text{Ash}$$

The process performance is dependent upon a number of process variables, for example, reaction temperature, reaction time, oxygen pressure, solid–liquid ratio, oxidizer content, and mixing speed for stirred processes (Demesa et al. 2015). In wet oxidation process, degradation of MSW happens at critical temperature and pressure conditions because water undergoes a considerable change in its properties both physical and chemical, e.g., its dielectric constant, viscosity, and surface tension decrease while diffusion rate increases that make the water a good solvent for extraction and solubilization processes (Zhang et al. 2017).

In comparison with anaerobic digestion and landfilling, this technique can greatly reduce the amount of MSW in shorter time span and can treat wet and mixed waste without pre-drying (a costly step) and separation process. Cost estimation process of various waste-to-energy conversion techniques is provided in Table 5, where capital cost is the representation of total initial expenditures calculated in the US dollars per ton of MSW, while the operational cost is daily ongoing cost such as labor cost and maintenance cost.

In some situations, the wet oxidation only relies on pure oxygen for the oxidation process, but depending upon the nature of products required and stability of waste materials, some catalysts are also added to achieve the required degree of oxidation comparatively at lower temperature and pressure (Bhargava et al. 2006). There are two options to lower the reaction pressure and temperature. One is to supply the oxygen with an appropriate catalyst, and the other is to add an oxidant instead of directly providing oxygen. One example of such an oxidant is hydrogen peroxide, which degrades at higher temperature and serves as the source of oxygen. So depending upon the reaction pathways, the wet oxidation can be classified as shown in Fig. 5.

Table 5 Cost comparison of waste-to-energy conversion techniques for MSW (Kumar et al. 2017)

Waste-to-energy conversion techniques	Capital cost US$/ton	Operational cost US$/ton
Incinerating	400–700	40–70
Landfilling	10–30	1–3
Anaerobic digestion	50–350	5–35
Pyrolysis	400–700	50–80
Gasification	250–850	45–85

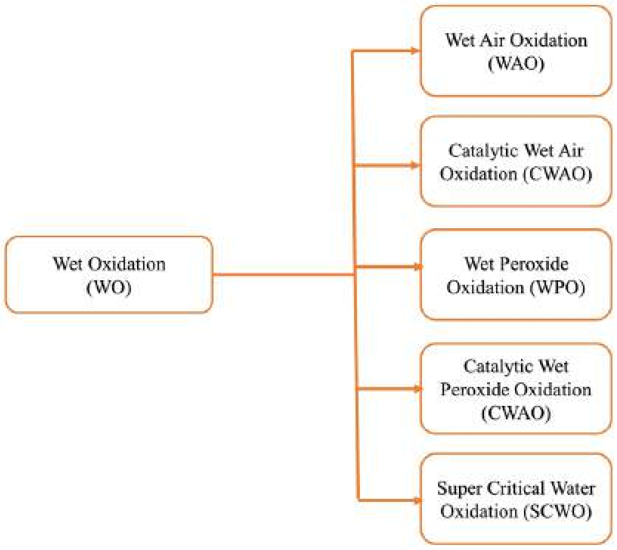

Fig. 5 Classification of wet oxidation

Wet air oxidation

Wet air oxidation (WAO) is the process of oxidizing the organic and inorganic waste in the presence of air, containing oxygen in gaseous form at certain conditions of temperatures 175–320℃ and 20–200 bar of pressure, respectively, but the conditions widely depend upon the treated material (Mishra et al. 1995). The powerful driving force for this destructive technique is the high degree of reactivity of oxygen with organic compounds and the increased reaction rate at elevated temperatures and free radical formation. The sole purpose of the process is not the complete degradation of organic matter but the production of intermediate valuable products. At high enough pressures, water will remain in its liquid form and acts as a catalyst for oxidation, processes can take place at temperatures that are much lower than the temperatures required if the same materials were oxidized through open flame combustion process. Water acts as a heat transfer medium and removes surplus heat via evaporation, hence normalizing oxidation rates (Bhargava et al. 2006).

The procedure is environmentally friendly because no potentially hazardous chemical reagents are used as reactants, and products are water and CO_2 in case of complete oxidation. However, most notable aspect related to WAO process is that it typically necessitates the utilization of high temperatures (and pressures) to accomplish required oxidation levels of organic compounds containing long chains of carbons in a less amount of time. But on the other hand, partial oxidation takes place at low temperatures and less reaction times, resulting the development of intermediate-molecular-weight carboxylic acids, which are not easy to oxidize further and can be the compounds of primary interest. This special behavior of carbon-based compounds in a modest oxidative atmosphere gives us a thought that WAO or oxi-liquefaction process has the potential to convert the MSW into valuable products mainly the compounds with low molecular weight, e.g., carboxylic acids and has the high potential of waste-to-resource recovery.

Krisner et al. (2000) used WAO to degrade the solid polymers, both synthetic (a blend of plastics) and natural (cellulose substances), at a pressure of less than 3 MPa and at a temperature less than 300 ℃. Below stoichiometric condition, no vaporizable products were detected, but at comparatively higher pressure and increased oxygen concentration, all polymeric materials were decomposed in one hour. The maximum degradation yield was 80%, and the primary intermediate products, which are resistant to further oxidation, were acetic acid and benzoic acid.

Anthraper et al. (2018) investigated conversion of solid waste materials including plastics, lumber, tires, cardboards, and sanitary into valuable products via WAO process. The starting pressure of the process was kept 35 bar, and the process involves the breaking down of the complex carbon structure of treated waste and converting the solids into useful chemical products like carboxylic acids, resulting in a significant reduction in solid waste. At 280 °C, each material produced at least 1500 (mg/L) of acetic acid, and slightly over 90% of the total suspended particles were effectively reduced, and acetic acid production from the compounds representing non-recyclable stream of waste materials was 3000 mg/L. But solubilization and oxidation had opposing effects and trends in the soluble chemical oxygen requirement varied across materials.

According to Dietrich et al. (1985), WAO process demonstrated to be extremely operative in handling a variety of toxic and hazardous industrial chemicals in bench, pilot, and full-scale experiments and can be used to safely dispose of wastes containing phenolic compounds, a large proportion of insecticides, defoliants, and other toxic organic chemicals. In most circumstances, wastewater containing high quantities of these substances can be detoxified to make way for further biological treatment or even direct discharge.

In above presented research works, various types of solid waste materials and industrial wastes including the polymeric materials have seen significant reductions in volume resulting in production of useful chemical compounds highlighting the potential of WAO to treat the mixed composition of MSW. The treatment of waste of the same composition or waste including blends of different synthetic and natural polymers seen in municipal solid waste, hospital waste, and agricultural waste can be done industrially using this method. Limiting the release of acidic gaseous effluents is one of the benefits of WAO process. Depending on how well the process is controlled, the high amounts of acetic acid output can yield considerable commercial and environmental benefits.

Catalytic wet air oxidation (CWAO)

CWAO is a suggested process to successfully degrade the complex organic compounds at comparatively lower temperatures and pressures with suitable catalysts, partially in low-molecular-weight organic compounds or completely into water and CO_2. One of the main purposes of this technique is the conversion of toxic organic compounds to biodegradable intermediates, paving the ways for the application of biological methods for further treatment (Pintar 2003). CWAO is less energy demanding, and the presence of catalyst helps to achieve much higher oxidation rates in less severe reaction conditions as compared to non-catalytic processes. For reaction governing by solid catalyst including both volatile (oxygen) and nonvolatile (organic compounds) reactants, a three-phase reactor is the necessity (Mills and Chaudhari 1997). Depending on the reaction conditions, this process can transform organic nitrogen gas into ammonia or nitrates as well as hazardous substances such as phosphorus into phosphate, halogens into halides, and sulfur into sulfates (Guo et al. 2015). The long chains hydrocarbons, pyridine, phenol, and chlorophenols are transformed to intermediate carboxylic acids, products of key interests. Reduction of the waste and production of required products of special chemical composition are dependent upon the reaction pathways so the selection of proper catalyst is the heart of the process.

Catalysts

When the catalyst components and reaction substrates are combined in one phase, usually the liquid phase, this is referred to as a homogeneous catalytic system, and homogenous catalysts are best applicable (Cole-Hamilton 2003). Salts of different metals including copper, iron, and manganese are mostly used as homogenous catalysts. The process is quite simpler with high conversion efficiencies and better process control, and reactor design is less complex as compared to process involving heterogenous catalysts. Initiation, propagation, and termination are the basic steps involve in completing the reaction through promotion of free radicals (Sheldon 2001). Another form of the catalysts used in this process is the coordination catalysts, which can play the role of both homogeneous or heterogeneous catalysts, and a crucial step is the oxidation of the coordinated substrate using metal ions, and the oxidized form of the metal can be restored by the reaction of the reduced form with oxygen. One of the important heterogenous catalyst models is Mars–Van Krevelen Adsorption Model. Chemical process involves redox mechanism based on lattice oxygen (Bhargava et al. 2006). An oximetal species oxidizes the substrate in this chemical process, oxygen then reoxidizes the reduced form in the redox cycle, and the reaction's rate-determining step is the exchange of oxygen between the catalyst and hydrocarbons, or the impact of oxygen negative ions on the after-mentioned product. Use of the heterogenous catalyst has been supported to reduce the organic compounds on large scales. It is comparatively cheaper method to treat various types of organic compounds. Both noble and non-noble metals are used for this purpose. The three noble metals that are most frequently utilized in the CWAO process are platinum (Pt), palladium (Pd), and ruthenium (Ru). But the activity of these metals is highly dependent upon the reaction conditions, solution pH value, and type of organic compounds (Johnstone et al. 1985). No doubt noble metals have very high reactivity and strongly support the oxidation process, but they are not cheap and can also be contaminated by existence of halogens and sulfur-based compounds. In such situations, the oxides of metals such as iron, copper, manganese, and nickel serve as best alternative.

Table 6 presents all the review articles published in the field of WAO and CWAO, these articles summarize the work done in this field, and it can be seen that WAO and CWAO process has great success in treating the organic compounds in wastewater streams, for dyes degradation, for treating the industrial wastes, but unfortunately, no literature could be found that highlights the use of these processes to treat the mix MSW. But the higher potential of treating industrial waste containing persistent organic pollutants, used solvents, polychlorinated biphenyls, and complex organic compounds gives us a thought to use this technique for treating the MSW. However, the factors that require careful consideration include the leaching and sintering of metal-based catalysts, loss of surface area of supporting materials, active sites poisoning by CO assessment, and accumulation of inorganic and organic compounds on the catalyst surfaces.

Wet and catalytic wet peroxide oxidation (CWPO)

While dealing with WAO process during the initial stages, the gaseous oxygen is converted to liquid phase, and in later stages, this oxygen needs to dissolve in water but it faces significant resistance at the gaseous/liquid interface so high pressure is needed to solve this problem. Adding aqueous hydrogen peroxide to the system in place of oxygen is another option for lowering the pressure and that is the base of WPO. No doubt the WPO oxidation has the potential to stand alone but use of metal salts in combination with peroxide greatly reduces the complex organic compounds in low-molecular-weight organic acids.

The CWPO process is considered as low-cost technology, because it works under mild condition of temperature and pressure and with simple reaction arrangements (Ribeiro et al. 2016). In CWPO technique, the hydrogen peroxide (H_2O_2) is used as oxygen source, and catalyst mostly the metal based is used for its partial degradation to produce hydroxyl radicals ($HO^{\cdot}$) with strong oxidation power, capable of oxidizing the large organic compounds (Rokhina et al. 2011). Moreover, the complete degradation of H_2O_2 results in production of oxygen and water which make it more environmentally friendly reagent and CWPO-based techniques more supportive in environmental point of view. Still proper choice of catalyst and its subsequent design is important to justify the CWPO process as a most efficient process to degrade the organic compounds.

CWPO oxidation was first reported by Fenton (1894) when he observed that H_2O_2 in the presence of iron slats has a very high potential to degrade the organic compounds as Fe^{2+} plays its role as catalyst, and small amount of these ferrous ions is sufficient enough to degrade the high content of organic matter. Later studies indicated that the reaction between H_2O_2 and Fe^{2+} in acidic conditions leads to the oxidation of Fe^{2+} to ferric ions (Fe^{3+}) and the breakdown of peroxide along with the generation of hydroxide ions (OH^-) and ($HO\cdot$) radicals (Haber and Weiss 1932). Barb et al. (1951) provided a more thorough explanation of the CWPO's two-step mechanism. In the first step, H_2O_2 reacts with $HO^{\cdot}$ radicals to produce hydroperoxyl ($HOO^{\cdot}$) radicals and water, and in the second step, the hydroperoxyl radicals participate in the regeneration of Fe^{2+} through the reduction of Fe^{3+} to complete the catalytic cycle.

Table 6 Summary of work already done in field of wet oxidation and catalytic wet oxidation

Title	Comprehensive discussion	Treatment conditions	Outcomes	References
Wet Air Oxidation	A thorough examination of every facet of WO and CWO			Mishra et al. (1995)
Advances in Catalytic Wet Air Oxidation of Wastewater			COD removal = 72–74%, carboxylic acids, concentrations = 50–60 wt%, organic nitrogen compounds conversion = ammonium (85%), dinitrogen (10%), and nitrates (5%)	Wang et al. (1995)
Recent Progress of Waste Treatment by Wet Oxidation Process	Destruction of organic compounds	For industrial sludge 400 ℃ and 30 min,	Conversion efficiency = 99%	Wakakura and Fumio (1995)
		For municipal sludge 450 ℃, 5 min	Conversion efficiency = 95%	
A Review of Industrial Catalytic Wet Air Oxidation Processes	The effect of using five different catalysts on normalizing the reaction conditions for wet oxidation of organic compounds in wastewater has been studied		COD removal Without catalyst = 76.2% With $MnSO_4$ = 74.7% With $CuSO_4$ = 97.6% Total Solid reduction Without catalyst = 85.3% With $MnSO_4$ = 84.2% With $CuSO_4$ = 95.6%	Luck (1996)
Technical and Economic Feasibility of Wet Oxidation: Treatment in a Full-scale Plant. Part 1	Review of cost and technologies involve in wet oxidation of biomass			Collivignarelli et al. (1997)
Wastewater Treatment by Wet Oxidation	Review on selecting the best technique for destruction of organic compounds in water			Zarzycki et al. (1997)
Catalytic Abatement of Water Pollutants	Catalytic destruction of organic compounds	For aromatic compounds with CuO–ZnO–CoO Temp. = 90–150 ℃, Press. = 30 atm	Conversion efficiency = 90%	Matatov–Meytal and Sheintuch (1998)
		For aliphatic compounds with Pt/TiO_2 Temp. = 380 ℃, Press. = 230 atm	Conversion efficiency = 98%	
Technological Progress of Heterogeneous Catalytic Oxidation for Treating Wastewater	A heterogeneous copper catalyst supported by activated carbons	Temp. = 200 ℃, Time = 90 min, Press. = 2.65 MPa	For catalyst with 59 mg/g of Cu impregnation COD = 2200 TOC = 1171 For catalyst with 96 mg/g of Cu impregnation COD = 1980 TOC = 1144	Chen and Li (1999)
Wet Air Oxidation: Past, Present, and Future	Chemistry of WAO and CWO has been briefly discussed			Luck (1999)
Some Aspects of Total Catalytic Wet Oxidation of Organic Substances in an Aqueous Phase				Sune and de Soares. (1999)

Table 6 (continued)

Title	Comprehensive discussion	Treatment conditions	Outcomes	References
Wet Air Oxidation and Catalytic Wet Air Oxidation Process for Wastewater Treatment				Tan et al. (1999)
Lumped Kinetic Model for Catalytic Wet Oxidation of Organic Compounds in Industrial Wastewater	Mass of the catalyst charged into reactor and TOC	Temp. = 393–443 ℃ Reaction time = 60 min	For 0.2, 0.5, and 1 g of catalyst TOC = 40–50%, 60–70%, and 80%, respectively	Zhang and Chuang (1999)
Wet Air Oxidation: A Review of Process Technologies and Aspects in Reactor Design	Detailed discussion of kinetics and mass transfer and WO and CWO processes			Kolaczkowski et al. (1999)
Catalytic and Non-catalytic Wet Oxidation	Chemistry of homogeneous copper-based catalysts and various metal-based catalysts have been discussed in detail			Imamura (1999)
Water pollution abatement by catalytic wet air oxidation in a trickle bed reactor		Temp. = 160 ℃, Press. = 1.2 MPa, Reaction time = 45 mints	COD reduction = 90% Oxalic acid = 1000 mg/L Formic acid = 700 mg/L Acetic acid = 500 mg/L	Fortuny et al. (1999)
Wet Air Oxidation for the Treatment of Industrial Wastes. Chemical Aspects, Reactor Design, and Industrial Applications in Europe	The mechanisms and kinetics of WAO and CWO in chemical terms are briefly discussed	Temp. = 200–325 ℃ Press. = 175 bar	COD reduction = 89.9%	Debellefontaine and Foussard (2000)
Catalytic wet air oxidation of low-molecular-weight carboxylic acids using a carbon supported platinum catalyst		Temp. = 200–325 ℃ Reaction time = 120 mints	Acetic acid conversion = 60.2% Propanoic acid conversion = 75% Butyric acid conversion = 59.4%	Gomes et (al. 2000)
Mechanism and Mathematical Modeling of Wet Oxidation Processes	WO processes are mathematically modeled, and their reaction mechanisms are discussed in detail			Zarzycki and Imbierowicz (2001)
Catalytic Wet Air Oxidation				Yang et al. (2002)
Wet Air Oxidation: A Review of Commercial Sub-critical Hydrothermal Treatment	Commercial WAO processes have been discussed in detail			Maugans and Ellis (2002)
Catalytic Technology for Water Purification				Imamura (2003)
Wet Air Oxidation of Nitrogen-Containing Organic Compounds and Ammonia in Aqueous Media	Only nitrogen-containing compounds were mentioned in the WAO			Oliviero et al. (2003)
Progress of Wet Catalytic Air Oxidation Technology				Cai et al. (2004)

Table 6 (continued)

Title	Comprehensive discussion	Treatment conditions	Outcomes	References
Advanced Oxidation Processes for Water and Wastewater Treatmen	Synergetic effect of different metals on TOC removal	Temp. = 98 ℃ Reaction time = 60 mints	TOC removal for Fe–Cu–Mn synergy = 95% For Cu–Mn synergy = 75–80%	Cretenot et al. (2004)

$$H_2O_2 + HO^{\cdot} \rightarrow HOO^{\cdot} + H_2O$$

$$Fe^{3+} + HOO^{\cdot} \rightarrow H^+ + O_2 + Fe^{2+}$$

Hence, in both WPO and CWPO processes, the conversion efficiency is highly dependent upon the concentration of HO· radicals, while the HO· radicals are created in both Fenton’s reaction and WPO oxidation through the thermo-scission of hydrogen peroxide, while OH radicals are generated through the catalysis of ferrous ions in Fenton's reaction. Thus, raising the temperature of the reaction can increase the concentration of HO· radicals but, if the temperature is too high, it will cause the hydrogen peroxide to decompose into H_2O and O_2. Fenton reagent oxidation is typically performed at room temperature, but elevated temperatures are used to attain higher oxidation rates during WPO processing (Malik and Saha 2003). In addition, iron-based CWPO processes are only applicable for low pH values solution so overcome this problem the other option is carbon-supported metal-based catalysts but influence of carbon material properties, metal impurities, surface chemistry, acidic oxygen-containing functionalities, basic active sites, sulfur-containing functionalities, textural features, and surface area porosity are very important factors when applying the CWPO process for degradation of organic compounds on larger scales.

Supercritical water oxidation (SCWO)

SCWO method involves treating the organic fractions of waste in the presence of water at supercritical conditions of temperature and pressure as in this state the water’s important properties, i.e., density, dielectric constant, and viscosity, changed dramatically. Water as a medium for chemical reaction depending upon its density, supercritical water (SCW) exhibits both liquid-like and gas-like properties. Gas-like properties exhibiting the low viscosities are suitable for promoting mass transfer while liquid-like properties are suitable for solvation. The three phases of heat transfer, normal heat transfer with average heat transfer values, degraded heat transfer with a low heat transfer coefficient, and enhanced heat transfer with higher values of heat transfer coefficient, can all occur during the supercritical stage. The deteriorated heat transfer is mostly related to high values of heat fluxes and subordinate mass fluxes. A low dielectric constant is helpful in dissolution of nonorganic materials while high temperature increases the thermal reaction rates. These special properties of water make it a suitable solvent for dissolving organic compounds nearer to supercritical point. In SCWO, the source of oxygen is mostly the oxidants such as H_2O_2, O_2, and air, and the conversion efficiency of organic species to CO_2 and H_2O is 99% dependent on the reaction circumstances, such as the oxygen content, operating temperature, final pressure, reaction time, and reactant concentrations (Onwudili and Williams 2008).

Water in supercritical state owns the properties of weak electrolyte so it favors free radical mechanism. Where the atoms or groups of atoms with free/unpaired electrons generated during the covalent bond secession under special conditions are known as free radicals and trigger the free radical reaction with the main steps of initiation, propagation, and termination. Alkenes may be changed to alkanes by hydrogenation through a partial oxidation process while alkanes can normally undergo the isomerization, hydration, and hydrogenation processes in SCW (Wei et al. 2021). In case of alkanes, the studies are mostly focused on the treatment of alkanes with longer carbon chains that degrade at much faster rate than aromatic compounds as aromatic compounds possess higher C–C bond energy, and they tend to accumulate for a long time (Okoh 2006). In the case of SCWO of cellulose, the preliminary step is hydrolysis where the products are oligomers and monomers that can further be hydrolyzed to produce glucose whose isomerization results in fructose. Through a variety of dehydration, condensation, isomerization, and polymerization actions, these hydrolyzed products can be transformed into certain intermediates, such as phenolic compounds, furfurals, and low-molecular-weight organic compounds, primarily acids, aldehydes, and ketones and alcohols (Wei et al. 2021). SCWO process is also used to treat the waste plastic in the work reported by Liu et al. (2019) where the total carbon conversion efficiency, hydrogen conversion efficiency, and total yield of gaseous products were examined. The main oil components identified in this study were mostly the aromatic compounds, benzene, propane nitrile, toluene, ethylbenzene, styrene, naphthalene, 2-methyl naphthalene, and biphenyls and p-terphenyl. There further other studies (Abeln et al. 2001; Barner et al. 1992; Bermejo et al. 2006; Marrone 2013; Schmieder and Abeln 1999; Thomason and Modell 1984) reported in which this technique is used to treat various types of organic materials to produce the useful products, but in this process, the main focus is mostly the gaseous products.

However, the process has very high conversion efficiencies but due to the involvement of high temperature and pressure, the process has limitations to accept on a wide scale. High energy is required to obtain the supercritical temperature and pressure conditions, then at the end of the reaction, depressurization and heat recovery are the cases that need special attention to make this process economically favorable. In addition, this process comes with harsh operational conditions and chances for corrosion of the reactor. So, there is a lot of scope for the researcher to proceed with their work related to the choice of the reactor and reactor design, solve the problems related to SCWO, and application of this technique on large scale to deal with MSW for the production of useful liquids and solid products.

The general chemistry of oxidation in wet environments and role of water

In the current study, the intermediate products mostly the carboxylic acids are the main concern, and they are primarily partial oxidation products of almost all types of wet oxidation processes, often occurring simultaneously in most systems and sharing mostly the same reaction pathways.

The primary objective of the WO process, which is to degrade organic molecules by converting them into useful chemical products, is simple to explain, but the chemistry that occurs during WO of both individual organic compounds and mixtures of organic compounds is highly complicated. These complexities can be attributed to the numerous chemical reactions (both oxidative and non-oxidative) that can occur for various organic molecules under normal WO circumstances and the numerous reactions that can occur during the WO of even a single organic component.

Under typical WO conditions, a variety of chemical reactions, including auto-oxidation, also known as free radical reactions involving oxygen, heterolytic/homolytic cleavage (oxidative or non-oxidative thermal degradation), hydrolysis, decarboxylation, alkoxide formation followed by subsequent oxidation (alkaline solution), and carbanion formation, can result in or lead to the oxidation of organic compounds. The overall number of reactions that can occur during the WO can be very high, even for a simple low-molecular-weight organic molecule like propionic acid. For the WO of propionic acid, (Day et al. 1973) hypothesized a free radical reaction process with 16 distinct stages.

The WO of an organic compound can be divided into two main stages (Bhargava et al. 2006), which are the following: (i) A physical stage, in which the gaseous oxygen is converted to the liquid form and (ii) chemical stage which involves the reaction of oxygen from the first stage with the organic compounds in the solution to start the oxidation process. These two stages are considered as rate determining stages of WO of any organic compound directly or indirectly. No doubt several other singularities, such as co-oxidation through intermediate free radicals produced during the oxidation of other compounds in the solution, can influence overall WO process.

The physical stage of WO in which oxygen transition happens from the gas phase to the liquid phase and solubilizes in water is described in great depth by (Debellefontaine and Foussard 2000). According to the conducted study, there is a significant resistance to gas transfer on gas–liquid interface, and there are three types of interaction of oxygen with water, i.e., (i) oxygen reacts only within the film due to a rapid chemical reaction and resistance offered by liquid surface to transfer inside, (ii) oxygen reacts rapidly within the bulk liquid, where its concentration is nearly zero, and finally, iii) the oxygen react with liquid in such a way that its concentration in bulk liquid is nearer to stoichiometric conditions, that is, an important interaction in wet oxidation. According to Debellefontaine and Foussard (2000), high mixing efficiency is the only solution to often eliminate the influence of oxygen transfer rate on overall rate of reaction, allowing the determination of unencumbered chemical kinetic rates.

The rate and breadth of the chemical reaction stage of the WO process can be affected by a variety of variables such as temperature, oxygen partial pressure (dissolved oxygen concentration), geometry of the reactors, wall composition, and solution pH, which must be taken into account. The overall time required for the degradation of organic compound, and total volume is dependent upon the type of reactor, reaction rate, and degree of oxidation required (Khan and Kr. Ghoshal 2000). An increased reaction rate is beneficial as it decreases the overall volume of the reactor. A balance is maintained while choosing the necessary operating conditions between the process's total cost and safety repercussions, as well as the mass transfer and response rate with rising temperature and pressure. Detailed kinetic studies for treatment of real-life organic compounds are not widely available; thus, reactor design calculations are mostly based on empirical methods. During the WAO process, the oxidation reaction is exothermic and follows the Arrhenius dependence (Aquilanti et al. 2010) which suggests the increase reaction rate with increase in temperature.

$$R_\mathrm{r} = A \times e^{(E/RT)} \times \left(C_\mathrm{or}\right)^m \left(C_{\mathrm{O}_2}\right)^n$$

where R_r is the rate of reaction s^{-1}, A is the pre-exponential factor s^{-1}, E is the activation energy kJ/mol, R is the universal gas constant kJ·(kmol K)$^{-1}$, T is the reaction temperature K, C_or is the normalized concentration of organic compounds, and $\mathrm{C}_{\mathrm{O}_2}$ is the normalized concentration of oxygen in bulk liquid, and m and n are the order of reaction mostly first order with respect to pollutant concentration and between zero and one for oxygen.

In order to maintain the oxygen partial pressure, an increase in temperature necessitates an increase in the total operating pressure. Since the reaction is exothermic, additional heat is released, raising the liquid's present temperature and causing it to evaporate. So, water can also serve as heat sink to adsorb the excess heat and preventing the reaction from running away. But the oxidation occurs in aqueous phase so it's necessary that some proportion of water should be remain in liquid state (Kolaczkowski et al.1999). To maintain such situation, the pressure is an important parameter as latent heat of vaporization can be controlled through the variation in applied pressure in addition at elevated pressures, the pressure impact is also expressed as an additional variable in determining the rate constant, i.e., $R_\mathrm{r} = f(T,p)$. In decomposition of organic compounds, a free radical reaction has been observed in batch systems, with the presence of slow oxidation rates, followed by steady state rapid reaction steps (Rivas et al. 1999). The extent of induction step that represents the time required establish minimum concentration of free radicals decreases with increase in both applied temperature and pressure. The situation gets more complex as the reaction proceeds as the oxygen and formed radicals start reacting with reaction intermediates. These types of unpredicted reactions result in consumption and generation of new radicals, including some different radicals with some interesting reactive properties. Due to the involvement of free radicals, the overall rate of reaction is dependent upon the concentration of organic compounds and their degradation mechanism.

Owing to the involvement of free radicals in the reaction, all the aspects affecting the initiation, propagation, and termination stages should be considered while dealing with the reactor design. The geometry and nature of design has a significant effect on heterogenous free radical initiation and termination with the kinetic constant involving the wall of reactor which is specific for each wall material (Kolaczkowski et al. 1999). Emanuel et al. reported that in WO termination of radicals, supporting the oxidation process is much higher in reactor with the metallic walls. This situation provides the difficulties in scaling up the process on industrial scale for degradation of organic compounds and comparison of results from different reactor setups. The significance of operating conditions can be investigated in more details by considering some other non-oxidative reactions, for example, thermal hydrolysis and isomerization.

To summarize, a rise in temperature increases water vapor pressure in addition to the reaction rate and oxygen solubility. Exothermic reactions cause the temperature of the reactor to rise and cause water to vaporize. As pressure rises, oxygen becomes more soluble, and less water is evaporated at equilibrium, which lowers the latent heat of vaporization overall. Therefore, pressure may be utilized to regulate the amount of water in the liquid state and keep the fluid temperature constant. The overall oxidation rate depends on both mass transfer and reaction kinetics when designing moist air oxidation reactors. The rate-controlling step is influenced by a variety of variables, such as the reactor type, operational conditions, and the kind of organic compounds taking part in the reaction. Additionally, the rate-controlling step may alter over time and in relation to type of reactor.

Considering above-discussed issues in depth, the WO technique can be used on industrial scale for decomposition of organic compounds in mixed MSW to recover the resources in the form of converted valuable products.

Conclusions

The composition of mix MSW is complex, and it varies from city to city and for different seasons within Poland but the organic content always remains at the top not only showing its potential to be converted into valuable products but also its availability throughout the year. All types of WO processes have a high potential to deal with mix municipal waste to recover organic resources. WAO process can result in moderate yield of intermediate products, and it also controls the emission of acidic gaseous effluents but the rate of reaction is very slow so a long time would be needed to treat the stable structures. CWAO can show very high conversion rates, and the rate of reaction would also be enhanced but the proper choice of catalyst, catalyst contamination, leaching, and catalyst recovery would be the problems to consider. WPO is a direct source of providing oxygen that eliminates the mixing requirements to make the reactor design less complex. SCWO would mostly result in gaseous products, depressurization and heat recovery, harsh operating conditions, and reactor corrosion would be major problems. Overall, the WO process is carried out comparatively at low temperatures and has ability to treat the complex waste compositions with almost no flue gases production so willingness of society to accept this process for effective waste management is higher. Future research can be oriented to solve the problems related to various types of WO to apply this process on an industrial scale to recover the resources from mix MSW. In addition, the potential of WO can be checked for the waste from composite materials that have high organic content but have not been treated effectively because of the complex composition.

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Data availability Enquiries about the data availability will be entertained by the corresponding author.

Declarations

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Appendix F

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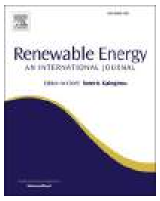

Optimizing advanced oxidative liquefaction of municipal solid waste and personal protective equipment of medical sector for solid reduction and secondary compounds production

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ABSTRACT

Escalating proportion of polymer waste from medical sector (personal protective equipment (PPEs)) and increasing concentration of municipal solid waste (MSW) need to be recycled effectively to ensure sustainable waste management. The current research entails a comparative analysis of a novel oxidative liquefaction technique to disintegrate organic fraction of MSW and PPEs into oxygenated chemical compounds (OCCs) having secondary applications in chemical industry. When examined through ultimate and proximate analysis PPEs and MSW samples have a carbon content of 80.13 ± 2.34 % & 50.30 ± 0.50 % respectively sufficiently higher for secondary compounds production. The oxidative liquefaction process of selected wastes is performed through a meticulously organized experimental framework that integrates Central Composite Design with Fractional Factorial Design employing three critical parameters: 200–300 °C of temperature, 30–60 % of oxidant concentration, and 3–7 % waste-to-liquid ratio. An inverse analysis of the process heating behavior was performed to identify the temperature span over which major degradation of organic matrix occurs and specify exothermic or endothermic nature of various halves of reaction. At the end of the experiments, the total solid reduction (TSR) was in the range of 50–95 % for MSW and (45–97 %) for PPEs, supporting the process efficacy. Gas chromatography with flame ionization detection (GC-FID) was employed to identify the various liquid chemical fractions, and oxygenated chemical compounds (OCCs) yield was in the range of 13–51 g/kg MSW and 37–212 g/kg PPEs. Energy consumed during the process is monitored for both MSW and PPE samples and recorded from 0.7 to 1.4 kWh. Based on the obtained results employing one-way analysis of variance (ANOVA), detailed optimization of the experimental plan was carried out to obtain the most optimal values of the tested parameters that result maximum TSR and OCCs against the minimum resource consumption to support the industrialization of the suggested process.

1. Introduction

The process of oxidative liquefaction involves reacting organic matter with oxygen or an oxygen donor at high pressures and elevated temperatures to convert it into useful liquid products. The process entails decomposing complex organic compounds into more manageable and useful chemical entities. The effectiveness of the method in treating the composite waste from wind turbine blades has already been proven by Mumtaz et al., where the focus was recovering the glass fibers [1]. Furthermore, the study from the same research group shows the concept of degrading the complex organic matrix through oxidative attacks and producing oxygenated liquid chemical compounds including volatile fatty acids (VFAs) [2]. The successful application of oxidative liquefaction to intricate materials has motivated scientists to investigate its efficacy in dealing with two of the most common and widespread waste streams: polymeric waste generated from PPEs related to healthcare industry and MSW.

The escalating use of energy and service products, together with fast population expansion and higher living standards, has caused a notable rise in MSW production, posing severe environmental issues. MSW

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includes a wide range of solid wastes that are regularly disposed of in both urban and rural areas. Every individual is estimated to produce 0.74 kg of waste each day on average [3]. According to current estimates, 2 billion tons of MSW are produced each year globally, of which about 33 % is not collected by municipal services [4]. According to World Bank projections, the production of MSW might reach more than 3 billion tons by 2050 [5]. Roughly 70 % of the MSW that is collected is sent to dumps and landfills, 19 % and 11 % are the number for effective recycling and energy recovery respectively [6]. The US Census Bureau (2020) estimates that there are more than 7 billion people on the planet, and approximately half of them are barred from accessing basic waste management facilities [7]. The projection indicates an increase to 5.6 billion by the year 2050, highlighting the critical necessity for enhanced waste management approaches.

The advancements in technology and the growth of modern healthcare facilities have led to a notable escalation in generation of polymeric waste in the medical sector [8]. The observed rise can be attributed to the extensive utilization of disposable medical products, the adoption of novel medical procedures that primarily rely on single-use items, and the overall expansion of healthcare services to meet the growing demands of the population. Following radiation exposure, medical waste (MW) is recognized as one of the most hazardous types of waste globally [9]. With the declaration from the World Health Organization (WHO) reported in 2020 the worldwide population faced an outbreak of COVID-19, a severe acute respiratory condition triggered by coronavirus SARS-CoV-2, in end of year 2019, which further highlighted the seriousness of this problem [10]. To mitigate the transmission of this virus, the World Health Organization has put forth a series of recommendations, including the complete closure of public venues such as transportation hubs, markets, hotels, restaurants, and educational facilities. Additionally, they have advised restrictions on travel, the enforcement of social distancing, and the use of face masks along with other PPEs. The implementation of masks and PPEs was mandated by the WHO as a critical response through the pandemic that resulted in an increased demand for PPEs, frequently produced from plastic, for frontline healthcare workers and the general population. Plastic polymers such as polystyrene (PS), polypropylene (PP), polyester (PEs), polyacrylonitrile (PAN), and polyurethane (PU) are primarily employed in the production of PPEs including disposable face masks, N95 masks, boots, aprons, and face shields [11]. While around 60 % of textile fraction that include synthetic fibers i.e., acrylic, polyester, and nylon fibers are used in fabric masks [12]. Furthermore, polyethylene (PE), latex, and nitrile are frequently utilized in the manufacturing of gloves [13]. The approximate monthly quantity of gloves and face masks used globally during the pandemic was around 65–66 billion and 130 billion, respectively [14]. This notable increase in polymeric waste production throughout the period of COVID-19 pandemic, which continues in healthcare industry alongside the growth of worldwide populations, poses a serious environmental risk, negatively impacting both marine lives and land-dwelling ecosystems.

To solve the problem of escalating polymeric waste from the medical industry and MSW streams, various recycling techniques, including mechanical recycling, anaerobic digestion, material recovery facilities (MRFs), waste-to-energy recovery techniques (pyrolysis, incineration, gasification), and chemical recycling, have been adopted in the past. Mechanical recycling efficiently sorts and recycles MSW commodities such as plastics, metals, paper, and glass based on segregation quality and contamination levels [15]. The application of mechanical recycling for PPE waste is restricted due to significant contamination and material variety, making it acceptable only for certain clean, single-type PPEs [16]. Composting and anaerobic digestion are effective for converting the organic components of MSW into compost or biogas [17]. However, they are not ideal for synthetic, non-biodegradable PPE waste, unless it is advanced and biodegradable PPE. Material recovery facilities are essential for sorting MSW into recyclable categories. However, their ability to handle PPE waste is limited due to the requirement for specialist sorting methods to deal with the particular material compositions and varieties of PPE. Pyrolysis is an another well mature technology used to manage the waste from PPEs in medical sector [18,19] and MSW [20,21]. The process of pyrolysis applied to MSW, and PPEs presents a viable approach for waste management and energy recovery, facilitating the degradation of carbon-based fractions in oxygen-deprived atmosphere [22]. The process yields syngas, bio-oil, and char, each of which serves distinct purposes: syngas for energy generation, bio-oil for fuel production, and char as a carbon source [23]. Pyrolysis is a sustainable waste management and energy recovery method; however, it has certain drawbacks. The diverse composition of waste leads to inconsistencies in product quality, increased operational complexity, and significant requirements for pre-treatment processes such as sorting, drying, or shredding [24]. The procedure is energy-intensive, expensive, and may release dioxins and furans, especially from PPEs. Improper regulation of pyrolytic decomposition may result in the emission of detrimental gases for example hydrogen chloride, carbon monoxide, carbon dioxide, and volatile organic compounds, thereby contributing to environmental pollution [25]. The process is characterized by high energy consumption and yields low-value byproducts such as syngas and char, which restricts the potential for material recovery. Table 1 summarizes the techniques used to recycle PPEs and MSW.

Hydrothermal liquefaction (HTL) is a thermochemical technique that is widely used for treating various kinds of waste comparatively at a temperature of 250–400 °C with an end goal of bio-crude oil production characterized by its reduced oxygen content. This necessitates further upgrading processes, including hydrodeoxygenation, to enhance the fuel properties of the resultant bio-crude [37]. Another limitation of HTL is its propensity to produce heavy oil fractions and tar-like compounds characterized by elevated molecular weights, thereby constraining its direct applicability without the catalytic upgrading [38].

Moreover, HTL exhibits reduced efficacy in the decomposition of specific polymeric waste materials, including highly crosslinked resins

Table 1
Details of techniques used in recycling of PPEs and MSW.

Waste type	Recycling technique	Process parameters	Out puts	Ref.
PPEs	Extrusion	T = 200 °C, P = 6000 Pa, for 3 min	Polypropylene (PP)	[26]
	Pyrolysis	T = 100–500 °C with cooling water at 17.59 °C.	Liquid, wax, gases (product real composition is not presented)	[27]
	Fast pyrolysis	LCA is performed, N/A	Ethylene, Propylene Propane, Butane, Bauxite	[28]
	Catalytic fast pyrolysis	T = 500, 600 and 700 °C with different feed-to-catalyst ratios 1:2, 1:4, and 1:6 (w/w)	Aromatic hydrocarbons, BTEX, Naphthalene	[29]
	Hydrothermal deconstruction	T = 250–350 °C, P = 30 bar	Volatile fatty acids, Ammonia, CO_2, O_2	[30]
	Hydrothermal treatment	T = 250–350 °C, t = 90–180 min	Volatile fatty acids, CO_2	[31]
MSW	Pyrolysis	T = 400–700 °C, Heating rate = 10K/min, t = 1 h	Char, CO_2, CO, H_2, CH_4, C_2H_6 and C_3H, Pyrolytic oil	[32]
	Slow & Fast pyrolysis	T = 550 °C, Heating rate = 4K/min, t = 1 h	Poly(ethylene-co-propylene) wax	[33]
	Hydrothermal treatment	T = 220 °C, P = 2.4 MPa, t = 30 min	MSW in uniform powder sample	[34]
	Hydrothermal liquefaction	T = 300–350 °C, t = 15–45 min	Bio-crude oil	[35]
	Hydrothermal carbonization	T = 120–280 °C, t = 0–6h, 0.05 to 0.25. B/W	hydro char with HHV of 22–32.5 MJ/kg	[36]

and thermoset plastics, which demonstrate increased resistance to hydrothermal conditions [39]. Furthermore, the HTL process is characterized by its high energy demands, functioning at elevated temperatures ranging from 250 to 400 °C and under pressures between 10 and 25 MPa. This operational framework contributes to significant energy consumption costs [40].In the context of above-presented limitations, i.e., high energy intensity, pre-separation requirements, material contamination, high operational costs, and emission concerns of available waste management techniques, the situation demands a unified and innovative recycling technique that has the potential to treat simple as well as diverse and complex waste streams without pre-requirements. To fill this void, for the first time, a novel technique called oxidative liquefaction has been examined to test its potential to treat MSW and PPE waste with the common aims of solid waste reduction and OCCs production in the context of sustainable waste management and waste-to-resource recovery. Detailed analytical and chemical analysis of both types of waste are presented, and a comprehensive experimental matrix was constructed to perform the oxidative liquefaction process and study the effects of three reaction parameters i.e., temperature, oxidant concentration, waste-to-liquid ratio. Inside reactor temperature was recorded, temperature profiles were generated, and inverse analysis of process heating was performed to compare the heating behavior and decomposition pattern of both types of wastes under the oxidative liquefaction process. TSR was calculated to highlight process efficacy, yield of OCCs was estimated through GC-FID. Based on recorded energy consumptions, and obtained TSR and OCCs yield, optimization of the experimental plan was performed to achieve the final goals of a comprehensive and sustainable waste management framework.

2. Materials and methods

2.1. Details of the materials

To reduce possibility of viral spread among personnel dealing with materials, unused PPEs were obtained from a nearby healthcare center. The PPEs assortment comprises single used face masks, N-95 respirators, polymeric gloves, protective gowns, and bedsheets that were manually trimmed into 1–3 cm fragments using scissors for further handling. All these selected PPEs are mainly made up off polypropylene (PP), polyethylene (PE), polyester (PEs), textile, and high-density polyethylene (HDPE) according to studies published by Purnomo.et al. [41] The MSW analyzed in current research is a heterogenous waste stream typically prevalent in urban and suburban areas in Poland. The chosen MSW sample includes a wide variety of materials, including polymers, organic compounds, a small proportion of metals, glass, and other components, all of which were carefully sorted before being analyzed in experiments. One thing was important while dealing with MSW sample to have a less chlorine content to avoid the rusting of reactor under oxidative environments. The interaction between H_2O_2 and high chlorine compounds results in the generation of oxidative species, including chlorine radicals (Cl•) and hypochlorous acid (HOCl). These species exhibit high reactivity and play a significant role in the material rusting or degradation.

Nevertheless, when the concentration of chlorine is reduced, hydrogen peroxide by itself does not demonstrate the same level of corrosiveness. As under specified reaction conditions, it predominantly decomposes into oxygen and water, thereby rendering it a comparatively safer oxidant with respect to the integrity of the reactor.

2.1.1. Ultimate and proximate analysis of municipal solid waste and personal protective equipments

In detailed analyses were conducted for both MSW and PPEs, to have an insight into the composition and to estimate the existing amount of moisture, ash, volatile matter, and organic carbon. The instrumental details and standards followed are already available elsewhere [1].

2.1.2. FTIR of municipal solid waste and personal protective equipment

The FTIR tests were conducted utilizing a Nicolet 6700 spectrometer (Thermo Scientific, USA), covering a wavenumber range from 650 to 3200 cm^{-1}, with a resolution set at 0.05 cm^{-1}. Measurements were conducted at room temperature, averaging 8 scans per sample. The attenuated total reflection (ATR) method was employed, with each sample pressed against a single-reflection diamond crystal. Spectral data were processed using OMNIC software, version 9.

2.2. Experimental section's details

2.2.1. Experimental setup for oxidative liquefaction of selected wastes

The detail experimentation was performed by using the Parr reactor (model No. 4650), having an internal volume of 500 ml with batch type, manufactured by Parr Instruments (Parr Instr., ILL, USA). Complete details about the experimental setup have already been published by Mumtaz et al. during the discussion on oxidative liquefaction of wind turbine blades [42,43].

2.2.2. Designing of experimental framework

Current study thoroughly carried out empirical research on the oxidative liquefaction of PPEs and MSW using a cohesive experimental design approach. A total of 17 runs (excluding random repetition) were performed for individual waste types based on a design framework integrated with the techniques of Central Composite and Fractional Factorial Designs. The experimental design approach thoroughly evaluated the impacts of three individual reaction parameters: temperature, waste-to-liquid ratio (%), and oxidant concentrations and their interaction for both types of waste. During the experiments pressure and reaction time remained unchanged, whereas the variables indicated before were the major focus of the investigation.

2.2.3. Details of sample processing protocols

The solid samples from both MSW and PPEs mixed with water and hydrogen peroxide H_2O_2, were placed in glass liners inside the reactor. The reactor was then sealed and purged with nitrogen to create an inert environment. It was essential to keep the starting pressure at 30 bars to ensure the reactants were retained in a liquid state while heating. After pressurization, the reactor was observed for 30 min to confirm complete airtightness. Then the reactor was heated using a heating spiral to reach the required temperature (Table 2) and kept at that temperature for 45 min as actual reaction time. Temperature measurements were taken using six K-type thermocouples in sets of two (redundant measurement) placed in three different locations: on the reactor's surface, within the reactor (main focus), and on the walls of the heating spiral.

After the oxidative liquefaction process completes under the conditions in Table 1, the heating spiral was switched off, letting the reactor to cool down naturally to reach normal conditions. Once the reactor cooled down to room temperature, it was depressurized and opened and the obtained mixture was subjected to filtration process to segregate the liquid and solid fractions. A detailed experimental scheme is shown in Fig. 1.

2.2.4. Study of heating behavior and inverse analysis of the process heating

Investigating the heating behavior inside the reactor and inverse analysis of process heating was performed to identify the nature of oxidative liquefaction reaction, i.e., exothermic or endothermic,

Table 2
Indication of levels of tested parameters for MSW and PPEs.

	Levels of tested parameters		
	Lowest (−1)	Average (0)	Highest (1)
Temperature (°C)	200	250	300
Waste-to-liquid ratio (%)	3	5	7
Oxidant concentration (%)	30	45	60

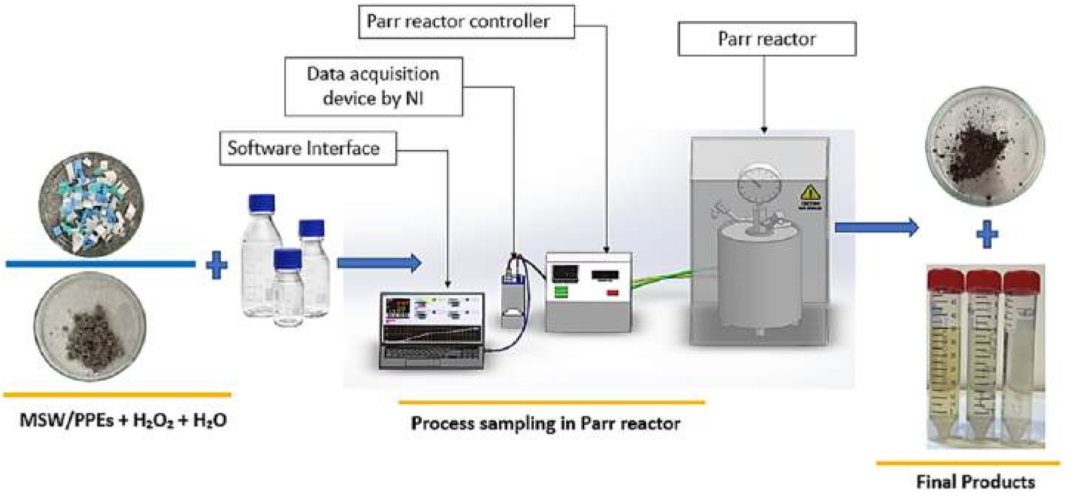

Fig. 1. Sample processing approach for oxidative liquefaction of MSW and PPEs.

calculate the amount of heat absorbed or released, and image the temperature range in which major decomposition of waste happened. For this purpose, modeled experiments, replicating the original one at 200 °C and 250 °C were performed for both types of wastes under the optimized experimental conditions with waste-to-liquid ratio at minimum level for both types of wastes and oxidant concentration at minimum for PPEs and average for MSW (later discussed in section 3.4). The temperature inside the reactor (reaction temperature) was recorded after each 10-s interval by using K-type thermocouples connected to a data acquisition device from National Instruments (NI), error of 0.75 % of the measured temperature, Parr readout and setpoint resolution of 1K. Two dummy runs (without waste samples) replicating the modeled reaction were performed with (i) oxidant + water (ii) water only under same reaction conditions. During these dummy reactions, the temperature was also recorded in the same pattern. A dummy run with only water (heating water) is completely endothermic, as there are no chances of additional reactions that can be absorbed or release heat, so the generated heating profile is considered as a baseline. to judge the nature of reactions (endothermic or exothermic) that happened during the modeled reaction at 200 °C and 250 °C. To exhibit the heating behavior the temperature inside the reactor for the modeled reactions and dummy runs was plotted against the time. To observe the change of heating rates during each time interval, dT/dt (K/minute) was plotted against the inside reactor temperature in degrees Celsius. In-depth curve analysis was performed to identify the additional peaks (as compared to the dummy run with water) that appeared during the modeled reaction. The number of additional peaks, height of peaks, and total curve area were found during the analysis. As the appearance of these additional peaks in the heating profiles of the modeled reaction is an indication of additional heat supplied that was missing during the dummy runs with water.

2.3. Product analysis

2.3.1. Total solid reduction (TSR)

TSR is an estimation of the degradation of the organic matrix that occurs during the oxidative liquefaction of MSW and PPEs and calculated based on the approach discussed by Mumtaz et al. while calculating TSR for WTBs [44].

2.3.2. Quantification of oxygenated chemical compounds through liquid product analysis in GC-FID

The Clarus 500 Gas Chromatograph industrialized by PerkinElmer in the United States was utilized to detect a variety of OCCs, including short chain carboxylic acid with carbon chain lengths ranging from C_2 to C_{16}, and aromatic and aliphatic hydrocarbon-based esters and compounds. An Agilent Technologies, USA, DB-FAT WAX UI capillary column, having dimensions as length and diameter of 30 m and 0.25 mm respectively, with film thickness of 0.25 μm, was employed. The oven was first set to a temperature of 40 °C for a duration of 4 min, following which it was raised to 240 °C incrementally at a rate of 5 °C per minute. Quantitative analysis was performed using calibration curves specific to respective compound. The obtained results were in μg/mL of total liquid media that were converted to g/kg of sample by using equation (1). In upcoming sections, the discussion will be based on OCCs instead of individual fraction.

$$\sum \mathrm{OCCs} = \frac{\mathrm{OCCs}\cdot V_{liq\_samp}}{m_{sample}\cdot 1000}\left[\frac{g}{kg_{waste}}\right] \qquad (1)$$

$\sum$ OCCs - sum of OCCs [g/kg $_{OCCs}$]
OCCs- OCCs in the liquid sample from oxidative liquefaction [μg/mL]
V_{liq_samp} – the volume of the liquid sample from oxidative liquefaction in [mL]
m_{sample} – mas of waste used to oxidative liquefaction [g]

2.3.3. Optimization of overall experimental process: maximum total solid reduction and oxygenated chemical compounds yield against minimum energy consumption

The research utilizes an analytical framework that integrates Pareto charts, predicted value profiles, and response surface contours, along with desirability analysis. The utilization of these graphical tools facilitates a comprehensive assessment of the influence of parameters on process outputs. Furthermore, P-values are employed in conjunction with ANOVA to investigate the intricate relationships that exist between independent and dependent variables. Details of process optimization have been documented, emphasizing the enhancement of TSR and OCCs yield alongside the reduction of energy consumption by Mumtaz et al.

3. Results and discussions

3.1. Ultimate and proximate analysis of municipal solid waste and personal protective equipment

Results from ultimate and proximate analysis of both waste types, i.e. MSW and PPEs, have been provided in Table 3.

In the context of Table 2, M^a, A^a, VM, C^a, H^d, N^a, S^a O^{diff} represent moisture content, ash content, volatile matter, carbon, hydrogen, nitrogen, sulfur content, and oxygen by difference, while ^{a} in superscript

Table 3
Ultimate and proximate analysis results of MSW and PPE samples.

Parameter, wt%	M^a	A^a	VM	C^a	H^a	N^a	S^a	O^{diff}
MSW	2.5 ± 0.2	15.1 ± 0.8	84.9 ± 0.3	50.3 ± 2.3	7.2 ± 0.2	1.1 ± 0.1	<0.5	23.3
PPE	0.1 ± 0.2	8.7 ± 0. 5	97.0 ± 3.8	80.1 ± 2.3	12.8 ± 0.6	0.17 ± 0.01	0.03 ± 0.00<0.03	0.0

represents "as analyzed". Analysis of PPE waste, primarily composed of various polymers, relative to MSW indicates significant differences in feedstock composition that may considerably influence the outcomes of the applied process. Referring Table 2, PPEs waste contained higher concentrations of volatile fractions and carbon content when contrasted with MSW, which comprises a heterogeneous blend of organic and inorganic materials, including food residues, paper products, and plastics. The elevated levels of volatile matter in PPE could lead to a more efficient conversion into liquid and gaseous products under oxidative conditions, consequently producing a greater amount of valuable oxygenated chemical compounds. Conversely, municipal solid waste is expected to present challenges stemming from its heterogeneous nature and the potential for elevated ash content, which can result in diminished reaction efficiency and the risk of product contamination. The fluctuation in carbon content represents a crucial variable. An elevated carbon content in PPE can enhance the generation of liquid chemical compounds, thereby improving the suitability of PPE for oxidative liquefaction aimed at the production of targeted chemicals.

3.2. FTIR analysis of municipal solid waste and personal protective equipment

The diverse chemical composition and different structural orientations of MSW and PPE wastes are suspected to significantly influence the final yield and quality of liquid products after the oxidative liquefaction process. Graphical illustration below depicts the variations in the FTIR spectra of both analyzed samples, highlighting the bands corresponding to vibrations from each group in the MSW and PPE samples, as shown in Fig. 2.

The FTIR spectrum of the MSW sample exhibited pronounced peaks at 2950, 2920, and 2850 cm^{-1}, which can be ascribed to C-H stretching vibrations in CH_2 and CH_3 groups, resulting from the degradation of lipids and hydrocarbons. A moderate-intensity peak observed at 1710 cm^{-1} is associated with C=O stretching vibrations, which are presumably sourced from cellulose fibers and organic matter. Furthermore, a prominent peak observed at 1460 cm^{-1}, succeeded by a distinct peak at 1380 cm^{-1}, correlates with the asymmetric and symmetric deformation vibrations of CH_3 and CH_2 groups, respectively. The peak observed at 1230 cm^{-1} was determined to originate from O-C-O stretching vibrations, suggesting the presence of aromatic ethers, hydrocarbons, or polysaccharides within the sample. Additionally, the broad band detected within the range of 1100–870 cm^{-1} substantiated the heterogeneous nature of the MSW sample. The observed range encompassed signals linked to silicates (Si-O-Si), aromatic ethers, polysaccharides (C-H vibrations), and a combination of plastic materials, thereby reinforcing the multi-material composition of the sample [45].

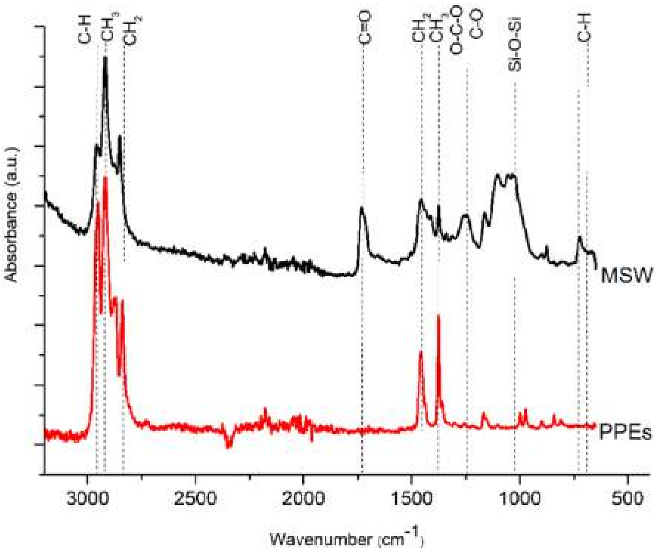

Fig. 2. FTIR spectra of MSW and PPEs.

The FTIR spectrum of the PPE sample exhibited distinct bands that are typically linked to polypropylene (PP). Significant peaks observed at approximately 2950 and 2920 cm^{-1} were associated with the antisymmetric stretching vibrations of CH_3 and CH_2 groups. In contrast, the less intense peaks at 2890 and 2850 cm^{-1} were attributed to the symmetric stretching vibrations of these identical groups. A prominent and significant band observed at 1460 cm^{-1} has been linked to in-plane antisymmetric deformation vibrations of CH_2, whereas the band located at 1380 cm^{-1} has been designated to in-plane symmetric deformation vibrations of CH_3 [46].

3.3. Inverse analysis of process heating

During the oxidative liquefaction of MSW and PPE, temperature profiles based on inside reactor temperature have been shown in Fig. 3 (a). The overall pattern of heating profiles for tested waste materials is the nearly same, but this pattern significantly varies from the heating profile recorded for dummy runs with water only. After 20 min of the experiment, the intersection of heating profiles can be observed (Fig. 3 (a), enlarged). After that, an additional temperature bump appeared for tested wastes and dummy run with oxidant, which is an indication of additional heat added to the system that was absent during the dummy runs with water only. The situation can be observed more clearly in Fig. 3(b), where the heating rates were plotted against the inside reactor temperature. No sharp peak with significant height can be observed for a dummy run with water, highlighting the uniform heating rates. For dummy run with oxidant, a sharp peak can be observed from 110 to 140 °C. But for a modeled run with MSW, two adjacent peaks at 90–120 °C exhibiting the higher heating rates of 1–1.5 K/s appeared while for PPEs, a single large peak with a heating rate of 5 K/s is observed around 130–150 °C. The appearance of these peaks with enhanced heating rates is an indication of the decomposition of oxidant + waste materials under the oxidative liquefaction process. It is assumed that during the temperature ranges at which these extended peaks appeared, a major portion of waste together with oxidant is decomposed, exhibit an exothermal behavior and additional heat is added to the system that results extend heating rates that were absent during the dummy run with water only. Additionally, to achieve the same temperature of 250 and 200 °C the oxidative liquefaction reaction of both types of waste (MSW and PPEs) finished 12–14 min earlier than the time recorded for the dummy run with water, which also indicates the supply of additional heat.

This additional heat is calculated using the following equation (2):

$$dQ = mCv(T)dt \tag{2}$$

Where dQ stands for change in internal energy of system in joules (J), containing the mass (m) of substance in grams, with specific heat at constant volume (C_v) in (J/g. K), over the temperature interval dT,

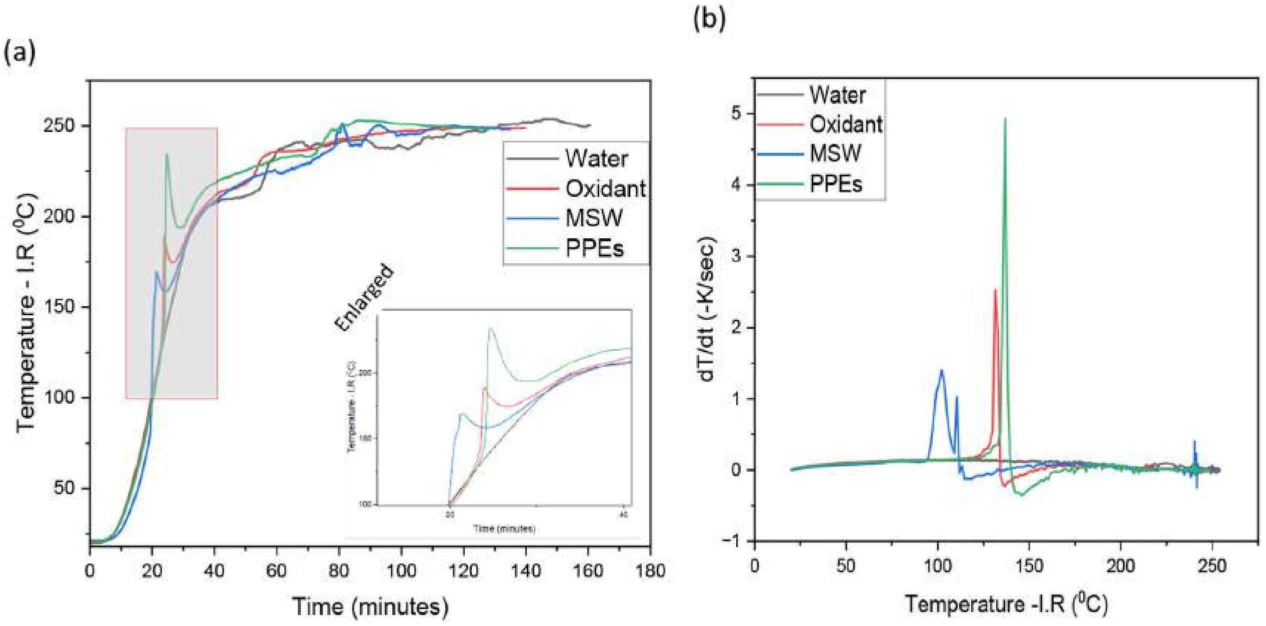

Fig. 3. Comparison of (a)inside reactor temperature profiles (b) heating rates for MSW and PPEs.

measure in K. During these calculations, the following assumptions were made.

(i) Molar specific heat for solid waste at constant pressure $C_p \approx C_v$,
(ii) Temperature based approximation of C_v for both water and oxidant,
(iii) PPEs waste mostly consists of equal proportions of rubber, polypropylene (PP), polyethylene (PE) polyester (PET).

Integration of the energy equation (i) based on the mass of reactants and specific heats at constant volume and changing temperatures over the whole reaction period helped to calculate the heat of the reaction. As the heating of water is completely endothermic, the heating power absorbed during the dummy run with water is considered the baseline for showing the heating behavior of waste materials. Heating power absorbed during the dummy runs with water calculated on the basis of equation (i) using the interpolation method for the value of C_v of water was 66 ± 1.1 W at 200 °C & 86.13 ± 0.75 W at 250 °C. To achieve the same temperature level of 200 °C & 250 °C, heat absorbed during the modeled run with PPEs waste was 53.38 ± 0.21 W & 67.78 ± 0.82 W calculated based on assumptions (i) and (iii), while the absorbed heat for MSW was 55.31 ± 0.47 W & 68.30 ± 0.94 W also calculated based on assumption (i) and using the cp value of 2 J/g.k already reported in the literature [47]. The absorption of less heating power as compared to dummy runs with water indicates that this time an additional 10.69 ± 0.63 W & 17.83 ± 0.19 W for MSW and 12.6 ± 0.89 W &18.35 ± 0.07 W for PPEs is provided by the reaction itself. So, it can be said that the oxidative liquefaction of MSW and PPEs is exothermal over a specific temperature range as compared to heating water, but it is not exothermal overall to continue the reaction on its own.

3.4. *Comparison of total solid reduction for municipal solid waste and personal protective equipment*

The extent of TSR attained for both MSW and PPEs is illustrated in Fig. 4. This figure depicts the varying levels of tested parameters—minimum, average, and maximum levels—along the x-axis, with TSR represented on the y-axis. The maximum TSR for MSW was observed in experiment 7, reaching a 95 % reduction at a temperature of 300 °C (1), with an oxidant concentration of 60 % (1) and a waste-to-liquid ratio of 3 (−1). The achievement was realized with an energy consumption of 1.4 kWh. The maximum TSR for PPEs waste was recorded in experiment 7 also, achieving a reduction of 96.67 % under the same conditions as MSW, with a slightly reduced energy consumption of 1.2 kWh.

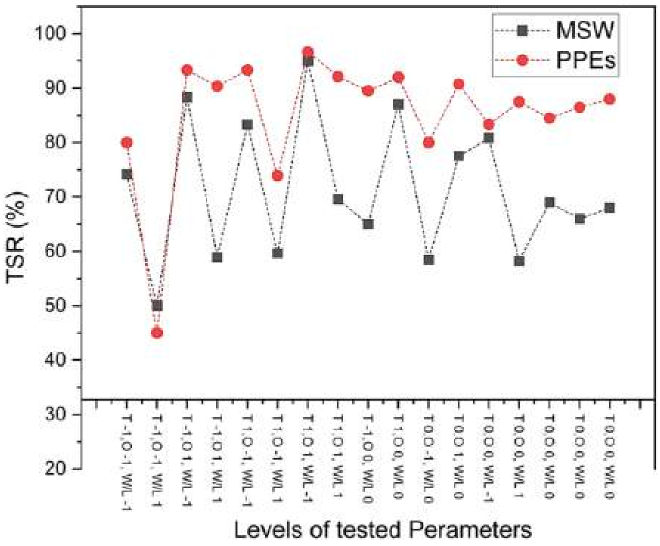

Fig. 4. Comparison of % total solid reduction achieved for MSW and PPEs.

The analysis revealed an increase in TSR for both MSW and PPEs waste as temperatures and oxidant concentrations were elevated. This suggests that elevated temperatures and an increased presence of reactive oxygen facilitate the breakdown of organic materials, leading to a more significant reduction in solid matter. The optimal waste-to-liquid ratio identified is approximately 3, which demonstrates the highest efficacy in enhancing TSR, as evidenced by the findings in Experiment 7 for both types of waste. This ratio likely indicates a balanced state that ensures sufficient reactant availability alongside conducive heat and mass transfer conditions.

The waste generated from PPE predominantly consists of plastics like PP, PE, and PVC, exhibiting a more uniform degradation trend compared to the heterogeneous makeup of MSW. These unique thermal degradation pathways are effectively utilized under the conditions studied, particularly at high temperatures and oxidant concentrations, resulting in more complete decomposition and enhanced TSR relative to MSW. Higher ash content indicated from proximate analysis, some organic fractions, for example, cellulose from wood can be converted to char than liquid products which can reduce TSR for MSW. In addition, the existence of heteroatom in MSW acting as impurity can hinder the oxidant catalytic capacity and overall heterogenicity of the sample can result in uneven reaction dynamics i.e., some fractions are not completely reacting under the same reaction conditions.

The experiments underscore the importance of refining operational parameters to improve TSR while managing energy consumption. The waste generated from PPE consistently exhibits a higher TSR compared to municipal solid waste across different conditions, highlighting the impact of waste composition on the effectiveness of oxidative processes. The results demonstrate that targeted adjustments to temperature, oxidant concentration, and waste-to-liquid ratio can significantly enhance waste reduction outcomes, particularly for consistent waste streams like PPE. This offers critical insights for enhancing and refining waste treatment methodologies within the context of environmental preservation and sustainability efforts. Random repetitions of experiments were performed, and standard deviations were in the range of 0.58–1.76 for MSW and 0.5 to 3.53 for PPEs, which ensured the technical repeatability of results.

3.5. Quantification of liquid compounds yields resulted from oxidative liquefaction of municipal solid waste and personal protective equipment

Based on Fig. 5 oxidative liquefaction of MSW results in the production of OCCs lying in the range of 13.04–51.51 g/kg $_{\text{of MSW}}$ while this range was quite higher (37.43–212.66 g/kg $_{\text{of PPEs}}$) for the liquid products obtained from processing of PPEs. The findings reveal notable variations in the production of OCCs when comparing MSW to PPEs sourced from the medical sector, particularly during oxidative liquefaction across different conditions. The influence of temperature on both categories of waste was significant. In the context of PPE, it was noted that elevated yields were recorded at reduced temperatures, specifically at 200 °C, while a decrease was evident at increased temperatures, such as 300 °C. This decline is presumably attributable to the decomposition of oxygenated compounds into gaseous forms at elevated temperatures. In a similar manner, MSW exhibited diminished yields at elevated temperatures, yet its total generation of oxygenated compounds remained consistently lower than that of PPE. This discrepancy can likely be attributed to its heterogeneous composition and the inclusion of non-reactive materials such as glass and metals.

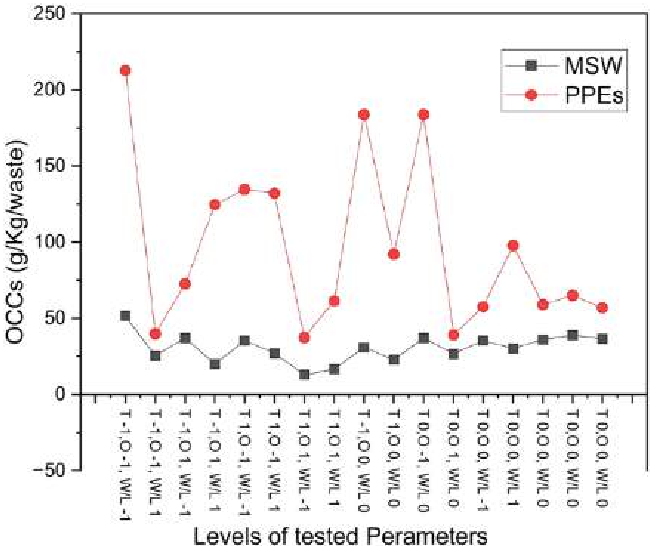

Fig. 5. Yields of oxygenated chemical compounds obtained for MSW and PPEs.

The concentration of oxygen had a significant impact on the results observed. In the context of PPE, reduced oxygen levels (30 %) resulted in enhanced yields when contrasted with 60 % oxygen, indicating that an excess of oxygen may have led to over-oxidation, which in turn contributed to the degradation of oxygenated products. A comparable pattern was noted for MSW, indicating that elevated oxygen levels diminished the yield, albeit the impact was less significant than that observed for PPE. The ratio of H_2O to waste had a significant effect on the yields observed. Increasing the ratio from 3:1 to 7:1 reduced the production of oxygenated compounds for both waste types, less availability of reaction media reduced the efficiency of the oxidative liquefaction process. At a temperature of 200 °C, a notable decrease in the yield of oxygenated compounds for PPE was observed as the water ratios increased.

In the comparison of the two waste types, it was observed that PPE consistently yielded significantly higher results than MSW under all tested conditions. This observation can be linked to the uniform composition of PPEs, which is predominantly made up of synthetic polymers that exhibit significant reactivity in oxidative environments. The variability present in MSW, characterized by a combination of organic and inorganic components, constrained its conversion efficiency and diminished the output of oxygenated products. The results underscore the significance of refining reaction parameters, including temperature, oxygen concentration, and H_2O/waste ratio, to enhance the yield of valuable compounds, with PPE showing increased potential for effective processing in these scenarios.

Overall higher production of OCCs from PPEs can be attributed to the more straightforward composition of PPE and the regulated nature of the oxidation process involved. The heterogeneity of MSW results in the occurrence of competing side reactions, incomplete oxidation processes, and the secondary degradation of oxygenated intermediates. Furthermore, MSW may encompass constituents such as various metals that can initiate undesirable side reactions, thereby hindering the yield of (OCC). Hydrogen peroxide exhibits a higher efficiency in the oxidation of PPE polymers, whereas the diverse fractions of MSW experience intricate transformations that restrict the formation of OCCs.

3.6. Identification and comparison of optimal reaction conditions for municipal solid waste and personal protective equipment

Optimizing experimental conditions for both PPEs and MSW revolved on three key parameters: temperature, oxidant concentration, and waste-to-liquid ratio, with pressure and residence time held constant (Fig. 6). Regarding PPE, the ideal conditions were defined by red dashed lines. These lines show that although raising the temperature enhances TSR, it causes a minor drop in the production of OCCs and leads to a linear rise in energy consumption. An inverse correlation exists between energy use and temperature, indicating that lower temperatures are more favorable in terms of energy efficiency. Decreased levels of oxidants promote the formation of OCCs by minimizing excessive oxidation. An ideal scenario involves a low waste-to-liquid ratio, as it allows for full reactions to occur without a notable increase in energy consumption, due to the reduced amount of waste per unit volume of liquid.

Regarding MSW, it was noted that the same patterns were evident about temperature, with lower values being more desirable to optimize the trade-off between energy consumption and the production of oxygenated compounds. Nevertheless, the average levels of oxidant were considered to be ideal in order to achieve a balance between TSR and the production of oxygenated compounds, highlighting the necessity of making a compromise between both results. Similar to PPEs it is ideal to have lower waste-to-liquid ratios, as higher liquid content might lead to increased energy consumption per unit weight of waste. This research underscores the need to meticulously balance operational

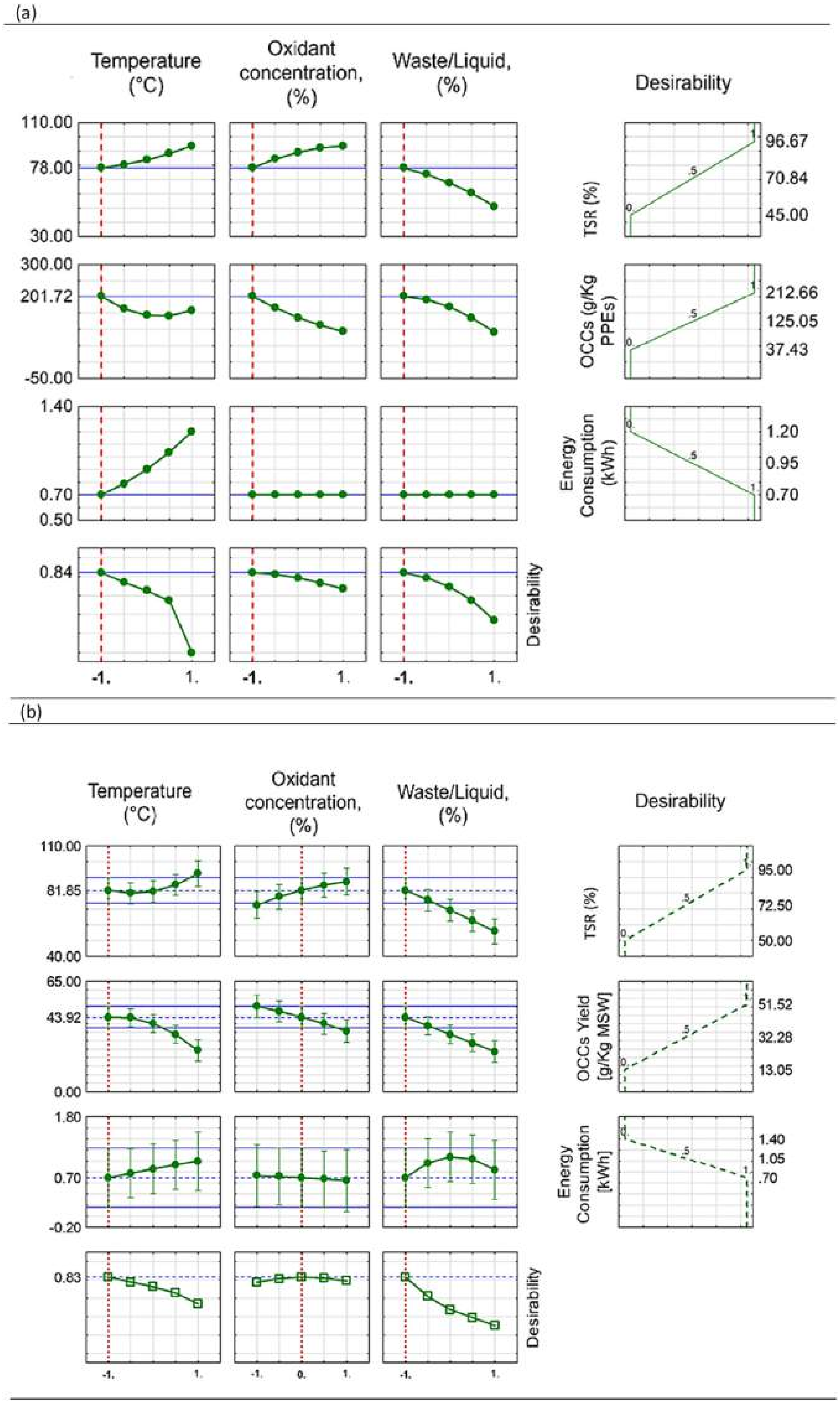

Fig. 6. Identification of optimal reaction conditions for (a) PPEs and (b) MSW.

factors in order to enhance results for waste processing. Based on Fig. 6 the optimal reaction condition for oxidative liquefaction of MSW and PPEs waste, with the aims maximum TSR and OCCs yields against the minimum energy consumption have been shown in Table 4.

4. Practical implications of study

The oxidative liquefaction has proved to be a promising approach for the potential waste valorization of MSW and PPEs. Nonetheless, various challenges must be considered to facilitate its large-scale application.

The heterogeneous composition of MSW presents a significant challenge, as it encompasses a variety of polymeric and organic fractions that may exhibit distinct reactions under oxidative conditions. The observed variability has the potential to influence process efficiency, yield, and the consistency of the final products.

In contrast to pyrolysis, oxidative liquefaction exhibits significantly lower energy demands. Nonetheless, the optimization of reaction conditions is critical for enhancing energy efficiency and achieving superior conversion rates. Investigations should focus on the optimization of catalytic enhancements and the development of process control strategies aimed at maximizing efficiency while concurrently minimizing energy input.

The generation of gaseous emissions during oxidative liquefaction is predominantly attributed to the over-oxidation of intermediate products, rather than the formation of toxic by-products. Consequently, subsequent investigations ought to concentrate on the mechanisms of reaction control to mitigate over-oxidation and enhance selectivity for preferred liquid products. Furthermore, the optimization of reaction parameters has the potential to improve the overall yield while simultaneously minimizing the production of undesirable gaseous emissions.

A critical component of forthcoming investigations pertains to the design of reactors and the scalability of processes. The advancement of continuous-flow reactors featuring meticulous regulation of temperature and oxygen levels has the potential to significantly improve process efficiency and ensure product consistency. Furthermore, investigations should concentrate on reactor materials and configurations that enhance heat distribution and mixing, thereby ensuring uniform reactions throughout the feedstock.

In order to establish industrial viability, it is imperative that further investigations be undertaken regarding the recovery of products and the potential applications of the liquid fraction derived from oxidative liquefaction. It is imperative to investigate potential applications in fuel production, chemical feedstocks, and material recovery. Additionally, conducting life cycle assessment (LCA) studies will be essential to evaluate the associated environmental and economic benefits.

5. Conclusions

The thorough comparative investigation of the oxidative liquefaction of MSW and PPEs, supplemented by ultimate and proximate analysis, and inverse analysis of process heating, disclosed unique features favorable to waste valorization. The higher carbon and volatile matter content highlighted by the elemental analysis resulted in a higher potential for conversion into secondary carbon compounds and energy-rich products for PPEs while inorganic fractions in MSW were suspected to limit the process efficiency. Inverse analysis of process heating showed that the oxidative liquefaction process for both MSW and PPEs is exothermic during the intermediate half of the reaction where most of the (waste + oxidant) decomposition takes place providing sufficient oxygen for oxidative liquefaction of the sample, but the release of energy is not high enough to carry out the whole reaction on its own. The TSR results highlighted PPE's better capacity for reduction due to higher volatile content than MSW, and also the OCC yields confirm PPE's favorable carbon profile for producing oxygenated liquid compounds. Temperature increases have a more prominent linear effect on TSR for PPEs, MSW also experienced higher TSR with increasing temperature, but higher temperatures result in degradation of intermediate products reducing the overall OCCs yield for both types of wastes. Oxidant concentration is important to achieve the suitable TSR but higher concentration results in overoxidation affecting the OCCs yield. The waste-to-liquid ratio is also an important parameter governing the process efficiency, as lower waste-to-liquids ratios ensure better mixing, enhanced mass transfer of oxidative species, proper dilution, and even heat transfer across waste samples. Optimal reaction conditions, which prioritize lower temperatures, oxidant concentrations lower for PPEs and intermediate for MSW, and low waste-to-liquid ratios offer an efficient pathway for oxidative degradation of different kinds of waste with minimum energy consumption against maximum resource recovery. The findings of this study underscore the necessity for continued progress in the domains of process optimization, reactor design, and waste feedstock management. Subsequent investigations ought to prioritize scalable methodologies, economic viability, and regulatory frameworks to effectively incorporate oxidative liquefaction within circular economy paradigms.

Table 4
The optimal parameters for treating MSW and PPEs under oxidative liquefaction.

	Temperature, (°C)	H_2O_2 Concentration (wt. %)	Waste-to-Liquid ratio (wt.%)
PPE	200	30	3
MSW	200	45	3

During the experimentation the pressure was kept constant to 30 bar and reaction time for 45 min.

CRediT authorship contribution statement

Hamza Mumtaz: Writing – original draft, Visualization, Validation, Software, Investigation, Data curation, Conceptualization. **Szymon Sobek:** Writing – review & editing, Methodology, Conceptualization. **Marcin Sajdak:** Writing – review & editing, Formal analysis. **Roksana Muzyka:** Writing – review & editing, Formal analysis. **Sebastian Werle:** Writing – review & editing, Funding acquisition.

Data availability

All the data used in developing this study will be made available on request.

Declaration of competing interest

I on the behalf of all authors, declare that there is no conflict of interest and all the elements of the submission are also in compliance with the journal publishing ethics. By submitting this manuscript, the authors agreed that the copyright for their article should be transferred to this journal if the article is accepted for publication. The work contained within the research paper is our original contribution and has not been published anywhere.

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Appendix G

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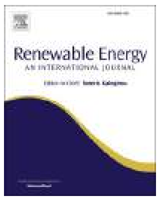

Innovative recycling of end-of-life photovoltaic panels with the aim of polymer degradation and valuable chemical production

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ABSTRACT

Recycling end-of-life photovoltaic (PV) panels is challenging, as multiple-layer structure makes separation and material recovery processes complex and resource-intensive. This study embarks on an innovative chemical recycling technique based on the liquefaction of organic fractions of PV panels in an oxidative environment. Thermogravimetric analysis (TGA) of virgin PV waste showed the mass loss in three stages, with residual mass left in the range of 32–40 %. During oxidative liquefaction following a well-constructed experimental (Central Composition and Fractional Factorial) design effects of three different parameters, including temperature ranging from 200 to 300 °C, hydrogen peroxide serving as an oxidant (30–60 % overall volume of liquid), and the waste-to-liquid ratio of 12.5–37.5 %, were studied. Total polymer degradation (TPD) was calculated in the range of 20–100 %. The liquid fraction obtained after the process was analyzed through gas chromatography with flame ionization detection (GC-FID), to quantify the yield of oxygenated chemical compounds (OCCs). Fourier transform infrared spectroscopy (FTIR) analysis identified various structural modifications and the degradation of polymeric components. An inverse analysis of the process heating behavior was performed to identify the temperature span over which degradation of polymers occurs and specify the nature of the reaction (exothermic or endothermic). An analysis of variance ANOVA was performed to identify the optimal values of parameters supporting maximum TPD and OCCs yield against the minimum energy consumption, a meaningful input for a potential scale-up of the PV panel recycling technique.

Symbols
M – moisture content, wt.%
A – ash content, wt.%
VM – volatile matter, wt.%
C – carbon, wt.%
O – oxygen, wt.%
H – hydrogen, wt.%
N – nitrogen, wt.%

Superscripts
^{a} – analytical state
^{d} – dry state
$^{diff.}$ – calculated as difference

1. Introduction

Photovoltaic (PV) panels have gained significant attention in recent years due to their pivotal role in the worldwide shift towards renewable energy production and can be linked to the interplay of various factors. The utilization of energy across its various forms plays a crucial role in the economic and social advancement of societies, as well as in the daily lives of individuals. The technological advancements and societal structures towards a non-fossil fuel-based society is garnering significant attention. It has become increasingly evident that the energy consumption patterns observed in recent decades are unsustainable, primarily due to the depletion of fossil energy resources and the consequential impact of this consumption on climate change [1]. The energy sector plays a crucial role in addressing climate change, as it is responsible for approximately two-thirds of global carbon dioxide emissions. After 2020, the total proven energy reserves of the primary

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fuels—namely oil, natural gas, and coal—indicated a potential duration of 53.5 years for oil, 48.8 years for natural gas, and 139 years for coal. Fossil fuels constitute 85 % of the total primary energy consumption on a global scale [2]. The contemporary period is confronted with the significant challenge of global warming, which stands as the foremost environmental concern. Consequently, the reduction of carbon emissions has become a focal point of international environmental policy. Thus, the energy sustainability, targets set by Paris Agreement, energy for sustainable development, decarbonization plans, and efforts towards reduced CO_2 emission, all set a roadmap for renewable energy sources adoption.

Solar energy, among available renewable resources, presents numerous benefits including energy security, reliability, efficiency, and environmentally benign, with extensive potential for worldwide distribution [3]. Solar energy, particularly photovoltaic (PV) technology, has emerged as a subject of significant global interest. The utilization of photovoltaic power has surged over the past few decades, contributing to the global initiative to enhance clean energy production, and it offers significant market potential. Photovoltaic power is anticipated to generate a substantial share of global energy consumption and to emerge as a principal energy source in this century [4]. In the recent past the total installed PV capacity worldwide ranged from 1.4 GW in 2000 to over 102 GW in 2012, including over 70 GW in Europe, 8.3 GW in China, 7.77 GW in the US, and 6.9 GW in Japan. From year 20007, the production of PV solar energy had increased by 60 %, while wind energy and hydroelectricity had grown by 25 % and 3.3 %, respectively and this growth is still progressing [4]. Research findings predicted that the global capacity for solar photovoltaic power generation was expected to reach almost 600 GW and fast-rising China would continue to dominate the world in solar PV execution by a wide margin and hold almost 40 % of installed PV capacity in 2023, with solar PV capacity installations surpassing all other renewable energy inventions and technologies combined in future. The fastest-growing rising country, India, who's RE capacity would treble, is expected to overtake the United States of America as the second-largest market for solar PV growth [5].

PV panels can be divided into four generations depending on their production method. The first generation, which is silicon-based, and the second generation, which is thin-film cells, are widely used commercial PV panels, while the third and fourth generation cells are still in the experimental stage [6,7]. Crystalline silicon is 92 % more abundant than the other mentioned varieties due to its superior efficiency and lower manufacturing costs [8,9]. The performance degradation rate of PV modules operating under various environmental conditions ranges from 0.58 % to 0.83 % annually [10,11]. A PV module is deemed end-of-life (EOL) after 25–30 years of operation when actual power is less than 20 % of its rated power [12]. Based on this principle according to International Renewable Energy Agency (IRENA) by 2030, 1.7–8 million tons of PV panels while till 2050, when installed capacity will reach 4500 GW, 60 to 78 million tons of photovoltaic panels will be needed to be scrapped [13].

Silicon-based PV panels have complicated and multiple-layer sandwich structure that has an outer aluminum frame supporting and securing internal components. From bottom to top it consists of:

1. Back sheet, made up of different polymers mostly fluorinated polymers [14,15].
2. Encapsulate mostly ethylene vinyl acetate (EVA), helping solar cells to adhere to tempered glass and back sheet. It also prevents solar cells from moisture and accidental damages [16].
3. At the middle, there are solar cells with an antireflective layer on top [17].

The originating predominance of PV panels in the energy production sector, no doubt is a notable accomplishment in fostering ecological sustainability, but the complex composition presents a crucial challenge of efficient waste management after their EOL phase [18].

Regulatory framework and policies, environmental concerns, factors affecting economic implications, the existing technology and infrastructure along with geographic and resource considerations, as well as the dynamics of the industry and market, are the factors that play critical roles in the selection of effective recycling techniques for EOL PV waste [19–22].

Depending upon the final goals, various waste management techniques, including landfilling, mechanical recycling or physical separation, and thermal or chemical treatments, have been adopted to manage the complex waste from EOL PV panels. The materials that constitute photovoltaic panels encompass a range of valuable elements, including silicon, silver, and indium [23]. The disposal of these panels in landfills results in the loss of valuable resources and represents a significant oversight in the potential to recover and repurpose these valuable materials for the manufacturing of new panels [24]. The reduction of available resources compels an escalation in resource extraction activities, which may subsequently lead to an increase in production costs. In Physical separation or mechanical recycling, the PV panels are dismantled parts by parts starting from aluminum frame [15,25]. Nevala et al. introduced electrohydraulic shredding (EHF) as a viable alternative to traditional shredding methods. The procedure involves the insertion of photovoltaic c-Si pieces (12 cm × 18 cm) into the EHF reactor, which is filled with water. This setup facilitates the detachment and fragmentation of the photovoltaic layers through the application of shock wave technology, thereby enhancing selectivity by concentrating the target metals into defined particle size fractions. This process demonstrates significant potential for the preparation of materials intended for the subsequent extraction of valuable metals [26]. Song et al. utilized high-voltage pulsed discharge in water, referred to as high-voltage fragmentation (HVF), under various discharge circumstances as a recycling method for polycrystalline c-Si solar panels [27]. Li et al. reported the mechanical recycling of EVA by irradiation through an infrared fiber optic pulsed laser. The laser traversed the rear of the EVA to access the solar cell/EVA contact [28]. Lovato et al. examined the efficacy of supercritical fluid technology in the delamination of solar panels, targeting the recovery of high-value components like Ag, Si, Pb, polymers, and glass. The process employed supercritical carbon dioxide ($ScCO_2$) in conjunction with toluene and ball milling [29].

Pyrolysis is well mature waste management technology that involves a thermal degradation of specific waste in an inert atmosphere that enables the breakdown of long-chain polymers into valuable secondary compounds, including monomers and oligomers [30]. Xin Chen and colleagues conducted a comprehensive study on kinetics of the (co–) pyrolysis, characterization of thermodynamic products, and degradation pathways associated with PV encapsulant and back sheet materials. The EPV pyrolysis process encompassed side-chain scission occurring within the temperature range of 262–392 °C, subsequently leading to main-chain breakdown between 392 and 518 °C, which resulted in the release of acetic acid and hydrocarbons [31]. Pablo Dias et al. mentioned in their study, that the recycling process of photovoltaic modules typically initiates with the extraction of the polymeric ethylene-vinyl acetate (EVA) resin through pyrolysis, a method that facilitates the recovery of valuable materials including silicon, copper, and silver. The implementation of pyrolysis, however, requires enhancement due to its significance. This research involved the characterization of polymers in photovoltaic modules through Fourier transform infrared spectroscopy (FTIR), alongside an investigation and optimization of the pyrolytic removal of EVA resin [32]. Various other studies have also been reported in the recent past using thermal [33–35] or chemical methods for recycling the PV waste [35–37]. These already existing and traditional recycling methods encounter several constraints, including toxicity, cost-effectiveness, quality degradation, and issues related to environmental pollution.

The objective of current research is to introduce an innovative technique in the field of PV waste recycling, titled "oxidative liquefaction" which comprises the mixing of PV waste in the form of chips, with water (H_2O) and oxidant, hydrogen peroxide (H_2O_2) in this case, and heating the mixture at suitable temperatures for subsequent amount of heating periods. PV waste before being subjected to experimentation is analyzed through ultimate and proximate analysis, FTIR, later thermogravimetric (TG) and derivative TG analyses were performed to study the response of PV waste against the increasing heating rates and to identify the existence of more than one polymeric compound. Based on well structured experimental design oxidative liquefaction experiments were performed and through recorded inside reactor temperature profiles, inverse analysis of process heating (IHA) was performed to highlight the major degradation stage of oxidant and waste and to identify the nature of the reaction. Total polymer degradation was calculated and resulted oxygenated chemical compounds (OCCs) were analyzed to identify the composition and yield. Energy consumption during each experiment was recorded and analysis of variance (ANOVA) was performed, optimal reaction conditions were identified for oxidative liquefaction of PV waste to ensure the best process outputs against minimum resource consumptions justifying the viability of oxidative liquefaction process.

2. Materials and methods

2.1. Materials used in the study

In the current study, the focused waste material was EOL PV waste obtained from the local market in the form of damaged PV panel. This panel was cut into pieces of 6 inches × 6 inches by using an electrically powered circular saw. Due to the dimensional limitation of the reactor, pieces of PV panels are converted to chips of size 1 cm × 1 cm using mechanical scissors. Small sizes of chips are suitable to obtain high area-to-volume ratios (waste-to-liquid). H_2O_2 solution (40 %) obtained from Chemland company is used as an oxidant, while 95 % pure nitrogen is supplied to obtain the initial pressure.

2.1.1. Elemental analysis of end-of-life photovoltaic (PV) panels

The elemental composition of PV waste materials was analyzed through ultimate and proximate analysis using LECO TruSpec CHN and SC 632 analyzer. The elements like carbon (C), hydrogen (H), and nitrogen (N) were quantified using the CHN analyzer, whereas SC 632 analyzer was used to analyze the sulfur (S) content. The moisture, volatile matter, and ash content were quantified through a conventional gravimetric technique. The standards used during the analysis process have already been published by Mumtaz et al. [38].

2.1.2. Scanning electron microscope (SEM) and energy dispersive system (EDS) analysis of raw PV sample before experimentation

The surface morphology of raw PV samples was examined utilizing SEM in conjunction with an EDAX/Octane Elect Plus X-ray energy dispersive system (EDS). The current study utilized SEM with model details: the FEI/INSPECT S50, sourced from Hillsboro, Oregon, USA. The incident electron acceleration voltages in basic SEM operations were recorded at 5 kV and 15 kV while the pressure within the chamber was approximately 10^{-7} mbar. The test results presented in the later section should be regarded as the aggregate of all elements isolated from the PV and analyzed, with a total of approximately 160 measurements conducted. The findings are expressed in atomic percent.

2.1.3. Fourier transform infrared spectroscopy (FTIR) of raw PV panels before experimentation and after oxidative liquefaction

FTIR analysis was conducted using a Nicolet iS50-TRACE 1300 ISQ 7000 spectrometer (Thermo Scientific, USA) within a wavenumber range of 650–3200 cm^{-1} with a resolution of 0.05 cm^{-1}. Measurements were performed at room temperature, with an average of 21 measurements taken for each sample. Data acquisition utilized the attenuated total reflection (ATR) technique. Each sample was pressed onto a single-reflection diamond crystal. Spectral processing was carried out using OMNIC software, version 9.

2.1.4. Thermogravimetric analysis of end-of-life photovoltaic (PV) panels

The temperature range over which thermal deterioration of PV panels is investigated was 30–800 °C. To ensure a comprehensive analysis, the heating rates were systematically varied at 2, 4, 8, and 16 K/min. The experiment was conducted under controlled conditions to maintain an inert atmosphere. This was achieved by carefully regulating the flow of argon gas at a constant rate of 35 cm^3/min. The details of instrumentation and used standards have already been published [39].

2.2. Details of the experimental section

2.2.1. Experimental detailed setup for oxidative liquefaction end-of-life photovoltaic (PV) panels

The oxidative liquefaction process was conducted using a 500 mL batch reactor (Parr Instruments series 4650, Parr Instr., IL, USA). The precise temperature control in this reactor was achieved by utilizing a Parr 4838 reactor controller. The high-temperature spiral heater allowed for temperatures to be reached as high as 800 °C. Complete details about the setup, readout and setpoint resolution, and accuracies have already been published elsewhere [40].

2.2.2. Details of the experimental design framework

The influence of key factors on the oxidative liquefaction process was statistically evaluated through the implementation of seventeen experiments, excluding random repetition. These experiments were conducted using a central composite design (CCD) and a fractional factorial design (FFD) to ensure robust statistical analysis. The study primarily investigated three crucial variables: reaction temperature, waste-to-liquid ratio expressed as a percentage, and oxidant concentration. Based on previous experience with the minimal effect of initial pressure and reaction time on the process, these factors were kept constant during the experimental investigation.

2.2.3. Sample preparation protocols for oxidative liquefaction of end-of-life photovoltaic panels

Sample Preparation and Reactor Loading: The pre-processed end-of-life (EOL) photovoltaic (PV) panel material (see the materials section) was introduced into glass liners with a subsequent amount of H_2O and H_2O_2 placed inside the Parr series 4650 batch reactor. The reactor was subsequently sealed to establish an impermeable environment. It is of utmost importance to maintain an initial pressure of 30 bar to ensure that the reaction mixture remains in a liquid state throughout the entirety of the process. After the process of pressurization, the reactor underwent a monitoring period of 30 min to confirm its absolute airtightness.

2.2.4. Reaction conditions and monitoring

The reactor was subsequently subjected to heating using the high-temperature spiral to attain the target reaction temperature, as specified in the experimental design (Table 1). The temperature was carefully controlled and kept constant throughout the entire duration of the reaction, which lasted for a precise period of 45 min. The experiment involved the utilization of six thermocouples, which were strategically placed in sets of two at three distinct locations: the reactor surface, interior, and heating spiral. These thermocouples were employed to

Table 1
Details of tested parameter levels for PV waste.

	Levels of tested parameters		
	Lowest (−1)	Average (0)	Highest (1)
Temperature (°C)	200	250	300
Waste-to-liquid ratio (%)	12.5	25	37.5
Oxidant concentration (%)	30	45	60

effectively monitor and record temperature data throughout the duration of the experiment.

2.2.5. Post-reaction processing and sample collection

Following the predetermined duration of the reaction, the heating element was deactivated, and the reactor was left to undergo natural cooling until it reached the surrounding temperature. After the reactor had cooled, it was depressurized and cautiously opened. Subsequently, the reaction mixture was subjected to filtration to separate the liquid and solid constituents for further analysis. Fig. 1 provides a comprehensive depiction of the whole experimental strategy.

2.2.6. Study of heating behavior and inverse analysis of the process of heating

In order to investigate the thermal behavior and to determine the temperature range associated with significant PV waste decomposition during the oxidative liquefaction process, a series of experiments were conducted. The study focused on modeled reactions conducted at a temperature of 200 °C and 250 °C, with remaining parameters at optimal levels determined in later sections. The temperature within the reactor, referred to as the reaction temperature, was systematically observed at intervals of 10 s during the entire duration of the reaction. Additionally, two dummy runs (without waste) were carried out to replicate the modeled reaction:

Dummy run 1: Oxidant + Water: The purpose of this experimental condition was to investigate the influence of the oxidant on the thermal profile while excluding any waste material from consideration.

Dummy run 2: Water Only: The implementation of this dummy run aimed to create a reference temperature profile, effectively simulating a purely endothermic phenomenon characterized by the heating of water, without the influence of any additional chemical reactions that might lead to the release or absorption of heat.

The temperature profiles of the modeled reaction, along with those from both dummy runs, were plotted over time to illustrate their distinct heating behaviors. To have a clearer insight into temperature behaviors inside the reactor the rate of temperature change (dT/dt - K/sec) for modeled runs and dummy runs was plotted against the internal reactor temperature measured in °C. Very clear and distinct peaks related to heating rates are observed for the modeled reaction profiles as compared to heating profiles of dummy runs. The identification of these supplementary peaks suggests the release of thermal energy due to exothermic reactions occurring during the modeled reaction with waste material, a phenomenon absent in the control experiments.

2.3. Product analysis

2.3.1. Total polymer degradation (TPD)

After opening the batch reactor the mixture of solid fractions mostly inorganic (glass) and liquid is obtained. This mixture is filtered and liquid fractions are stored for further analysis. The obtained solid fraction was dried in an oven at 105 °C for 8 h. After the completion of the drying process, the solid fraction is weighed and Total polymer degradation was calculated as (i)

$$TPD = \frac{m_i - m_f}{m_i(1 - A)} \cdot 100\% \tag{i}$$

where m_i is the initial mass of the waste and m_f is the final mass of the solid fraction after drying and A is the ash content.

2.3.2. Quantification of OCCs through liquid product analysis in GC-FID

The liquid products obtained are subjected to analysis through gas chromatography employing flame ionization detection methodology. The comprehensive information regarding the instrumentation has been previously documented by Mumtaz et al. [40].

2.3.3. Process optimization for maximizing the TPD and OCCs yield against the minimum energy consumption

The experimental data obtained after detailed experimentation was subjected to in-depth statistical analysis, and a comprehensive framework was used to optimize the overall oxidative liquefaction process. The enhanced framework was implemented through the integration of specific techniques:

Pareto charts of standardized effects. These charts help us to identify the parameters that have the most significant effect on the overall process and assist in the prioritization of optimization efforts.

Profiling of predicted values. The current methodology proved to be an effective way of comparison between the anticipated and observed values of response variables, thus providing insight into the model accuracy and possible areas that can be subjected to specific improvements.

The desirability function and response surface contours. The desirability function and response surface contours are utilized to visually illustrate the overall influence of the examined factors on the targeted outcomes of the process. For example, desirability function and response surface contours proficiently demonstrated the impact of various factors on critical process outcomes, including TPD, OCC yield, and energy consumption. The application of desirability functions, along with the

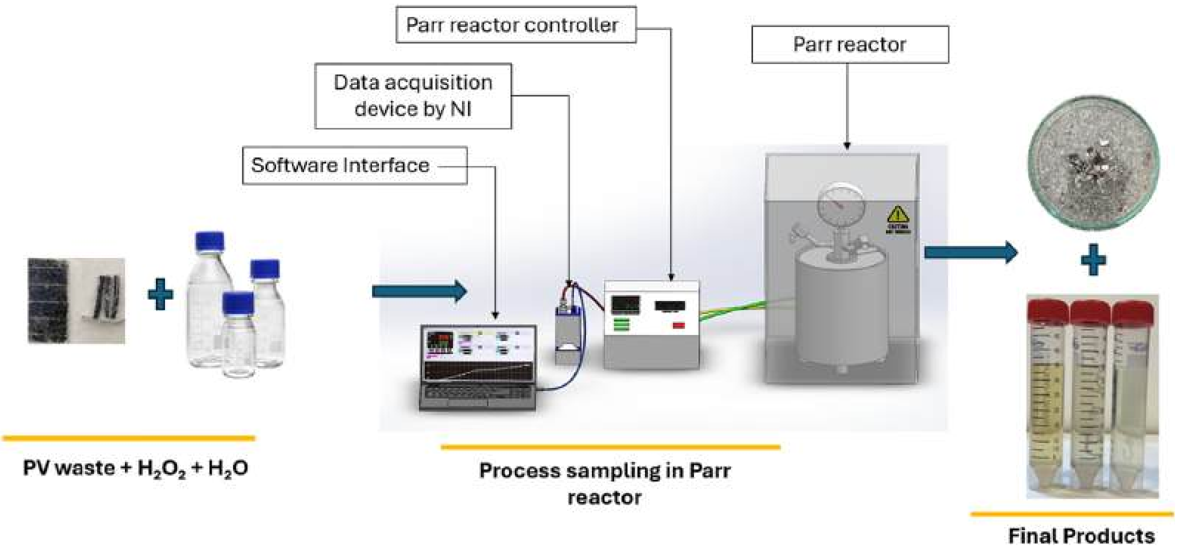

Fig. 1. Sample processing approach for oxidative liquefaction of PV waste.

plotting of response surface contours, facilitated the identification of optimal operating conditions that resulted in the most beneficial integration of these response variables. The current investigation utilized the analysis of variance (ANOVA) approach to statistically assess the significance of the interactions among the independent variables, which include reaction temperature, waste-to-liquid ratio, and oxidant concentration, as well as the dependent response variables, such as TPD, OCC yield, and energy consumption. The assessment of these interactions and statistical significance was conducted through the calculation of p-values.

3. Details of obtained results

3.1. Ultimate and proximate analysis of end-of-life photovoltaic panels

Table 2 summarizes the results from the ultimate and proximate analysis of PV waste, summarizing the content of ash (A^a) volatile matter (VM), carbon, hydrogen, nitrogen, sulfur, and content of oxygen calculated based on mass difference.

Upon conducting a comprehensive examination of the PV waste sample provided, it has been determined that the sample exhibits a substantial ash content, accounting for 93.2 % ± 4.8 of its total weight. The results suggest that a significant portion of the sample may comprise inorganic materials, including glass, ceramics, or metallic components derived from the photovoltaic panel's structure. The existence of elevated ash content in the feedstock may adversely impact the overall efficiency of oxidative liquefaction processes. The levels of volatile matter and fixed carbon are comparatively low, comprising 6.3 % and 6.4 % of the sample's weight, respectively. The results suggest a limited presence of readily degradable organic polymers in the analyzed sample. The low organic content observed in the sample could have significant implications for the potential generation of oxygenated chemical compounds (OCC) during oxidative liquefaction processes.

3.2. SEM and EDS analysis of raw PV sample

The analysis conducted using SEM and EDS on the raw photovoltaic (PV) sample elucidates its elemental composition. The analysis reveals the following primary elements: carbon (C) at an atomic percentage of 53.7, oxygen (O) at 19.2 at.%, silicon (Si) at 16.3 at.%, fluorine (F) at 5.91 at.%, aluminum (Al) at 1.85 at.%, sodium (Na) at 1.36 at.%, calcium (Ca) at 0.56 at.%, magnesium (Mg) at 0.38 at.%, and titanium (Ti) at 0.24 at.%. The presence of these elements is likely in the form of various compounds, such as oxides, silicates, and fluorides, which collectively account for 99.5 % of the total sample mass.

In the analyzed sample, trace elements were detected with the following concentrations: phosphorus (P) at 0.050 at.%, bromine (Br) at 0.056 at.%, chlorine (Cl) at 0.008 at.%, potassium (K) at 0.009 at.%, iodine (I) at 0.002 at.%, cerium (Ce) at 0.003 at.%, praseodymium (Pr) at 0.002 at.%, neodymium (Nd) at 0.002 at.%, copper (Cu) at 0.011 at.%, molybdenum (Mo) at 0.004 at.%, tin (Sn) at 0.001 at.%, lead (Pb) at 0.001 at.%, vanadium (V) at 0.004 at.%, and zinc (Zn) at 0.004 at.%. These elements collectively accounted for less than 0.2 % of the sample. The difference of 0.3 % that appears in overall summation could be because of an error or the existence of an element that was not detected during the analysis. The potential value of elements such as copper (Cu) and rare earth elements (Ce, Pr, Nd) is contingent upon market prices and the viability of extraction methods. Nevertheless, the relatively small amounts of these substances may pose a challenge in terms of economic viability for recovery efforts. So in current study is primarily focused on degrading the polymeric content and producing the OCCs instead of elemental recovery.

3.3. FTIR analysis of raw PV panels before experimentation and after oxidative liquefaction

The diversity of the chemical composition of PV panels and their complex, multi-layered sandwich structure significantly impacts the differences observed in the solid products formed after the oxidative condensation process. The chart below illustrates the differences in the FTIR spectra obtained for the analyzed samples, identifying the bands corresponding to vibrations, as shown in Fig. 2.

The spectrum of the raw PV sample exhibited typical bands observed for the EVA spectrum (ethylene-vinyl acetate copolymer). Intense bands at approximately 2920 and 2860 cm^{-1} were attributed to the antisymmetric stretching vibrations of CH_3 and CH_2 groups. A broad and intense band at 1730 cm^{-1} was assigned to C=O vibrations originating from a ketone group, while the band at 1250 cm^{-1} was attributed to O-C-O vibrations from a carboxyl group. Additionally, the spectrum confirmed bands at 1460 cm^{-1} and 1380 cm^{-1}, which were attributed to asymmetric in-plane bending vibrations of CH_3 and CH_2. A single band at 1060 cm^{-1} was assigned to Si-O-Si vibrations from silicates.

The registered spectrum of the PV sample after the oxidative liquefaction process shows significant changes resulting from both the efficiency of the applied process and the degradation of individual protective layers. The bands at 2950 and 2880 cm^{-1}, which exhibit increased intensity and a shift toward higher wavenumbers, were attributed to the antisymmetric stretching vibrations of CH_3 and CH_2 groups. These changes are a direct effect of the degradation of polymeric protective layers, such as EVA (ethylene-vinyl acetate copolymer), during the oxidation process. The broad and intense band at 1750 cm^{-1}, which also shows a shift and broadening, was assigned to C=O vibrations from additional ketone groups formed as a result of oxidation. These changes indicate intensive oxidative processes within the encapsulant layer. In contrast, the reduced intensity of the band at 1280 cm^{-1} was attributed to O-C-O vibrations associated with carboxyl groups and the detachment into the liquid phase of acetic acid. This acid is one of the degradation products of EVA under oxidative conditions. The

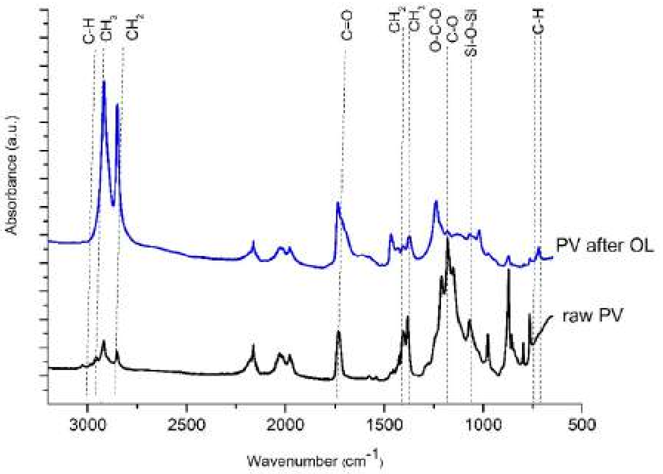

Fig. 2. FTIR spectra of raw PV panels before experimentation and after oxidative liquefaction.

Table 2
Ultimate and proximate analysis results of PV waste samples.

Parameter, wt%	M^a	A^a	VM	C^a	H^d	N^a	S^a	O^{diff}
PV waste	N/A	93.2 ± 4.8	6.3 ± 0.2	6.4 ± 0.2	0.70 ± 0.03	0.03	<0.03	0.0

spectrum also identified broadened and less intense bands at 1480 and 1380 cm^{-1}. These bands correspond to asymmetric bending vibrations of CH_3 and CH_2 groups in planes, further indicating structural changes caused by the degradation of polymeric protective layers. Meanwhile, the single band at 1060 cm^{-1}, assigned to Si-O-Si vibrations originating from the glass layer or antireflective coatings, shows reduced intensity. This observed weakening results from the separation of the complex multilayer PV structure into individual components during the liquefaction process.

3.4. *Thermal degradation behavior of end-of-life photovoltaic panels*

TGA and DTG runs were performed at 4 different heating rates and the trends of decomposition were the same just with a slight change in decomposition temperatures. For the sake of simplicity, TGA and DTG trends are presented on two heating rates only i.e., 4 and 16 K/min (Fig. 3).

Based on the analysis of the TGA curve, it can be inferred that the initial portion of the curve corresponds to a stable region characterized by minimal mass loss. These findings indicate that the sample does not contain a significant amount of moisture or volatile substances. The application of TG-DTG analysis to PV panel waste indicates the identification of two separate stages of decomposition later. This observation yields significant insights into the complex thermal behavior exhibited by the materials in the study. Initially, it is noted that the TGA curves demonstrate a gradual reduction in weight within the temperature interval of 300–385 °C. The emergence of this phenomenon can be attributed primarily to the processes of evaporation or the release of moisture, if present, volatile organic compounds (VOCs), and low molecular weight degradation products. However, the most significant factor is the removal of acetic acid from the vinyl acetate monomer within the EVA structure during the initial decomposition stage 300–385 °C [16,17]. The present phase being examined exemplifies the mechanisms through which organic materials, such as polymers, encapsulants, and adhesives, utilized in the fabrication of PV panels experience degradation and disintegration.

Subsequently, the second and major stage of weight loss for PV waste is observed during temperature range of 385–500 °C and subjected to the decomposition that occurs specifically in the more stable organic components. The current phase under consideration encompasses the process of decomposing intricate organic molecules and polymers, resulting in the production of supplementary volatile compounds and the creation of char residues. Polymers that are commonly observed to undergo degradation within the specified temperature range encompass small fractions of polyethylene (PE), polypropylene (PP), polyvinyl butyral (PVB), polyester resins, and silicone-based polymers but more specifically, ethylene-vinyl acetate (EVA) [41]. The details about residual mass, rate of mass loss, and percentage change in mass are presented in Table 3.

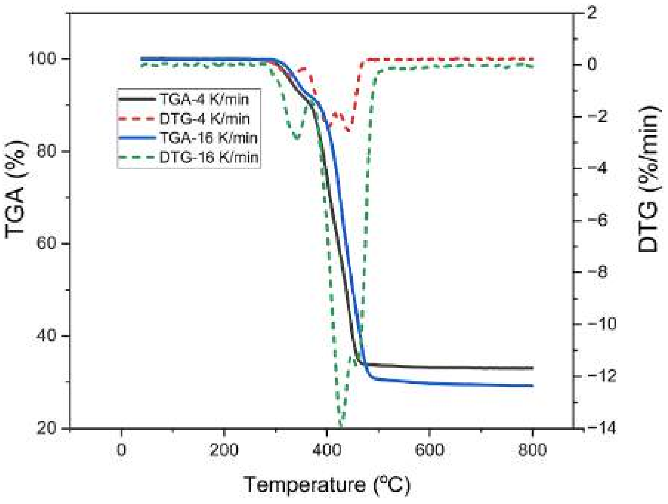

Fig. 3. Thermal decomposition patterns of end-of-life PV panels at 4 and 16 K/min.

3.5. *Inverse analysis of process heating*

During the oxidative liquefaction of PV waste, temperature profiles based on inside reactor temperature (maximum 250 °C) have been shown in Fig. 4 (a). The overall pattern of heating profiles for modeled run with PV waste is the same as for dummy runs with water + oxidant, but this pattern significantly varies from the heating profile recorded for dummy runs with water only. After 22–25 min of the experiment, the intersection of heating profiles can be observed Fig. 4 (a) and an additional temperature bump appeared (Fig. 4 (a) enlarged), which is an indication of additional heat added to the system that was absent during the dummy runs with water. Similar situations happened but at lower levels around 70–80 min of experimental duration. The situation can be observed more clearly in Fig. 4 (b), where the heating rates were plotted against the inside reactor temperature. No sharp peaks with significant height can be observed for a dummy run with water, highlighting the uniform heating rates. For dummy runs with water + oxidant, a sharp peak can be observed from 125 to 140 °C, representing the decomposition of oxidant. In the case of the modeled run with PV waste, two peaks appeared, first double headed peak slightly at a lower temperature than dummy runs of water + oxidant with sharp heating rates of 1.5–2.3 K/s, and second small peak around 230 °C with heating rates reaching to 0.5 K/s. The appearance of these peaks with enhanced heating rates is an indication of the decomposition of waste materials + oxidants under the oxidative liquefaction process. It is assumed that during the temperature ranges at which these extended peaks appeared, a major portion of waste and oxidant is decomposed, exhibits an exothermal behavior, and additional heat is added to the system, resulting in extended heating rates that were absent during the dummy run with water only. Additionally, to achieve the same temperature of 250 °C the oxidative liquefaction reaction of PV waste finished 8–10 min earlier than the time recorded for the dummy run with water, which also indicates the supply of additional heat.

This additional heat is calculated using the following equation:

$$dQ = mCv(T)dt\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad \text{(i)}$$

where dQ stands for change in internal energy of system in joules (J), containing the mass (m) of substance in grams, with specific heat at constant volume (C_v) in (J/g.K), over the temperature interval dT, measure in K. During these calculations, the following assumptions were made.

(i) Molar specific heat for solid waste at constant pressure $C_p = C_v = Cp_{EVA}$
(ii) Temperature based approximation of C_v for both water and oxidant

Integration of the energy equation (i) based on the mass of reactants and specific heats at constant volume and changing temperatures over the whole reaction period helped to calculate the heat of the reaction. As the heating of water is completely endothermic, the heating power absorbed during the dummy run with water is considered the base line for showing the behavior of waste materials. Heating power absorbed during the dummy runs with water at 250 and 200 °C calculated on the basis of equation (i) using the interpolation method for the value of C_v of water was 86.13 ± 0.75 W and 66 ± 1.1 W consumed during the reaction time of 160 and 130 min respectively. To achieve the same temperature level of 250 and 200 °C, heat absorbed during the modeled run with PV waste was 46.09 ± 0.57 and 35.81 ± 0.43 W also calculated

Table 3
Detail parameters of the TG-DTG analysis of PV waste.

	β, (K/min)	R_m (%)	*Stage 1*		*Stage 2*	
			r_m (%/min)	Δm (%)	r_m (%/min)	Δm (%)
PV waste	4	33.09	−0.43 to −0.70	−8.12	−2.36 to −3.10	−27.52 to −30.61
	16	29.18	−1.43 to −2.82	−7.96	−11.20 to −13.85	−21.61 to −40.62

R_m = Residual mass, %.
r_m = Mass loss rate, %/min.
Δm = Change is mass %.

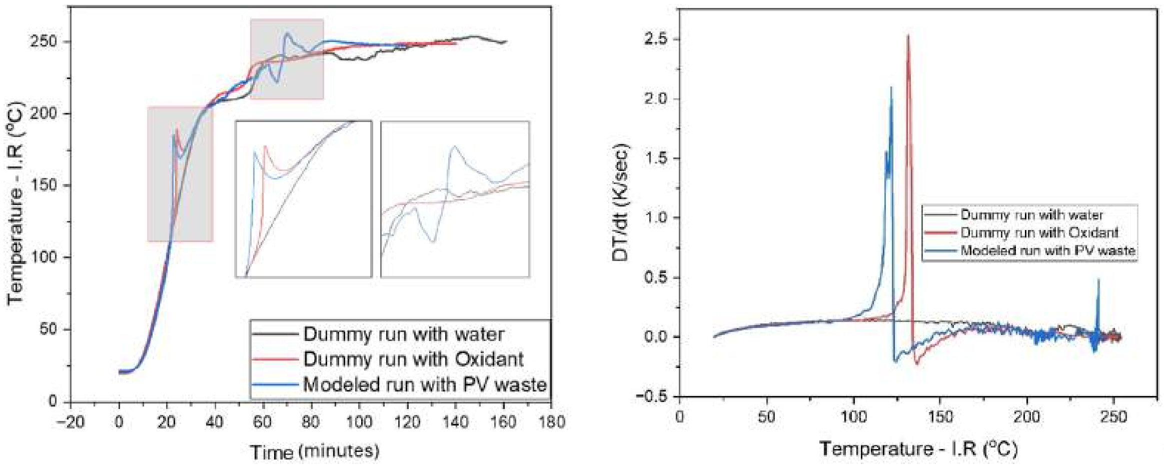

Fig. 4. Comparison of (i)inside reactor temperature profiles (b) heating rates for PV waste and dummy runs.

based on assumption (i) and using the cp value of 2.04 J/g.K already reported in the literature. The absorption of less heating power as compared to dummy runs with water indicates that this time an additional 40.04 ± 0.92 W at 250 °C and 30.19 ± 1.18 W at 200 °C for PV waste is provided by the reaction itself, through the decomposition of PV waste and oxidant. So, it can be said that the oxidative liquefaction of PV waste is exothermal over a specific temperature range as compared to heating water, but it is not exothermal overall to carry out the whole reaction on its own.

3.6. *Yields of total polymer degradation (TPD) attained*

The data illustrating the trends of TPD during the oxidative liquefaction of PV waste is presented in Fig. 5. In this figure, TPD is represented on the y-axis, while the x-axis delineates the levels of each parameter tested, as detailed in Table 1. An analysis of the data concerning polymer degradation across varying temperatures, oxidant concentrations, and waste-to-liquid ratios is conducted to identify nuanced combinations that are critical for understanding and enhancing this process. The peak TPD is observed at a temperature of 200 °C, with a waste-to-liquid ratio of 12.5 % and an oxidant concentration of 60 %. This observation suggests that an increased concentration of oxidant may be necessary to effectively facilitate the degradation process at reduced temperatures. Conversely, the minimum TPD observed at 200 °C occurs at a 30 % oxidant concentration and a 37.5 % waste-to-liquid ratio. This indicates that an excessive amount of waste or an insufficient oxidant concentration may impede the degradation efficiency.

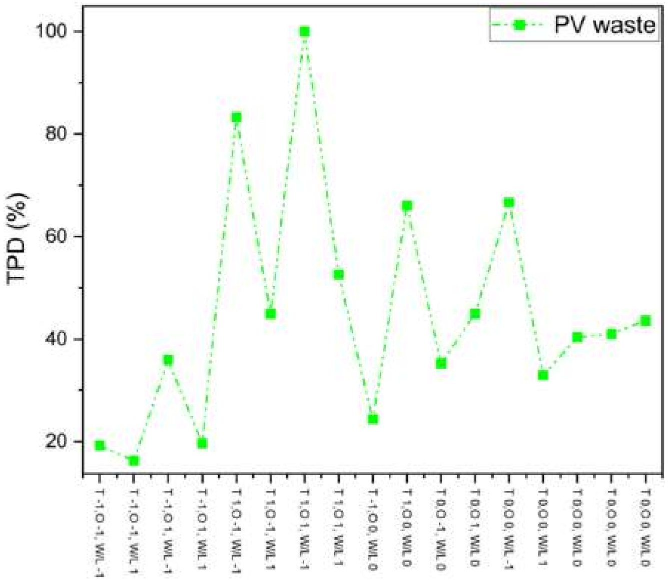

Fig. 5. Yields of total polymer degradation (TPD) attained after the oxidative liquefaction process of end-of-life photovoltaic (PV) panels.

At 250 °C, the findings indicate that, regardless of the waste-to-liquid ratio, a critical oxidant concentration of 45 % is necessary to achieve maximal TPD. This suggests that the oxidant plays a crucial role in facilitating polymer degradation at this intermediate temperature, likely by enhancing oxidative mechanisms and increasing reaction velocities. Conversely, the minimal TPD observed at 250 °C occurs at an oxidant concentration of 30 %, indicating that the oxidation process may lack sufficient intensity to induce significant polymer degradation below a specific threshold. An in-depth analysis of the overarching deterioration patterns at this temperature can be achieved through a more detailed examination of the average TPD at 250 °C.

The findings indicate a distinct difference at 300 °C, where the peak TPD is reached under complete degradation conditions (100 %) at an oxidant concentration of 60 % and a waste-to-liquid ratio of 12.5 %. This indicates that even low levels of oxidants may facilitate significant polymer degradation at higher temperatures, likely due to enhanced reaction kinetics and favorable thermodynamic conditions. Conversely, the minimum TPD observed at 300 °C occurs at a 30 % oxidant concentration and a 37.5 % waste-to-liquid ratio. This suggests that suboptimal conditions can impede degradation efficiency, despite elevated temperatures. The overall performance of the process under these extreme temperatures is represented by the average TPD at 300 °C. The standard deviations of results when calculated based on random repetitions of experiments lie in range of 0–6 % subjected to the inhomogeneous nature PV waste sample when cut with scissors.

In conclusion, systematic analysis reveals the intricate relationships between temperature, oxidant concentration, waste-to-liquid ratio, and polymer degradation. Understanding these correlations is essential for improving degradation processes and developing sustainable waste management strategies applicable across various sectors.

3.7. The quantification of OCCs resulted from the oxidative liquefaction of PV waste

Through a detailed examination of the data presented in Fig. 6, which illustrates the overall concentration of OCCs under varying conditions such as temperature, oxidant concentration, and waste-to-liquid ratio, one can derive substantial insights into the complex dynamics of the PV waste degradation process, and secondary compounds generation. The experimental findings indicate that at a temperature of 200 °C, the maximum OCC yield is achieved when the oxidant concentration is held at a moderate level of 30 % and the waste-to-liquid ratio is maintained at a relatively low level of 12.5 %. This observation indicates that the identified conditions facilitate the production of oxygenated compounds. Conversely, it has been noted that elevated levels of oxidants and increased waste-to-liquid ratios correspond to the lowest recorded OCC. This indicates that an excess of oxidants and higher concentration of waste could hinder the synthesis of OCCs.

Upon elevating the temperature to 250 °C, the experimental findings demonstrate that the peak OCC concentrations are recorded at an oxidant concentration of 60 %, while the waste-to-liquid ratio is kept at a moderate level of 25 %. This indicates that particular combinations of these parameters are advantageous for facilitating the formation of oxygenated compounds at the specified temperature. Conversely, it is important to highlight that the minimum recorded OCC is observed under particular conditions, despite the oxidant concentration being held constant. This observation highlights the intricate interplay among multiple factors influencing OCC production.

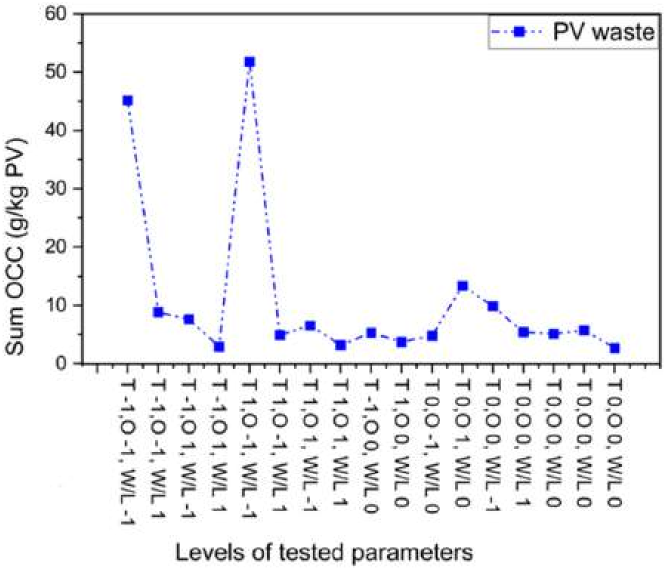

Fig. 6. Yields of oxygenated chemical compounds obtained for PV waste.

At a temperature of 300 °C, the experimental findings demonstrate distinct patterns in the production of OCC, suggesting a significant influence of elevated temperatures on the degradation mechanism. The data indicates that the peak observed OCC is associated with a lower oxidant concentration, particularly at 30 %, and a reduced waste-to-liquid ratio, specifically at 12.5 %. This indicates that elevated temperatures may lead to particular combinations of parameters that can enhance the production of oxygenated compounds. Conversely, it has been noted that the lowest recorded OCC correlates with elevated levels of oxidants and waste-to-liquid ratios. This indicates that an abundance of oxidants and waste may impede the synthesis of OCC in scenarios characterized by elevated temperatures.

During each experiment, the energy consumption was recorded in the range of 0.8–1.1 KWh. From the above discussion it's very evident that there is a complex relation between the tested parameters and expected outcomes, that are highly affected by sample inhomogeneity. To make the experimental process less resource-intensive and justify the oxidative liquefaction of PV waste a promising waste management technique was important to identify the optimal reaction conditions.

3.8. Identification of optimal reaction conditions for the oxidative liquefaction of PV waste

Sections discussing TPD and yields of OCCs highlighted the importance of optimizing the process parameters such as temperature, waste-to-liquid ratio, and oxidant concentration, as these parameters and the complex interaction between these parameters play a crucial role in obtaining the maximum OCCs yield and complete polymer degradation from PV waste. In Fig. 7 the red lines represent the optimal levels of reaction parameters while on the other hand, the blue lines provide an illustration of the trends in the variation of yields of OCCs and total TPD in relation to tested parameters.

Commencing with the variable of temperature, it is observed that lower temperatures exhibit a concomitant reduction in the overall degradation of polymers, whereas an escalation in temperature is found to be associated with an increase in polymer degradation. On the other hand, the influence of temperature on the production of oxygenated compounds is insignificant. Nevertheless, it is worth noting that as temperatures increase, there is a corresponding increase in energy consumption in relation to the level of polymer degradation that is achieved. Therefore, it can be observed that under optimal conditions, as indicated by the red line, there is a tendency for the temperature values to converge towards the average.

Through meticulous analysis of the oxidant concentrations, a clear relationship emerges between elevated oxygen levels and a modest rise in the overall degradation of polymers. This observation indicates that elevated levels of oxygen could play a role in the degradation process of polymers. It has been noted that increased concentrations of oxidants result in a decrease in the synthesis of oxygenated compounds. The phenomenon observed may be linked to a higher concentration of oxygen, which could lead to the over-oxidation of intermediate compounds. The process of excessive oxidation leads to the generation of gaseous byproducts that are considered undesirable. The concentration of oxygen appears to have a minimal effect on energy consumption throughout the process. This observation suggests that employing minimum levels of oxidant may serve as the optimal parameters.

The waste-to-liquid ratio is recognized as a vital parameter that considerably influences the overall process yield as higher ratios have been observed to result in decreased levels of polymer degradation and yields of oxygenated compounds. Optimizing the waste-to-liquid ratios is crucial in order to provide an adequate amount of reaction media to support the required degradation reactions, thereby enabling the attainment of required outcomes. Thus, the optimization of overall experiment plans plays a crucial role in attaining the desired outcomes while simultaneously minimizing energy consumption and maximizing process efficiency. Based on the trends observed in Fig. 7 and the above

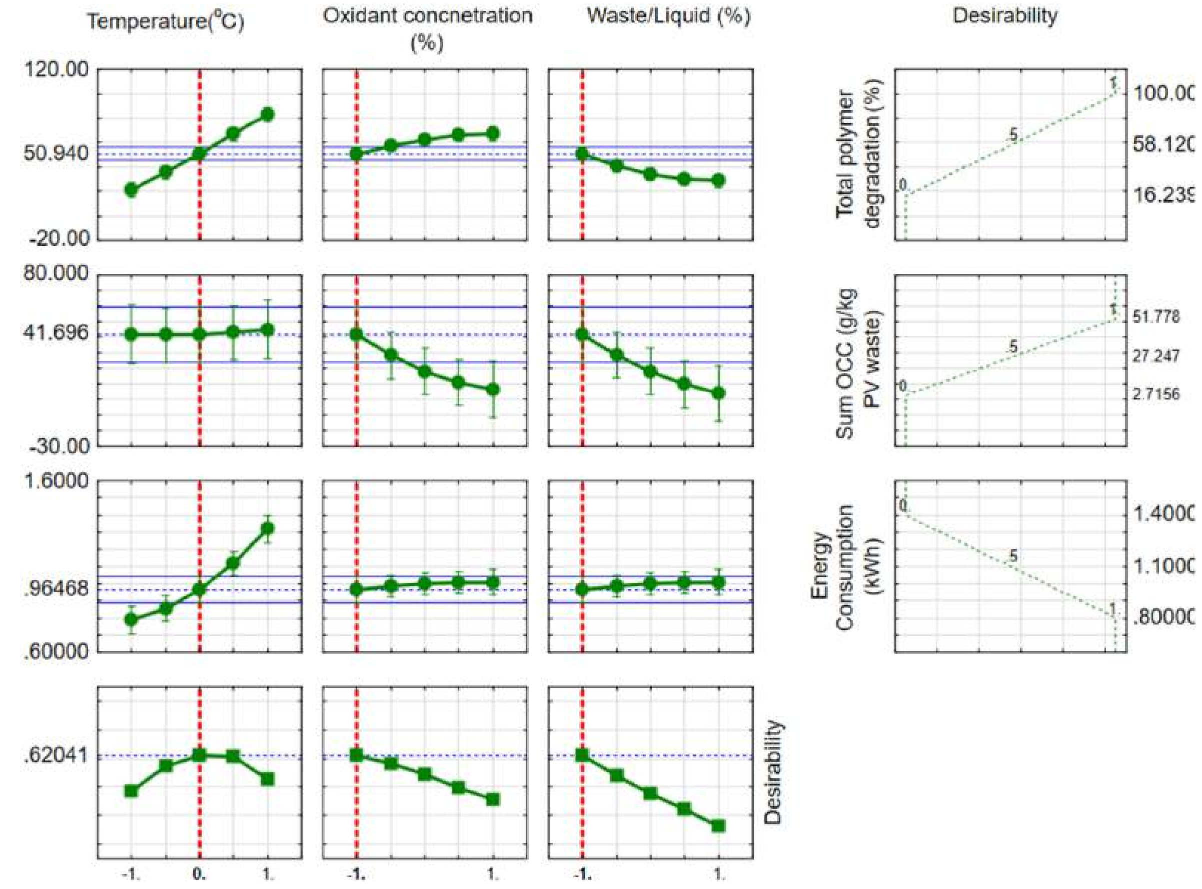

Fig. 7. Identification of optimal reaction conditions for PV waste.

discussion, the optimal reaction conditions for maximum TPD and OCC yield against the minimum energy consumption has been shown in Table 4.

During the experimentation, the initial pressure was kept constant to 30 bar and reaction time for 45 min.

4. Discussion

The utilization of oxidative liquefaction has recently been presented as a promising approach for recycling composite wind turbine blades [13,14] and results obtained in the current study i.e. photovoltaic (PV) waste recycling, present notable benefits in contrast to conventional techniques. Although conventional methods such as mechanical or physical recycling methods encounter difficulties in effectively extracting the valuable components contained within the intricate structure of photovoltaic (PV) panels [20,21], oxidative liquefaction demonstrates a greater capacity to degrade organic part of PV waste into useable secondary products. The aforementioned statement can be interpreted as an indication of a heightened level of material recovery, wherein polymers are subjected to a process of degradation into smaller molecular units to facilitate subsequent processing in to secondary compounds. Moreover, it also encompasses the possibility of conversion of organic constituents such as encapsulants into oxygenated chemical compounds (OCCs) that possess significant value as they provide an opportunity for the development of alternative fuel sources and chemical feedstocks. This approach not only improves the efficiency of the recycling process but also opens up new opportunities for revenue generation. The process of oxidative liquefaction aims to minimize the volume of waste directed to landfills by decomposing a substantial fraction, if not all, the technique can be used to extract useful materials like metals if existing in matrix. The implementation of a circular economy framework is being noted, with the objective of improving resource efficiency and reducing ecological consequences. Furthermore, the incorporation of high-value products, including fuels and chemicals, adds an extra dimension of appeal to this methodology.

Table 4
Optimal reaction conditions for oxidative liquefaction of PV waste.

	Temperature, (°C)	H_2O_2 Concentration (wt.%)	Waste-to-Liquid ratio (wt.%)
PV waste	250	30	12.5

Energy efficiency efficiency is a crucial parameter that should be the point of key interest when evaluating various effects of waste management techniques. The specific process design allows for the optimization of oxidative liquefaction, which can lead to a reduction in energy consumption. The utilization of low-temperature methods, such as liquefaction, presents distinct advantages compared to high-temperature methods like pyrolysis [22,23], primarily due to their operational capacity at reduced temperatures. This approach not only minimizes energy consumption but also facilitates the potential recovery of energy from the exothermic reactions (waste & oxidant decomposition) that take place during the liquefaction process. Additionally, it is important to highlight that oxidative liquefaction demonstrates favorable attributes that position it as a potentially more sustainable alternative to traditional methods, which frequently require the application of severe chemical reagents, and catalysts or elevated thermal conditions. The implementation of strategies designed to minimize landfill waste and enhance the recovery of valuable resources offers a more effective alternative for the management of photovoltaic (PV) waste.

It is essential to acknowledge that oxidative liquefaction is still an emerging technology in the context of composite waste recycling. In comparison to current methodologies, further investigations and development are essential to improve the process and ensure its viability for commercial applications. It is essential to maintain precise regulation of process parameters to enhance the desired outputs while reducing the formation of unwanted byproducts. Moreover, it is essential to perform a thorough evaluation of the economic and environmental feasibility (similar efforts are made by Sobek.et al.) linked to the extraction of valuable resources from the liquefaction products [42]. In conclusion, the findings indicate that oxidative liquefaction holds significant promise for the efficient recycling of PV waste but is crucial to highlight that further research initiatives are necessary to fully harness its potential at an industrial scale.

5. Conclusions

The recycling of end-of-life PV panels poses a significant challenge mainly due to the complex composition and multi-layered structure. The application of oxidative liquefaction has demonstrated its vast potential as a viable alternative for managing PV waste in terms of waste reduction and valuable secondary compound production. The proximate analysis of PV waste, indicates a significant presence of ash content alongside a diminished ratio of volatile matter suggesting a limited accessibility of polymers or organic materials that can be efficiently decomposed into valuable secondary carbon compounds and energy-dense products. The FTIR analysis of raw PV panels and those subjected to oxidative liquefaction revealed significant structural and chemical changes, including degradation of protective layers, oxidation of encapsulant materials, and separation of multilayer components.

The thermal degradation profiles of the photovoltaic waste reveal two distinct stages of mass loss. In the preliminary stage, an occurrence of minimal significance is observed, while the following stage reveals the presence of polymers, primarily ethylene vinyl acetate (EVA). The characteristics observed in this second stage indicate that the waste exhibits a relatively narrow temperature range for degradation, thereby offering further evidence for the existence of a significant inorganic component. The oxidative liquefaction process for PV waste exhibits exothermic characteristics at a particular reaction phase that aligns with the significant breakdown of organic material and oxidant. The interaction among various reaction parameters and their respective levels plays a crucial role in influencing both the TPD and OCC yields. The analysis of variance (ANOVA) suggests that prioritizing intermediate reaction temperatures, in conjunction with reduced oxidant concentrations and minimized waste-to-liquid ratios, facilitates the attainment of a more efficient degradation strategy. The optimization of these parameters is essential for developing a sustainable and efficient methodology for the treatment of PV waste. This process plays a significant role in promoting the advancement of a more sustainable energy source for the future.

CRediT authorship contribution statement

Hamza Mumtaz: Writing – original draft, Visualization, Validation, Investigation, Data curation, Conceptualization. **Szymon Sobek:** Writing – review & editing, Supervision. **Marcin Sajdak:** Writing – review & editing, Formal analysis. **Roksana Muzyka:** Writing – review & editing, Writing – original draft, Formal analysis. **Sebastian Werle:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **Marcin Procek:** Formal analysis.

Data availability

All the data used in developing this study will be made available on request.

Declaration of competing interest

I on the behalf of all authors, declare that there is no conflict of interest and all the elements of the submission are also in compliance with the journal publishing ethics. By submitting this manuscript, the authors agreed that the copyright for their article should be transferred to this journal if the article is accepted for publication. The work contained within the research paper is our original contribution and has not been published anywhere.

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