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Ph.D. DISSERTATION

APPLICATION OF ISOTOPE METHODS FOR DETERMINATION OF BIOCOMPONENTS IN LIQUID FUELS

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Acknowledgements

The Ph.D. thesis is not only an academic achievement, but also a monumental life achievement that requires various supports. I still find it hard to believe that I have reached this milestone. I want to raise a toast to everyone who has been a part of this incredible journey with me.

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I would be remiss in not mentioning my family, especially my parents, spouse, brothers, and sisters. Their belief in me has kept my spirits and motivation high during this process.

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Abstract

In many European countries, isotope methods are being used to investigate environmental changes. To determine the biocomponents of liquid fuels using radiocarbon (^{14}C) content analysis, it is necessary to adapt the sample preparation to the conditions of the Gliwice Radiocarbon and Mass Spectrometry Laboratory.

In this study, the accelerator mass spectrometry (AMS) and liquid scintillation counting (LSC) methods were tested using liquid fuel samples submitted in 2018 by an external oil company in large quantity, including a purely bio-based hydrotreated vegetable oil (HVO) and one petrodiesel sample of infinite ^{14}C age (ON/UF-BC), bio-oil samples, and one reference sample of 100 % biomass and several fuel blends produced from ON/UF-BC and HVO with various proportions.

For AMS, samples for ^{14}C measurements were prepared using tin capsules for liquids for combustion in elemental analyser (EA) and graphitisation in an automated system (AGE). For the LSC method, the benzene sample was prepared. To safely enable the conversion of the fuel samples to lithium carbide (Li_2C_2) without causing any explosion, each liquid fuel was mixed with purified quartz sand. Benzene resublimation method was also tested to speed up the procedure. IRMS measurements were conducted for benzene to determine the $\delta^{13}C$ and account for isotopic fractionation.

The background values were acquired based on the ^{14}C measurement results for pure petrodiesel. The results for liquid fuel blends proved that the ^{14}C content agreed between the AMS and LSC methods. Additionally, a linear relation between the ^{14}C and the HVO contents confirmed the reproducibility between the two methods and allowed to validate them. The reproducibility of the AMS results was verified in several aliquots of one of the blends and the results were deemed consistent. Moreover, the bio-oil results allowed to detect that one of the samples was not produced from the investigated reference biomass.

The results of the study showed that both AMS and LSC are effective radiocarbon dating methods but their choice depends on specific research needs, balancing accuracy, sample size, and available resources. AMS is superior for small samples and high precision while LSC is more practical for larger samples.

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List of abbreviations

HVO: Hydrogenated Vegetable Oil

AMS: Accelerator Mass Spectrometry

LSC: Liquid Scintillation Counting

IRMS: Isotope-ratio mass spectrometry

AGE: Automated Graphitisation Equipment

EA: Elemental Analyser

CV: Critical Value

MICADAS: Mini Carbon Dating System

ASTM: American Society for Testing and Materials

pMC: Percent Modern Carbon

GdS: sample ID for GADAM LSC measurements

GdA: sample ID for GADAM AMS measurements

GADAM: Gliwice Absolute Dating Methods Centre

SUT: Silesian University of Technology

1. Description of the research topic

In this world of rapid development, global energy demand is undoubtedly rising due to economic and population growth. Liquid fuels play a significant role in both transportation and economic development (Krištof and Kožar Logar 2013). Over the years, the extensive use of fossil fuels, which have been considered the driving force behind modern lifestyles and the global economy, particularly in energy production and transportation sectors, has led to environmental degradation due to increased carbon dioxide (CO_2) in the atmosphere (Dijs et al. 2006; Liaquat et al. 2012; Guo et al. 2022).

Due to environmental concerns such as water pollution, air pollution, and global warming associated with the use of fossil fuels, member states of the European Union (EU) and other countries around the world are developing alternative energy sources such as biomass, solar panels, using wind and wave energy, as well as nuclear energy (Rajasekhar et al. 2015; Matsakas et al. 2017; Neha and Remya 2022). Furthermore, to reduce CO_2 emissions to the atmosphere, many countries are focussing on using liquid fuels derived from environmentally friendly renewable resources (De Souza et al. 2013). One such liquid fuel, called bio-oil, produced from biomass has several environmental benefits. It is considered CO_2 neutral, as CO_2 is sequestered during growth of its feedstock, and it can generate CO_2 credits without emitting sulphur oxides (SO_X) (Fan et al. 2011). Furthermore, the amount of nitrogen oxides (NOx) emitted by bio-oil combustion is 50% lower than that emitted by biodiesel from gas turbines (Boucher et al. 2000; Gutiérrez et al. 2018).

Additionally, many European countries, including Poland, have implemented fuel blending strategies with the aim of reducing the net flux of carbon into the atmosphere and decreasing the dependence on fossil fuels. These blends often include biofuels derived from renewable resources such as crops such as sugarcane, corn, as well as biodiesel from vegetable oil (Dobrzyńska et al. 2020; Verger et al. 2022).

There are three carbon isotopes in nature. ^{13}C and ^{12}C are stable carbon isotopes with abundances of 1.11 % and 98.89 %, respectively (Wagner et al. 2016). Furthermore, there is a cosmogenic radiocarbon isotope (^{14}C) produced in the upper atmosphere of the Earth by the reaction of nitrogen (^{14}N) with cosmic ray neutrons, that further forms CO_2 by oxidation with oxygen contained in the atmosphere. Relative to stable ^{12}C carbon isotope, the radiocarbon fraction is ca. 10^{-10} % (Hajdas et al. 2021).

Contrary to the contemporary biosphere with a high concentration of ^{14}C, fossil fuels are devoid of this radioisotope due to their age (Dijs et al. 2006).

Therefore, biofuels or fuel blends containing biocomponents are referred to as renewable fuels, as derived from contemporary organic sources, including animal fats and plants that contain a relatively large proportion of radiocarbon (Culp 2017; Hajdas et al. 2021).

As a result, in addition to increasing energy production from renewable resources, member states of the European Union decreased biocomponent taxes due to higher production costs compared to fossil fuels (Dijs et al. 2006; Krištof and Kožar Logar 2017; Karaaslan and Gezen 2022). Based on (Lee et al. 2022), the ^{14}C content in biofuel feedstocks can vary depending on the type, age, and geographic origin of the biomass used to produce fuels. In particular, the CO_2 emitted from burning fossil fuels and nuclear weapons tests can contribute to the variation of the ^{14}C concentration in the atmosphere.

The ^{14}C content of liquid fuels is measured using the methods listed in a standard D6866 of the American Society for Testing and Materials (ASTM), for which the latest version was published in 2022. They are standard analytical methods used for determining the biobased carbon contents of solid, liquid and gaseous samples using radiocarbon method (Culp et al. 2014; Idoeta et al. 2014).

Accelerator mass spectrometry (AMS) is one of the most precise and accurate methods for ^{14}C determination, and it is listed in ASTM D6866-22. In general, AMS is an ultrasensitive technique for the analysis of cosmogenic isotopes such as ^{14}C, ^{10}Be, ^{36}Cl, and ^{26}Al analysis (Tuniz et al. 2001; Lee et al. 2020). For the AMS ^{14}C analysis, the investigated samples require the prior preparation process to form graphite targets. The AMS technique has the main advantages of using a small sample size and greater precision (Culp et al. 2014; Haverly et al. 2019). The second method is liquid scintillation counting (LSC), which requires different procedures to produce scintillation cocktails. In the LSC-A method, the ^{14}C determination is based on the preparation of CO_2 by combusting the sample in the controlled environment and absorption in a mixture with scintillator. For benzene or LSC-B method, the sample under investigation is transformed into benzene for ^{14}C measurement in three main steps such as carbide formation, hydrolysation, and trimerization to get benzene (Horvatinčić et al. 2004), which is then mixed with organic scintillator. Another procedure (LSC-C) does not require any pretreatment of the sample, but only a relevant cocktail is mixed with the investigated sample (Krištof 2015; Krajcar Bronić et al. 2017; Doll et al. 2021).

To report the accurate and precise ^{14}C measurement results, it is required to correct for isotope fractionation, which occurred during sample preparation and ^{14}C measurements processes. Although both AMS and LSC require the corrections for isotope fractionation, the methodology used to apply these corrections vary.

For the LSC the isotope ratio mass spectrometry (IRMS) is required for stable carbon isotope measurements used for the corrections (Maruccio et al. 2017).

In AMS the fractionation rate is measured in a spectrometer and the corrections are directly incorporated in the calculations and data reduction process (Wacker et al. 2010b)

2. Scope of the research project

To ensure the accuracy of the results, the development of the suitable procedure for the preparation of samples to measure the biobased carbon content in various substances is required to guarantee the reliability of the results. The basis is formed by the normative acts.

Measurements of the ^{14}C content in fuels are carried out with the methods listed in the American Society for Testing and Materials (ASTM) standard D6866 introduced in Poland so far as PN-EN 16640:2017 ("Bio-based products - Bio-based carbon content - Determination of the bio-based carbon content using the radiocarbon method") and PN-EN 16785-1:2016-01 ("Biobased products -- Bio-substance content -- Part 1: Determination of bio-substance content using radiocarbon and elemental analysis").

The research was planned primarily for liquid fuels, but also for others, sometimes unusual materials such as biomass used to produce the liquid fuels. As a part of this research project, the adaptation of the described methods including accelerator mass spectrometry (AMS) and liquid scintillation beta spectrometry (LSC) methods in the introduced standards was carried out. In addition, systematic tests were performed in the ^{14}C and Mass Spectrometry Laboratory. The results of these measurements allowed to correct for the isotope fractionation occurring during the preparation and measurement processes. The fractionation may alter the carbon isotope compositions of investigated material, which can affect the final results.

3. Research significance

Liquid fuels are the multicomponent mixtures of various compounds such as olefins, paraffins, and aromatic hydrocarbons with broad molecular weight, heterorganic components, and improvers. The group composition of liquid fuels depends on the initial parameters of the raw materials used to produce their components, as well as the characteristics of the respective refinery used in the process of blending (Malinowski et al. 2015). It is important to analyse the composition of liquid fuels that are expected to go to market to confirm their uniform quality, which may result from several variables that affect fuel properties throughout its entire life cycle (Sulek et al. 2010; Haverly et al. 2019; Morone and D'Amato 2019).

Due to their promising solutions to reduce greenhouse gas emissions and dependence on fossil fuels, the worldwide demand for sustainable energy has led to widespread adoption of using biocomponents in bio-fuels as alternatives to conventional fossil fuels.

However, researchers and industry professionals face substantial hurdles in accurately determining and characterising biocomponents in bio-fuels. One of the main challenges in the use of bio-fuels is the use of traditional analytical methods designed to quantify and characterise the biocomponents in fossil fuels. These methods may not be directly applicable to biofuels depending on their complex matrices and chemical composition. Consequently, it is essential to develop sensitive, robust, and cost-effective methods for determining the biocomponents of bio-fuels. Additionally, to ensure compliance with quality specifications and environmental challenges, the regulatory landscape governing the production and use of bio-fuels requires standardised analytical procedures. However, existing methods frequently lack harmonisation, which may lead to inconsistency of the results, hindering the widespread adoption and bio-fuels commercialization.

4. Objectives and contents

4.1. Dissertation objectives

The goal of this doctoral project was to adapt the methodology for determining the content of biocarbon using isotope methods in the Gliwice Radiocarbon and Mass Spectrometry Laboratory and to verify the accuracy of this methodology.

Moreover, in this study, uncertainties in radiocarbon determination caused by several factors such as sample preparation, the surrounding environment, and measurement procedures were reported for all measurement results. Understanding these uncertainties is crucial as it leads to more accurate and reliable results, which are essential for informed decision-making in environmental and climate sciences.

4.2. Dissertation main contents

This doctoral thesis is prepared on the basis of three published research papers:

1. Baranyika JB, Piotrowska N, Kłusek M, Michczyński A, Pawlyta J. 2022. Testing the methods for determination of radiocarbon content in liquid fuels in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. Radiocarbon. 64(6):1447–1456. doi:10.1017/rdc.2022.35.

2. Baranyika JB, Piotrowska N. 2023. Determination of radiocarbon content in bio-oil samples by MIni Carbon Dating System in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. Geochronometria. 50:21–27. doi:10.2478/geochr-2023-0005.

3. Baranyika JB, Piotrowska N, Michczyński A. 2024. Determination of radiocarbon content in liquid fuel blends by accelerator mass spectrometry and liquid scintillation counting in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. Radiocarbon.:1–12. doi:10.1017/RDC.2024.51.

In the following chapters the main contents of these works are briefly described:

4.2.1. Testing of methods for determination of radiocarbon content at liquid fuels in the Gliwice Radiocarbon and Mass Spectrometry Laboratory

In general, in determining the biocomponents in liquid fuels using radiocarbon (^{14}C) isotope analysis, samples must be prepared according to protocols adapted to laboratory conditions. This paper (Baranyika et al. 2022) aimed to test methods for determining the content in liquid fuels at the Gliwice Radiocarbon and Mass Spectrometry Laboratory. The accuracy of these methods for biocarbon quantification was also tested.

Therefore, the section 2.3 and section 2.4 of (Baranyika et al. 2022) paper presented both AMS and LSC methods for ^{14}C measurements, respectively. For AMS, in this work, a batch of liquid fuel samples was prepared and combusted in Elemental Analyser (EA) without any chemical processing prior to combustion to obtain CO_2 that was transferred to the reactors for graphitisation with H_2 and using an iron powder as catalyst. The obtained graphite was used for ^{14}C measurement using AMS.

For the LSC method, at the Gliwice Laboratory, we used the benzene method known as the LSC-B method. To obtain the benzene sample for the liquid fuel LSC method, we mixed the samples with purified pre-heated sand in a reactor in order to obtain the lithium carbide. The Li_2C_2 was hydrolysed to obtain acetylene, which was trimerized to benzene, which was subsequently used for ^{14}C measurement using LSC. For most of the liquid fuel samples, two subsamples of benzene were prepared. The first was kept for 30 days in a laboratory freezer (–20 °C) to remove radon contamination (^{222}Rn) and the second was used in resublimation as a quick removal of ^{222}Rn without waiting in the freezer.

Furthermore, to report the accurate and precise results of radiocarbon determination using LSC method, it was important to correct for isotopic fractionation using the $^{13}C/^{12}C$ ratio, expressed as $\delta^{13}C$, that was obtained using the IRMS technique. For AMS, the correction was made along with the ^{14}C measurement process using the AMS-derived $^{13}C/^{12}C$ ratios.

The main results of (Baranyika et al. 2022) are presented in Section.3. In Table 1 from this paper, it can be observed that liquid fuel samples were subjected to EA combustion to investigate the carbon content required to decide the amount of samples needed for graphitisation and required by standards to calculate the bio-based carbon content.

Carbon concentrations for the combusted samples considering only the calculated mass without weighting were not relevant, as they surpassed 100 % for all subsamples, while the combusted samples considering the weighted masses showed carbon concentrations of <100 % for all subsamples. The observed inconsistence of the calculated carbon concentrations did not affect the expected range of radiocarbon concentrations of the samples, but it was due to the loss of the sample due to the small capsule size relative to the pipette used in the subsampling procedure.

The procedure of tight sealing the tin capsules was tested to confirm the change in sample mass over time. The results in Table.1 showed that the mass of samples sealed in tin capsules that were kept in the laboratory for 24 hours before combustion varied by up to 22 %. There was no relation observed between the measured carbon concentration and the change of mass. Similar testing procedures were reported by (Santos Arévalo et al. 2015). The same results were obtained for samples stored for 48 hours prior to EA combustion. As a result, monitoring sample evaporation was unnecessary; however, controlling the EA cross-contamination by running empty analyses ("RunIn") in-between the samples and increasing the number of subsamples was critical.

The ^{14}C measurement results for both the AMS and LSC methods are also reported in (Baranyika et al. 2022). Stable isotopes ^{13}C and ^{12}C were used to quantify the ($\delta^{13}C$) isotopic ratio of the ANU-sucrose and NBS-22 oil standards, resulting in values of -10.5 and -30, respectively. As shown in Table.2, the results of all isotope measurements of liquid fuels were ranging from -26.9 ‰ to -30 ‰, and they were used to correct the radiocarbon content after measurements by the LSC.

The ^{14}C concentration measured for the background sample (ON/UF-BC) was used to test the contamination of the samples with modern carbon. The measurement results obtained using the AMS (0.32 ± 0.06 pMC) and LSC (0.25 ± 0.10 pMC) methods were satisfactory and comparable, given the combined uncertainty (with 0.07 ± 0.12 pMC difference). However, the resublimed background sample did not yield the intended result using LSC method (Table.2). This variation may be due to the inclusion of modern contamination when handling benzene. In addition, this background sample may be affected by the interaction with atmospheric CO_2 during many steps in the resublimation process.

Table 1. Results (% C) of liquid fuels combustion in EA in various experiments (see text).

**Result disregarded in average calculations.*

Sample name	Initial mass [mg]	Mass loss after 24 h [mg]	Mass loss after 48 h [mg]	Final mass [mg]	% C
B30 Experiment 1	1.3	-	-	1.3	127.22
	1.3	-	-	1.3	228.19
B30 Experiment 2	1.852	0.219	-	1.633	66.67
	1.887	0.136	-	1.751	66.72
	1.841	0.053	-	1.788	85.00
				Average	*72.8 ± 10.6*
B30 Experiment 3	1.900	-	0.110	1.790	29.14*
	1.884	-	0.090	1.794	75.38
	1.788	-	0.069	1.719	80.99
				Average	*78.2 ± 4.00*
B37 Experiment 1	1.3	-	-	1.3	262.68
	1.3	-	-	1.3	185.95
B37 Experiment 2	1.792	0.053	-	1.739	82.99
	1.802	0.073	-	1.729	90.49
	1.952	0.065	-	1.887	72.88
				Average	*82.1 ± 8.80*
B37 Experiment 3	1.892	-	0.084	1.808	81.25
	1.776	-	0.171	1.605	79.83
	1.846	-	0.111	1.735	66.03
				Average	*75.7 ± 8.40*
SN-204 Experiment 2	1.943	-	-	1.943	73.31
	1.858	-	-	1.858	65.42
	1.577	-	-	1.577	72.86
				Average	*70.5 ± 4.40*
SN-204 Experiment 3	1.897	-	0.177	1.720	88.33
	2.108	-	0.182	1.926	51.17
	2.189	-	0.202	1.987	54.17
				Average	*64.6 ± 20.60*
ON/UF-BC Experiment 3	1.828	-	0.122	1.706	85.50
	1.646	-	0.186	1.460	86.33
	1.872	-	0.206	1.666	83.45
				Average	*85.1 ±1.50*
Diesel BP Experiment 3	1.913	-	0.079	1.834	49.58
	1.893	-	0.420	1.473	63.75
	1.872	-	0.133	1.739	72.66
				Average	*62.0 ±11.60*
HVO Experiment 3	1.892	-	0.054	1.838	88.92
	1.853	-	0.068	1.785	67.45
	1.569	-	0.110	1.459	42.17
				Average	*66.2 ± 23.40*

Table 2. Results of radiocarbon concentration (pMC), and isotope fractionation (δ^{13}C) measurements.

Sample name	**δ^{13}C IRMS [‰]**	**Lab. ID**	**^{14}C concentration [pMC]**	**Method**
ON/UF-BC	GdMS-58627 -26.90±0.10	GdS-4368	0.25±0.10 0.25±0.10	LSC uncorrected LSC corrected
		GdS-4398 *resublimation*	1.63±0.13 1.64±0.13	LSC uncorrected LSC corrected
		GdA-5724	0.256±0.02	AMS
		GdA-5627	0.343±0.02	AMS
		GdA-5623	0.24±0.01	AMS
		GdA-5803	0.392±0.02	AMS
		GdA-6605	0.38±0.10	AMS
			0.32±0.06	*AMS average*
B30	GdMS-58633 -30.00±0.10	GdS-4333	39.67±0.43 40.07±0.43	LSC uncorrected LSC corrected
		GdS-4377 *resublimation*	34.16±0.42 34.50±0.42	LSC uncorrected LSC corrected
		GdA-6607	30.07±0.10	AMS
B37	GdMS-58638 -29.90±0.10	GdS-4334	28.50±0.48 28.78±0.48	LSC uncorrected LSC corrected
		GdA-6608	22.14±0.17	AMS
SN-204	GdMS-59026 -30.00±0.10	GdS-4009	9.74±0.22 9.84±0.22	LSC uncorrected LSC corrected
		GdS-4400 *resublimation*	9.33±0.19 9.42±0.19	LSC uncorrected LSC corrected
		GdA-6606	9.54±0.19	AMS
		GdA-5722	8.84±0.08	AMS
			9.19±0.49	*AMS average*
Diesel-BP	GdMS-58636 -30.00±0.10	GdS-4335	37.64±0.53 38.01±0.53	LSC uncorrected LSC corrected
		GdA-6609	33.92±0.20	AMS
HVO	GdMS-59022 -28.10±0.10	GdS-4379	99.49±0.81 100.10±0.81	LSC uncorrected LSC Corrected
		GdS-4386 *resublimation*	100.18±0.80 100.8±0.80	LSC uncorrected LSC corrected
		GdA-6610	101.45±0.33	AMS
ANU-sucrose	GdMS-58611 - 10.45±0.10			
NBS-22 oil	GdMS-58613 -30.00±0.10			

Furthermore, the measurement results demonstrate the reproducibility and reliability of both the AMS and LSC methods in determining the ^{14}C content in the HVO and SN-204 fuel samples. For HVO, the corrected results yielded values of 100.10 ± 0.81 and 100.8 ± 0.8 pMC for benzene kept 30 days, and the resublimed benzene samples, respectively, agreed with the AMS result (101.45±0.33 pMC). The δ^{13}C-corrected LSC results for both non-resublimed (9.74 ± 0.22 pMC) and resublimed (9.33 ± 0.19 pMC) are in line with the average AMS result (9.19 ± 0.49 pMC), given calculated uncertainties and expected biocarbon content in the SN-204 sample (see Table.2). The close agreement of these results enhanced confidence in the accuracy of the reported ^{14}C values.

The ^{14}C results measured by the LSC for B30 sample were 40.07 ± 0.43 pMC and 34.50 ± 0.40 pMC for sample kept 30 days in the laboratory freezer and the resublimed sample, respectively. They showed a discrepancy from AMS result (30.07 ± 0.10 pMC). Similarly, the LSC results for diesel-BP (38.01±0.53 pMC) and B37 (28.87±0.48 pMC) samples kept for 30 days in the freezer to remove radon, were not consistent with the AMS results of 33.92 ± 0.20 and 22.14 ± 0.17 pMC, respectively. However, no resublimation experiments were conducted on B37 and diesel-BP samples in this study. These differences for the three samples with ^{14}C results ~30 pMC for B30, B37, and diesel-BP are illustrated in Fig.1. There is no good explanation for this phenomenon presently. One reason may be an incomplete reaction with lithium, and we plan to improve reaction monitoring in the future.

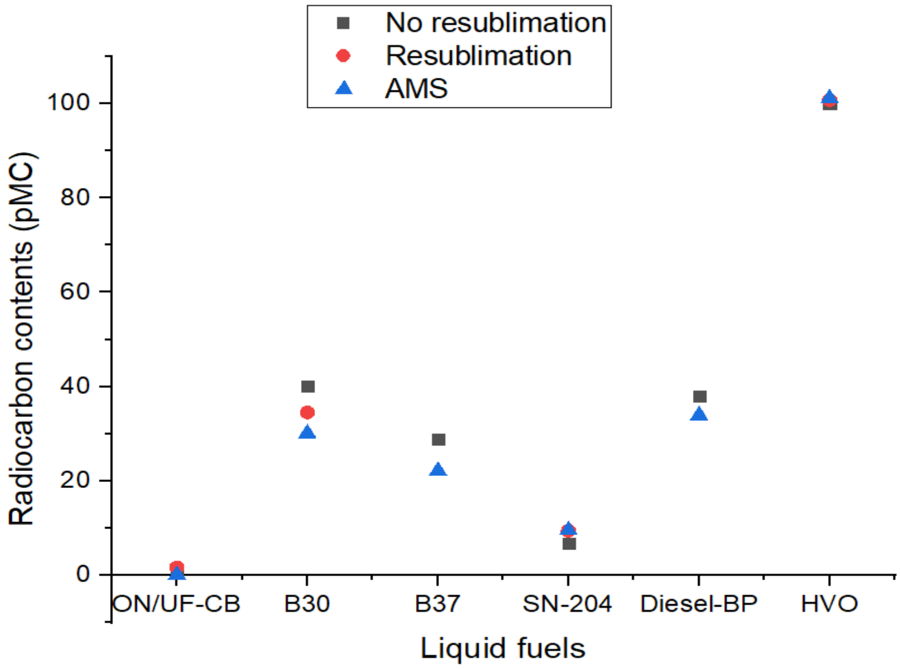

Figure 1. Radiocarbon (^{14}C) contents of tested liquid fuels grouped according to different methods of sample preparation (LSC-non resublimation, LSC-resublimation and AMS). Error bars are not visible at this scale.

4.2.2. Determination of radiocarbon content in bio-oil samples by Mini Carbon Dating System in the Gliwice Radiocarbon and Mass Spectrometry Laboratory

Isotope methods are invaluable tools for studying environmental changes in European countries and beyond. These methods involve analysing the isotopic composition of elements present in various environmental samples. In the Gliwice Radiocarbon and Mass Spectrometry Laboratory, a compact modern AMS system known as the Mini Carbon Dating System (MICADAS) is used to determine the ^{14}C content in different environmental samples, including liquid fuels.

The goal of this paper (Baranyika and Piotrowska 2023) was to determine the ^{14}C content of bio-oils using the MICADAS in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. The ^{14}C measurements for the tested biofuels and the biomass used as reference material were compared.

As mentioned in the section 2 of this research paper, three bio-oil samples from the catalytic process of biomass depolymerisation and the biomass (pistachio shells) used for their production were submitted by a manufacturer for ^{14}C measurement in the Gliwice Radiocarbon Laboratory. The methodology of the ^{14}C measurement process is summarised using Fig.2 in (Baranyika and Piotrowska 2023).

This ^{14}C measurement process using MICADAS required graphite targets (Lee et al. 2020) that were obtained by converting the original sample materials into graphite. Each bio-oil sample was subsampled into the tin capsule for liquids while the biomass was subsampled in the tin capsule for solid samples. To avoid loss of the sample due to evaporation, each bio-oil subsample was sealed in the second capsule for solid samples.

All samples were combusted in EA to produce CO_2, which was graphitised in AGE by reaction with hydrogen H_2 using iron powder as a catalyst (Němec et al. 2010; Wacker et al. 2010a). The obtained graphite targets consisting of 1 mg carbon and 5 mg iron were pressed using a pneumatic sample press (PSP) and measured by the MICADAS spectrometer to obtain a ^{14}C content in the tested bio-oil fuels. The Oxalic Acid II standard was used for normalisation and ^{14}C-free petroleum prepared in the same way was used as a background sample.

The results of the ^{14}C measurement were reported in percentage of modern carbon (pMC), which is a percentage of ^{14}C isotope concentration in the so-called modern biosphere.

Furthermore, biocarbon content calculations were performed in accordance with EN 16640:2017 (E) using the following equation for biogenic content relative to reference value (x_B):

$$x_B = \frac{F^{14}C_{sample}}{F^{14}C_{ref}} \cdot 100 \qquad (1)$$

where: $F^{14}C_{sample}$ is the radiocarbon content in a sample, and $F^{14}C_{ref}$ is the radiocarbon content in a reference material.

The biogenic carbon content in % by mass (x^{TC}_B) was calculated as follows:

$$x_B^{TC} = \frac{x_B}{x_{TC}}$$

(2)

where x_{TC} is the total carbon content of the sample. As a reference value ($F^{14}C_{ref}$), the ^{14}C content obtained for the pistachio shells was used.

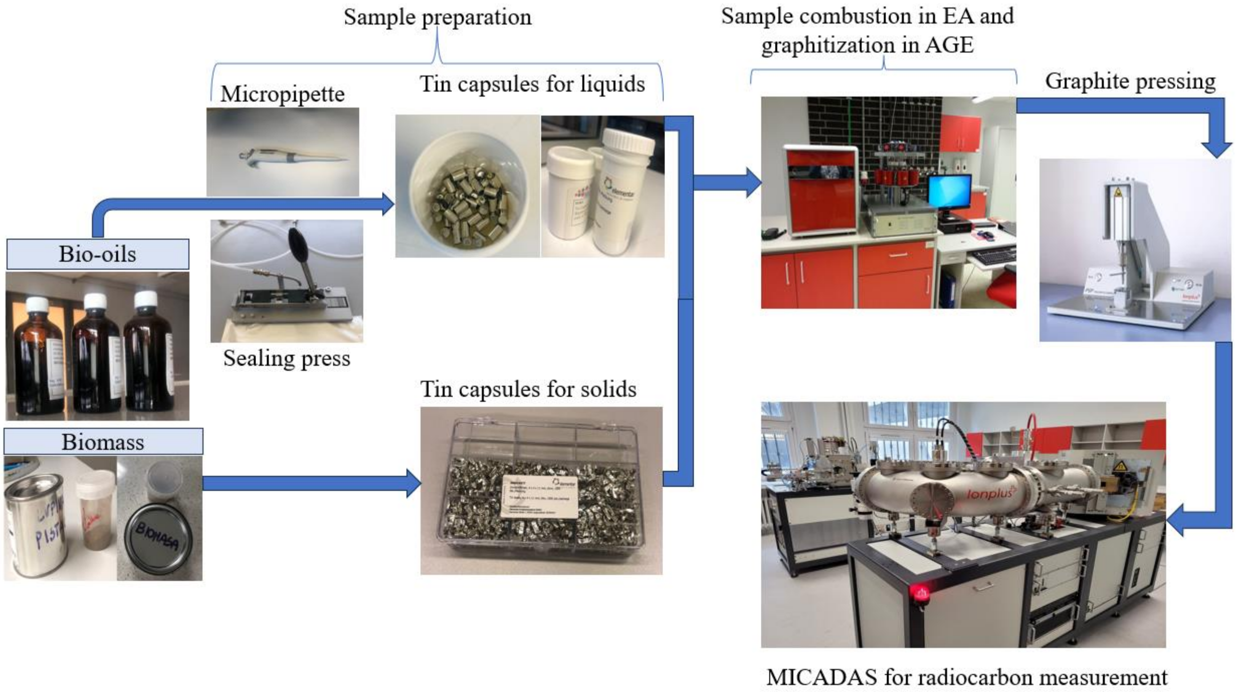

Figure 2. Radiocarbon measurement process by AMS technique in the Gliwice Radiocarbon and Mass Spectrometry Laboratory

As shown in section 3 of (Baranyika and Piotrowska 2023), the first parameter of interest in this study was the carbon content in percentage (% C) by mass. Based on the obtained % C content results in each sample such as 79.7 ± 1.7 %, 68.7 ± 2.1 %, 47.0 ± 1.1 %, and 48.82 ± 0.3 % for bio-oil-1, bio-oil-2, bio-oil-3, and the pistachio shell respectively, the sufficient amount of each investigated sample to obtain at least 1 mg of carbon to produce graphite targets for ^{14}C measurement by MICADAS accelerator was decided.

As presented in Table 3, several measurements of ^{14}C content were performed to test the reproducibility for each investigated sample. The average ^{14}C measurement results were 28.14 ± 0.4 pMC, 74.95 ± 0.22 pMC, 112.92 ± 0.07 pMC, and 102.61 ± 0.21 pMC for bio-oil-1, bio-oil-2, bio-oil-3, and the reference material (pistachio shell). However, the main objective of this study was to assess the consistency of the sample preparation technique in the Gliwice Laboratory rather than to merely obtain radiocarbon results. The graphical presentation of the radiocarbon measurement results for all bio-oil samples and the reference material is shown in Figure.3. A chi-square (χ^2) test was performed to confirm the reproducibility of the measurement results as well. In case of unsatisfactory test results, the outlying data were removed from the calculations.

As can be seen in Table 3, at a confidence level, α = 0.05, the final calculated χ^2 values were 1.21, 1.08, 0.15 and 0.41 for bio-oil-1, bio-oil-2, bio-oil-3, and the pistachio shell, respectively. As a result, all χ^2 values were less than CV, confirming non-significant differences, showing that the sample preparation procedure and the ^{14}C measurement using MICADAS yielded repeatable results. However, the preparation of multiple aliquots is crucial to detect inhomogeneity in the sample material.

Table 3. Reproducibility test for radiocarbon measurements in bio-oil fuels. The results are presented as pMC, and the uncertainties are calculated from AMS measurements.

Sample name	**Laboratory code**	**Number of experiment**	**^{14}C concentration (pMC)**	**Average ^{14}C concentration (pMC)**	**χ^2 test For α= 0.05 CV= 5.99**
Bio-oil-1	GdA6968.1.5	Experiment-1	27.72 ± 0.59	28.14 ± 0.36	χ^2 = 1.21 Significant
	GdA6968.1.3	Experiment-2	28.31 ± 0.18		
	GdA-6968.1.4	Experiment-3	28.40 ± 0.19		
	GdA-6968.1.2	Experiment-4	29.46 ± 0.56*		
Bio-oil-2	GdA-6969.1.1	Experiment-1	74.71 ± 0.32	74.95 ± 0.22	χ^2 = 1.08 Significant
	GdA-6969.1.2	Experiment-2	74.95 ± 0.32		
	GdA-6969.1.3	Experiment-3	75.18 ± 0.32		
	GdA-6969.1.5	Experiment-4	76.07 ± 0.32*		
	GdA-6969.1.4	Experiment-5	73.29 ± 0.32*		
Bio-oil-3	GdA-6970.1.1	Experiment-1	113.00 ± 0.28	112.92 ± 0.07	χ^2 =0.15 Significant
	GdA-6970.1.2	Experiment-2	112.85 ± 0.28		
	GdA-6970.1.5	Experiment-3	112.91 ± 0.28		
	GdA-6970.1.3	Experiment-4	110.85 ± 0.40*		
	GdA-6970.1.4	Experiment-5	110.11 ± 0.41*		
Pistachio shell (Reference material)	GdA-6971.1.1	Experiment-1	102.58 ± 0.29	102.61 ± 0.21	χ^2 = 0.41 Significant
	GdA-6971.1.2	Experiment-2	102.82 ± 0.29		
	GdA-6971.1.3	Experiment-3	102.61 ± 0.29		

*Shows inhomogenous sub-samples

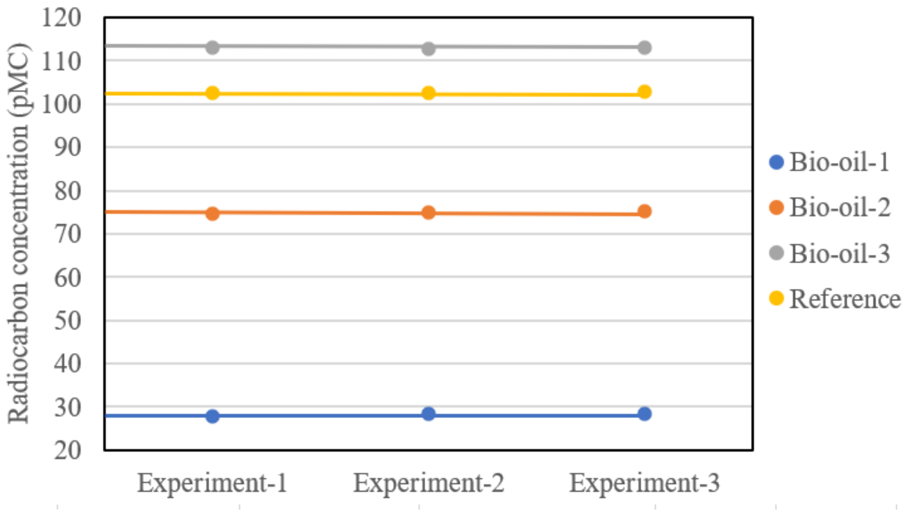

Figure 3. Graphical presentation of the reproducibility test for radiocarbon measurement in bio-oils by AMS; 2-sigma error bars are invisible at this scale.

Based on the ^{14}C concentration, the biogenic carbon was determined for all investigated samples. The determined biogenic carbon contents relative to the measured ^{14}C of the reference material (102.61 ± 0.21 pMC) are presented in Table 4. Surprisingly, the measurement results revealed a higher ^{14}C value for Bio-oil-3 (112.92 ± 0.07 pMC) compared to the biomass used as a reference material (102.61 ± 0.21 pMC). The calculated biogenic carbon content relative to the reference value was also higher for bio-oil-3 (110.04 ± 0.22 %) compared to the reference sample (100.00 ± 0.29 %).

Furthermore, as illustrated in Fig. 4, the results in Fig. 4A indicated that bio-oil-3 was probably grown in AD 1993-1994, while the reference material was grown in AD 2012-2016. This phenomenon revealed that only two samples, bio-oil-1 and bio-oil-2, were produced from the investigated pistachio shell, while bio-oil-3 was produced from an unknown biomass that was not provided by the sample submitter. This conclusion was confirmed by the company that provided the samples, but the additional information was confidential.

Table 4. Calculated radiocarbon, carbon, and biocarbon contents in bio-oil samples

Sample name	Lab. code	Carbon content in % by mass	^{14}C content (average) [pMC]	Biogenic carbon content relative to the reference value (x_B)	Biogenic carbon content in % by mass (x^{TC}_B)
Bio-oil-1	GdA-6968	79.7 ± 1.7	28.14 ± 0.36	27.43 ± 0.42	21.87 ± 1.76
Bio-oil-2	GdA-6969	68.7 ± 2.1	74.95 ± 0.22	73.04 ± 0.30	50.16 ± 2.09
Bio-oil-3	GdA-6970	47.0 ± 1.1	112.92 ± 0.07	110.04 ± 0.22	51.73 ± 1.10
Reference material	GdA-6971	48.82 ± 0.25	102.61 ± 0.21	100.00 ± 0.29	48.82 ± 0.39

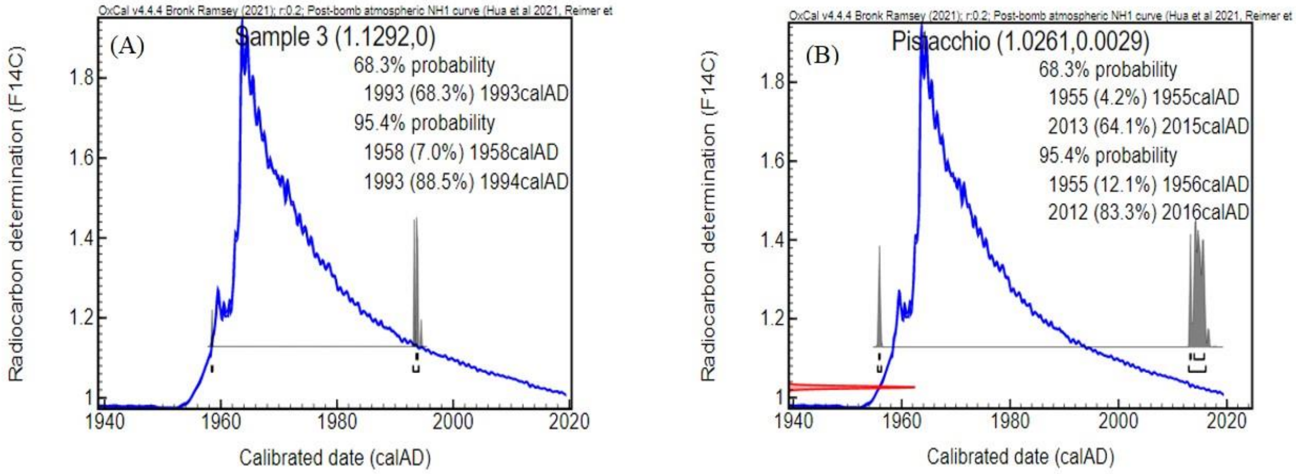

Figure 4. Calibration of F^{14}C results for bio-oil sample-3 (A) and the pistachio shell reference sample (B) and Ox Cal v.4.4 (Bronk Ramsey 2009) using the post-bomb atmospheric NH1 curve (Reimer et al. 2004; Hua et al. 2022). The F^{14}C values are commonly used in calibration process, and the relationship with pMC is pMC=F^{14}C*100 (Stenström et al. 2011).

4.2.3. Determination of radiocarbon content in liquid fuel blends by accelerator mass spectrometry and liquid scintillation counting in the Gliwice Radiocarbon and Mass Spectrometry Laboratory

The increased use of biobased products necessitates the development of verification methods to analyse the actual biocarbon content of such materials, including liquid fuel. This study (Baranyika et al. 2024) aimed to use both AMS and LSC methods to investigate the ^{14}C content in liquid fuel blends of known bio- to fossil fuel ratios. The ^{14}C measurement methods (LSC and AMS) are described in sections 2.2 and 2.3, respectively.

Fuel blend samples were produced from a sample of HVO and a petrodiesel sample of infinite ^{14}C age (ON/UF-BC) that were submitted in the Gliwice Laboratory in 2018 by an external oil company in large quantity, which allowed them to be used for testing purposes for years (Baranyika et al. 2022). The ON/UF-BC has been extensively used as a background sample for liquid fuels.

The ^{14}C measurement results were reported in the section.3 of (Baranyika et al. 2024). As presented in Table.5, the ^{14}C content of the background sample (ON/UF-BC) was the foremost parameter to test the contamination of the samples. The weighted average of 14 independent 24-hour background measurements by the LSC Quantulus 1220 spectrometer was 0.3598 ± 0.0052 cpm (counts per minute). The consistency of individual measurements was confirmed using the χ^2 test. For AMS, the nine measurements conducted yielded an average of 0.41 ± 0.18 pMC for the ON/UF-BC background sample. The respective values obtained for the ON/UF-BC sample were used for background correction for all subsequent AMS and LSC analyses.

For HVO, the LSC method yielded a ^{14}C measurement of 100.10 ± 0.81 pMC. This result agreed with the AMS result (101.45 ± 0.33 pMC).

Figure 5 depicts the graphical representation of the ^{14}C measurement results of the tested fuel blends (Bld) for both the methods (LSC and AMS) and the components (HVO and ON/UF-BC) used for their production. As shown in the Figure, all values fall within the 2-sigma uncertainty range, indicating that both the sample preparation methods and ^{14}C measurements yielded reliable results. As the ^{14}C content in HVO is ca.100 pMC, the results for all other fuel blends follow a linear trend.

In addition, the linear regression plot was used to compare the ^{14}C results for the six fuel blends. As shown in Figure 6, the linear regression equation ($y = ax + b$; $a=1.022 \pm 0.025$, $b=0.07 \pm 0.43$) with $R^2= 0.9975$ demonstrated a strong correlation between the AMS and LSC measurement results. The distribution of the ^{14}C values along the regression line indicated good reproducibility between the two methods, with the exception of blend-15, where the measurement results for the two methods deviated further apart compared to the other samples.

Table 5. Results of radiocarbon content measurement (in pMC with 1-sigma uncertainty) in fuel blends and background sample for both LSC and AMS methods and isotope fractionation (δ^{13}C, measured for ON/UF-BC and HVO, calculated for blend samples-see text for methodology).

Sample name	**δ^{13}C IRMS [‰]**	**δ ^{13}C AMS**	**Lab. ID**	**^{14}C content [pMC]**	**Method**
ON/UF-BC	-26.90	-26.5	GdS-4547	1.30 ± 0.11	LSC
			GdA-6821	0.50 ± 0.25 0.45 ± 0.11 0.39 ± 0.21 0.36 ± 0.22 0.42 ± 0.21 0.38 ± 0.30 0.36 ± 0.22 0.38 ± 0.20 0.32 ± 0.22	AMS
				0.41 ± 0.18	AMS average
Blend-5	-26.96	-27.7	GdS-4546	5.02 ± 0.14	LSC
			GdA-6820	5.12 ± 0.15	AMS
Blend-7.5	- 26.99	-27.4	GdS-4545	7.45 ± 0.14	LSC
			GdA-6819	7.72 ± 0.16	AMS
Blend-10	-27.02	-29.4	GdS-4502	11.03 ± 0.22	LSC
			GdA-6817	10.71 ± 0.16	AMS
Blend-15	-27.08	-27.2	GdS-4538	14.03±0.22	LSC
			GdA-6818	15.27 ± 0.16	AMS
Blend-20	-27.14	-29.2	GdS-4501	20.62 ± 0.29	LSC
			GdA-6816	21.06 ± 0.17	AMS
Blend-30	-27.26	-28.9	GdS-4496	30.67 ± 0.36	LSC
			GdA-6815	31.33 ± 0.19	AMS
HVO	-28.1	ND	GdS-4379	100.10 ± 0.81	LSC
			GdA-6610	101.45 ± 0.33	AMS

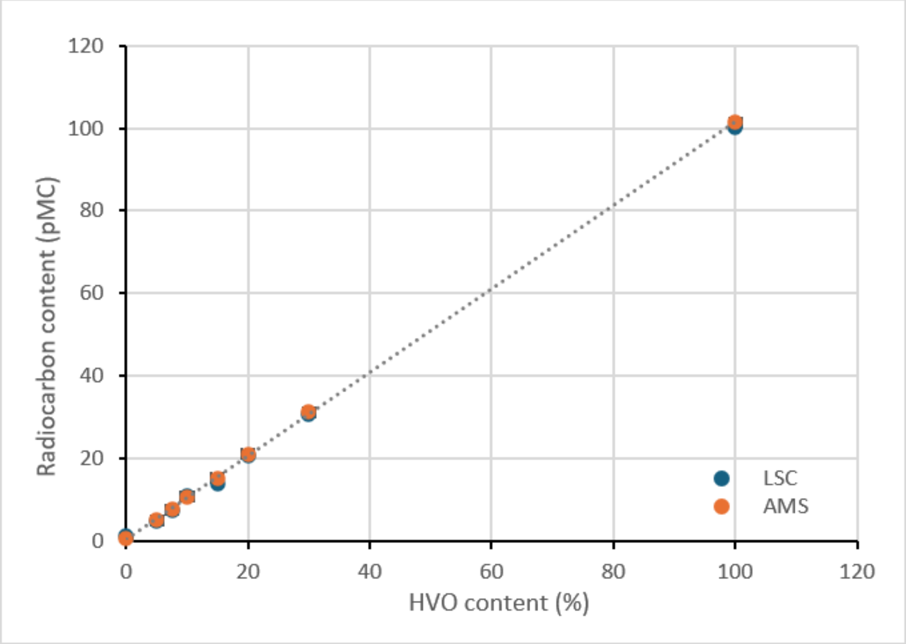

Figure 5. Radiocarbon content of the tested fuel blends (Bld) and the components (HVO and ON/UF-BC) used for their production for both methods (LSC and AMS). The 2-sigma error bars are not visible at the given scale.

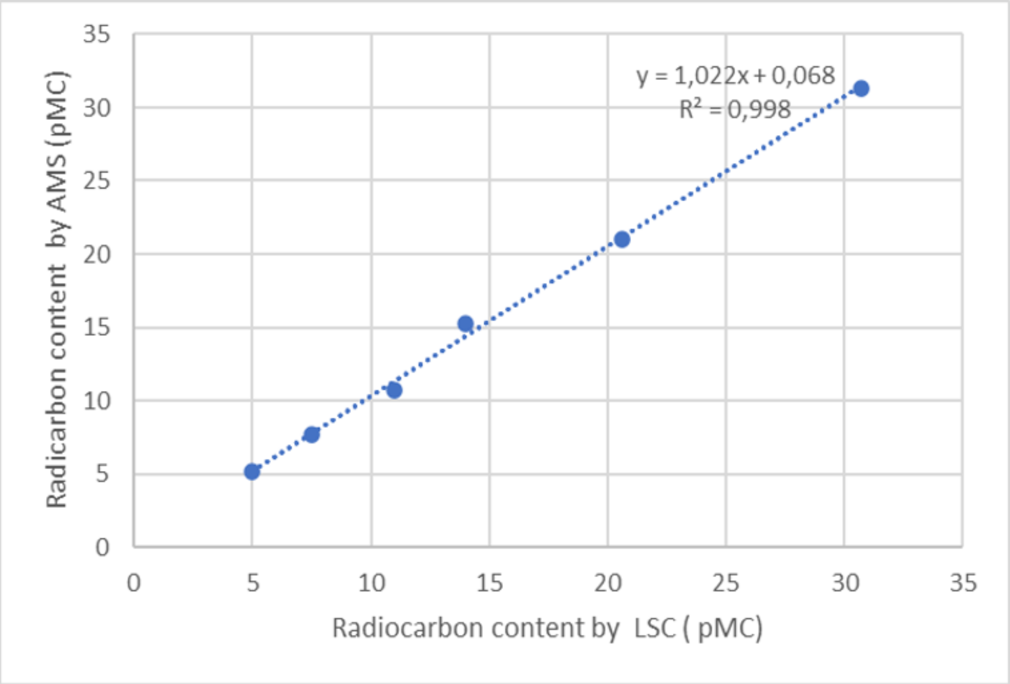

Figure 6. Comparison of radiocarbon content results in six fuel blends for LSC and AMS using the regression method. The 2-sigma error bars are invisible due to low uncertainty values.

To investigate the reproducibility of the results produced by the MICADAS accelerator in the Gliwice laboratory, additional measurements were conducted for 10 subsamples of blend-15 with the same volume (2 µl). The results of the ^{14}C measurement for these subsamples are presented in Table 6 of (Baranyika et al. 2024) and the calculated average was 15.12 ± 0.10 pMC. Compared to the prior measurement for Blend-15 (15.27 ± 0.16 pMC), this ^{14}C average value was reproducible. The results of the reproducibility test are also shown in Figure 7. They were within a 2-sigma range, demonstrating that from sample preparation using a tin capsule for liquids, through the sealing procedure and combustion in the elemental analyser, to graphitisation by AGE, reproducible results were obtained from the MICADAS system in our laboratory. The reproducibility test was confirmed by a chi-square (χ^2). From Table 6 in this paper, it can be observed that the computed χ^2 value was 7.72, and the critical value (CV) was 21.67 (with a confidence level, $\alpha = 0.01$). Since the χ^2 value was less than the CV, there was no significant difference between the results from all 10 aliquots, indicating that the results were reproducible and consistent.

Table 6. Results of radiocarbon content for the reproducibility test using the MICADAS system.

Sample name	**Subsample number**	**Lab code**	**^{14}C content [pMC]**	**χ^2 test**
Blend-15	1	GdA-6818.1.3	15.05 ± 0.11	For α= 0.01, CV=21.67 χ^2 = 7.72
	2	GdA-6818.1.5	15.13 ± 0.11	
	3	GdA-6818.1.6	15.07 ± 0.11	
	4	GdA-6818.1.7	14.98 ± 0.12	
	5	GdA-6818.2.1	15.18 ± 0.11	
	6	GdA-6818.2.2	15.16 ±0.11	
	7	GdA-6818.2.3	15.24 ± 0.12	
	8	GdA-6818.2.4	15.14 ± 0.11	
	9	GdA-6818.2.5	14.94 ± 0.11	
	10	GdA-6818.2.6	15.26 ± 0.11	
			Mean= 15.12 ± 0.10	χ^2<CV, there is no significant difference

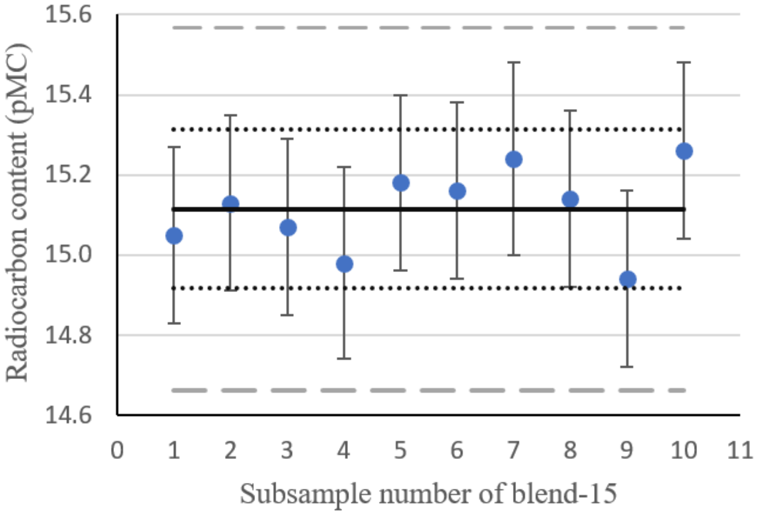

Figure 7. Graphical presentation of the radiocarbon content for the reproducibility test of the MICADAS system in our laboratory. Error bars show 2-sigma uncertainties. The solid line shows the average, the dotted lines show the double standard deviation from the average, and the dashed line shows the 3 % acceptability limits as provided by the ASTM D6866-22 standard.

5. Summary of own contribution to the Ph.D. project

In the course of Ph.D. research, I have carried out the following activities:

Review of literature: I reviewed the relevant literature to identify gaps and limitations, and to ensure that my work is in line with the current state of knowledge in the field. I studied published experiments on radiocarbon method applied for biocarbon content determinations and contributed to refining the methodology for specific challenges encountered in the Gliwice Laboratory.

Research design and planning: I contributed to the development of the research objectives and framework for application of isotope methods to investigate liquid fuels composition. This included identifying relevant issues to adapt the methodology for biocarbon content determination in liquid fuels in the Gliwice Radiocarbon and Mass Spectrometry Laboratory and to verify the accuracy of this methodology. I also tested and improved the methodology for sample preparation, in particular the technique for sealing samples in tin capsules for liquids. I tested this method through a series of experiments, which significantly contributed to increasing the accuracy and precision of the measurement results.

Sample selection and preparation. I carried out the selection of liquid fuel samples from the samples archived in the Gliwice Laboratory and worked with other samples submitted by companies in Poland during the course of my studies. The selection adhered to best practices to prevent contamination and ensure homogenisation of sample material. I performed preparation of the samples for isotope analysis, using relevant techniques.

This involved benzene synthesis for LSC, preparation of graphite for AMS analysis, and CO_2 for IRMS analysis. For sample combustion and determination of carbon content by mass I used the elemental analyser (EA), which is coupled to the automated system AGE-3 for converting the CO_2 to graphite. I used vacuum lines for benzene synthesis and for CO_2 production and purification. In total, I prepared 13 benzene samples, 224 graphite targets and 72 CO_2 samples.

Laboratory measurements: Under the supervision of my advisor, I performed the measurements with use of AMS MICADAS spectrometer for ^{14}C content analysis, and IRMS IsoPrime spectrometer for stable carbon isotope analysis. In addition, I processed the raw data acquired during measurement using specialised software such as BATs (for AMS) and IonVantage (for IRMS), as well as OxCal software to calibrate the radiocarbon data to convert them into calendar dates.

Writing publications, applications and reports: I am the lead author of the three manuscripts forming this Ph.D. thesis. I performed writing of the text, preparation of all figures and tables and submission to journals, as well as responding to the comments of the reviewers. In addition, I wrote the extended abstract as a part of my Ph.D. thesis based on published papers. I am also the lead author of other five manuscripts, stemming from my BSc and MSc thesis. I applied for the internal SUT funding for young scientists three times with success. I wrote the three annual reports for Doctoral School, including the mid-term report, which were positively evaluated by relevant Commissions.

Presentations on scientific meetings: I presented my results at 6 international scientific conferences, including 3 oral and 3 poster presentations. I provided two seminars at the Division meetings, and one lecture at the workshop for young scientists.

6. General conclusions

In conclusion, the primary aim of this study was to test, evaluate and optimise the sample preparation and measurement methods in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. The choice between AMS and LSC methods for radiocarbon dating largely depends on specific study requirements, such as sample size, age, desired precision, and available resources.

In the three published papers, liquid fuel sample preparations were tested using both AMS and LSC methods. As demonstrated by the results in Table 5, AMS exhibited greater sensitivity and precision, making it highly suitable for small samples. Aside from sample loss due to the small size relative to the pipette tip, the sealing press was effective for AMS samples. For the LSC method, more complex sample preparation, such as converting the sample to benzene, was required.

The ^{14}C content of the background samples measured using both AMS and LSC without resublimation, confirmed that the results for the ^{14}C-free sample were stable and enabled the necessary corrections. Additionally, the minimum detectable ^{14}C content in liquid fuels at the Gliwice Laboratory was determined to be approximately 0.4 pMC for AMS and around 1 pMC for LSC (see Tables 2 and 5).

The ^{14}C measurement results for fuel blends using both AMS and LSC methods showed good reproducibility of sample processing. Minor differences between the results obtained with two methods may stem from variations in carbon conversion efficiency during benzene production for LSC compared to combustion in the elemental analyser for AMS. This is despite corrections for isotope fractionation ($^{13}C/^{12}C$ ratio measured by IRMS) being applied to ensure accurate and precise LSC ^{14}C results.

The findings of the study on bio-oil and fuel blend samples demonstrated that the reproducibility test yielded reliable results, indicating that the AMS technique using the MICADAS spectrometer provided satisfactory precision for ^{14}C measurements in the Gliwice Radiocarbon and Mass Spectrometry Laboratory.

References

Baranyika JB, Piotrowska N. 2023. Determination of radiocarbon content in bio-oil samples by Mini Carbon Dating system in the Gliwice Radiocarbon and Mass spectrometry Laboratory. Geochronometria. 50:21–27. doi:10.2478/geochr-2023-0005.

Barayika JB, Piotrowska N, Kłusek M, Michczyński A, Pawlyta J. 2022. Testing the Methods for Determination of Radiocarbon Content in Liquid Fuels in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. Radiocarbon. 64(6):1447–1456. doi:10.1017/rdc.2022.35.

Baranyika JB, Piotrowska N, Michczyński A. 2024. Determination of radiocarbon content in liquid fuel blends by accelerator mass spectrometry and liquid scintillation counting in the Gliwice Radiocarbon and Mass spectrometry Laboratory. Radiocarbon.:1–12. doi:https://doi.org/10.1017/RDC.2024.51.

Boucher ME, Chaala A, Roy C. 2000. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part I: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase. Biomass and Bioenergy. 19(5):337–350. doi:10.1016/S0961-9534(00)00043-X.

Bronk Ramsey C. 2009. Bayesian analysis of radiocarbon dates. Radiocarbon. 51(1):337–360. doi:10.1017/s0033822200033865.

Culp R. 2017. Radiocarbon Analysis for Biofuel Quantification in Fuel Blends. Encyclopedia of Analytical Chemistry.:1–13. doi:10.1002/9780470027318.a9587.

Culp R, Cherkinsky A, Ravi Prasad G V. 2014. Comparison of radiocarbon techniques for the assessment of biobase content in fuels. Applied Radiation and Isotopes. 93:106–109. doi:10.1016/j.apradiso.2014.01.007.

Dijs IJ, van der Windt E, Kaihola L, van der Borg K. 2006. Quantitative determination by ^{14}C analysis of the biological component in fuels. Radiocarbon. 48(3):315–323. doi:10.1017/S0033822200038777.

Dobrzyńska E, Szewczyńska M, Pośniak M, Szczotka A, Puchałka B, Woodburn J. 2020. Exhaust emissions from diesel engines fueled by different blends with the addition of nanomodifiers and hydrotreated vegetable oil HVO. Environmental Pollution. 259. doi:10.1016/j.envpol.2019.113772.

Doll CG, Plymale AE, Cooper A, Kutnyakov I, Swita M, Lemmon T, Olarte M V., Wang H. 2021. Determination of low-level biogenic gasoline, jet fuel, and diesel in blends using the direct liquid scintillation counting method for ^{14}C content. Fuel. 291(November 2020):120084. doi:10.1016/j.fuel.2020.120084.

Fan J, Kalnes TN, Alward M, Klinger J, Sadehvandi A, Shonnard DR. 2011. Life cycle assessment of electricity generation using fast pyrolysis bio-oil. Renewable Energy. 36(2):632–641. doi:10.1016/j.renene.2010.06.045.

Guo X, Liang C, Umar M, Mirza N. 2022. The impact of fossil fuel divestments and energy transitions on mutual funds performance. Technological Forecasting and Social Change. 176(December 2021):121429. doi:10.1016/j.techfore.2021.121429.

Gutiérrez J, Galán CA, Suárez R, Álvarez-Murillo A, González JF. 2018. Biofuels from cardoon pyrolysis: Extraction and application of biokerosene/kerosene mixtures in a self-manufactured jet engine. Energy Conversion and Management. 157:246–256. doi:10.1016/j.enconman.2017.12.006.

Hajdas I, Charlotte L. Pearson , Gianluca Quarta , Kirsty L. Spalding HY, Yoneda and M. 2021. Radiocarbon dating. Encyclopedia of Earth Sciences Series. 0123456789:689–702. doi:10.1007/978-1-4757-9694-0_3.

Haverly MR, Fenwick SR, Patterson FPK, Slade DA. 2019. Biobased carbon content quantification through AMS radiocarbon analysis of liquid fuels. Fuel. 237(October 2018):1108–1111. doi:10.1016/j.fuel.2018.10.081.

Horvatinčić N, Barešić J, Bronić IK, Obelić B. 2004. Measurement of low 14C activities in a liquid scintillation counter in the Zagreb Radiocarbon Laboratory. Radiocarbon. 46(1):105–116. doi:10.1017/S0033822200039412.

Hua Q, Turnbull JC, Santos GM, Rakowski AZ, Ancapichún S, De Pol-Holz R, Hammer S, Lehman SJ, Levin I, Miller JB, et al. 2022. Atmospheric Radiocarbon for the Period 1950-2019. Radiocarbon. 64(4):723–745. doi:10.1017/RDC.2021.95.

Idoeta R, Pérez E, Herranz M, Legarda F. 2014. Characteristic parameters in the measurement of 14C of biobased diesel fuels by liquid scintillation. Applied Radiation and Isotopes. 93:110–113. doi:10.1016/j.apradiso.2014.01.019.

Karaaslan A, Gezen M. 2022. The evaluation of renewable energy resources in Turkey by integer multi-objective selection problem with interval coefficient. Renewable Energy. 182(2022):842–854. doi:10.1016/j.renene.2021.10.053.

Krajcar Bronić I, Barešić J, Horvatinčić N, Sironić A. 2017. Determination of biogenic component in liquid fuels by the 14C direct LSC method by using quenching properties of modern liquids for calibration. Radiation Physics and Chemistry. 137:248–253. doi:10.1016/j.radphyschem.2016.01.041.

Krištof R. 2015. Quantification of biocomponents in fuels by 14C. Ph.D thesis. University of Nova Gorica Graduate School.

Krištof R, Kožar Logar J. 2013. Direct LSC method for measurements of biofuels in fuel. Talanta. 111:183–188. doi:10.1016/j.talanta.2013.03.009.

Krištof R, Kožar Logar J. 2017. Liquid Scintillation Spectrometry as a Tool of Biofuel Quantification. In: Frontiers in Bioenergy and Biofuels. p. 60–69.

Lee JE, Li ZH, Wang H, Plymale AE, Doll CG. 2022. Quantification of biogenic carbon in fuel blends through LSC 14C direct measurement and assessment of uncertainty. Fuel. 315:122859. doi:10.1016/j.fuel.2021.122859.

Lee P, Hoon S, Kong M, Kim Y. 2020. A new compact AMS facility at the Dongguk University. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 465:15–18. doi:10.1016/j.nimb.2019.12.027.

Liaquat AM, Masjuki HH, Kalam MA, Varman M, Hazrat MA, Shahabuddin M, Mofijur M. 2012. Application of blend fuels in a diesel engine. Energy Procedia. 14:1124–1133. doi:10.1016/j.egypro.2011.12.1065.

Malinowski A, Wrzosek P, Turlej A, Wardzińska D. 2015. A Review of Selected Methods of Measurement Used for the On-Line Analysis of Liquid Fuels. In: IntechOpen. p. 189–204.

Maruccio L, Quarta G, Braione E, Calcagnile L. 2017. Measuring stable carbon and nitrogen isotopes by IRMS and 14C by AMS on samples with masses in the microgram range: Performances of the system installed at CEDAD-University of Salento. International Journal of Mass Spectrometry. 421:1–7. doi:10.1016/j.ejbt.2017.01.004.

Matsakas L, Gao Q, Jansson S, Rova U, Christakopoulos P. 2017. Green conversion of municipal solid wastes into fuels and chemicals. Electronic Journal of Biotechnology. 26:69–83. doi:10.1016/j.ejbt.2017.01.004. http://dx.doi.org/10.1016/j.ejbt.2017.01.004.

Morone P, D'Amato D. 2019. The role of sustainability standards in the uptake of bio-based chemicals. Current Opinion in Green and Sustainable Chemistry. 19:45–49. doi:10.1016/j.cogsc.2019.05.003.

Neha S, Remya N. 2022. Co-production of biooil and biochar from microwave co-pyrolysis of food-waste and plastic using recycled biochar as microwave susceptor. Sustainable Energy Technologies and Assessments. 54:102892. doi:10.1016/j.seta.2022.102892.

Němec M, Wacker L, Gäggeler H. 2010. Optimization of the graphitization process AT AGE-1. Radiocarbon. 52(3):1380–1393. doi:10.1017/S0033822200046464.

Rajasekhar M, Rao NV, Rao GC, Priyadarshini G, Kumar NJ. 2015. Energy Generation from Municipal Solid Waste by Innovative Technologies – Plasma Gasification. Procedia Materials Science. 10:513–518. https://doi.org/10.1017/S0033822200033154.

Reimer PJ, Brown TA, Reimer RW. 2004. Discussion: Reporting and calibration of post-Bomb 14C data. Radiocarbon. 46(3):1299–1304. https://doi.org/10.1016/S0969-806X(01)00255-9.

Santos Arévalo FJ, Gómez Martínez I, Agulló García L, Reina Maldonado MT, García León M. 2015. 14C determination in different bio-based products. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 361:354–357. doi:10.1016/j.nimb.2015.01.033.

De Souza JE, Scherer MD, Cáceres JAS, Caires ARL, M'Peko JC. 2013. A close dielectric spectroscopic analysis of diesel/biodiesel blends and potential dielectric approaches for biodiesel content assessment. Fuel. 105:705–710. doi:10.1016/j.fuel.2012.09.032.

Stenström KE, Skog G, Georgiadou E, Genberg J, Johansson A. 2011. A guide to radiocarbon units and calculations Lund University , Department of Physics , Division of Nuclear Physics.(LUNFD6(NFFR-3111)/1-17/(2011)). Lund University, Nuclear Physics.

Sulek MW, Kulczycki A, Malysa A. 2010. Assessment of lubricity of compositions of fuel oil with biocomponents derived from rape-seed. Wear. 268(1):104–108. doi:10.1016/j.wear.2009.07.004.

Tuniz C, John Rb, David F, Gregory FH. 2001. Accelerator mass spectrometry: Ultra-sensitive analysis for global science. Radiation Physics and Chemistry. 61:317–322. https://doi.org/10.1016/S0969-806X(01)00255-9.

Verger T, Azimov U, Adeniyi O. 2022. Biomass-based fuel blends as an alternative for the future heavy-duty transport: A review. Renewable and Sustainable Energy Reviews. 161:112391. https://doi.org/10.1016/j.rser.2022.112391.

Wacker L, Synal HA, Marcus C. 2010b. Bats: A new tool for AMS data reduction. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 268(7–8):976–979. http://dx.doi.org/10.1016/j.nimb.2009.10.078.

Wacker L, Němec M, Bourquin J. 2010a. A revolutionary graphitisation system: Fully automated, compact and simple. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 268(7–8):931–934. doi:10.1016/j.nimb.2009.10.067.

Wagner T, R. Magill C, O. Herrle J. 2016. Carbon isotopes. In: Encyclopedia of Earth Sciences Series. Vol. Part 2. p. 73–78.

POLITECHNIKA ŚLĄSKA

INSTYTUT FIZYKI – CENTRUM NAUKOWO-DYDAKTYCZNE
ZAKŁAD GEOCHRONOLOGII I BADAŃ IZOTOPOWYCH ŚRODOWISKA

PRACA DOKTORSKA

ZASTOSOWANIE METOD IZOTOPOWYCH DO OZNACZANIA BIOKOMPONENTÓW W PALIWACH CIEKŁYCH

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Podziękowania

Praca doktorska to nie tylko osiągnięcie akademickie, ale także monumentalne osiągnięcie życiowe, które wymaga wsparcia różnego rodzaju. Wciąż trudno mi uwierzyć, że osiągnąłem ten kamień milowy. Chciałbym wznieść toast za wszystkich, którzy byli częścią tej niesamowitej podróży ze mną.

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Streszczenie

W wielu krajach europejskich metody izotopowe są wykorzystywane do badania zmian środowiskowych. W celu oznaczenia biokomponentów w paliwach płynnych z wykorzystaniem analiz zawartości radiowęgla (^{14}C) konieczne jest dostosowanie sposobu przygotowania próbek do warunków Gliwickiego Laboratorium Radiowęglowego i Spektrometrii Mas.

W niniejszej pracy zostały przetestowane metody akceleratorowej spektrometrii mas (AMS) i ciekłoscyntylacyjnej (LSC) przy użyciu próbek paliw ciekłych dostarczonych w 2018 r. przez zewnętrzną firmę paliwową w dużych ilościach, w tym czysto bio-bazowego hydrorafinowanego oleju roślinnego (HVO) i jednej próbki oleju napędowego o nieskończonym wieku ^{14}C (ON/UF-BC). Analizom poddano też próbki bio-oleju i próbki referencyjnej 100% biomasy oraz kilku mieszanek paliwowych wyprodukowanych z ON/UF-BC i HVO w różnych proporcjach.

W przypadku AMS próbki do pomiarów ^{14}C przygotowano przy użyciu cynowych kapsułek do cieczy do spalania w analizatorze elementarnym (EA) i grafityzacji w systemie automatycznym (AGE). Dla metody LSC przygotowano próbkę benzenu. Aby bezpiecznie umożliwić konwersję próbek paliwa do węglika litu (Li_2C_2) bez powodowania eksplozji, każde ciekłe paliwo zmieszano z oczyszczonym piaskiem kwarcowym. Przetestowano również metodę resublimacji benzenu w celu przyspieszenia procedury. Pomiary IRMS przeprowadzono dla benzenu w celu określenia $\delta^{13}C$ i uwzględnienia frakcjonowania izotopowego.

Wartości tła uzyskano na podstawie wyników pomiarów ^{14}C dla czystego oleju napędowego. Wyniki dla mieszanek paliw płynnych dowiodły, że zawartość ^{14}C jest zgodna między metodami AMS i LSC. Dodatkowo, liniowa zależność między zawartością ^{14}C i HVO potwierdziła powtarzalność obu metod i pozwoliła na ich walidację. Powtarzalność wyników AMS została zweryfikowana w kilku podpróbkach jednej z mieszanek, a wyniki zostały uznane za spójne. Ponadto wyniki uzyskane dla biooleju pozwoliły wykryć, że jedna z próbek nie została wyprodukowana z badanej biomasy referencyjnej.

Wyniki badania wykazały, że zarówno AMS, jak i LSC są skutecznymi metodami datowania radiowęglowego, ale ich wybór zależy od konkretnych potrzeb badawczych, równoważenia dokładności, wielkości próbki i dostępnych zasobów. AMS jest lepsza dla małych próbek i wysokiej precyzji, podczas gdy LSC jest bardziej praktyczna dla większych próbek.

Spis treści

Wykaz tabel

Wykaz wykresów

Lista skrótów

HVO: Uwodorniony olej roślinny (*Hydrogenated Vegetable Oil)*

AMS: Akceleratorowa spektrometria mas (*Accelerator Mass Spectrometry)*

LSC: Licznik ciekłoscyntylacyjny (*Liquid Scintillation Counting*)

IRMS: Izotopowa spektrometria masowa (*Isotope-Ratio Mass Spectrometry*)

AGE: Zautomatyzowany sprzęt do grafityzacji (*Automated Graphitisation Equipment*)

EA: Analizator elementarny (*Elemental Analyser*)

CV: Wartość krytyczna (*Critical Value*)

MICADAS: =nazwa własna spektrometru AMS (*Mini Carbon DAting System*)

ASTM: Amerykańskie Stowarzyszenie Badań i Materiałów (*American Society for Testing and Materials*)

pMC: Procent współczesnego węgla (*Percent Modern Carbon*)

GdS: Identyfikator próbki dla pomiarów LSC w Gliwicach

GdA: identyfikator próbki dla pomiarów AMS w Gliwicach

GADAM: Gliwickie Centrum Absolutnych Metod Datowania (*Gliwice Absolute DAting Methods Centre*)

PŚ: Politechnika Śląska

1. Opis tematu badawczego

W świecie szybkiego rozwoju nie ma wątpliwości, że globalne zapotrzebowanie na energię gwałtownie rośnie w wyniku wzrostu gospodarczego i wzrostu liczby ludności. Paliwa płynne odgrywają ważną rolę w transporcie i wzroście gospodarczym (Krištof i Kožar Logar 2013). Przez wiele lat intensywne wykorzystanie paliw kopalnych, które są uważane za siłę napędową stylu życia i światowej gospodarki w sektorach produkcji energii i transportu, doprowadziło do degradacji środowiska ze względu na wyższą emisję dwutlenku węgla (CO_2) do atmosfery (Dijs et al. 2006; Liaquat et al. 2012; Guo et al. 2022).

Ze względu na obawy dotyczące środowiska, takie jak zanieczyszczenie wody, zanieczyszczenie powietrza i globalne ocieplenie związane z wykorzystaniem paliw kopalnych, państwa członkowskie Unii Europejskiej (UE) i inne kraje na całym świecie rozwijają alternatywne źródła energii, takie jak biomasa, panele słoneczne, wykorzystujące energię wiatru i fal, a także energię jądrową (Rajasekhar i in. 2015; Matsakas i in. 2017; Neha i Remya 2022). Ponadto, w celu zmniejszenia emisji CO_2 do atmosfery, wiele krajów koncentruje się na wykorzystaniu paliw płynnych pochodzących z przyjaznych dla środowiska zasobów odnawialnych (De Souza et al. 2013). Paliwo ciekłe zwane bioolejem produkowane z biomasy ma kilka korzyści dla środowiska. Jest ono uważane za neutralne pod względem emisji CO_2, ponieważ CO_2 jest sekwestrowany podczas wzrostu surowca, i może generować kredyty CO_2 bez emisji tlenków siarki (SO_X) (Fan et al. 2011). Ponadto ilość tlenków azotu (NO_x) emitowanych podczas spalania bioolejú jest o 50% niższa niż w przypadku biodiesla z turbin gazowych (Boucher et al. 2000; Gutiérrez et al. 2018).

Ponadto wiele krajów europejskich, takich jak Polska, wdrożyło strategie mieszania paliw w celu zmniejszenia strumienia netto węgla do atmosfery i zależności od paliw kopalnych. Mieszanki te często obejmują biopaliwa pochodzące z zasobów odnawialnych, takich jak uprawy trzciny cukrowej, kukurydzy, a także biodiesel z oleju roślinnego (Dobrzyńska i in. 2020; Verger i in. 2022).

W przyrodzie występują trzy izotopy węgla. ^{13}C i ^{12}C to stabilne izotopy węgla o udziale odpowiednio 1,11 %i 98,89% (Wagner et al. 2016). Ponadto istnieje kosmogeniczny radiowęgiel (^{14}C) wytwarzany w górnej atmosferze Ziemi w reakcji azotu (^{14}N) z neutronami promieniowania kosmicznego, który następnie tworzy CO_2 w wyniku utleniania zawartym w atmosferze tlenem. W stosunku do stabilnego izotopu węgla ^{12}C, zawartość radiowęgla wynosi około 10^{-10}% (Hajdas i in. 2021).

W przeciwieństwie do współczesnej biosfery o wysokim stężeniu ^{14}C, paliwa kopalne są pozbawione tego radioizotopu ze względu na ich wiek (Dijs et al. 2006). Dlatego biopaliwa lub mieszanki paliwowe zawierające biokomponenty są określane jako paliwa odnawialne, ponieważ pochodzą ze współczesnych źródeł organicznych, w tym tłuszczów zwierzęcych i roślin, które zawierają stosunkowo dużą ilość radiowęgla. (Culp 2017; Hajdas i in. 2021).

W rezultacie, oprócz zwiększenia produkcji energii ze źródeł odnawialnych, państwa członkowskie Unii Europejskiej obniżyły podatki od biokomponentów ze względu na wyższe koszty produkcji w porównaniu z paliwami kopalnymi (Dijs i in. 2006; Krištof i Kožar Logar 2017; Karaaslan i Gezen 2022). Na podstawie (Lee et al. 2022), zawartość ^{14}C w surowcach do produkcji biopaliw może się różnić w zależności od rodzaju, wieku i pochodzenia geograficznego biomasy wykorzystywanej do produkcji paliw. W szczególności CO_2 emitowany w wyniku spalania paliw kopalnych i testów broni jądrowej może przyczyniać się do zmian stężenia ^{14}C w atmosferze.

Zawartość ^{14}C w paliwach ciekłych jest mierzona przy użyciu metod wymienionych w normie D6866 Amerykańskiego Towarzystwa Badań i Materiałów (ASTM), której najnowsza wersja została opublikowana w 2022 roku. Są to standardowe metody analiz stosowane do określania zawartości węgla biobazowego w próbkach stałych, ciekłych i gazowych przy użyciu metody radiowęglowej (Culp et al. 2014; Idoeta et al. 2014).

Akceleratorowa spektrometria mas (AMS) jest jedną z najbardziej precyzyjnych i dokładnych metod oznaczania ^{14}C i jest wymieniona w ASTM D6866-22. Ogólnie rzecz biorąc, AMS jest ultraczułą techniką analizy izotopów kosmogenicznych, takich jak ^{14}C, ^{10}Be, ^{36}Cl i ^{26}Al (Tuniz et al. 2001; Lee et al. 2020). W przypadku analizy AMS ^{14}C badane próbki wymagają wcześniejszego procesu przygotowania w celu utworzenia tarcz grafitowych. Główną zaletą techniki AMS jest niewielki rozmiar próbki i większa precyzja (Culp et al. 2014; Haverly et al. 2019). Drugą metodą jest technika liczników ciekłoscyntylacyjnych (LSC), która wymaga zastosowania procedur do produkcji koktajli scyntylacyjnych. W metodzie LSC-A oznaczanie ^{14}C opiera się na przygotowaniu CO_2 poprzez spalenie próbki w kontrolowanym środowisku i absorpcję w mieszaninie ze scyntylatorem. W przypadku metody benzenowej lub LSC-B badana próbka jest przekształcana w benzen do pomiaru ^{14}C w trzech głównych etapach, takich jak tworzenie węglików, hydroliza i trymeryzacja w celu uzyskania benzenu (Horvatinčić et al. 2004), który jest następnie mieszany z organicznym scyntylatorem. Kolejna procedura (LSC-C) nie wymaga wstępnej obróbki próbki, a jedynie wymieszania odpowiedniego koktajlu z badaną próbką (Krištof 2015; Krajcar Bronić et al. 2017; Doll et al. 2021).

Aby przedstawić dokładne i precyzyjne wyniki pomiarów ^{14}C, wymagana jest korekta frakcjonowania izotopowego, które wystąpiło podczas przygotowywania próbek i pomiarów ^{14}C. Chociaż zarówno AMS, jak i LSC wymagają poprawek na frakcjonowanie izotopowe, metodologia stosowana do stosowania tych poprawek jest różna. W przypadku LSC spektrometria masowa stosunków izotopowych (IRMS) jest wymagana do analiz zawartości stabilnych izotopów węgla wykorzystywanych do korekt (Maruccio i in. 2017). W przypadku AMS wielkość frakcjonowania jest poddana pomiarowi w spektrometrze, a poprawki są bezpośrednio włączane do obliczeń i procesu redukcji danych (Wacker i in. 2010b).

2. Zakres projektu badawczego

Aby zapewnić dokładność wyników, konieczne jest opracowanie odpowiedniej procedury przygotowania próbek do pomiaru zawartości biowęgla w różnych substancjach. Podstawę stanowią akty normatywne.

Pomiary zawartości ^{14}C w paliwach wykonywane są metodami wymienionymi w normie American Society for Testing and Materials (ASTM) D6866 wprowadzonej w Polsce dotychczas jako PN-EN 16640:2017 ("Produkty biobazowe. Zawartość węgla biobazowego. Oznaczanie węgla biobazowego przy zastosowaniu metody radiowęglowej") oraz PN-EN 16785-1:2016-01 ("Produkty biobazowe. Zawartość bio-substancji. Część 1: Oznaczanie zawartości bio-substancji z zastosowaniem analizy radiowęglowej i analizy elementarnej").

Badania zaplanowano przede wszystkim dla paliw ciekłych, ale także dla innych, czasem nietypowych materiałów, takich jak biomasa wykorzystywana do produkcji paliw ciekłych. W ramach tego projektu badawczego wykonano adaptację opisanych metod, w tym metod akceleratorowej spektrometrii mas (AMS) i ciekłoscyntylacyjnej spektrometrii beta (LSC) we wprowadzonych standardach. Ponadto przeprowadzono systematyczne testy i walidację metod w Laboratorium ^{14}C i Spektrometrii Mas. Wyniki tych pomiarów pozwoliły skorygować frakcjonowanie izotopów występujące podczas preparatyki i procesu pomiarowego. Frakcjonowanie może zmienić skład izotopowy węgla badanego materiału, co może wpłynąć na ostateczne wyniki.

3. Znaczenie pracy

Paliwa ciekłe są wieloskładnikowymi mieszaninami różnych związków, takich jak olefiny, parafiny i węglowodory aromatyczne o dużej masie cząsteczkowej, komponenty heteroorganiczne oraz dodatki uszlachetniające. Skład grupowy paliw ciekłych zależy od parametrów wyjściowych surowców wykorzystywanych do produkcji ich komponentów, a także charakterystyki danej rafinerii wykorzystywanej w procesie blendowania (Malinowski i in. 2015). Ważne jest, aby analizować skład paliw ciekłych, które mają trafić na rynek, w celu potwierdzenia ich jednolitej jakości, która może wynikać z kilku zmiennych wpływających na właściwości paliwa w całym jego cyklu życia (Sulek et al. 2010; Haverly et al. 2019; Morone and D’Amato 2019).

Ze względu na obiecujące rozwiązania w zakresie redukcji emisji gazów cieplarnianych i zależności od paliw kopalnych, światowe zapotrzebowanie na zrównoważoną energię doprowadziło do powszechnego stosowania biokomponentów w biopaliwach jako alternatywy dla konwencjonalnych paliw kopalnych. Jednak naukowcy i specjaliści z branży napotykają znaczne przeszkody w dokładnym określaniu i charakteryzowaniu biokomponentów w biopaliwach. Jednym z głównych wyzwań związanych z wykorzystaniem biopaliw jest stosowanie tradycyjnych metod analitycznych zaprojektowanych w celu ilościowego określenia i scharakteryzowania biokomponentów w paliwach kopalnych. Metody te mogą nie mieć bezpośredniego zastosowania do biopaliw ze względu na ich złożone matryce i skład chemiczny. W związku z tym konieczne jest opracowanie czułych, solidnych i opłacalnych metod oznaczania biokomponentów biopaliw. Ponadto, aby zapewnić zgodność ze specyfikacjami jakościowymi i wyzwaniami środowiskowymi, otoczenie regulacyjne regulujące produkcję i wykorzystanie biopaliw wymaga znormalizowanych procedur analitycznych. Jednak istniejące metody często nie są zharmonizowane, co może prowadzić do niespójności wyników, utrudniając powszechne przyjęcie i komercjalizację biopaliw.

4. Cele i treść

4.1. Cele pracy doktorskiej

Celem niniejszego projektu doktorskiego było dostosowanie metodyki oznaczania zawartości biowęgla metodami izotopowymi w Gliwickim Laboratorium ^{14}C i Spektrometrii Mas oraz weryfikacja dokładności tej metodyki.

Co więcej, dla wszystkich wyników pomiarów zostały określone niepewności w oznaczaniu radiowęgla spowodowane kilkoma czynnikami, takimi jak przygotowanie próbki, otaczające środowisko i procedury pomiarowe. Zrozumienie tych niepewności ma kluczowe znaczenie, ponieważ prowadzi do dokładniejszych i bardziej wiarygodnych wyników, które są niezbędne do podejmowania świadomych decyzji w naukach o środowisku i klimacie.

4.2. Główna treść dysertacji

Niniejszą pracę doktorską przygotowano na podstawie trzech opublikowanych prac badawczych:

1. Baranyika JB, Piotrowska N, Kłusek M, Michczyński A, Pawlyta J. 2022. Testing the methods for determination of radiocarbon content in liquid fuels in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. Radiocarbon. 64(6):1447–1456. doi:10.1017/rdc.2022.35.

2. Baranyika JB, Piotrowska N. 2023. Determination of radiocarbon content in bio-oil samples by MIni Carbon Dating System in the Gliwice Radiocarbon and Mass

Spectrometry Laboratory. Geochronometria. 50:21–27. doi:10.2478/geochr-2023-0005.

3. Baranyika JB, Piotrowska N, Michczyński A. 2024. Determination of radiocarbon content in liquid fuel blends by accelerator mass spectrometry and liquid scintillation counting in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. Radiocarbon.:1–12. doi:10.1017/RDC.2024.51.

W kolejnych rozdziałach pokrótce opisano główną treść tych prac:

4.2.1. Testowanie metod oznaczania zawartości radiowęgla w paliwach ciekłych w Gliwickim Laboratorium ^{14}C i Spektrometrii Mas

Zasadniczo, przy oznaczaniu biokomponentów w paliwach ciekłych za pomocą analiz zawartości izotopu promieniotwórczego węgla (^{14}C) próbki muszą być przygotowane zgodnie z protokołami dostosowanymi do warunków danego laboratorium. Niniejsza praca (Baranyika et al. 2022) miała na celu przetestowanie metod oznaczania zawartości biokomponentów w paliwach ciekłych w Gliwickim Laboratorium ^{14}C i Spektrometrii Mas. Przetestowano również dokładność tych metod do ilościowego oznaczania biowęgla.

Dlatego w sekcji 2.3 i sekcji 2.4 artykułu (Baranyika et al. 2022) przedstawiono odpowiednio metody AMS i LSC do pomiarów ^{14}C. W przypadku AMS, w niniejszej pracy przygotowano partię próbek paliwa ciekłego i spalono je w analizatorze elementarnym (EA) bez jakiejkolwiek obróbki chemicznej przed spalaniem, w celu uzyskania CO_2, który został przeniesiony do reaktorów w celu grafityzacji za pomocą H_2 i przy użyciu proszku żelaza jako katalizatora. Uzyskany grafit został wykorzystany do pomiaru ^{14}C przy użyciu AMS.

W przypadku metody LSC w Laboratorium w Gliwicach zastosowaliśmy metodę benzenową znaną jako metoda LSC-B. Aby uzyskać próbkę benzenu do pomiaru metodą LSC, próbki paliwa ciekłego zmieszano z oczyszczonym, wstępnie wygrzanym piaskiem kwarcowym w reaktorze w celu uzyskania węglika litu (Li_2C_2). Węglik ten poddano hydrolizie, aby otrzymać acetylen, który następnie trymeryzowano do benzenu. Uzyskany benzen wykorzystano do pomiaru ^{14}C metodą LSC. Dla większości próbek paliwa ciekłego przygotowano dwie podpróbki benzenu: pierwsza była przechowywana przez 30 dni w zamrażarce laboratoryjnej (-20 °C) w celu usunięcia zanieczyszczeń radonem (^{222}Rn), a drugą poddano resublimacji w celu szybszego usunięcia ^{222}Rn bez konieczności długotrwałego przechowywania w zamrażarce.

Ponadto, aby uzyskać dokładne i precyzyjne wyniki oznaczania radiowęgla metodą LSC, ważne było skorygowanie wyniku z uwzględnieniem frakcjonowania izotopowego za pomocą stosunku $^{13}C/^{12}C$, wyrażonego jako $\delta^{13}C$, który wyznaczono techniką IRMS. W przypadku AMS korekta została dokonana wraz z procesem pomiaru ^{14}C przy użyciu stosunku $^{13}C/^{12}C$ uzyskanego za pomocą spektrometru AMS.

Główne wyniki badania (Baranyika et al. 2022) przedstawiono w sekcji 3. W Tabeli 1 tego artykułu można zauważyć, że próbki paliw ciekłych poddano spalaniu EA w celu zbadania zawartości węgla wymaganej do podjęcia decyzji o ilości materiału i liczbie podpróbek potrzebnych do grafityzacji i wymaganych przez normy do obliczenia zawartości węgla pochodzenia biologicznego. Zawartości węgla dla spalonych próbek, uwzględniające jedynie obliczoną masę, bez ważenia, nie były poprawne, ponieważ przekraczały 100% we wszystkich podpróbkach. Natomiast próbki spalone z uwzględnieniem ich ważonych mas wykazały stężenia węgla poniżej 100% dla wszystkich podpróbek. Zaobserwowana niespójność obliczonych zawartości węgla nie miała wpływu na koncentrację radiowęgla w próbkach, lecz wynikała z utraty próbki ze względu na wielkość małych kapsułek w stosunku do pipety wykorzystanej w procedurze pobierania podpróbek.

Procedura szczelnego zamykania kapsułek cynowych została przetestowana w celu potwierdzenia zmiany masy próbki w czasie. Wyniki przedstawione w tabeli 1 wykazały, że masa zamkniętych w kapsułkach próbek, które były przechowywane w laboratorium przez 24 godziny przed spaleniem, zmieniała się nawet o 22%. Nie zaobserwowano związku między zmierzonym stężeniem węgla a zmianą masy. Podobne procedury testowe zostały opisane przez (Santos Arévalo et al. 2015). Takie same wyniki uzyskano dla próbek przechowywanych przez 48 godzin przed spaleniem w EA. W rezultacie monitorowanie parowania próbek nie było konieczne, jednak kluczowe znaczenie miało kontrolowanie zanieczyszczenia krzyżowego w EA poprzez przeprowadzanie pustych analiz ("RunIn") pomiędzy próbkami oraz zwiększenie liczby podpróbek.

Wyniki pomiarów ^{14}C zarówno dla metody AMS, jak i LSC są również raportowane w pracy (Baranyika et al. 2022). Stabilne izotopy ^{13}C i ^{12}C wykorzystano do ilościowego określenia stosunku izotopowego ($\delta^{13}C$) we wzorcach ANU-sucrose i oleju NBS-22, uzyskując wartości odpowiednio -10,5 i -30. Jak pokazano w tabeli 2, wyniki wszystkich pomiarów izotopowych paliw ciekłych zawierały się w zakresie od -26,9 ‰ do -30 ‰ i zostały wykorzystane do skorygowania zawartości radiowęglowej po pomiarach za pomocą LSC.

Koncentracja ^{14}C zmierzona dla próbki tła (ON/UF-BC) została wykorzystana do określenia zanieczyszczenia próbek węglem współczesnym. Wyniki pomiarów uzyskane przy użyciu metod AMS (0,32 ± 0,06 pMC) i LSC (0,25 ± 0,10 pMC) były zadowalające i porównywalne, biorąc pod uwagę rozszerzoną niepewność (z różnicą 0,07 ± 0,12 pMC).

Jednak resublimowana próbka tła nie uzyskała zamierzonego wyniku przy użyciu metody LSC (Tabela 2). Różnica ta może być spowodowana dodaniem współczesnych zanieczyszczeń podczas pracy z benzenem. Ponadto na tę próbkę tła może mieć wpływ interakcja z atmosferycznym CO_2 podczas wielu etapów w procesie resublimacji.

Koncentracja ^{14}C zmierzona dla próbki tła (ON/UF-BC) została wykorzystana do określenia zanieczyszczenia próbek węglem współczesnym. Wyniki pomiarów uzyskane przy użyciu metod AMS (0,32 ± 0,06 pMC) i LSC (0,25 ± 0,10 pMC) były zadowalające i porównywalne, biorąc pod uwagę rozszerzoną niepewność (z różnicą 0,07 ± 0,12 pMC). Jednak resublimowana próbka tła nie uzyskała zamierzonego wyniku przy użyciu metody LSC (Tabela 2). Różnica ta może być spowodowana dodaniem współczesnych zanieczyszczeń podczas pracy z benzenem. Ponadto na tę próbkę tła może mieć wpływ interakcja z atmosferycznym CO_2 podczas wielu etapów w procesie resublimacji.

Tabela 1. Wyniki (% C) spalania paliw ciekłych w EA w różnych doświadczeniach (zob. tekst).

**Wynik pominięty w obliczeniach średnich.*

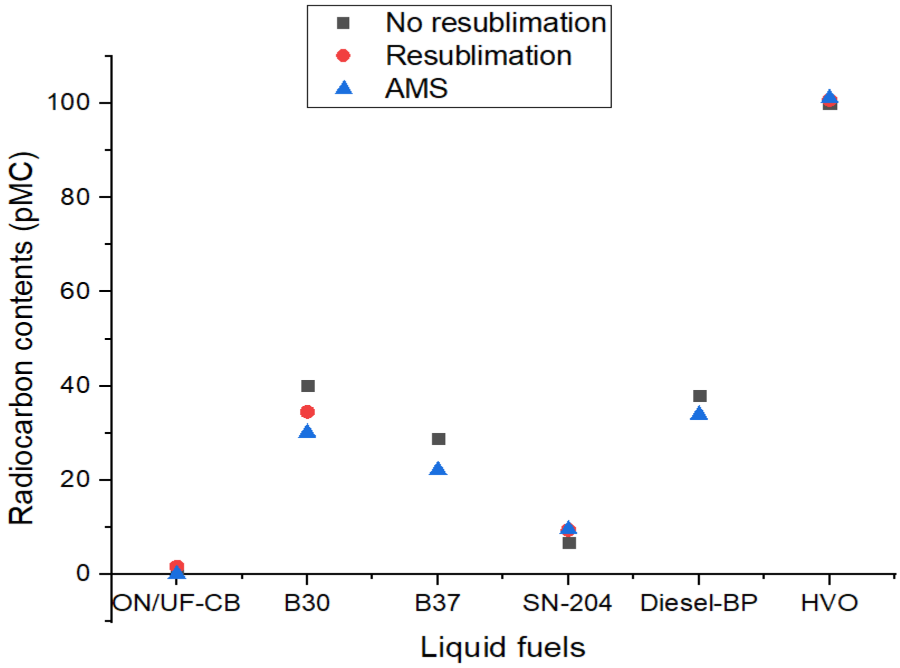
Nazwa próbki	**Masa początkowa [mg]**	**Utrata masy po 24 godzinach [mg]**	**Utrata masy po 48 godzinach [mg]**	**Masa końcowa [mg]**	**% C**
B30 Eksperyment 1	1.3	-	-	1.3	127.22
	1.3	-	-	1.3	228.19
B30 Eksperyment 2	1.852	0.219	-	1.633	66.67
	1.887	0.136	-	1.751	66.72
	1.841	0.053	-	1.788	85.00
				Średnia	*72.8 ± 10.6*
B30 Eksperyment 3	1.900	-	0.110	1.790	29.14*
	1.884	-	0.090	1.794	75.38
	1.788	-	0.069	1.719	80.99
				Średnia	*78.2 ± 4.00*
B37 Eksperyment 1	1.3	-	-	1.3	262.68
	1.3	-	-	1.3	185.95
B37 Eksperyment 2	1.792	0.053	-	1.739	82.99
	1.802	0.073	-	1.729	90.49
	1.952	0.065	-	1.887	72.88
				Średnia	*82.1 ± 8.80*
B37 Eksperyment 3	1.892	-	0.084	1.808	81.25
	1.776	-	0.171	1.605	79.83
	1.846	-	0.111	1.735	66.03
				Średnia	*75.7 ± 8.40*
SN-204 Eksperyment 2	1.943	-	-	1.943	73.31
	1.858	-	-	1.858	65.42
	1.577	-	-	1.577	72.86
				Średnia	*70.5 ± 4.40*
SN-204 Eksperyment 3	1.897	-	0.177	1.720	88.33
	2.108	-	0.182	1.926	51.17
	2.189	-	0.202	1.987	54.17
				Średnia	*64.6 ± 20.60*
W DNIU/UF-BC Eksperyment 3	1.828	-	0.122	1.706	85.50
	1.646	-	0.186	1.460	86.33
	1.872	-	0.206	1.666	83.45
				Średnia	*85.1 ±1.50*
Olej napędowy BP Eksperyment 3	1.913	-	0.079	1.834	49.58
	1.893	-	0.420	1.473	63.75
	1.872	-	0.133	1.739	72.66
				Średnia	*62.0 ±11.60*
HVO Eksperyment 3	1.892	-	0.054	1.838	88.92
	1.853	-	0.068	1.785	67.45
	1.569	-	0.110	1.459	42.17
				Średnia	*66.2 ± 23.40*

Tabela 2. Wyniki pomiarów stężenia radiowęgla (pMC) i frakcjonowania izotopowego (δ^{13}C).

Nazwa próbki	**δ ^{13}C IRMS** [‰]	**ID laboratoryjne**	**Koncentracja ^{14}C [pMC]**	**Metoda**
ON/UF-BC	GdMS-58627 —26,90±0,10	GdS-4368	0.25±0.10 0.25±0.10	LSC nieskorygowane LSC skorygowane
		GDS-4398 *resublimacja*	1.63±0.13 1.64±0.13	LSC nieskorygowane LSC skorygowane
		GdA-5724	0.256±0.02	AMS
		GdA-5627	0.343±0.02	AMS
		GdA-5623	0.24±0.01	AMS
		GdA-5803	0.392±0.02	AMS
		GdA-6605	0.38±0.10	AMS
			0.32±0.06	*Średnia AMS*
B30	GdMS-58633 —30,00±0,10	GdS-4333	39.67±0.43 40.07±0.43	LSC nieskorygowane LSC skorygowane
		GdS-4377 *resublimacja*	34.16±0.42 34.50±0.42	LSC nieskorygowane LSC skorygowane
		GdA-6607	30.07±0.10	AMS
B37	GdMS-58638 —29,90±0,10	GdS-4334	28.50±0.48 28.78±0.48	LSC nieskorygowane LSC skorygowane
		GdA-6608	22.14±0.17	AMS
SN-204	GdMS-59026 —30,00±0,10	GdS-4009	9.74±0.22 9.84±0.22	LSC nieskorygowane LSC skorygowane
		GdS-4400 *resublimacja*	9.33±0.19 9.42±0.19	LSC nieskorygowane LSC skorygowane
		GdA-6606	9.54±0.19	AMS
		GdA-5722	8.84±0.08	AMS
			9.19±0.49	*Średnia AMS*
Diesel-BP	GdMS-58636 —30,00±0,10	GdS-4335	37.64±0.53 38.01±0.53	LSC nieskorygowane LSC skorygowane
		GdA-6609	33.92±0.20	AMS
HVO	GdMS-59022 —28.10±0,10	GdS-4379	99.49±0.81 100.10±0.81	LSC nieskorygowane LSC skorygowane
		resublimacja GdS- *4386*	100.18±0.80 100.8±0.80	LSC nieskorygowane LSC skorygowane
		GdA-6610	101.45±0.33	AMS
ANU-sucrose	GdMS-58611 – 10.45±0,10			
Olej NBS-22	GDMS-58613-30.00±0,10			

Ponadto, wyniki pomiarów wykazują powtarzalność i wiarygodność zarówno metody AMS, jak i LSC w określaniu zawartości ^{14}C w próbkach paliw HVO i SN-204. W przypadku HVO skorygowane wyniki dały wartości 100,10 ± 0,81 i 100,8 ± 0,8 pMC odpowiednio dla benzenu przechowywanego przez 30 dni i próbki benzenu po resublimacji, oraz zgadzały się z wynikiem AMS (101,45 ± 0,33 pMC). Wyniki LSC z korektą δ^{13}C zarówno dla próbek nieresublimowanych (9,74 ± 0,22 pMC), jak i resublimowanych (9,33 ± 0,19 pMC) są zgodne ze średnim wynikiem AMS (9,19 ± 0,49 pMC), biorąc pod uwagę obliczone niepewności i oczekiwaną zawartość biowęgla w próbce SN-204 (patrz Tabela 2).

Bliska zgodność tych wyników zwiększyła zaufanie do dokładności podanych wartości ^{14}C. Wyniki ^{14}C zmierzone przy użyciu LSC dla próbki B30 wyniosły odpowiednio 40,07 ± 0,43 pMC i 34,50 ± 0,40 pMC dla próbki przechowywanej 30 dni w zamrażarce laboratoryjnej i próbki resublimowanej. Wykazały one rozbieżność z wynikami AMS (30,07 ± 0,10 pMC). Podobnie, wyniki LSC dla próbek diesel-BP (38,01±0,53 pMC) i B37 (28,87±0,48 pMC) przechowywanych przez 30 dni w zamrażarce w celu usunięcia radonu, nie były zgodne z wynikami AMS wynoszącymi odpowiednio 33,92 ± 0,20 i 22,14 ± 0,17 pMC. Jednak w tym badaniu nie przeprowadzono eksperymentów resublimacji na próbkach B37 i diesel-BP. Te różnice dla trzech próbek z wynikami ^{14}C około 30 pMC dla B30, B37 i Diesel BP zostały zilustrowane na Rys.1. Obecnie nie ma dobrego wyjaśnienia tego zjawiska. Jedną z przyczyn może być niekompletna reakcja z litem i planujemy poprawić monitorowanie przebiegu tej reakcji w przyszłości.



Rysunek 1. Zawartość radiowęgla (^{14}C) w badanych paliwach ciekłych pogrupowanych według różnych metod przygotowania próbek (LSC-bez resublimacji, LSC-resublimacja i AMS). Słupki błędów nie są widoczne w tej skali.

4.2.2. Oznaczanie zawartości radiowęgla w próbkach bio-oleju przy pomocy Mini Carbon Dating System w Gliwickim Laboratorium ^{14}C i Spektrometrii Mas

Metody izotopowe są nieocenionymi narzędziami do badania zmian środowiskowych w krajach europejskich i poza nimi. Metody te polegają na analizie składu izotopowego pierwiastków obecnych w różnych próbkach środowiskowych. W Gliwickim Laboratorium ^{14}C i Spektrometrii Mas stosuje się kompaktowy, nowoczesny system AMS znany jako Mini Carbon Dating System (MICADAS) do oznaczania zawartości ^{14}C w różnych próbkach środowiskowych, w tym paliwach ciekłych.

Celem tego artykułu (Baranyika i Piotrowska 2023) było określenie zawartości ^{14}C w bio-olejach przy użyciu MICADAS w Gliwickim Laboratorium. Porównano wyniki analiz ^{14}C dla testowanych biopaliw oraz biomasy użytej jako materiał referencyjny.

Jak wspomniano w rozdziale 2 tego artykułu, trzy próbki bio-oleju pochodzące z katalitycznego procesu depolimeryzacji biomasy oraz biomasa (łupiny pistacji) użyta do ich produkcji zostały dostarczone przez producenta do analiz ^{14}C w Gliwickim Laboratorium Radiowęglowym. Metodologię procesu pomiaru ^{14}C przedstawiono za pomocą Ryc. 2 z pracy (Baranyika i Piotrowska 2023). Proces analiz ^{14}C przy użyciu MICADAS wymagał wykonania tarcz grafitowych (Lee et al. 2020), które uzyskano poprzez konwersję oryginalnych materiałów próbnych na grafit. Każda próbka bio-oleju została pobrana do kapsułki cynowej przeznaczonej do cieczy, podczas gdy biomasa użyta do ich produkcji również była badana. Aby uniknąć utraty próbki wskutek parowania, każdą kapsułkę z próbką bio-oleju zamknięto w dodatkowej kapsułce przeznaczonej do próbek stałych.

Wszystkie próbki zostały spalone w EA w celu wytworzenia CO_2, który został poddany grafityzacji w AGE w reakcji z wodorem H_2 przy użyciu proszku żelaza jako katalizatora (Němec et al. 2010; Wacker et al. 2010a). Uzyskany materiał, składający się z 1 mg węgla i 5 mg żelaza, został sprasowany za pomocą pneumatycznej prasy (PSP) i poddany pomiarowi przy użyciu spektrometru MICADAS w celu uzyskania zawartości ^{14}C w badanych bio-olejach. Do normalizacji użyto standardu, kwasu szczawiowego II (*Oxalic Acid* II), a paliwo pozbawione ^{14}C, przygotowane w ten sam sposób, zastosowano jako próbkę tła.

Wyniki pomiarów ^{14}C zostały podane jako procent współczesnego węgla (pMC), który jest procentem stężenia izotopu ^{14}C w tak zwanej współczesnej biosferze.

Ponadto, obliczenia zawartości biowęgla przeprowadzono zgodnie z normą EN 16640:2017 (E), korzystając z następującego równania dla zawartości biogennej względem wartości referencyjnej (x_B):

$$x_B = \frac{F^{14}C_{sample}}{F^{14}C_{ref}} \cdot 100 \qquad (1)$$

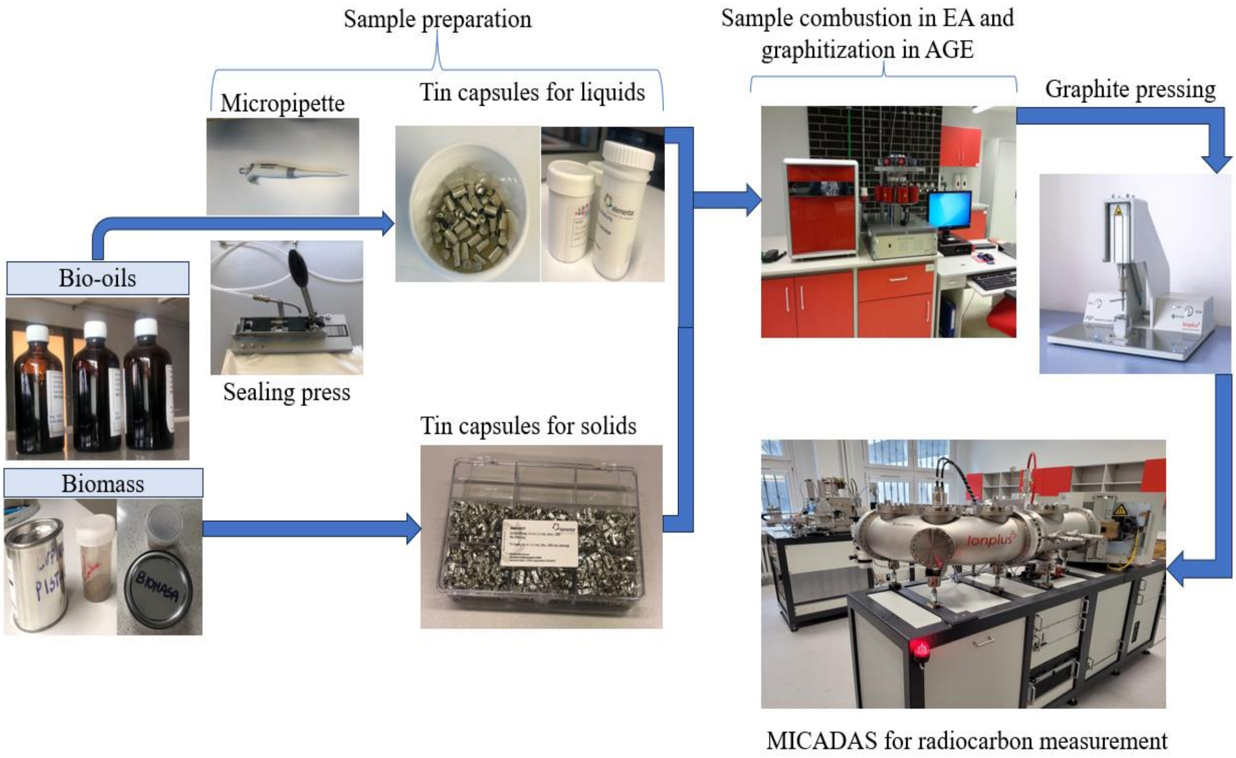
gdzie: $F^{14}C_{próbka}$ jest zawartością radiowęgla w próbce, a $F^{14}C_{ref}$ jest zawartością radiowęgla w materiale odniesienia.

Zawartość węgla biogenicznego w % (m/m) ($x^{TC}{}_{B}$) obliczono w następujący sposób:

$$x_B^{TC} = \frac{x_B}{x_{TC}}$$

(2)

gdzie x_{TC} oznacza całkowitą zawartość węgla w próbce. Jako wartość odniesienia ($F^{14}C_{ref}$) wykorzystano zawartość ^{14}C uzyskaną dla łupin pistacji.



Rysunek2. Proces pomiaru radiowęglowego metodą AMS w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach

Jak pokazano w sekcji 3 (Baranyika and Piotrowska 2023), pierwszym parametrem interesującym w tym badaniu była zawartość węgla w procentach (% C) (m/m). Na podstawie uzyskanej zawartości procentowej C w każdej próbce, takich jak 79,7 ±1,7 %,68,7 ±2,1 %, 47,0 ±1,1 % i 48,82 ±0,3 %, odpowiednio w przypadku biooleju-1, biooleju-2, biooleju-3 i łupin pistacji, zdecydowano o odpowiedniej ilości każdej badanej próbki, aby uzyskać co najmniej 1 mg węgla do wytworzenia tarcz grafitowych do pomiaru ^{14}C za pomocą spektrometru MICADAS.

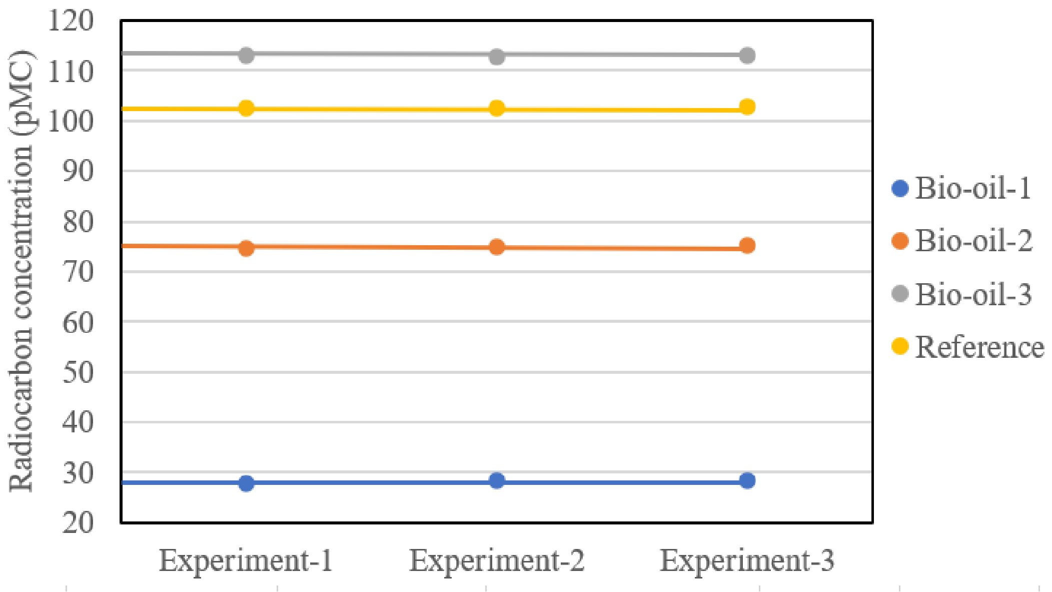
Jak przedstawiono w Tabeli 3, przeprowadzono kilka pomiarów zawartości ^{14}C, aby przetestować powtarzalność dla każdej badanej próbki. Średnie wyniki pomiarów ^{14}C wynosiły odpowiednio 28,14 ± 0,4 pMC, 74,95 ± 0,22 pMC, 112,92 ± 0,07 pMC oraz 102,61 ± 0,21 pMC dla bio-oleju-1, bio-oleju-2, bio-oleju-3 oraz materiału referencyjnego (łupiny pistacji). Głównym celem tego badania była jednak ocena techniki przygotowania próbek w Laboratorium w Gliwicach, a nie jedynie uzyskanie wyników analiz radiowęgla. Graficzne przedstawienie wyników pomiarów koncentracji radiowęgla dla wszystkich próbek bio-oleju i materiału referencyjnego pokazano na Rysunku 3. Przeprowadzono również test chi-kwadrat (χ^2), aby potwierdzić powtarzalność wyników. W przypadku niezadowalających wyników testu, odstające wyniki były usuwane z obliczeń.

Jak można zauważyć w Tabeli 3, przy poziomie ufności $\alpha = 0,05$, ostateczne obliczone wartości χ^2 wynosiły odpowiednio 1,21, 1,08, 0,15 i 0,41 dla bio-oleju-1, bio-oleju-2, bio-oleju-3 oraz łupin pistacji. W związku z tym, wszystkie wartości χ^2 były mniejsze niż wartość krytyczna (CV), co potwierdziło brak istotnych różnic i wskazało, że procedura przygotowania próbek i pomiary ^{14}C przy użyciu systemu MICADAS dały powtarzalne wyniki. Jednak przygotowanie wielu podpróbek jest kluczowe, aby wykryć niejednorodność materiału próbki.

Tabela 3. Badanie odtwarzalności pomiarów radiowęglowych w paliwach (bio-olejach). Wyniki przedstawione są jako pMC, a niepewność obliczona na podstawie wyników pomiarów AMS.

Nazwa próbki	**Kod laboratoryjny**	**Numer doświadczenia**	**Stężenie^{14}C (pMC)**	**Średnia Stężenie^{14}C (pMC)**	**Test χ^2 dla α= 0,05 CV = 5,99**
Bioolej-1	GdA-6968.1.5	Eksperyment-1	27.72 ± 0.59	28.14 ± 0.36	χ^2 = 1,21 Znaczące
	GdA-6968.1.3	Eksperyment-2	28.31 ± 0.18		
	GdA-6968.1.4	Eksperyment-3	28.40 ± 0.19		
	GdA-6968.1.2	Eksperyment 4	29.46 ± 0.56*		
Bioolej-2	GdA-6969.1.1	Eksperyment-1	74.71 ± 0.32	74.95 ± 0.22	χ^2 = 1,08 Znaczące
	GdA-6969.1.2	Eksperyment-2	74.95 ± 0.32		
	GdA-6969.1.3	Eksperyment-3	75.18 ± 0.32		
	GdA-6969.1.5	Eksperyment 4	76.07 ± 0.32*		
	GdA-6969.1.4	Eksperyment 5	73.29 ± 0.32*		
Bioolej-3	GdA-6970.1.1	Eksperyment-1	113.00 ± 0.28	112.92 ± 0.07	χ^2 = 0,15 Znaczące
	GdA-6970.1.2	Eksperyment-2	112.85 ± 0.28		
	GdA-6970.1.5	Eksperyment-3	112.91 ± 0.28		
	GdA-6970.1.3	Eksperyment 4	110.85 ± 0.40*		
	GdA-6970.1.4	Eksperyment 5	110.11 ± 0.41*		
Łupiny pistacji (Materiał referencyjny)	GdA-6971.1.1	Eksperyment-1	102.58 ± 0.29	102.61 ± 0.21	χ^2 = 0,41 Znaczące
	GdA-6971.1.2	Eksperyment-2	102.82 ± 0.29		
	GdA-6971.1.3	Eksperyment-3	102.61 ± 0.29		

*wskazuje niejednorodne podpróbki



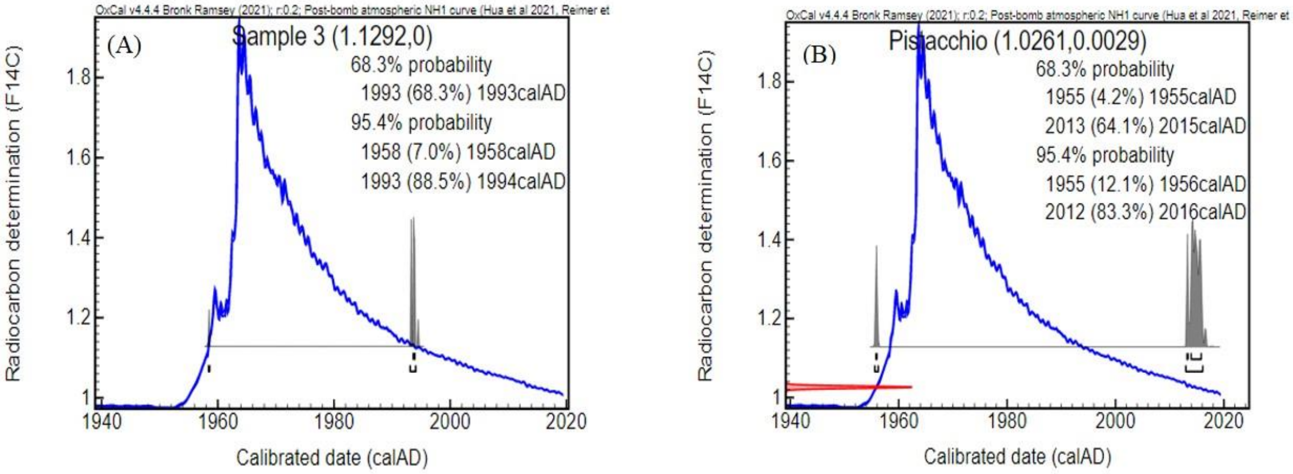
Rysunek3. Graficzna prezentacja testu odtwarzalności dla pomiarów radiowęglowych w bio-olejach metodą AMS; słupki błędów 2-sigma są niewidoczne w tej skali.

Na podstawie koncentracji ^{14}C określono zawartość węgla biogenicznego dla wszystkich badanych próbek. Ustaloną zawartość węgla biogenicznego w stosunku do materiału odniesienia (102,61 ± 0,21 pMC) przedstawiono w tabeli 4. Co zaskakujące, wyniki pomiarów wykazały wyższą wartość ^{14}C dla biooleju-3 (112,92 ±0,07 pMC) w porównaniu z biomasą stosowaną jako materiał odniesienia (102,61 ± 0,21 pMC). Obliczona zawartość węgla biogenicznego w stosunku do wartości odniesienia była również wyższa w przypadku biooleju-3 (110.04 ± 0.22 %) w porównaniu z próbką referencyjną (100,00 ± 0,29 %).

Ponadto, jak pokazano na Rys. 4, wyniki na Rys. 4A wskazują, że bio-olej-3 prawdopodobnie pochodzi z lat 1993-1994, podczas gdy materiał referencyjny pochodzi z lat 2012-2016. Osobliwość ta ujawniła, że tylko dwie próbki, bio-olej-1 i bio-olej-2, zostały wyprodukowane z badanych łupin pistacji, natomiast bio-olej-3 został wyprodukowany z nieznanej biomasy, która nie została dostarczona przez nadawcę próbek. Ten wniosek został potwierdzony przez firmę dostarczającą próbki, jednak dodatkowe informacje były poufne.

Tabela 4. Obliczone zawartości radiowęgla, węgla i biowęgla w próbkach bio-oleju

Nazwa próbki	**Kod laboratoryjny**	**Zawartość węgla w % (m/m)**	**Zawartość ^{14}C (średnia) [pMC]**	**Zawartość węgla biogenicznego w stosunku do wartości odniesienia (x_B)**	**Zawartość węgla biogenicznego w % (m/m) (X^{TC}_B)**
Bio-olej-1	GdA-6968	79.7 ± 1.7	28.14 ± 0.36	27.43 ± 0.42	21.87 ± 1.76
Bio-olej-2	GdA-6969	68.7 ± 2.1	74.95 ± 0.22	73.04 ± 0.30	50.16 ± 2.09
Bio-olej-3	GdA-6970	47.0 ± 1.1	112.92 ± 0.07	110.04 ± 0.22	51.73 ± 1.10
Materiał odniesienia	GdA-6971	48.82 ± 0.25	102.61 ± 0.21	100.00 ± 0.29	48.82 ± 0.39



Rysunek4. Kalibracja wyników F^{14}C dla próbki bio-oleju-3 (A) i próbki referencyjnej łupin pistacji (B) przy pomocy programu OxCal v.4.4 (Bronk Ramsey 2009) z wykorzystaniem post-bombowej krzywej atmosferycznej NH1 (Reimer et al. 2004; Hua et al. 2022). Wartości F^{14}C są powszechnie stosowane w procesie kalibracji, a relacja z pMC wynosi pMC=F^{14}C*100 (Stenström et al. 2011).

4.2.3. Oznaczanie zawartości radiowęgla w mieszankach paliw ciekłych metodą akceleratorowej spektrometrii mas i licznika ciekłoscyntylacyjnego w Gliwickim Laboratorium ^{14}C i Spektrometrii Mas

Zwiększone wykorzystanie produktów biopochodnych wymaga opracowania metod weryfikacji do analizy rzeczywistej zawartości biowęgla w takich materiałach, w tym w paliwach ciekłych. Badania przedstawione w pracy (Baranyika et al. 2024) miały na celu zastosowanie metod AMS i LSC do określenia zawartości ^{14}C w mieszankach paliw ciekłych o znanych proporcjach bio- i kopalnego węgla. Metody pomiaru ^{14}C (LSC i AMS) opisano odpowiednio w sekcjach 2.2 i 2.3.

Próbki mieszanek paliw wyprodukowano z próbki HVO i paliwa o nieskończonym wieku ^{14}C (ON/UF-BC), które zostały dostarczone do Laboratorium w Gliwicach w 2018 roku przez zewnętrzną firmę naftową w dużej ilości, co pozwoliło na ich wykorzystanie do celów testowych przez lata (Baranyika et al. 2022). ON/UF-BC był szeroko wykorzystywany jako próbka tła dla paliw ciekłych.

Wyniki pomiarów ^{14}C zostały przedstawione w sekcji 3 (Baranyika et al. 2024). Jak pokazano w Tabeli 5, zawartość ^{14}C w próbce tła (ON/UF-BC) była kluczowym parametrem do przetestowania zanieczyszczenia próbek. Średnia ważona z 14 niezależnych, 24-godzinnych pomiarów tła za pomocą spektrometru LSC Quantulus 1220 wyniosła 0,3598 ± 0,0052 cpm (zliczeń na minutę). Spójność pomiarów potwierdzono za pomocą testu χ^2. Dla AMS, pomiary wykonane dla dziewięciu oddzielnych tarcz grafitowych dały średnią 0,41 ± 0,18 pMC dla próbki tła ON/UF-BC. Odpowiednie wartości uzyskane dla próbki ON/UF-BC zostały wykorzystane do korekty tła dla wszystkich kolejnych analiz AMS i LSC.

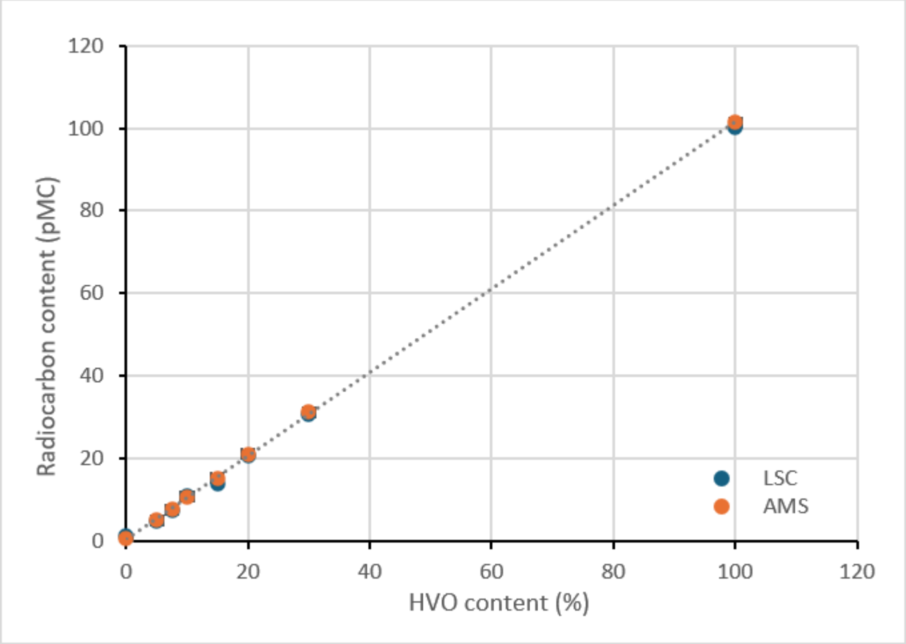
W przypadku HVO metodą LSC uzyskano wynik pomiaru ^{14}C wynoszący 100,10 ± 0,81 pMC. Wynik ten był zgodny z wynikiem AMS (101,45 ± 0,33 pMC).

Rysunek 5 przedstawia graficzną prezentację wyników pomiarów ^{14}C badanych mieszanek paliwowych (Bld) dla obu metod (LSC i AMS) oraz komponentów (HVO i ON/UF-BC) użytych do ich produkcji. Jak pokazano na rysunku, wszystkie wartości mieszczą się w zakresie niepewności 2-sigma, co wskazuje, że zarówno metody przygotowania próbek, jak i pomiary ^{14}C dały wiarygodne wyniki. Ponieważ zawartość ^{14}C w HVO wynosi około 100 pMC, wyniki dla wszystkich innych mieszanek paliwowych wykazują tendencję liniową.

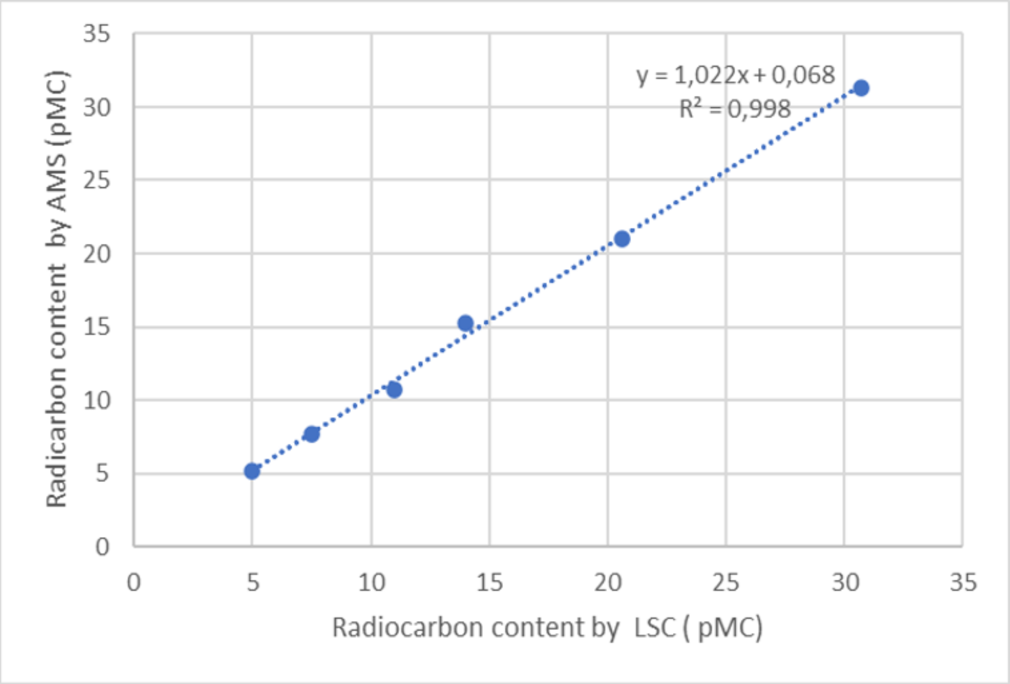
Ponadto do porównania wyników ^{14}C dla sześciu mieszanek paliwowych wykorzystano wykres zależności liniowej. Jak pokazano na rysunku 6, równanie regresji liniowej (y =ax + b; a=1,022 ± 0,025, b=0,07 ± 0,43) z R^2= 0,9975 wykazało silną korelację między wynikami pomiarów AMS i LSC. Rozrzut wartości ^{14}C wzdłuż linii regresji wskazywał na dobrą odtwarzalność między dwiema metodami, z wyjątkiem mieszanki Blend-15, gdzie wyniki pomiarów dla obu metod różniły się bardziej w porównaniu z innymi próbkami.

Tabela 5. Wyniki pomiarów zawartości radiowęgla (w pMC z niepewnością 1-sigma) w mieszankach paliw i próbce tła zarówno dla metod LSC, jak i AMS oraz frakcjonowania izotopów (δ^{13}C, zmierzone dla ON/UF-BC i HVO, obliczone dla próbek mieszanek – zob. tekst dotyczący metodyki).

Nazwa próbki	δ^{13}C IRMS	δ ^{13}C AMS	Identyfikator laboratoryjny	Zawartość ^{14}C [pMC]	Metoda
ON/UF-BC	-26.90	-26.5	GdS-4547	1.30 ± 0.11	LSC
			GdA-6821	0.50 ± 0.25 0.45 ± 0.11 0.39 ± 0.21 0.36 ± 0.22 0.42 ± 0.21 0.38 ± 0.30 0.36 ± 0.22 0.38 ± 0.20 0.32 ± 0.22	AMS
				0.41 ± 0.18	AMS average
Blend-5	-26.96	-27.7	GdS-4546	5.02 ± 0.14	LSC
			GdA-6820	5.12 ± 0.15	AMS
Blend-7.5	- 26.99	-27.4	GdS-4545	7.45 ± 0.14	LSC
			GdA-6819	7.72 ± 0.16	AMS
Blend-10	-27.02	-29.4	GdS-4502	11.03 ± 0.22	LSC
			GdA-6817	10.71 ± 0.16	AMS
Blend-15	-27.08	-27.2	GdS-4538	14.03±0.22	LSC
			GdA-6818	15.27 ± 0.16	AMS
Blend-20	-27.14	-29.2	GdS-4501	20.62 ± 0.29	LSC
			GdA-6816	21.06 ± 0.17	AMS
Blend-30	-27.26	-28.9	GdS-4496	30.67 ± 0.36	LSC
			GdA-6815	31.33 ± 0.19	AMS
HVO	-28.1	ND	GdS-4379	100.10 ± 0.81	LSC
			GdA-6610	101.45 ± 0.33	AMS



Rysunek 5. Zawartość radiowęgla w badanych mieszankach paliwowych (Bld) i komponentach (HVO i ON/UF-BC) użytych do ich produkcji dla obu metod (LSC i AMS). Słupki błędów 2-sigma nie są widoczne w podanej skali.



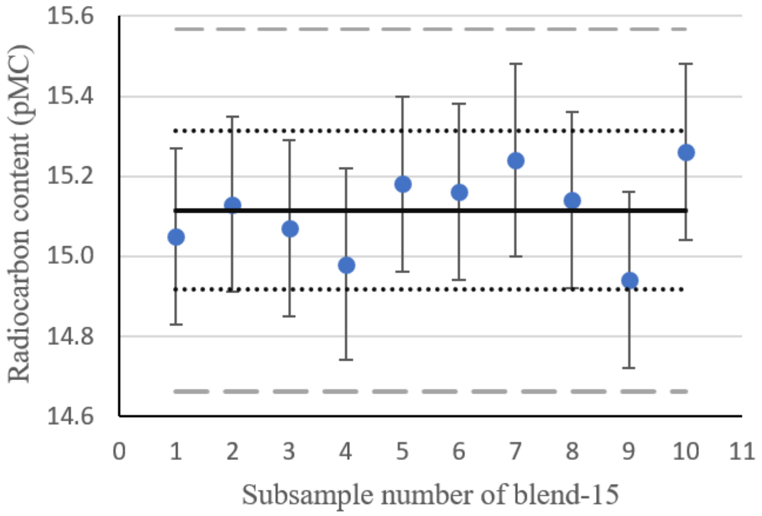
Rysunek 6. Porównanie wyników zawartości radiowęgla w sześciu mieszankach paliwowych dla LSC i AMS przy użyciu metody regresji. Słupki błędu 2-sigma są niewidoczne ze względu na niskie wartości niepewności.

Aby zbadać powtarzalność wyników uzyskanych przez spektrometr MICADAS w Laboratorium w Gliwicach, przeprowadzono dodatkowe pomiary dla 10 podpróbek mieszanki Blend-15 o tej samej objętości (2 µl). Wyniki pomiarów ^{14}C dla tych podpróbek przedstawiono w Tabeli 6 (Baranyika et al. 2024), a obliczona średnia wyniosła 15,12 ± 0,10 pMC.

W porównaniu do wcześniejszego pomiaru dla Blend-15 (15,27 ± 0,16 pMC), wartość ta była powtarzalna. Wyniki testu powtarzalności pokazano również na Rysunku 7. Znajdowały się one w zakresie 2-sigma, co pokazuje, że od przygotowania próbki przy użyciu kapsułki cynowej do cieczy, przez proces uszczelniania i spalanie w analizatorze elementarnym, aż do grafityzacji w AGE, w naszym laboratorium uzyskano powtarzalne wyniki z systemu MICADAS. Test powtarzalności został potwierdzony testem chi-kwadrat (χ^2). Z Tabeli 6 w tym artykule wynika, że obliczona wartość χ^2 wyniosła 7,72, a wartość krytyczna (CV) wyniosła 21,67 (przy poziomie ufności $\alpha = 0{,}01$). Ponieważ wartość χ^2 była mniejsza niż CV, nie stwierdzono istotnych różnic między wynikami ze wszystkich 10 podpróbek, co wskazuje na powtarzalność i spójność wyników.

Tabela 6. Wyniki zawartości radiowęgla dla testu odtwarzalności przy użyciu systemu MICADAS.

Nazwa próbki	**Numer podpróbki**	**Kod laboratoryjny**	**Zawartość ^{14}C [pMC]**	**Test χ^2**
Blend-15	1	GdA-6818.1.3	15.05 ± 0.11	Dla α= 0,01, CV=21,67 χ^2 = 7,72
	2	GdA-6818.1.5	15.13 ± 0.11	
	3	GdA-6818.1.6	15.07 ± 0.11	
	4	GdA-6818.1.7	14.98 ± 0.12	
	5	GdA-6818.2.1	15.18 ± 0.11	
	6	GdA-6818.2.2	15.16 ±0.11	
	7	GdA-6818.2.3	15.24 ± 0.12	
	8	GdA-6818.2.4	15.14 ± 0.11	
	9	GdA-6818.2.5	14.94 ± 0.11	
	10	GdA-6818.2.6	15.26 ± 0.11	
			średnia = 15.12 ±0.10	χ^2 <CV, brak istotnej różnicy



Rysunek 7. Graficzna prezentacja zawartości radiowęgla w teście odtwarzalności systemu MICADAS w naszym Laboratorium. Słupki błędów pokazują niepewności 2-sigma. Linia ciągła pokazuje średnią, linie kropkowane pokazują podwójne odchylenie standardowe od średniej, a linia przerywana pokazuje 3-procentowe granice akceptowalności zgodnie z normą ASTM D6866-22.

5. Podsumowanie wkładu własnego w projekt doktorancki

W trakcie badań doktoranckich przeprowadziłem następujące działania:

Przegląd literatury: Dokonałem przeglądu odpowiedniej literatury w celu zidentyfikowania luk i ograniczeń oraz upewnienia się, że moja praca jest zgodna z aktualnym stanem wiedzy. Przeanalizowałem opublikowane eksperymenty dotyczące metody radiowęglowej stosowanej do oznaczania zawartości biowęgla i przyczyniłem się do udoskonalenia metodologii pod kątem konkretnych wyzwań napotkanych w Laboratorium w Gliwicach.

Planowanie i projektowanie prac badawczych: Przyczyniłem się do opracowania celów i ram prac badawczych dla zastosowania metod izotopowych do badania składu paliw ciekłych. Obejmowało to identyfikację zagadnień istotnych dla dostosowania metodyki oznaczania zawartości biowęgla w paliwach ciekłych w Gliwickim Laboratorium Radiowęglowym i Spektrometrii Mas oraz weryfikacji dokładności tej metodyki. Przetestowałem również i udoskonaliłem metodologię przygotowania próbek, w szczególności technikę zamykania próbek w cynowych kapsułkach przeznaczonych do cieczy. Przetestowałem tę metodę poprzez serię eksperymentów, które znacząco przyczyniły się do zwiększenia dokładności i precyzji wyników pomiarów.

Wybór i przygotowanie próbek: Przeprowadziłem selekcję próbek paliw ciekłych z próbek zarchiwizowanych w Laboratorium w Gliwicach i pracowałem z innymi próbkami dostarczonymi przez polskie firmy podczas moich studiów. Selekcja odbywała się zgodnie z najlepszymi praktykami, aby zapobiec zanieczyszczeniom i zapewnić homogenizację materiału próbki. Przygotowałem próbki do analizy izotopowej przy użyciu odpowiednich technik. Obejmowało to syntezę benzenu do LSC, przygotowanie grafitu do analiz AMS i CO_2 do analiz IRMS. W celu spalania próbek i oznaczania zawartości węgla pierwiastkowego używałem analizatora elementarnego (EA), który jest sprzężony ze zautomatyzowanym systemem AGE-3 do konwersji CO_2 na grafit. Wykorzystałem linie próżniowe do syntezy benzenu oraz do produkcji i oczyszczania CO_2. W sumie przygotowałem 13 próbek benzenu, 224 próbek grafitu i 72 próbek CO_2.

Pomiary laboratoryjne: Pod nadzorem promotora wykonałem pomiary z wykorzystaniem spektrometru AMS MICADAS do analizy zawartości ^{14}C oraz spektrometru IRMS IsoPrime do analizy składu izotopów stabilnych węgla. Ponadto opracowywałem surowe dane uzyskane podczas pomiarów przy użyciu specjalistycznego oprogramowania, takiego jak BATs (dla AMS) i IonVantage (dla IRMS), a także oprogramowania OxCal do kalibracji dat radiowęglowych w celu ich konwersji na daty kalendarzowe.

Pisanie publikacji, wniosków i raportów: Jestem głównym autorem trzech manuskryptów składających się na niniejszą pracę doktorską. Napisałem teksty, przygotowałem wszystkie rysunki i tabele oraz złożyłem je do czasopism, a także odpowiadałem na komentarze recenzentów. Ponadto napisałem rozszerzone streszczenie jako część mojej pracy magisterskiej w oparciu o opublikowane prace. Jestem również głównym autorem pięciu innych manuskryptów, zawierających wyniki mojej pracy licencjackiej i magisterskiej. Trzykrotnie z powodzeniem ubiegałem się o wewnętrzne finansowanie PŚ dla młodych naukowców. Napisałem trzy roczne raporty dla Szkoły Doktorskiej, w tym raport śródokresowy, które zostały pozytywnie ocenione przez odpowiednie Komisje.

Prezentacje na spotkaniach naukowych: Swoje wyniki prezentowałem na 6 międzynarodowych konferencjach naukowych, w tym 3 prezentacje ustne i 3 plakatowe. Przeprowadziłem dwa seminaria na spotkaniach Zakładu oraz jeden wykład na warsztatach dla młodych naukowców.

6. Ogólne wnioski

Podsumowując, głównym celem pracy doktorskiej było przetestowanie, ocena i optymalizacja metod przygotowania próbek oraz pomiarów w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach. Wybór między metodami AMS i LSC w analizach radiowęglowych zależy głównie od specyficznych wymagań badania, takich jak wielkość próbki, wiek, pożądana precyzja oraz dostępne zasoby.

W trzech opublikowanych manuskryptach testowano przygotowanie próbek paliw ciekłych przy użyciu obu metod. Jak wykazały wyniki z Tabeli 5, technika AMS wykazała większą czułość i precyzję, co czyni ją bardziej odpowiednią dla małych próbek. Oprócz strat próbki związanych z niewielkimi rozmiarami względem końcówki pipety, prasa do uszczelniania była skuteczna dla próbek AMS. W przypadku metody LSC wymagane było bardziej złożone przygotowanie próbek, takie jak konwersja próbek do postaci benzenu.

Zawartość ^{14}C w próbkach tła zmierzona zarówno przy użyciu AMS, jak i LSC bez resublimacji, potwierdziła, że wyniki dla próbki wolnej od ^{14}C były stabilne i spójne oraz umożliwiła wprowadzenie niezbędnych korekt. Dodatkowo, minimalna wykrywalna zawartość ^{14}C w paliwach ciekłych w Laboratorium w Gliwicach została określona na około 0,4 pMC dla AMS i około 1 pMC dla LSC (patrz Tabele 2 i 5).

Wyniki pomiarów ^{14}C dla mieszanek paliwowych przy użyciu obydwóch metod AMS i LSC wykazały dobrą powtarzalność przetwarzania próbek.

Niewielkie różnice między wynikami uzyskanymi za pomocą dwóch metod mogą wynikać z różnic w wydajności konwersji węgla podczas produkcji benzenu w przypadku LSC w porównaniu do całkowitego spalania materiału próbki w analizatorze elementarnym w przypadku AMS. Dzieje się tak pomimo zastosowania poprawek na frakcjonowanie izotopowe (stosunek $^{13}C/^{12}C$ mierzony metodą IRMS) w celu zapewnienia dokładnych i precyzyjnych wyników LSC ^{14}C.

Wyniki badań uzyskane dla próbek bio-olejów i mieszanek paliw wykazały, że test odtwarzalności dał wiarygodne wyniki, wskazując, że technika AMS z wykorzystaniem spektrometru MICADAS zapewnia zadowalającą precyzję pomiarów ^{14}C w Gliwickim Laboratorium ^{14}C i Spektrometrii Mas.

Referencje

Baranyika JB, Piotrowska N. 2023. Determination of radiocarbon content in bio-oil samples by Mini Carbon Dating system in the Gliwice Radiocarbon and Mass spectrometry Laboratory. Geochronometria. 50:21–27. doi:10.2478/geochr-2023-0005.

Barayika JB, Piotrowska N, Kłusek M, Michczyński A, Pawlyta J. 2022. Testing the Methods for Determination of Radiocarbon Content in Liquid Fuels in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. Radiocarbon. 64(6):1447–1456. doi:10.1017/rdc.2022.35.

Baranyika JB, Piotrowska N, Michczyński A. 2024. Determination of radiocarbon content in liquid fuel blends by accelerator mass spectrometry and liquid scintillation counting in the Gliwice Radiocarbon and Mass spectrometry Laboratory. Radiocarbon.:1–12. doi:https://doi.org/10.1017/RDC.2024.51.

Boucher ME, Chaala A, Roy C. 2000. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part I: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase. Biomass and Bioenergy. 19(5):337–350. doi:10.1016/S0961-9534(00)00043-X.

Bronk Ramsey C. 2009. Bayesian analysis of radiocarbon dates. Radiocarbon. 51(1):337–360. doi:10.1017/s0033822200033865.

Culp R. 2017. Radiocarbon Analysis for Biofuel Quantification in Fuel Blends. Encyclopedia of Analytical Chemistry.:1–13. doi:10.1002/9780470027318.a9587.

Culp R, Cherkinsky A, Ravi Prasad G V. 2014. Comparison of radiocarbon techniques for the assessment of biobase content in fuels. Applied Radiation and Isotopes. 93:106–109. doi:10.1016/j.apradiso.2014.01.007.

Dijs IJ, van der Windt E, Kaihola L, van der Borg K. 2006. Quantitative determination by 14c analysis of the biological component in fuels. Radiocarbon. 48(3):315–323. doi:10.1017/S0033822200038777.

Dobrzyńska E, Szewczyńska M, Pośniak M, Szczotka A, Puchałka B, Woodburn J. 2020. Exhaust emissions from diesel engines fueled by different blends with the addition of nanomodifiers and hydrotreated vegetable oil HVO. Environmental Pollution. 259. doi:10.1016/j.envpol.2019.113772.

Doll CG, Plymale AE, Cooper A, Kutnyakov I, Swita M, Lemmon T, Olarte M V., Wang H. 2021. Determination of low-level biogenic gasoline, jet fuel, and diesel in blends using the direct liquid scintillation counting method for 14C content. Fuel. 291(November 2020):120084. doi:10.1016/j.fuel.2020.120084.

Fan J, Kalnes TN, Alward M, Klinger J, Sadehvandi A, Shonnard DR. 2011. Life cycle assessment of electricity generation using fast pyrolysis bio-oil. Renewable Energy. 36(2):632–641. doi:10.1016/j.renene.2010.06.045.

Guo X, Liang C, Umar M, Mirza N. 2022. The impact of fossil fuel divestments and energy transitions on mutual funds performance. Technological Forecasting and Social Change. 176(December 2021):121429. doi:10.1016/j.techfore.2021.121429.

Gutiérrez J, Galán CA, Suárez R, Álvarez-Murillo A, González JF. 2018. Biofuels from cardoon pyrolysis: Extraction and application of biokerosene/kerosene mixtures in a self-manufactured jet engine. Energy Conversion and Management. 157:246–256. doi:10.1016/j.enconman.2017.12.006.

Hajdas I, Charlotte L. Pearson , Gianluca Quarta , Kirsty L. Spalding HY, Yoneda and M. 2021. Radiocarbon dating. Encyclopedia of Earth Sciences Series. 0123456789:689–702. doi:10.1007/978-1-4757-9694-0_3.

Haverly MR, Fenwick SR, Patterson FPK, Slade DA. 2019. Biobased carbon content quantification through AMS radiocarbon analysis of liquid fuels. Fuel. 237(October 2018):1108–1111. doi:10.1016/j.fuel.2018.10.081.

Horvatinčić N, Barešić J, Bronić IK, Obelić B. 2004. Measurement of low 14C activities in a liquid scintillation counter in the Zagreb Radiocarbon Laboratory. Radiocarbon. 46(1):105–116. doi:10.1017/S0033822200039412.

Hua Q, Turnbull JC, Santos GM, Rakowski AZ, Ancapichún S, De Pol-Holz R, Hammer S, Lehman SJ, Levin I, Miller JB, et al. 2022. Atmospheric Radiocarbon for the Period 1950-2019. Radiocarbon. 64(4):723–745. doi:10.1017/RDC.2021.95.

Idoeta R, Pérez E, Herranz M, Legarda F. 2014. Characteristic parameters in the measurement of 14C of biobased diesel fuels by liquid scintillation. Applied Radiation and Isotopes. 93:110–113. doi:10.1016/j.apradiso.2014.01.019.

Karaaslan A, Gezen M. 2022. The evaluation of renewable energy resources in Turkey by integer multi-objective selection problem with interval coefficient. Renewable Energy. 182(2022):842–854. doi:10.1016/j.renene.2021.10.053.

Krajcar Bronić I, Barešić J, Horvatinčić N, Sironić A. 2017. Determination of biogenic component in liquid fuels by the 14C direct LSC method by using quenching properties of modern liquids for calibration. Radiation Physics and Chemistry. 137:248–253. doi:10.1016/j.radphyschem.2016.01.041.

Krištof R. 2015. Quantification of biocomponents in fuels by 14C. Ph.D thesis. University of Nova Gorica Graduate School.

Krištof R, Kožar Logar J. 2013. Direct LSC method for measurements of biofuels in fuel. Talanta. 111:183–188. doi:10.1016/j.talanta.2013.03.009.

Krištof R, Kožar Logar J. 2017. Liquid Scintillation Spectrometry as a Tool of Biofuel Quantification. In: Frontiers in Bioenergy and Biofuels. p. 60–69.

Lee JE, Li ZH, Wang H, Plymale AE, Doll CG. 2022. Quantification of biogenic carbon in fuel blends through LSC 14C direct measurement and assessment of uncertainty. Fuel. 315:122859. doi:10.1016/j.fuel.2021.122859.

Lee P, Hoon S, Kong M, Kim Y. 2020. A new compact AMS facility at the Dongguk University. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 465:15–18. doi:10.1016/j.nimb.2019.12.027.

Liaquat AM, Masjuki HH, Kalam MA, Varman M, Hazrat MA, Shahabuddin M, Mofijur M. 2012. Application of blend fuels in a diesel engine. Energy Procedia. 14:1124–1133. doi:10.1016/j.egypro.2011.12.1065.

Malinowski A, Wrzosek P, Turlej A, Wardzińska D. 2015. A Review of Selected Methods of Measurement Used for the On-Line Analysis of Liquid Fuels. In: IntechOpen. p. 189–204.

Maruccio L, Quarta G, Braione E, Calcagnile L. 2017. Measuring stable carbon and nitrogen isotopes by IRMS and 14C by AMS on samples with masses in the microgram range: Performances of the system installed at CEDAD-University of Salento. International Journal of Mass Spectrometry. 421:1–7. doi:10.1016/j.ejbt.2017.01.004.

Matsakas L, Gao Q, Jansson S, Rova U, Christakopoulos P. 2017. Green conversion of municipal solid wastes into fuels and chemicals. Electronic Journal of Biotechnology. 26:69–83. doi:10.1016/j.ejbt.2017.01.004. http://dx.doi.org/10.1016/j.ejbt.2017.01.004.

Morone P, D'Amato D. 2019. The role of sustainability standards in the uptake of bio-based chemicals. Current Opinion in Green and Sustainable Chemistry. 19:45–49. doi:10.1016/j.cogsc.2019.05.003.

Neha S, Remya N. 2022. Co-production of biooil and biochar from microwave co-pyrolysis of food-waste and plastic using recycled biochar as microwave susceptor. Sustainable Energy Technologies and Assessments. 54:102892. doi:10.1016/j.seta.2022.102892.

Němec M, Wacker L, Gäggeler H. 2010. Optimization of the graphitization process AT AGE-1. Radiocarbon. 52(3):1380–1393. doi:10.1017/S0033822200046464.

Rajasekhar M, Rao NV, Rao GC, Priyadarshini G, Kumar NJ. 2015. Energy Generation from Municipal

Solid Waste by Innovative Technologies – Plasma Gasification. Procedia Materials Science. 10:513–518. https://doi.org/10.1017/S0033822200033154.

Reimer PJ, Brown TA, Reimer RW. 2004. Discussion: Reporting and calibration of post-Bomb 14C data. Radiocarbon. 46(3):1299–1304. https://doi.org/10.1016/S0969-806X(01)00255-9.

Santos Arévalo FJ, Gómez Martínez I, Agulló García L, Reina Maldonado MT, García León M. 2015. 14C determination in different bio-based products. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 361:354–357. doi:10.1016/j.nimb.2015.01.033.

De Souza JE, Scherer MD, Cáceres JAS, Caires ARL, M'Peko JC. 2013. A close dielectric spectroscopic analysis of diesel/biodiesel blends and potential dielectric approaches for biodiesel content assessment. Fuel. 105:705–710. doi:10.1016/j.fuel.2012.09.032.

Stenström KE, Skog G, Georgiadou E, Genberg J, Johansson A. 2011. A guide to radiocarbon units and calculations Lund University , Department of Physics , Division of Nuclear Physics.(LUNFD6(NFFR-3111)/1-17/(2011)). Lund University, Nuclear Physics.

Sulek MW, Kulczycki A, Malysa A. 2010. Assessment of lubricity of compositions of fuel oil with biocomponents derived from rape-seed. Wear. 268(1):104–108. doi:10.1016/j.wear.2009.07.004.

Tuniz C, John Rb, David F, Gregory FH. 2001. Accelerator mass spectrometry: Ultra-sensitive analysis for global science. Radiation Physics and Chemistry. 61:317–322. https://doi.org/10.1016/S0969-806X(01)00255-9.

Verger T, Azimov U, Adeniyi O. 2022. Biomass-based fuel blends as an alternative for the future heavy-duty transport: A review. Renewable and Sustainable Energy Reviews. 161:112391. https://doi.org/10.1016/j.rser.2022.112391.

Wacker L, Synal HA, Marcus C. 2010b. Bats: A new tool for AMS data reduction. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 268(7–8):976–979. http://dx.doi.org/10.1016/j.nimb.2009.10.078.

Wacker L, Němec M, Bourquin J. 2010a. A revolutionary graphitisation system: Fully automated, compact and simple. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 268(7–8):931–934. doi:10.1016/j.nimb.2009.10.067.

Wagner T, R. Magill C, O. Herrle J. 2016. Carbon isotopes. In: Encyclopedia of Earth Sciences Series. Vol. Part 2. p. 73–78.

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TESTING THE METHODS FOR DETERMINATION OF RADIOCARBON CONTENT IN LIQUID FUELS IN THE GLIWICE RADIOCARBON AND MASS SPECTROMETRY LABORATORY

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ABSTRACT. Determining the biocomponents in liquid fuels using radiocarbon radioisotope (^{14}C) dating requires sample preparation adaptations to the conditions of the Gliwice Radiocarbon and Mass Spectrometry Laboratory. Liquid scintillation counting (LSC), and accelerator mass spectrometry (AMS) were investigated using six samples, including one ^{14}C-free fuel and modern hydrotreated vegetable oil (HVO). For AMS, samples were prepared using tin capsules for liquids for EA combustion and graphitization in an AGE system. For LSC, liquid fuels were prepared by mixing with purified preheated sand and a benzene synthesis line. Benzene resublimation was also tested. IRMS measurements were also conducted for benzene to account for isotopic fractionation. Sample background measurements using both methods showed good performances by both AMS and LSC without resublimation. Comparable results were also obtained for HVO.

KEYWORDS: AMS, carbon isotopes, liquid fuels, LSC, radiocarbon.

INTRODUCTION

In this world of rapid development, global energy demand rises rapidly due to economic and population growth. Liquid fuels play a significant role in transportation and economic growth. In Poland, like in other European countries, the transportation sector contributes to increased energy consumption (Krištof and Kožar Logar 2013). As fossil fuel resources produce chemicals and energy, this made them known as the driving force behind the development of the world's lifestyle and economy (Krištof and Kožar Logar 2017).

In nature, there are three carbon isotopes. ^{12}C and ^{13}C are stable carbon isotopes with abundances of 98.89 and 1.11%, respectively (Wagner et al. 2016). Moreover, in the upper atmosphere a cosmogenic ^{14}C isotope is produced by the reaction of cosmic ray neutrons with nitrogen (^{14}N), followed by oxidization with oxygen in the atmosphere to form CO_2 (Hajdas et al. 2021). The fraction of ^{14}C in contemporary nature is ca. 10^{-10} % relative to stable carbon isotopes. During sample preparation and measurement, isotopic fractionation occurs. Isotope-ratio mass spectrometry (IRMS) verifies the fractionation processes that affect relative isotopic abundances in the given liquid fuel samples. IRMS plays a significant role in stable isotope analyses by measuring isotopic variation observed from fractionations of mass-dependent isotopes in natural systems (Maruccio et al. 2017).

The extreme age of fossil fuels means they no longer contain ^{14}C, though the current biosphere does contain this isotope. Because of that, European Union member states are encouraged to increase the use of energy from renewable resources. Moreover, they decrease biocomponent taxes due to higher production costs as compared to fossil fuels (Dijs et al. 2006; Krištof and Kožar Logar 2017; Karaaslan and Gezen 2022; Usman and Balsalobre-Lorente 2022).

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In addition, environmental changes due to greenhouse gas emissions have been observed. Previously, fossil fuel use in the transport sector or for energy production increased CO_2 levels in the atmosphere. Combustion of fossil fuels for transport, energy, and heating is the primary source of CO_2 emission from human activities in Poland (Piotrowska et al. 2020). One way to reduce CO_2 emissions comes from using renewable (biogenic) sources (Krištof 2015). Several accurate and reliable testing methods are being used to confirm the eligibility of reimbursed taxes by controlling the content of bio components in fuels. Biocomponent fractions reflect ^{14}C content, and numerous studies prove the suitability and robustness of ^{14}C dating for liquid fuels (Reddy et al. 2008; Krištof and Kožar Logar 2013; Culp et al. 2014; Santos Arévalo et al. 2015; Krajcar Bronić et al. 2017; Krištof and Kožar Logar 2017).

Accelerator mass spectrometry (AMS) and liquid scintillation counting (LSC) are among the techniques used to determine ^{14}C content in liquid fuels. AMS requires graphite, as sample graphitization is standard for ^{14}C measurements by high-precision accelerator mass spectrometry. To get the graphite, sample combustion by elemental analysis (EA) followed by CO_2 graphitization with H_2 on a catalyst (commonly iron powder).

During this process, the transfer of CO_2 from EA to the graphitization reactors occurs using a zeolite trap (Němec et al. 2010; Wacker et al. 2010). Sample preparation for LSC requires several procedures. In the carbamate method, also known as the LSC-A method (Horvatinčić et al. 2004), the determination of ^{14}C is based on CO_2 preparation by combusting a sample in a controlled environment. The second is the benzene method (LSC-B; Horvatinčić et al. 2004), where ^{14}C determination occurs after sample conversion to benzene by forming carbide followed by hydrolyzation to acetylene and the trimerization to get benzene (Horvatinčić et al. 2004; Krištof and Kožar Logar 2017). Another procedure avoids sample pretreatment altogether (LSC-C), and involves simply mixing an appropriate scintillation cocktail with the sample (Norton et al. 2012; Culp et al. 2014; Krištof 2015; Doll et al. 2017; Krajcar Bronić et al. 2017; Doll et al. 2021).

This work aimed to test and verify the methodology of determining ^{14}C content in liquid fuels at the Gliwice Radiocarbon and Mass Spectrometry Laboratory. Based on presented isotope studies, the biocarbon contents in liquid fuels may be determined. In addition, this study tested the accuracy of those methods for quantifying biocarbon in liquid fuels. This work moves towards accreditation for tested methods in the Radiocarbon and Mass Spectrometry Laboratory.

MATERIALS AND METHODS

To adapt the sample preparation methods and measurements to the conditions in Gliwice Laboratory, the determination of ^{14}C in liquid fuels was investigated using LSC and AMS.

Tested Sample Materials

Several archived samples of liquid fuels with the following expected biocontents were used in this study:

- ON/UF-BC/GdA-5623: 0%, background sample,
- SN-204: 7–8%,
- Diesel BP: unknown,

- B30: 30%,
- B37: 37%,
- Hydrotreated vegetable oil (HVO): 100%.

Place of Realization

In this project, all samples were prepared at the Gliwice Radiocarbon and Mass Spectrometry Laboratory Institute of Physics – Centre for Science and Education, Division of Geochronology and Environment Isotopes. Graphite targets were prepared for AMS at the Gliwice Laboratory (Piotrowska 2013). The targets accompanied by references were submitted to the Poznan Radiocarbon Laboratory for AMS measurements (Goslar et al. 2004). Stable isotopes analysis using IRMS was conducted at Gliwice as well.

Sample Preparation for AMS

Accelerator mass spectrometry precisely measures rare isotopic ratios. Ratios of ^{14}C/^{12}C and ^{13}C/^{12}C are needed to determine biocarbon contents. The method does quantitatively determine biocarbon contents but requires extensive sample treatment and expensive equipment. Normally, for ^{14}C AMS measurements, we need graphite (Wacker et al. 2010). To perform AMS measurements, a batch of liquid fuel samples was prepared. There was no chemical processing of samples before combustion. Liquid fuels were directly placed into tin capsules for liquid samples (0.04 mL) using an adjustable micropipette (0.1–2 μL) and sealed using a sealing press. At the Gliwice Laboratory, 2 μL of each liquid fuel type was subsampled and weighed on a Sartorius microbalance (precision = 0.001 mg) to get the mass of samples for combustion. The expected sample mass for 2 μL was 1.3 mg and the assumed percentage of carbon (% C) was 86%.

The samples were combusted in EA with 50 s of oxygen dosing and CO_2 was transferred from the EA to the reactors for graphitization with H_2 and an iron powder catalyst. Calculating the concentration of elements such as carbon in the sample, the system first measured the absolute elemental content, the concentration of that element was then calculated by the following formula:

$$C = \frac{a \cdot 100 \cdot f}{w} \tag{1}$$

C is the concentration of element in [%], a is the computed absolute elemental content in (mg), f is the daily factor, and w is the sample weight in (mg). To determine the daily factor, reference samples were analyzed along with unknowns. The ratio of known elemental concentrations of reference samples and the actual elemental concentration computed (CHNOS Elemental Analyzer manual 2013).

Sealing via capsule press was unchallenging and speedy. The only observed problem was the small size of the capsule for the liquid sample concerning the pipette tip, which kept some amount of the sample from sealing completely. A similar problem was reported previously (Santos Arévalo et al. 2015). This amount should evaporate in time, so experiments to test the evaporative effects of the samples were made. First, the samples were combusted directly after sealing, considering only the calculated mass of 1.3 mg, assumed from the expected carbon content and the 2 μL volume (experiment 1). Second, all samples were weighed after 24 hr in their sealed capsules to determine their evaporations rates (experiment 2). Finally, to verify the evaporation of sample residues over time, the samples were sealed in capsules for 48 hr before EA combustion (experiment 3). Blanks contained no liquid samples.

Sample Preparation for LSC Measurements

Liquid scintillation spectrometry measures radioactivity and is used primarily for β-emitting isotopes such as ^{14}C (Krištof and Kožar Logar 2017). Determining bicomponent content in liquid fuels using this method compares the counting rate for both fossil and modern origin samples. Gliwice Laboratory is equipped with two ultralow level liquid scintillation alpha and beta spectrometers (Quantulus1220). We used the LSC-B method (Pazdur et al. 2000, 2003; Horvatinčić et al. 2004).

To get the benzene sample for the LSC method, liquid fuels were prepared after mixing with purified preheated (500°C, 12 hr) sand using a benzene synthesis line. This process involved the use of 7 g of liquid fuels that reacted with 10.5 g of lithium at 700°C to form lithium carbide (Li_2C_2). Hydrolysis of Li_2C_2 produced acetylene (C_2H_2), which was purified by running through a mixture of potassium dichromate ($K_2Cr_2O_7$) and sulfuric acid. Trimerization at room temperature converted acetylene into benzene using a preheated (at 600°C) chromium catalyst on silica gel.

Benzene samples were stored over sodium metal for 24 hr to remove water, followed by sublimation. For most of the liquid fuel samples, two subsamples of benzene were prepared. The first one was kept for 30 days in a laboratory freezer (–20°C) to remove radon contamination and the second one used in the resublimation procedure described below.

Resublimation Method for Radon Removal

In the Gliwice Laboratory, benzene preparation is the fundamental step for LSC measurements. However, radon (^{222}Rn) inevitably contaminates these samples and can artificially inflate the biocarbon content. To remove ^{222}Rn from the benzene samples before measurements without waiting 30 days, the resublimation method was used (Tudyka et al. 2021). The key point of this method was to test the effectiveness of rapid radon removal. $\mathbf{^{222}}Rn$ was removed in three different benzene samples (ON/UF-BC, SN-204, and B30) via four resublimation steps using a mixture of alcohol and dry ice at –79°C or NaCl and ice at –20°C. The performance of this procedure was confirmed by comparison to the background activity sample.

$\delta^{13}C$ Determination by IRMS

IRMS sought to verify isotope fractionation that occurred during preparation and measurement processes. To provide accurate and precise ^{14}C determinations, it was important to correct for isotopic fractionation.

The $^{13}C/^{12}C$ ratio, expressed as $\delta^{13}C$, was used for this correction. For each benzene sample, ~5 μL was combusted in a glass tube with copper oxide (CuO), followed by CO_2 purification and subsampling with a syringe. CO_2 was introduced into a Multiflow device for IRMS measurements using an Isoprime continuous-flow mass spectrometer. Two standards, ANU-sucrose and NBS-22 were used to deduce the linear regression from which different $\delta^{13}C$ values were calculated.

The values of ^{14}C concentration were corrected for isotope fractionations using measured δ^{13}C according to equation (Stuiver and Polach 1977):

$$A_{SN} = A_S\left[1 - \frac{2(25 + \delta^{13}\mathrm{C})}{1000}\right] \tag{2}$$

A_{SN} is the corrected ^{14}C sample concentration, A_S is the measured ^{14}C concentration of the sample.

RESULTS AND DISCUSSION

To decide samples for graphitization, six different liquid fuels were subjected to EA combustion to test their carbon compositions. Table 1 gives the carbon concentration data obtained after combusting samples of different masses in three experiments.

Firstly, experiments were conducted considering the calculated mass. Thus, those carbon concentration results surpassed 100% for all subsamples used in experiment 1, which confirmed those results were not relevant. Based on this, we considered only the weighted mass of the samples. Secondly, fuel samples were combusted by considering the mass of each subsample directly after weighing. Those results showed carbon concentrations of <100% for all samples.

Even so, it did not significantly affect the expected range of sample carbon concentrations, but the calculated concentrations were inconsistent due to weight changes caused by sample residues lost because of small capsule size relative to the point of the pipette used in this subsampling procedure.

Despite the ease of sealing, it was tested to check sample mass changes over time. Different samples kept in the laboratory 24 hr after sealing in tin capsules showed their masses varied by up to 22% (see Table 1) (Santos Arévalo et al. 2015) reported similar testing procedures. Results for all subsamples showed carbon concentrations of less than 100%. Additionally, there is no relation between the change of mass (evaporated fuel after 24 hr) and measured carbon concentration. The same results occurred for samples kept for 48 hr before EA combustion. Therefore, it was not necessary to monitor sample evaporation but controlling EA cross-contamination by running empty analyses (“RunIn”) and increasing the number of sub-samples was important.

The carbon concentration averages (Experiment 2) were 72.8%, 82.1%, and 70.5% for B30, B37, and SN-204, respectively. The calculated carbon concentrations for experiment 3 were 78.2%, 75.7%, 64.6%, 85.1%, 62.0%, and 66.2% for B30, B37, SN-204, ON/UF-BC, Diesel BP, and HVO, respectively.

Testing the measurement methods for ^{14}C content were conducted on different liquid fuel samples. Measurements of the (δ^{13}C) isotopic ratio using stable isotopes ^{13}C and ^{12}C for both ANU-sucrose and NBS-22oil standards showed –10.5 and –30‰, respectively. Furthermore, Table 2 shows the results for all fuel samples and ranges from –26.9 to –30‰. The –30‰ was assumed for Diesel BP. The results for all isotope measurements from liquid fuels agreed with both standards (ANU-sucrose and NBS-22oil) and they were used for ^{14}C determination after measurements in the LSC laboratory.

To test sample contaminations, the ^{14}C content for background sample was first determined. ^{14}C content measured for the background samples (ON/UF-BC) in both AMS and LSC laboratories were 0.32 ± 0.06 pMC (average) and 0.25 ± 0.10 pMC, respectively. The 0.07

Table 1 Results (% C) of liquid fuels combustion in EA in various experiments (see text). *Result disregarded in average calculations.

Sample name	Initial mass (mg)	Mass loss after 24 hr (mg)	Mass loss after 48 hr (mg)	Final mass (mg)	% C
B30 Experiment 1	1.3	—	—	1.3	127.22
	1.3	—	—	1.3	228.19
B30 Experiment 2	1.852	0.219	—	1.633	66.67
	1.887	0.136	—	1.751	66.72
	1.841	0.053	—	1.788	85.00
				Average	*72.8 ± 10.6*
B30 Experiment 3	1.900	—	0.110	1.790	29.14*
	1.884	—	0.090	1.794	75.38
	1.788	—	0.069	1.719	80.99
				Average	*78.2 ± 4.00*
B37 Experiment 1	1.3	—	—	1.3	262.68
	1.3	—	—	1.3	185.95
B37 Experiment 2	1.792	0.053	—	1.739	82.99
	1.802	0.073	—	1.729	90.49
	1.952	0.065	—	1.887	72.88
				Average	*82.1 ± 8.80*
B37 Experiment 3	1.892	—	0.084	1.808	81.25
	1.776	—	0.171	1.605	79.83
	1.846	—	0.111	1.735	66.03
				Average	*75.7 ± 8.40*
SN-204 Experiment 2	1.943	—	—	1.943	73.31
	1.858	—	—	1.858	65.42
	1.577	—	—	1.577	72.86
				Average	*70.5 ± 4.40*
SN-204 Experiment 3	1.897	—	0.177	1.720	88.33
	2.108	—	0.182	1.926	51.17
	2.189	—	0.202	1.987	54.17
				Average	*64.6 ± 20.60*
ON/UF-BC Experiment 3	1.828	—	0.122	1.706	85.50
	1.646	—	0.186	1.460	86.33
	1.872	—	0.206	1.666	83.45
				Average	*85.1 ± 1.50*
Diesel BP Experiment 3	1.913	—	0.079	1.834	49.58
	1.893	—	0.420	1.473	63.75
	1.872	—	0.133	1.739	72.66
				Average	*62.0 ±11.60*
HVO Experiment 3	1.892	—	0.054	1.838	88.92
	1.853	—	0.068	1.785	67.45
	1.569	—	0.110	1.459	42.17
				Average	*66.2 ± 23.40*

Table 2 Results of ^{14}C concentration (pMC), and isotopes fractionation (δ^{13}C) measurements.

Sample name	δ^{13}C IRMS	Lab ID	^{14}C concentration (pMC)	Method
ON/UF-BC	GdMS-58627	GdS-4368	0.25 ± 0.10	LSC uncorrected
	–26.90 ± 0.10		0.25 ± 0.10	LSC corrected
		GdS-4398*	1.63 ± 0.13	LSC uncorrected
			1.64 ± 0.13	LSC corrected
		GdA-5724	0.256 ± 0.02	AMS
		GdA-5627	0.343 ± 0.02	AMS
		GdA-5623	0.24 ± 0.01	AMS
		GdA-5803	0.392 ± 0.02	AMS
		GdA-6605	0.38 ± 0.10	AMS
			0.32 ± 0.06	*AMS average*
B30	GdMS-58633	GdS-4333	39.67 ± 0.43	LSC uncorrected
	–30.00 ± 0.10		40.07 ± 0.43	LSC corrected
		GdS-4377*	34.16 ± 0.42	LSC uncorrected
			34.50 ± 0.42	LSC corrected
		GdA-6607	30.07 ± 0.10	AMS
B37	GdMS-58638	GdS-4334	28.50 ± 0.48	LSC uncorrected
	–29.90 ± 0.10		28.78 ± 0.48	LSC corrected
		GdA-6608	22.14 ± 0.17	AMS
SN-204	GdMS-59026	GdS-4009	9.74 ± 0.22	LSC uncorrected
	–30.00 ± 0.10		9.84 ± 0.22	LSC corrected
		GdS-4400*	9.33 ± 0.19	LSC uncorrected
			9.42 ± 0.19	LSC corrected
		GdA-6606	9.54 ± 0.19	AMS
		GdA-5722	8.84 ± 0.08	AMS
			9.19 ± 0.49	*AMS average*
Diesel-BP	GdMS-58636	GdS-4335	37.64 ± 0.53	LSC uncorrected
	–30.00 ± 0.10		38.01 ± 0.53	LSC corrected
		GdA-6609	33.92 ± 0.20	AMS
HVO	GdMS-59022	GdS-4379	99.49 ± 0.81	LSC uncorrected
	–28.10 ± 0.10		100.10 ± 0.81	LSC Corrected
		GdS-4386*	100.18 ± 0.80	LSC uncorrected
			100.8 ± 0.80	LSC corrected
		GdA-6610	101.45 ± 0.33	AMS
ANU-sucrose	GdMS-58611			
	–10.45 ± 0.10			
NBS-22 oil	GdMS-58613			
	–30.00 ± 0.10			

*Resublimated samples.

difference between AMS and LSC results was satisfactory given the combined uncertainty was 0.12 pMC. Compared to the expected value (0% pMC) and considering the calculated errors, results from both laboratories agreed, and satisfied the level of acceptability. Subsequently, ^{14}C measurements by LSC after radon removal by resublimation showed 1.63 ± 0.13 pMC. The result for resublimed background sample did not correlate with the expected value. This difference may be due to the addition of modern contamination while handling benzene

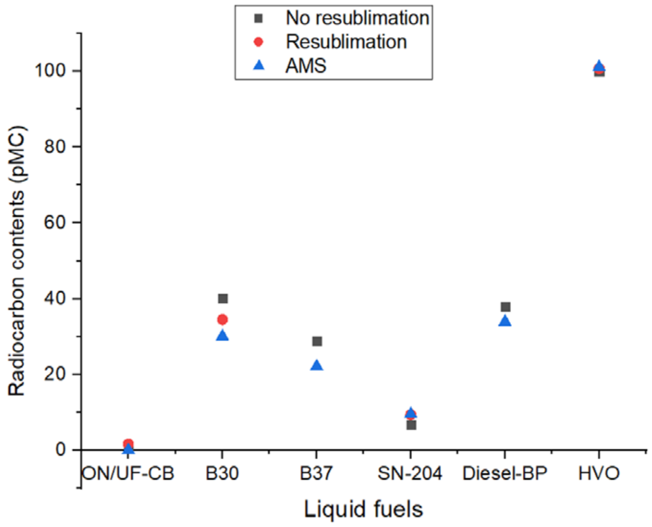

Figure 1 ^{14}C contents of tested liquid fuels grouped according to different methods of sample preparation (LSC-non resublimation, LSC-resublimation and AMS).

during resublimation. Many steps in this process interact with atmospheric CO_2, which affects the background sample.

Furthermore, ^{14}C contents for HVO fuel measured in the LSC laboratory yielded 99.49 ± 0.81pMC for the benzene sample kept for 30 days, and 100.18 ± 0.80 pMC for resublimed benzene. The results corrected for isotope fractionations yielded 100.10 ± 0.81 and 100.8 ± 0.8 pMC values for non-resublimed and resublimed benzene samples, respectively. Both values agreed with the AMS result of 101.45 ± 0.33 pMC.

For SN-204, the measured ^{14}C contents were 9.74 ± 0.22 and 8.84 ± 0.08 pMC by LSC and AMS, respectively. The expected result was between 7–8 pMC. To confirm the AMS measurement results, a second experiment yielded 9.54 ± 0.19 pMC. The average AMS results were 9.19 ± 0.49 pMC, and the difference between LSC was 0.55 ± 0.54 pMC. Also, the δ^{13}C-corrected results for both non-resublimed (9.74 ± 0.22 pMC) and resublimed (9.33 ± 0.19 pMC) samples showed good agreement (difference 0.41 ± 0.29 pMC), meaning these ^{14}C measurement results were in good agreement, given calculated errors and expected SN-204 biocarbon contents.

A comparison of the expected bio-content contents and the consistency of the results obtained via all methods for samples HVO and SN-204 confirmed that resublimation effectively avoided radon contamination.

For B30, the ^{14}C contents in the LSC laboratory were 39.67 ± 0.43 and 34.16 ± 0.40 pMC for benzene samples kept in the laboratory for 30 days and resublimed, respectively. To provide accurate ^{14}C contents, both results were corrected for isotopic fractionations using δ^{13}C. The corrected pMC values were 40.07 ± 0.43 and 34.50 ± 0.40 pMC for non-resublimed and resublimed samples, respectively. In addition, AMS measurement results showed a 30.07 ± 0.10 pMC, as expected, though uncertified bio-carbon content was 30%.

However, in this study, there were no resublimation experiments conducted for both Diesel BP and B37 samples. For both liquid fuels, the benzene samples were retained for 30 days in a freezer to remove radon. ^{14}C measurements from the LSC laboratory showed ^{14}C contents of 37.64 ± 0.53 and 28.50 ± 0.48 pMC for Diesel BP and B37, respectively. Both results were corrected for isotopic fractionation and showed 38.01 ± 0.53 and 28.87 ± 0.48 pMC. AMS measurement results were 33.92 ± 0.20 and 22.14 ± 0.17 pMC for both Diesel BP and B37, respectively. The lowest values were observed for B37 compared to the expected uncertified bio contents of 37%, and the highest pMC values were obtained for Diesel BP.

Figure 1 lists all results and shows significant differences for all three samples (results ~30 pMC for B30, B37, and Diesel BP). There is no good explanation for this phenomenon right now. One reason may be an incomplete reaction with lithium, and we plan to improve the reaction monitoring.

There is a similarity in factory production for all diesel fuels. Comparing expected bio-content levels, contamination from factory treatment processes may cause these differences. Therefore, additional tests will be conducted to determine a suitable explanation for these changes.

CONCLUSION

Sample preparations for both LSC and AMS methods were tested. Apart from sample loss due to its small size relative to the pipette point, the sealing press was effective. To provide accurate and precise radiocarbon determinations, isotopic ratio variations of (δ^{13}C) using ^{13}C and ^{12}C isotopes were measured by IRMS. Radiocarbon contents (pMC) of background samples measured using both AMS and LSC without resublimed samples confirmed there was no contamination by either sample preparation method. Several factors require consideration in the future to maintain reproducibility for liquid fuel measurements. A complete reaction requires improved control of Li_2C_2 synthesis. To minimize benzene loss and avoid contamination, vacuum control during resublimation must occur to minimize contact of the sample with atmospheric CO_2 and maintain the reproducibility of results. Finally, a new vacuum line is in construction in the Gliwice laboratory to allow combustion experiments with liquids in an oxygen stream.

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REFERENCES

CHNOS Elemental Analyzer manual. 2013. vario MICRO cube analyser. https://www.elementar.de/index.php?id=4531&L=1.

Culp R, Cherkinsky A, Ravi Prasad GV. 2014. Comparison of radiocarbon techniques for the assessment of biobase content in fuels. Applied Radiation and Isotopes 93:106–109. doi: 10.1016/j.apradiso.2014.01.007.

Dijs IJ, van der Windt E, Kaihola L, van der Borg K. 2006. Quantitative determination by ^{14}C analysis of the biological component in fuels. Radiocarbon 48(3):315–323. doi: 10.1017/S0033822200038777.

Doll CG, Plymale AE, Cooper A, Kutnyakov I, Swita M, Lemmon T, Olarte MV, Wang H. 2021. Determination of low-level biogenic gasoline, jet fuel, and diesel in blends using the direct liquid scintillation counting method for ^{14}C content. Fuel 291(November 2020):120084. doi: 10.1016/j.fuel.2020.120084.

Doll CG, Wright CW, Morley SM, Wright BW. 2017. Analysis of fuel using the Direct LSC method determination of bio-originated fuel in the presence of quenching. Applied Radiation and Isotopes 122(January):215–221. doi: 10.1016/j.apradiso.2017.01.040.

Goslar T, Czernik J, Goslar E. 2004. Low-energy ^{14}C AMS in Poznań Radiocarbon Laboratory, Poland. Nuclear Instruments and Methods in Physics Research Section B 223–224:5–11. doi: 10.1016/j.nimb.2004.04.005.

Hajdas I, Pearson CL, Quarta G, Kirsty L, Spalding HY, Yoneda M. 2021. Radiocarbon dating. Encyclopedia of Earth Science Series 0123456789:689–702. doi: 10.1007/978-1-4757-9694-0_3. http://doi.org/10.1038/s43586-021-00058-7.

Horvatinčić N, Barešić J, Bronić IK, Obelić B. 2004. Measurement of low ^{14}C activities in a liquid scintillation counter in the Zagreb Radiocarbon Laboratory. Radiocarbon 46(1):105–116. doi: 10.1017/S0033822200039412.

Karaaslan A, Gezen M. 2022. The evaluation of renewable energy resources in Turkey by integer multi-objective selection problem with interval coefficient. Renewable Energy 182(2022):842–854. doi: 10.1016/j.renene.2021.10.053.

Krajcar Bronić I, Barešić J, Horvatinčić N, Sironić A. 2017. Determination of biogenic component in liquid fuels by the ^{14}C direct LSC method by using quenching properties of modern liquids for calibration. Radiation and Physics Chemistry 137:248–253. doi: 10.1016/j.radphyschem.2016.01.041.

Krištof R. 2015. Quantification of biocomponents in fuels by ^{14}C [dissertation]. Nova Gorcia, Slovenia: University of Nova Gorcia.

Krištof R, Kožar Logar J. 2013. Direct LSC method for measurements of biofuels in fuel. Talanta. 111:183–188. doi: 10.1016/j.talanta.2013.03.009.

Krištof R, Kožar Logar J. 2017. Liquid scintillation spectrometry as a tool of biofuel quantification. Frontiers in Bioenergy and Biofuels. doi: 10.5772/65549.

Maruccio L, Quarta G, Braione E, Calcagnile L. 2017. Measuring stable carbon and nitrogen isotopes by IRMS and ^{14}C by AMS on samples with masses in the microgram range: Performances of the system installed at CEDAD-University of Salento. International Journal of Mass Spectrometry 421: 1–7. doi: 10.1016/j.ijms.2017.05.014.

Němec M, Wacker L, Gäggeler H. 2010. Optimization of the graphitization process AT AGE-1. Radiocarbon 52(3):1380–1393. doi: 10.1017/S0033822200046464.

Norton GA, Cline AM, Thompson GC. 2012. Use of radiocarbon analyses for determining levels of biodiesel in fuel blends—comparison with ASTM Method D7371 for FAME. Fuel 96:284–290. doi: 10.1016/j.fuel.2012.01.026.

Pazdur A, Fogtman M, Michczyński A, Pawlyta J. 2003. Precision of ^{14}C dating in Gliwice radiocarbon laboratory. FIRI programme. Geochronometria 22(September 1999):27–40.

Pazdur A, Michczyński A, Pawlyta J, Spahiu P. 2000. Comparison of the radiocarbon dating methods used in the Gliwice Radiocarbon Laboratory. Geochronometria 18:9–14.

Piotrowska N. 2013. Status report of AMS sample preparation laboratory at GADAM Centre, Gliwice, Poland. Nuclear Instruments and Methods in Physics Research Section B 294:176–181. doi: 10.1016/j.nimb.2012.05.017.

Piotrowska N, Pazdur A, Pawełczyk S, Rakowski AZ, Sensuła B, Tudyka K. 2020. Human Activity recorded in carbon isotopic composition of atmospheric CO_2 in Gliwice urban area and surroundings (southern Poland) in the years 2011–2013. Radiocarbon 62(1):141–156. doi: 10.1017/RDC.2019.92.

Reddy CM, Demello JA, Carmichael CA, Peacock EE, Xu L, Arey JS. 2008. Determination of biodiesel blending percentages using natural abundance radiocarbon analysis: testing the accuracy of retail biodiesel blends. Environmental Science & Technology 42(7):2476–2482. doi: 10.1021/es071814j.

Santos Arévalo FJ, Gómez Martínez I, Agulló García L, Reina Maldonado MT, García León M. 2015. ^{14}C determination in different bio-based products. Nuclear Instruments and Methods in Physics Research Section B 361:354–357. doi: 10.1016/j.nimb.2015.01.033.

Stuiver M, Polach HA. 1977. Reporting of ^{14}C data. Radiocarbon 19(3):355–363.

Tudyka K, Pawełczyk F, Michczyński A. 2021. Bias arising from ^{222}Rn contamination in standardized methods for biobased content determination and a simple removal method. Measurement 167. doi: 10.1016/j.measurement.2020.108263.

Usman M, Balsalobre-Lorente D. 2022. Environmental concern in the era of industrialization: Can financial development, renewable energy and natural resources alleviate some load? Energy Policy 162(January):112780. doi: 10.1016/j.enpol.2022.112780.

Wacker L, Němec M, Bourquin J. 2010. A revolutionary graphitisation system: Fully automated, compact and simple. Nuclear Instruments and Methods in Physics Research Section B 268(7–8):931–934. doi: 10.1016/j.nimb.2009.10.067.

Wagner T, Magill CR, Herrle JO. 2016. Carbon isotopes. In: Encyclopedia of earth sciences series. Part 2. p. 73–78.

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My contribution included: Sample selection and preparation of benzene and graphite for LSC and AMS analysis, preparation of CO_2 for IRMS analysis, calculations of carbon content based on EA results, ^{14}C and $\delta^{13}C$ measurements; writing of text, preparation of all figures and tables and paper submission in journal, as well as responding to reviewers' comments.

My participation to the work (Baranyika et al. 2022) was 75 %

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Mój wkład polegał na: Selekcji próbek i przygotowaniu benzenu oraz grafitu do analiz LSC i AMS, przygotowaniu CO_2 do analiz IRMS, obliczeniach zawartości węgla na podstawie wyników EA, pomiarach ^{14}C i $\delta^{13}C$; napisaniu tekstu, przygotowaniu wszystkich rycin i tabel oraz pracy, złożenie manuskryptu w czasopiśmie oraz odpowiadanie na uwagi recenzentów.

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My contribution was as follows: Supervision of PhD research, supervision of AMS analysis, calculations of ^{14}C content from AMS and assistance in paper revision

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był następujący: nadzór nad pomiarami IRMS, obliczenia zawartości $\delta^{13}C$ z IRMS oraz pomoc w redakcji artykułu.

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DETERMINATION OF RADIOCARBON CONTENT IN BIO-OIL SAMPLES BY MINI CARBON DATING SYSTEM IN THE GLIWICE RADIOCARBON AND MASS SPECTROMETRY LABORATORY

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Abstract
The applications of isotopes are used by many European countries to investigate environmental changes. A compact modern accelerator mass spectrometry (AMS) system known as Mini Carbon Dating System (MICADAS) is used in Gliwice Radiocarbon and Mass Spectrometry Laboratory for determining the ^{14}C content in different environmental samples including liquid fuels. For radiocarbon measurement using MICADAS, the liquid samples are accurately prepared using the tin capsules for liquids for combustion in elemental analyser (EA) and graphitisation in the AGE system. In this study, the determination of ^{14}C content in three different bio-oil samples and one reference sample of 100% biomass was conducted. Bio-oil samples were prepared using tin capsules for liquids sealed in the second capsules for solids to avoid sample evaporation while the reference sample was prepared using the tin capsule for solids for combustion in EA and graphitisation in the AGE system. Based on the ^{14}C measurement results, one of the bio-oils was not produced from the analysed reference biomass. Two others were determined as a mixture of bio- and fossil components, and based on ^{14}C the bio-carbon content was calculated. For all samples, the ^{14}C measurement showed reproducible and reliable results.

Keywords
bio-oils, radiocarbon, biomass, MICADAS, isotope methods

1. Introduction

Due to the environmental concerns associated with the use of fossil fuels, the member states of the European Union (EU) like other countries in the world are in the process of developing the use of alternative sources of energy including biomass, wave, and nuclear energies (Rajasekhar *et al*., 2015; Matsakas *et al*., 2017; Neha and Remya, 2022).

Among the sources of renewable energy, biomass used for biofuel production is obtained from forestry, microbial and agricultural systems (Kim *et al*., 2013). Biomass is an inexpensive and abundant source for biofuel production. Moreover, it has the potential for future sustainable development because it is characterised by zero net carbon dioxide (CO_2) emissions and promotes employment in the rural area of a given country (Gutiérrez *et al*., 2018; Neha and Remya, 2022).

Liquid form of fuel (known as bio-oil) produced from biomass has several environmental advantages. Bio-oil is considered CO_2 neutral and can produce the credits of CO_2 without emitting sulphur oxides (SO_X) (Fan *et al*., 2011). Furthermore, emissions of nitrogen oxides (NOX) by bio-oil are quantified 50% lower than those emitted by biodiesel in gas turbines (Boucher *et al*., 2000; Ikura *et al*., 2003; Gutiérrez *et al*., 2018). In addition to using bio-oil blends with heavy furnace oil to improve the quality of combustion, bio-oil is also used in diesel engines to replace fossil fuels and boilers and has several heating applications in furnaces (Soni and Karmee, 2020).

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The use of biomass to produce biofuels including bio-oils that provide renewable and clean energy is one of the initiatives of the United Nations (UN) implemented for sustainable development goals (SDG) (Arun *et al*., 2021). It was implemented to valorise biomass waste regarding the reduction of environmental pollution (Cho *et al*., 2020). The development of renewable energy is one of the tri-variate nexuses in the discourse of climate change and the agenda of sustainable development (Destek *et al*., 2021). Contrary, previous studies reported that though bio-oil enhances economic development depending on the methods used for their production, some bio-oils can contribute to environmental problems depending on the feedstock and the process of production by emitting more greenhouse gases (Jeswani *et al*., 2020; Destek *et al*., 2021). Due to that reason, several member states of the EU including Poland are developing systematic research on biofuels to understand their properties and deduce the consequences of biocomponent contents in the biofuels in different areas such as greenhouse gas emission, life cycles and toxicology (Hancsók *et al*., 2007; Do *et al*., 2014; Samson-Bręk *et al*., 2015).

To investigate the environmental changes that may be caused by the use of fuels in the member states of the EU, the isotope methods are being developed in several laboratories to determine the biocomponent contents in liquid fuels (Oinonen *et al*., 2010; Khundadze *et al*., 2022). In the Gliwice Radiocarbon and Mass Spectrometry Laboratory, a part of chronological purposes in geology and archaeology, the radiocarbon radioisotope (^{14}C) method is being used to determine the content of biocarbon in both solid and liquid samples such as liquid fuels using the accelerator mass spectrometry (AMS) (Baranyika *et al*., 2022).

Because of old age, fossil fuels no longer contain the measurable ^{14}C whereas the contemporary biosphere contains a lot of this radioisotope. As a result, the Member States of the EU are encouraged to produce energy from renewable resources such as biomass, and tax measures are applied to ensure that biofuel prices are comparable to those of fossil fuels (Dijs *et al*., 2006). According to Lee *et al*. (2022), the content of ^{14}C may vary in biofuels depending on the geographic origin of biomass and the age type. Moreover, several factors including CO_2 emissions from burning fossil fuels and the testing of nuclear weapons in the atmosphere may contribute to the variation of ^{14}C concentration in the atmosphere.

AMS is an ultrasensitive technique to analyse the cosmogenic isotope including ^{14}C, ^{26}Al, ^{10}Be and ^{36}Cl (Tuniz *et al*., 2001; Lee *et al*., 2020). Prior to analysis, the investigated samples have to undergo preparation procedures to form a target suitable for a specific ion source. In AMS measurements process, all atoms and molecules extracted from the target are ionized followed by the dissociation of ionized molecules into the accelerator. Depending on energy, momentum and charge, the ionized atoms go through changes in charge state, and at the end of AMS procedure, the isotopes are counted individually to determine the isotopic ratios. Moreover, ^{14}C is a significant AMS isotope in the studies of atmospheric processes, biomedicine, archaeology, and ocean circulation (Schuur *et al*., 2016; Lee *et al*., 2020).

This study aimed to determine the ^{14}C content in bio-oils by means of a compact modern AMS system known as the Mini Carbon Dating System (MICADAS) in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. The measurement results for the tested biofuels and the biomass used as the reference material were compared. Furthermore, this work will contribute to the accreditation of the tested method in the Gliwice Radiocarbon and Mass Spectrometry Laboratory.

2. Materials and Methods

2.1. Samples for Testing

In the present study, four samples were used: three samples of bio-oils from the catalytic process of biomass depolymerisation, and the biomass (pistachio shells) used for their production. The samples were provided by a manufacturer, and according to the information from the Safety Data Sheet the bio-oils are mixtures with the main constituent by weight of 30–90% of distillate-petroleum and hydrotreated heavy paraffinic oil. The other substances are 1H-Pyrrole (<10%) and 4-(2-Methoxyethyl)phenol (<10%), phenol (<8%), diisooctyl phthalate (<7%) and water (<5%).

2.2. Preparation of Sample for AMS Measurement

The ^{14}C measurement by AMS requires graphite targets (Wacker *et al*., 2010; Lee *et al*., 2020). As shown in **Fig. 1**, the process of graphitisation utilised to convert the original sample material into graphite is used in the Gliwice Radiocarbon and Mass Spectrometry for its fast, efficient, and convenient sample preparation for ^{14}C measurement by means of AMS. In this study, 2 µL of each bio-oil sample was subsampled into the tin capsule for liquid samples (0.4 mL) using the micropipette (0.1–2 µL) and sealed with the sealing press. Further, each sub-sample was sealed in the second capsule for solid samples to prevent the loss of the sample due to evaporation. Besides, 6 mg of biomass (pistachio shell) used as a reference material was sub-sampled in tin capsule for solid samples. Then, 3 to 5 subsamples for each investigated samples were combusted in elemental analyser (EA) at 95 ^{o}C with Ca.66.67 mL (2.98 mmol) of oxygen dosing. Both glutamic and aspartic acids were used as standards to calibrate the EA instrument while 0.1% is the standard uncertainty of the instrument for carbon.

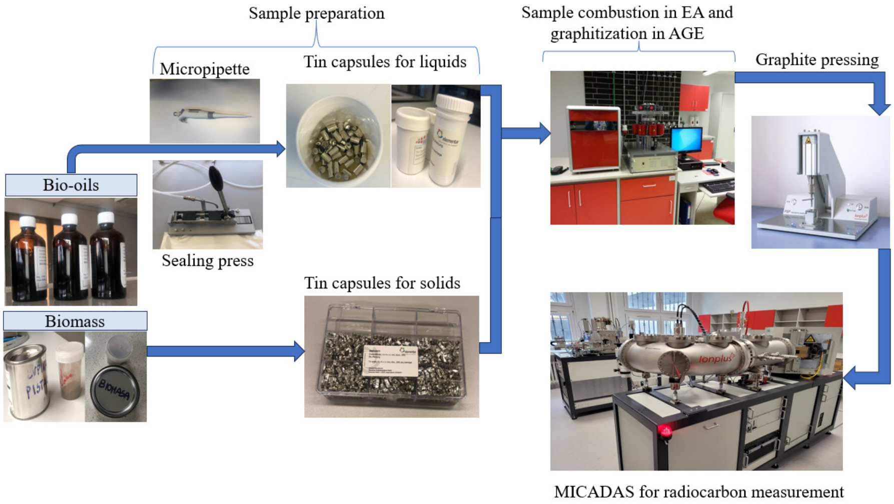

***Fig 1**. Radiocarbon measurement process by AMS technique in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. AMS, accelerator mass spectrometry.*

The produced CO_2 from the combusted samples was graphitized by its reaction with hydrogen (H_2) using iron powder as a catalyst. The obtained graphite targets consisting of 1 mg carbon and 5 mg iron were pressed using a pneumatic sample press (PSP) and measured by MICADAS accelerator to get radiocarbon content in the tested bio-oil fuels. Oxalic Acid II standard was used for normalisation, and the ^{14}C-free petroleum prepared in the same way was used as a blank reference. The correction for isotope fractionation is based on simultaneous analysis of ^{13}C and ^{12}C in the AMS spectrometer. The standard uncertainty of the MICADAS is 0.3% for Oxalic Acid II.

Radiocarbon measurement results of all bio-oils and the reference material were reported in percent modern carbon (pMC) which is a percentage of ^{14}C isotope concentration in the so-called modern biosphere. In addition, the calculations of biocarbon content were performed according to the EN 16640:2017 (E) using the following equation for biogenic carbon content relative to the reference value (x_B):

$$x_B = \frac{F^{14}C_{sample}}{F^{14}C_{ref}} \cdot 100 \tag{1}$$

where $F^{14}C_{sample}$ is the radiocarbon content of a sample, and $F^{14}C_{ref}$ is the radiocarbon content of a reference material.

The biogenic carbon content in% by mass (x^{TC}_{B}) was calculated as follows:

$$x_B^{TC} = \frac{\mathrm{x_B}}{\mathrm{x_{TC}}} \tag{2}$$

where x_{TC} is the total carbon content in the sample. The ^{14}C content obtained for pistachio shells was used as a reference value ($F^{14}C_{ref}$).

3. Results and Discussions

The content of carbon in percentage (% C) by mass was the foremost parameter of concern in this study. According to the results reported in **Table 2**, the calculated average of %C content was 79.7 ± 1.7%, 68.7 ± 2.1%, 47.0 ± 1.1%, and 48.82 ± 0.3% for bio-oil-1, bio-oil-2, bio-oil-3, and the pistachio shell, respectively. Based on the obtained carbon content results from each sample, 2 µL of each bio-oil sample and 6 mg of pistachio shell were sufficient to get at least 1 mg of carbon to produce graphite targets for measuring ^{14}C by means of MICADAS accelerator. Furthermore, as shown in **Table 1**, several measurements of ^{14}C content were conducted on different days and in different batches to test the reproducibility of each sample used for investigation.

As can be seen in **Table 1**, each fuel sample was measured 4 to 5 times to confirm the effect of the sample homogeneity on the final measurement results. The unreproducible ^{14}C measurement results indicated some inhomogeneity in the sample material. Therefore, the outlying results were discarded and were not used to calculate the average values. The recorded average values of ^{14}C measurement results for homogeneous sub-samples were 28.14 ± 0.4 pMC, 74.95 ± 0.22 pMC, 112.92 ± 0.07 pMC and 102.61 ± 0.21 pMC, respectively for bio-oil-1, bio-oil-2, bio-oil-3 and the pistachio shell, which is used as the reference material.

However, the main objective of this study was not only in getting the radiocarbon values, but in testing the reproducibility of the sample preparation procedure in the Gliwice radiocarbon laboratory. **Figure 2** graphically explains the reproducibility of the radiocarbon measurement results for all bio-oil samples and the reference material. To confirm the reproducibility of the measurement results, a chi-square (χ^2) test was carried out as well. As shown in **Table 1**, the calculated χ^2 values were 1.21, 1.08, 0.15 and

Table 1. *Reproducibility test for radiocarbon measurements in bio-oil fuels.*

Sample name	Laboratory code	Number of experiment	^{14}C concentration (pMC)	Average ^{14}C concentration (pMC)	χ^2 test for $\alpha = 0.05$ CV = 5.99
Bio-oil-1	GdA-6968.1.5	Experiment-1	27.72 ± 0.59	28.14 ± 0.36	$\chi^2 = 1.21$
	GdA-6968.1.3	Experiment-2	28.31 ± 0.18		Significant
	GdA-6968.1.4	Experiment-3	28.40 ± 0.19		
	GdA-6968.1.2	Experiment-4	29.46 ± 0.56*		
Bio-oil-2	GdA-6969.1.1	Experiment-1	74.71 ± 0.32	74.95 ± 0.22	$\chi^2 = 1.08$
	GdA-6969.1.2	Experiment-2	74.95 ± 0.32		Significant
	GdA-6969.1.3	Experiment-3	75.18 ± 0.32		
	GdA-6969.1.5	Experiment-4	76.07 ± 0.32*		
	GdA-6969.1.4	Experiment-5	73.29 ± 0.32*		
Bio-oil-3	GdA-6970.1.1	Experiment-1	113.00 ± 0.28	112.92 ± 0.07	$\chi^2 = 0.15$
	GdA-6970.1.2	Experiment-2	112.85 ± 0.28		Significant
	GdA-6970.1.5	Experiment-3	112.91 ± 0.28		
	GdA-6970.1.3	Experiment-4	110.85 ± 0.40*		
	GdA-6970.1.4	Experiment-5	110.11 ± 0.41*		
Pistachio shell (reference material)	GdA-6971.1.1	Experiment-1	102.58 ± 0.29	102.61 ± 0.21	$\chi^2 = 0.41$
	GdA-6971.1.2	Experiment-2	102.82 ± 0.29		Significant
	GdA-6971.1.3	Experiment-3	102.61 ± 0.29		

*Shows inhomogeneous sub-samples.
Results presented as pMC, and the uncertainties are calculated from AMS measurements.
AMS, accelerator mass spectrometry; CV, critical value; pMC, percent modern carbon.

Table 2. *Calculated radiocarbon, carbon and biocarbon contents in bio-oil samples.*

Sample name	Lab. code	Carbon content in % by mass	^{14}C content (average) [pMC]	Biogenic carbon content relative to the reference value (x_B)	Biogenic carbon content in % by mass (x^{TC}_B)
Bio-oil-1	GdA-6968	79.7 ± 1.7	28.14 ± 0.36	27.43 ± 0.42	21.87 ± 1.76
Bio-oil-2	GdA-6969	68.7 ± 2.1	74.95 ± 0.22	73.04 ± 0.30	50.16 ± 2.09
Bio-oil-3	GdA-6970	47.0 ± 1.1	112.92 ± 0.07	110.04 ± 0.22	51.73 ± 1.10
Reference material	GdA-6971	48.82 ± 0.25	102.61 ± 0.21	100.00 ± 0.29	48.82 ± 0.39

pMC, percent modern carbon.

0.41, respectively for bio-oil-1, bio-oil-2, bio-oil-3, and the pistachio shell. The calculated critical value (CV) for 3 measurements was 5.99 (at a confidence level $\alpha = 0.05$). Therefore, all χ^2 values were less than CV, which confirmed a non-significant difference, and this showed that the procedure for sample preparation and the radiocarbon measurement using MICADAS produced reliable results.

The biogenic carbon content values were determined based on ^{14}C concentration. The results in **Table 2** showed that the determined biogenic carbon content relative to the measured ^{14}C of pistachio shell as reference material (102.61 ± 0.29 pMC) value were 27.43 ± 0.42, 73.04 ± 0.30 and 110.04 ± 0.22 for bio-oil-1, bio-oil-2, and bio-oil-3, respectively. The biogenic carbon content in percent (%) by mass was 21.87 ± 1.76%, 50.16 ± 2.09% and 51.73 ± 1.10%, respectively for bio-oil-1, bio-oil-2, and bio-oil-3. For the reference material, the yielded biogenic carbon content in percent (%) by mass was 48.82 ± 0.39%.

Surprisingly, the results showed a higher ^{14}C value of bio-oil-3 (111.94 ± 0.31 pMC) compared to biomass used as reference material (102.61 ± 0.21 pMC). The calculated biogenic carbon content relative to the reference value was also higher for bio-oil-3 (110.04 ± 0.22) compared to the reference sample (100.00 ± 0.29). Additionally, as shown in **Fig. 3**, the results in **Fig. 3A** showed that the bio-oil-3 was most likely developed in AD 1993–1994 while the results in **Fig. 3B** showed that the reference material was developed in AD 2012–2016.

This phenomenon indicated that only two samples including bio-oil-1 and bio-oil-2 were produced by mixing distillate with the investigated pistachio shell while bio-oil-3 was produced from another unknown biomass whose

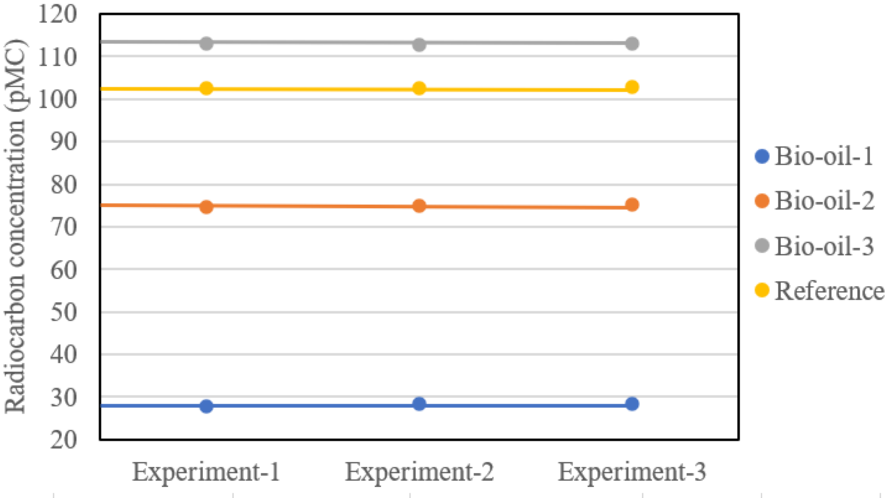

Fig 2. *Graphical presentation of reproducibility test for radiocarbon measurement in bio-oils by AMS; 2-sigma error bars are invisible at this scale. AMS, accelerator mass spectrometry.*

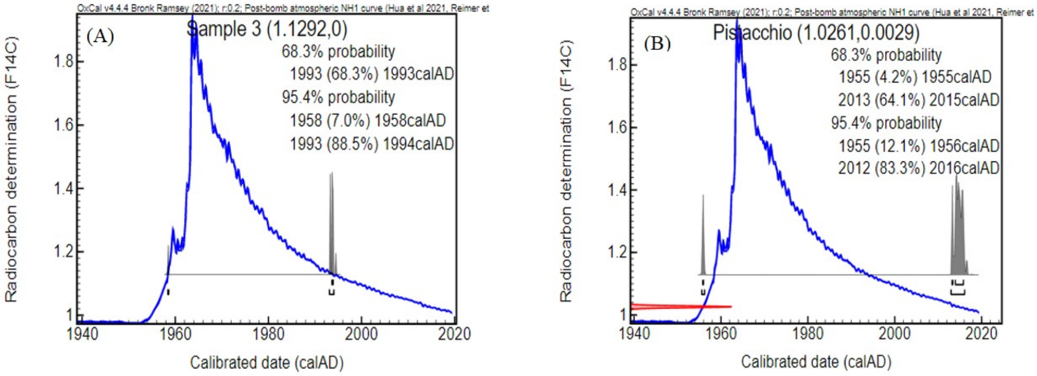

Fig 3. *Calibration of $F^{14}C$ results for bio-oil sample-3* ***(A)*** *and the pistachio shell reference sample* ***(B)*** *and Ox Cal v.4.4 (Bronk Ramsey, 2009) using the post-bomb atmospheric NH1 curve (Reimer et al., 2004; Hua et al., 2022). The $F^{14}C$ values are used commonly in the calibration process, and the relation to pMC is $pMC = F^{14}C*100$ (Stenström et al., 2011). pMC, percent modern carbon.*

details were not provided by the sample provider. This conclusion was confirmed by the company that provided the samples, but further information was confidential.

4. Conclusions

Each aliquot of the original bio-oil sample should always be representative for getting accurate and reproducible results, but in reality, it needs to be tested by running multiple measurements. The findings of the study showed reliable results for the reproducibility test of homogenous bio-oil samples, which proved the precision of the AMS technique by MICADAS for ^{14}C measurement in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. The results for radiocarbon content showed that the submitted reference material (Pistachio) was not used to produce the bio-oil-3. Furthermore, the biogenic carbon content was determined based on ^{14}C content because only carbon was taken into consideration, and no other biogenic elements, such as oxygen and hydrogen, were not considered. Moreover, due to the high increase in demand for biofuels for energy production in this rapidly developing world, many systematic studies on biofuels need to be done to deduce the consequences of biocomponents in different areas such as greenhouse gas emissions, toxicology, and life cycle. Eventually, in the future, additional tests will be conducted using different samples to confirm the precision of the AMS technique in the Gliwice Radiocarbon Laboratory.

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References

Arun J, Gopinath KP, Sivaramakrishnan R, Shyam S, Mayuri N, Manasa S and Pugazhendhi A, 2021. Hydrothermal liquefaction of Prosopis juliflora biomass for the production of ferulic acid and bio-oil. *Bioresource Technology 319*: 124116, DOI 10.1016/j.biortech.2020.124116.

Baranyika JB, Piotrowska N, Kłusek M, Michczyński A and Pawlyta J, 2022. Testing the methods for determination of radiocarbon content in liquid fuels in the Gliwice radiocarbon and mass spectrometry laboratory. *Radiocarbon 64*(6): 1447–1456, DOI 10.1017/rdc.2022.35.

Boucher ME, Chaala A and Roy C, 2000. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part I: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass and Bioenergy 19*(5): 337–350, DOI 10.1016/S0961-9534(00)00043-X.

Bronk Ramsey C, 2009. Bayesian analysis of radiocarbon dates. *Radiocarbon 51*(1): 337–360, DOI 10.1017/s0033822200033865.

Cho EJ, Trinh LTP, Song Y, Lee YG and Bae HJ, 2020. Bioconversion of biomass waste into high value chemicals. *Bioresource Technology 298*: 122386, DOI 10.1016/j.biortech.2019.122386.

Destek MA, Sarkodie SA and Asamoah EF, 2021. Does biomass energy drive environmental sustainability? An SDG perspective for top five biomass consuming countries. *Biomass and Bioenergy 149*: 106076, DOI 10.1016/j.biombioe.2021.106076.

Dijs IJ, van der Windt E, Kaihola L and van der Borg K, 2006. Quantitative determination by ^{14}C analysis of the biological component in fuels. *Radiocarbon 48*(3): 315–323, DOI 10.1017/S0033822200038777.

Do TX, Lim Y-I and Yeo H, 2014. Techno-economic analysis of bio-oil production process from palm empty fruit bunches. *Energy Conversion and Management 80*: 525–534, DOI 10.1016/j.enconman.2014.01.024.

Fan J, Kalnes TN, Alward M, Klinger J, Sadehvandi A and Shonnard DR, 2011. Life cycle assessment of electricity generation using fast pyrolysis bio-oil. *Renewable Energy 36*(2): 632–641, DOI 10.1016/j.renene.2010.06.045.

Gutiérrez J, Galán CA, Suárez R, Álvarez-Murillo A and González JF, 2018. Biofuels from cardoon pyrolysis: Extraction and application of biokerosene/kerosene mixtures in a self-manufactured jet engine. *Energy Conversion and Management 157*: 246–256, DOI 10.1016/j.enconman.2017.12.006.

Hancsók J, Krár M, Magyar S, Boda L, Holló A and Kalló D, 2007. Investigation of the production of high cetane number biogas oil from pre-hydrogenated vegetable oils over Pt/HZSM-22/Al2O3. *Microporous and Mesoporous Materials 101* (1-2 SPEC. ISS.): 148–152, DOI 10.1016/j.micromeso.2006.12.012.

Hua Q, Turnbull JC, Santos GM, Rakowski AZ, Ancapichún S, De Pol-Holz R, Hammer S, Lehman SJ, Levin I, Miller JB, Palmer JG and Turney CSM, 2022. Atmospheric radiocarbon for the Period 1950-2019. *Radiocarbon 64*(4): 723–745, DOI 10.1017/RDC.2021.95.

Ikura M, Stanciulescu M and Hogan E, 2003. Emulsification of pyrolysis derived bio-oil in diesel fuel. *Biomass and Bioenergy 24*(3): 221–232, DOI 10.1016/S0961-9534(02)00131-9.

Jeswani HK, Chilvers A and Azapagic A, 2020. Environmental sustainability of biofuels: A review. *Proceedings of the Royal Society A 476* (2234):1-37, doi.org/10.1098/rspa.2020.0351.

Khundadze N, Küppers C, Kammer B, Garbaras A, Masalaite A, Wissel H, Lücke A, Chankvetadze B, Rudolph J, Kiendler-Scharr A and Gensch I, 2022. Benchmarking source specific isotopic ratios of levoglucosan to better constrain the contribution of domestic heating to the air pollution. *Atmospheric Environment 268*: 118842, DOI 10.1016/j.atmosenv.2021.118842.

Kim KH, Kim TS, Lee SM, Choi D, Yeo H, Choi IG and Choi JW, 2013. Comparison of physicochemical features of bio-oils and biochars produced from various woody biomasses by fast pyrolysis. *Renewable Energy 50*: 188–195, DOI 10.1016/j.renene.2012.06.030.

Lee JE, Li ZH, Wang H, Plymale AE and Doll CG, 2022. Quantification of biogenic carbon in fuel blends through LSC ^{14}C direct measurement and assessment of uncertainty. *Fuel 315*: 122859, DOI 10.1016/j.fuel.2021.122859.

Lee SH, Park SH, Kong M and Kim Y, 2020. A new compact AMS facility at Dongguk University. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms 465*: 15–18, DOI 10.1016/j.nimb.2019.12.027.

Matsakas L, Gao Q, Jansson S, Rova U and Christakopoulos P, 2017. Green conversion of municipal solid wastes into fuels and chemicals. *Electronic Journal of Biotechnology 26*: 69–83, DOI 10.1016/j.ejbt.2017.01.004.

Neha S and Remya N, 2022. Co-production of bio-oil and biochar from microwave co-pyrolysis of food-waste and plastic using recycled biochar as microwave susceptor. *Sustainable Energy Technologies and Assessments 54*: 102892, DOI 10.1016/j.seta.2022.102892.

Oinonen M, Hakanpää-Laitinen H, Hämäläinen K, Kaskela A and Jungner H, 2010. Biofuel proportions in fuels by AMS radiocarbon method. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms 268*: 1117–1119, DOI 10.1016/j.nimb.2009.10.113.

Rajasekhar M, Rao NV, Rao GC, Priyadarshini G and Kumar NJ, 2015. Energy generation from municipal solid waste by innovative technologies – plasma gasification. *Procedia Materials Science 10*: 513–518, DOI 10.1016/j.mspro.2015.06.094.

Reimer PJ, Brown TA and Reimer RW, 2004. Discussion: Reporting and calibration of post-bomb ^{14}C data. *Radiocarbon 46*(3): 1299–1304.

Samson-Bręk I, Smerkowska B and Filip A, 2015. Environmental aspects in the life cycle of liquid biofuels with biocomponents, taking into account the storage process. In: Biernat K, eds., *Storage Stability of Fuels*. IntechOpen: 241–267, DOI 10.5772/59806.

Schuur EAG, Druffel E and Trumbore SE, 2016. *Radiocarbon and Climate Change, Mechanisms, Applications and Laboratory Techniques*. Springer, DOI 10.1007/978-3-319-25643-6.

Soni B and Karmee SK, 2020. Towards a continuous pilot scale pyrolysis based biorefinery for production of bio-oil and biochar from sawdust. *Fuel 271*: 117570, DOI 10.1016/j.fuel.2020.117570.

Stenström KE, Skog G, Georgiadou E, Genberg J and Johansson A, 2011. A guide to radiocarbon units and calculations Lund University, Department of Physics, Division of Nuclear Physics. (LUNFD6(NFFR-3111)/1-17/(2011)). Lund University, Nuclear Physics.

Tuniz C, John Rb, David F and Gregory FH, 2001. Accelerator mass spectrometry: Ultra-sensitive analysis for global science. *Radiation Physics and Chemistry 61*: 317–322, DOI 10.1016/S0969-806X(01)00255-9.

Wacker L, Němec M and Bourquin J, 2010. A revolutionary graphitisation system: Fully automated, compact, and simple. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms 268*(7–8): 931–934, DOI 10.1016/j.nimb.2009.10.067.

Gliwice, 07th July 2024

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Authorship statement

I hereby declare that my contribution to the paper that I first-authored:

Baranyika, J. B., and Piotrowska, N. (2023). Determination of radiocarbon content in bio-oil samples by Mini Carbon Dating System in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. *Geochronometria*, *49*, 1–7. https://doi.org/10.2478/geochr-2023-0005

My contribution included: Sample selection and preparation of graphite for AMS analysis. Calculations of carbon content based on EA results. ^{14}C measurements and data reduction. Writing of text, preparation of all figures and tables and paper submission in journal, as well as responding to reviewers' comments.

My participation to the work (Baranyika & Piotrowska, 2023) was 80 %

Signature

Gliwice, 7 lipca 2024

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Oświadczenie współautora

Oświadczam, że mój wkład w powstanie pracy, której jestem pierwszym autorem:

Baranyika, J. B., and Piotrowska, N. (2023). Determination of radiocarbon content in bio-oil samples by Mini Carbon Dating System in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. *Geochronometria*, 49, 1–7. https://doi.org/10.2478/geochr-2023-0005

Mój wkład polegał na: Selekcji próbek i przygotowaniu grafitu do analiz AMS. Obliczenia zawartości węgla na podstawie wyników EA. Pomiary ^{14}C i opracowanie wyników. Napisanie tekstu, przygotowanie wszystkich rycin i tabel oraz złożenie artykułu w czasopiśmie, a także odpowiadanie na uwagi recenzentów.

Mój udział w pracy (Baranyika & Piotrowska, 2023) wyniósł 80 %

Podpis

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Co-authorship statement

I hereby declare that my contribution to the paper:

Baranyika, J. B., and Piotrowska, N. (2023). Determination of Radiocarbon Content in Bio-Oil Samples by Mini Carbon Dating System in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. *Geochronometria*, *49*, 1–7. https://doi.org/10.2478/geochr-2023-0005

My contribution was as follows: Supervision of PhD research, supervision of AMS analysis, calculations of ^{14}C content from AMS and assistance in paper revision

My participation to the work was 20 %.

Signature

Gliwice, 5 czerwca 2024

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Politechnika Śląska

Polska

Oświadczenie współautora

Oświadczam, że w wyszczególnionej poniżej pracy:

Baranyika, J. B., and Piotrowska, N. (2023). Determination of Radiocarbon Content in Bio-Oil Samples by Mini Carbon Dating System in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. *Geochronometria*, *49*, 1–7. https://doi.org/10.2478/geochr-2023-0005

Mój wkład był następujący: nadzór nad badaniami doktoranckimi, nadzór nad analizą AMS, obliczenia zawartości ^{14}C z AMS i pomoc w poprawkach artykułu

Mój udział w powstaniu pracy wynosił 20 %.

Podpis

Radiocarbon (2024), pp. 1–11
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RESEARCH ARTICLE

Determination of radiocarbon content in liquid fuel blends by accelerator mass spectrometry and liquid scintillation counting in the gliwice radiocarbon and mass spectrometry laboratory

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Abstract
The increase in biobased material usage requires the methods of verification to investigate the actual content of biocarbon in such materials, including liquid fuels. The determination of biocarbon in liquid samples using ^{14}C required adaptation of existing sample preparation methods. In this study, both accelerator mass spectrometry (AMS) and liquid scintillation counting (LSC) methods were used to determine the content of ^{14}C in six different liquid fuel blends produced from purely bio-based hydrotreated vegetable oil (HVO) and a ^{14}C-free petrodiesel sample (ON/UF-BC). The results obtained for pure petrodiesel provide background values. The results indicate a good agreement between LSC and AMS, and a linear correlation between the ^{14}C measurement results for blended samples and HVO content affirmed the reproducibility between the two methods. The repeatability of AMS results was tested on 10 aliquots of one of the blends, and the results were deemed reproducible.

1. Introduction

Over many years, the intensive use of fossil fuels in transport and energy production sectors has led to environmental degradation due to the high emission of CO_2 into the atmosphere (Dijs et al 2006; Guo et al 2022; Liaquat et al 2012). According to (ICPP 2013) the combustion of fossil fuels for energy production, transport, and heating are the primary sources of CO_2 emission from human activities. Aiming to reduce the amount of CO_2 in the atmosphere, several countries are focused on using the liquid fuels to produce energy from renewable resources that are environmentally friendly (De Souza et al 2013).

Although bioenergy provides a greener alternative to fossil fuels, this method of energy production is still rare worldwide as it requires more efforts in research and production (Anyaoha and Zhang 2021; Casau et al 2022). Therefore, in Poland, as in other European countries, fuel blends have been put into use with the aim of reducing the net flux of carbon into atmosphere, and the research on the content of biocomponents within these blends has been undertaken (Dobrzyńska et al 2020; Howaniec and Smoliński 2014; Verger et al 2022).

Fuel blends involve the mixtures of fossil fuels with fuels derived from the contemporary biosphere in varying percentages to obtain a fuel that minimize the harmful effects while optimizing certain useful properties. They are relatively new to the market in comparison to pure fossil fuels (Culp 2017). The blending of liquid fuels must be carried out in a controllable and reproducible manner and requires knowledge of the fuel components that compose the blend mixtures, the reason for the blending, and the expected properties of the fuel blends (Alves and Poppi 2016).

Knowledge of the content of liquid fuels that are expected to be on the market is important in various sectors for defining fuel quality (Sulek et al 2010; Haverly et al 2019; Morone and D'Amato 2019). The characteristics of the fuel blend content are important factors which are used to avoid the interference of nonlinear blending effects on values of the parameters studied (Castillo et al 2017). A directive of the European Union Parliament (Directive 2009/30/EC 2009) aims to reduce the emission of greenhouse gases by 6% from road transport, causing the rapid implementation of strategies to produce new hybrid fuels that satisfy these requirements. Furthermore, this directive stated that liquid fuels must contain at least 10% fuel of biogenic origin by 2020 (Krajcar Bronić et al 2017). As a result, in the past few years, the biobased content of fuels has increased in most European countries.

One of the strategies developed was an increase in the blending of petroleum-based diesel with biobased fatty acid methyl esters (FAMEs) (Idoeta et al 2014; Schuurman et al 2013). FAMEs produced from animal fat or vegetable oil (by the transesterification of triglycerides) have physical properties closer to fossil diesel fuels, compared to pure vegetable oils. However, although the production of FAMEs is straightforward, they are not suitable for various uses as they can cause problems in the engine, such as internal diesel injector deposits, poor evaporation process and poor fuel-air mixing (Urzędowska and Stępień 2016; Zhang et al 2018). Moreover, due to the fact that the net energy value of these biofuels has been questioned, this blending method showed barriers that limited its potential for mass use and also had some negative impacts on the environment (Pimentel and Patzek 2005; Schuurman et al 2013; Serrano-Ruiz and Dumesic 2011).

For this reason, paraffinic hydrotreated vegetable oil (HVO) has been developed because of its suitable characteristics compared to those of FAMEs. Although HVO has a complicated production process and is expensive, its production from triglyceride-rich waste material is less complicated compared to diesel production, and when added to petrodiesel, the resulting products are extremely stable (Idoeta et al 2014; Türck et al 2021).

The use of fuel blends composed of HVO and other fuels such as petroleum-diesel have many advantages due to the low sulfur and aromatic content in HVO, that lead to lower emission of aromatics, SO_2, particulates and NOx. HVO combustion decreases greenhouse gas emissions more than fuels derived from petroleum (Vrtiška and Šimáček 2016).

The production of fuel blends led to the need for techniques to determine the content of their biocomponents precisely and accurately. Radiocarbon measurement is one way to quantify the contents of biocomponents in fuel blends. Contrary to plants, the primary recipients of the atmospheric $^{14}CO_2$, with the highest level of ^{14}C that represent the modern ^{14}C level, fossil fuels are devoid of ^{14}C due to their old age (Culp 2017; Hajdas et al 2021; Libby 1961).

Measurements of radiocarbon content in fuel blends are carried out with the methods listed in American Society for Testing and Materials (ASTM) standard D6866, with the most recent version released in 2022. These are currently the standard test methods used to determine the biobased contents in liquid, gaseous, and solid samples using the radiocarbon analysis (Alves and Poppi 2016; Culp et al 2014; Idoeta et al 2014; Oinonen et al 2010).

One of the most accurate and precise ASTM D6866-22 methods for ^{14}C determination is accelerator mass spectrometry (AMS). For the AMS method, the liquid samples are prepared using tin capsules for liquids and combusted to produce CO_2 which is graphitized to obtain graphite for ^{14}C measurements. The main advantages of the AMS technique are greater precision and the use of a small sample size (Baranyika et al 2022; Culp et al 2014; Haverly et al 2019). The second method is liquid scintillation counting (LSC).

The preparation of sample for LSC measurements requires various procedures. In the carbamate or LSC-A method, organic carbon is converted into CO_2. During this process, the sample is combusted in a special apparatus under a controlled environment to form CO_2 (Horvatinčić et al 2004). In the LSC-B or benzene method, the investigated sample is converted through three main steps such as carbide formation, hydrolyzation and trimerization to produce benzene for ^{14}C measurement (Horvatinčić et al 2004). A third one is the LSC-C method that does not requires any pretreatment of sample, but it simply

Table 1. *Blend samples prepared from archive liquid fuels (HVO and ON/UF-BC). Carbon content is a result from elemental analysis (EA), and benzene conversion efficiency was calculated based on these numbers*

Sample	Composition in mass (%)		Carbon content (%) (Average)	Benzene conversion efficiency (LSC) (%)
	HVO	ON/UF-BC		
Blend-30	30	70	85.8 ± 1.2	24.40 ± 0.38
Blend-20	20	80	76.5 ± 8.7	26.9 ± 3.1
Blend-15	15	85	81.5 ± 9.1	23.3 ± 2.6
Blend-10	10	90	84.65 ± 0.64	27.60 ± 0.26
Blend-7.5	7.5	92.5	78.4 ± 3.6	20.61 ± 0.97
Blend-5	5	95	85.1 ± 2.5	15.35 ± 0.48
ON/UF-BC	Background sample with expected 0% of biocarbon		84.97 ± 0.37	15.02 ± 0.17
HVO	Hydrogenated vegetable oil with expected 100% of biocarbon		84.74 ± 0.50	33.66 ± 0.30

involves a mixture of investigated sample with a relevant scintillator to form a scintillation cocktail (Norton et al 2012; Krištof and Kožar Logar 2013; Doll et al 2021).

To report precise and accurate ^{14}C measurement results, it is necessary to correct for isotope fractionation which occurred in the process of the sample preparation and ^{14}C measurements (Baranyika et al 2022; Maruccio et al 2017). For the LSC, isotope ratio mass spectrometry (IRMS) is required for stable carbon isotope measurements used for the corrections (Prasad et al 2019). On the contrary, during the AMS analysis the fractionation is determined and incorporated into the data reduction (Wacker et al 2010).

Nowadays, ^{14}C measurements are used in the Gliwice Radiocarbon and Mass Spectrometry Laboratory to investigate the biocarbon content in liquid and solid samples by AMS and LSC methods (Baranyika et al 2022; Gill et al 2022). The aim of this study is to test and verify methods for determining the ^{14}C content in liquid fuel blends of known bio- to fossil fuel ratios. The results of this study will contribute to the accreditation of the tested methods in the Gliwice Laboratory.

2. Materials and Methods

To investigate the precision and results accuracy in the Gliwice Radiocarbon and Mass Spectrometry Laboratory, both LSC and AMS methods are used for ^{14}C measurements.

2.1. Blend Sample Preparation

To obtain samples for radiocarbon measurements, six different fuel blends were produced from a sample of HVO and a petrodiesel sample of infinite ^{14}C age (ON/UF-BC; see Table 1) in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. These samples were submitted in 2018 by an external oil company in high quantity, which allowed to use them for testing purposes for years (Baranyika et al 2022).

Moreover, ON/UF-BC diesel has been extensively used as a background sample for liquid fuels. The liquids were transferred to 20-mL vials using the 230 mm-long glass Pasteur pipettes. The mass of HVO and ON/UF-BC was adjusted to obtain the required composition and provide a total of 15g for each blend.

2.2. LSC Method for Radiocarbon Measurement in Fuel Blends

In radiocarbon research laboratories, the extensive use of LSC is well established for the quantitative determination of biocomponents in samples by means of radiocarbon measurements.

Benzene was synthesized from each of the eight samples according to the benzene method (LSC-B). To enable a slow conversion of fuel samples to lithium carbide (Li_2C_2) without explosion, each liquid fuel blend, background and HVO sample was mixed with purified silica sand. The sand was pre-heated to remove organic impurities at 500 °C for 12h in a muffle oven. 7 g of fuel and 7g of lithium reacted at 700 °C to form Li_2C_2. Once cooled, the generated Li_2C_2 was hydrolyzed to obtain acetylene (C_2H_2), which was purified by being passed through a mixture of 40 g of potassium dichromate (99.9%), 100 mL sulfuric acid (95%), and 1000 mL H_2O. Purified C_2H_2 was trimerized to benzene using a chromium catalyst on silica gel (5.5% Cr_2O_3) purchased from "ATOM KOMPLEXPRYLAD" Llc research and production enterprise in Kyiv, Ukraine.

The overall efficiency of converting fuel sample to benzene (CE) reported in Table 1 was calculated as follows:

$$CE = \frac{m_{C6H6} \cdot C_{C6H6}}{m_f \cdot C_f} \tag{1}$$

where: m_{C6H6} – mass of obtained benzene; C_{C6H6} – carbon content of benzene, which is 93.3%; m_f – mass of combusted fuel; C_f – carbon content of fuel as analyzed by EA. The uncertainties were calculated according to the guide to the expression of uncertainty in measurement (BIPM et al 2008)

To remove water, the prepared benzene sample was stored with sodium for 24 hours (Gill et al 2022). The dried benzene sample was kept in a laboratory freezer for 30 days at -20 °C to remove contamination with radon (^{222}Rn). Afterwards the benzene was mixed with 26 mg of Butyl-PDB scintillator (Packard Canberra Company) to obtain the scintillation cocktail for 2 mL geometry. A Quantulus-1220 alpha and beta low-level LSC spectrometer was used for radiocarbon measurements (Pazdur et al 2003). In order to achieve appropriate precision, the sample measurement times using the LSC technique were 36 hours (Blend-10, Blend-20, Blend-30), 64 hours (HVO, Blend-15) and 72 hours (Blend-5, Blend-7.5), respectively. The total measurement time was divided into partial measurements of 30 or 40 minutes. For determination of machine background, 24-hour-long measurements were carried out. This procedure allowed for the control of the long-term stability of the measurements.

2.2.1. CO_2 Sample Preparation and $\delta^{13}C$ Determination by IRMS

Normally, radiocarbon data is corrected for isotopic fractionation that has occurred naturally, as well as that caused by sample preparation and measurement (Fahrni et al 2017; Stuiver and Polach 1977).

To verify the fractionation of isotopes during sample processing, the IRMS method was used (Baranyika et al 2022; Prasad et al 2019). For ON/UF-BC and HVO samples, after benzene preparation, 5 µl of benzene was combusted in a glass tube with copper oxide (CuO) at 560 °C for 24 h. After combustion, the glass tube was cracked, and the CO_2 was purified in a vacuum line. For IRMS measurement, CO_2 was subsampled with a syringe and introduced to an Isoprime continuous flow mass spectrometer. In this experiment, two reference materials, ANU-sucrose (5 mg) and NBS-22 (5 µl) were combusted with CuO and processed the same way for IRMS measurement (Baranyika et al 2022; Coplen et al 2006). The $^{13}C/^{12}C$ ratios expressed as $\delta^{13}C$ for reference materials were used to calculate the $\delta^{13}C$ for fuel samples by linear regression. The continuous flow isotope ratio mass spectrometer IsoPrime precision is 0.1 ‰ for $\delta^{13}C$, based on repeated measurements for reference materials.

To obtain the δ^{13}C values for fuel blend samples the mass-balance equation was used:

$$\delta^{13}C = \frac{\delta^{13}C \cdot f_{HVO} + \delta^{13}C \cdot f_{bg}}{f_{HVO} + f_{bg}} \tag{2}$$

Where: $\delta^{13}C_{HVO}$ and $\delta^{13}C_{bg}$ are the stable carbon composition of HVO and ON/UF-BC, and f_{HVO} and f_{bg} are the respective fractions of these components, so that $f_{HVO}+f_{bg}=1$.

The radiocarbon activities determined with use of LSC method were corrected for isotope fractionation using the obtained δ^{13}C values, according to the equation below (Stuiver and Polach 1977):

$$A_{SN} = A_S\left[1 - \frac{2(25 + \delta^{13}C)}{1000}\right] \tag{3}$$

$\boldsymbol{A_{SN}}$ is the corrected ^{14}C activity of the sample, $\boldsymbol{A_S}$ represents the measured (uncorrected) ^{14}C activity. Hereafter, the A_{SN} values are reported in pMC unit and referred to as ^{14}C or radiocarbon content.

2.3. Preparation of Graphite Samples for AMS Measurement

To obtain precise and accurate results for radiocarbon measurement by AMS in Gliwice Laboratory, it is necessary to prepare graphite targets.

In this study, after mixing the fuel blend samples from the HVO and background liquid fuels, there was no additional chemical processing before combustion. However, using an adjustable micropipette (0.1–2 μL), a volume of 2 μL for each blended liquid fuel was subsampled into a tin capsule for liquid samples and weighed with a Sartorius microbalance (precision = 0.001 mg) to obtain the mass used for combustion. The tin capsules were sealed using a sealing press and combusted in an Elemental Analyzer (EA, Vario Micro Cube model from Elementar^{TM}) at high temperature (950ºC), with ca. 42 mL (1.186 mmol) of oxygen dosing, to produce CO_2, which was transferred to a graphitization reactor. The obtained CO_2 was reduced to graphite with hydrogen (H_2) on an iron powder (325 mesh, purity 97%) catalyst from ALDRICH chemistry company using an AGE-3 graphitization system (Němec et al 2010). The efficiency of carbon conversion from sample to graphite measured by (Němec et al 2010) was ca. 92%. To obtain the radiocarbon content in fuel blends, the produced graphite targets, and reference samples (Oxalic Acid II, NIST 4990C) (Mann 1983; Stuiver 1983), were measured using a MICADAS accelerator mass spectrometer (Synal et al 2007). The measured currents and counts were recalculated to give radiocarbon concentrations using the BATs software (Wacker et al 2010). The results were normalized using δ^{13}C simultaneously measured by AMS and not corrected for date of sampling. The obtained F^{14}C were recalculated by multiplication by 100 to get the reported radiocarbon measurement results in pMC unit (Stenström et al 2011).

2.3.1. Reproducibility Test for Radiocarbon Measurements

To investigate the accuracy of the results for AMS measurements, a reproducibility test was conducted for one of the blends and the background sample. Multiple aliquots of fuel blend-15 and ON/UF-BC were graphitized on different days to produce graphite targets for radiocarbon measurement using the MICADAS accelerator mass spectrometer. To determine the reproducibility, the calculated average radiocarbon content for all aliquots was compared with the previous result, and they were analyzed statistically. For LSC, the measurement of the radiocarbon content in blend-15 was performed two times. Additionally, the chi-square statistical test was used to investigate the reproducibility of the measurement results for the 10 aliquots of blend-15.

Table 2. Measurement results of radiocarbon content (in pMC with 1-sigma uncertainty) in fuel blends and the background sample for both LSC and AMS methods and isotope fractionation ($\delta^{13\text{C, measured for}}$ ON/UF-BC and HVO, calculated for blend samples – see text for methodology)

Sample name	δ^{13}C IRMS [‰]	δ ^{13}C AMS	Lab. ID	^{14}C content [pMC]	Method
ON/UF-BC	–26.90	–26.5	GdS-4547	1.30 ± 0.11	LSC
			GdA-6821	0.50 ± 0.25	AMS
				0.45 ± 0.11	
				0.39 ± 0.21	
				0.36 ± 0.22	
				0.42 ± 0.21	
				0.38 ± 0.30	
				0.36 ± 0.22	
				0.38 ± 0.20	
				0.32 ± 0.22	
				0.41 ± 0.18	AMS average
Blend-5	–26.96	–27.7	GdS-4546	5.02 ± 0.14	LSC
			GdA-6820	5.12 ± 0.15	AMS
Blend-7.5	– 26.99	–27.4	GdS-4545	7.45 ± 0.14	LSC
			GdA-6819	7.72 ± 0.16	AMS
Blend-10	–27.02	–29.4	GdS-4502	11.03 ± 0.22	LSC
			GdA-6817	10.71 ± 0.16	AMS
Blend-15	–27.08	–27.2	GdS-4538	14.03 ± 0.22	LSC
			GdA-6818	15.27 ± 0.16	AMS
Blend-20	–27.14	–29.2	GdS-4501	20.62 ± 0.29	LSC
			GdA-6816	21.06 ± 0.17	AMS
Blend-30	–27.26	–28.9	GdS-4496	30.67 ± 0.36	LSC
			GdA-6815	31.33 ± 0.19	AMS
HVO	–28.1	—	GdS-4379	100.10 ± 0.81	LSC
			GdA-6610	101.45 ± 0.33	AMS

3. Results and Discussion

The radiocarbon results are presented in Table 2. For radiocarbon measurements, the first parameter of interest for both the LSC and AMS laboratories was the background sample (fuel of purely fossil origin, ON/UF-BC, Table 1). The radiocarbon content of the background sample was first determined to test for sample contamination. The results of the radiocarbon measurements for the background sample showed 1.30 ± 0.11 pMC. The LSC machine background used for correction was 0.3598 ± 0.0052 cpm (counts per minute). This value is a weighted average calculated from 14 independent 24-hour-long background measurements. The consistency of individual measurements was confirmed using the χ^2 test. For AMS, the nine measurements conducted yielded an average of 0.41 ± 0.18 pMC for the background sample, which is slightly higher than an average ^{14}C content for a phthalic anhydrite blank (ca. 0.35 pMC). The difference between the LSC and AMS measurements was 0.89 ± 0.27 pMC. Therefore, given the combined uncertainty and the expected uncertified biocarbon content (0%), the measurement results for both LSC and AMS methods were not reproducible. The value obtained for ON/UF-BC sample were used for background correction for all subsequent AMS analysis.

For HVO fuel, the measurement result of ^{14}C content using LSC method gives 100.10 ± 0.81 pMC. As shown in Figure 1 and 2, this result was in agreement with AMS result (101.45 ± 0.33 pMC).

The radiocarbon content measured for blend-5 using the LSC and AMS methods showed 5.02 ± 0.14 pMC and 5.12 ± 0.15 pMC, respectively. The measurement results for both methods showed good

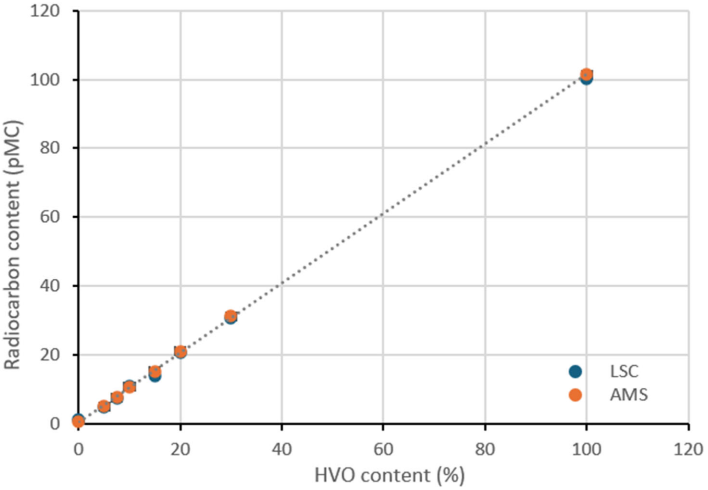

Figure 1. *Radiocarbon content of the tested fuel blends (Bld) and the components (HVO and ON/UF-BC) used for their production for both methods (LSC and AMS). 2-sigma error bars are not visible at the given scale.*

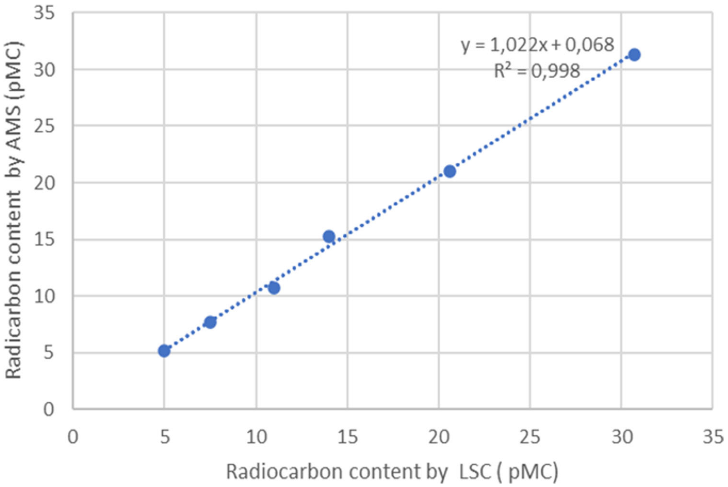

Figure 2. *Comparison of radiocarbon content results in six fuel blends for LSC and AMS using the regression method. 2-sigma error bars are invisible due to low uncertainty values.*

reproducibility with 0.1 pMC difference, which was less than the combined uncertainty (0.21). This study was aimed at testing the reproducibility of the sample preparation procedure, and in this regard the measurement results for the LSC and AMS methods were equivalent and in good agreement with each other, given the calculated uncertainty (difference 0.10 ± 0.21 pMC).

The radiocarbon content in blend-7.5 determined by the LSC method was 7.45 ± 0.14 pMC, while the AMS method gave 7.72 ± 0.16 pMC. Given the calculated uncertainty, the measurement results using both methods were reproducible and agreed with each other (difference of 0.27 ± 0.21 pMC) and with the expected uncertified biocontents (7.5%).

Table 3. *Radiocarbon content results for the reproducibility test using the MICADAS system*

Sample name	Subsample number	Lab code	^{14}C content [pMC]	χ^2 test
Blend-15	1	GdA-6818.1.3	15.05 ± 0.11	For α = 0.01, CV = 21.67
	2	GdA-6818.1.5	15.13 ± 0.11	
	3	GdA-6818.1.6	15.07 ± 0.11	$\chi^2 = 7.72$
	4	GdA-6818.1.7	14.98 ± 0.12	
	5	GdA-6818.2.1	15.18 ± 0.11	
	6	GdA-6818.2.2	15.16 ± 0.11	
	7	GdA-6818.2.3	15.24 ± 0.12	
	8	GdA-6818.2.4	15.14 ± 0.11	
	9	GdA-6818.2.5	14.94 ± 0.11	
	10	GdA-6818.2.6	15.26 ± 0.11	
			Mean = 15.12 ± 0.10	χ^2 < CV, there is no significant difference

Analyses of blend-10 for radiocarbon content were also conducted. The measurement using LSC, 11.03 ± 0.22 pMC, was in good agreement with the value of 10.71 ± 0.16 pMC from the AMS measurement, with a difference of 0.32 ± 0.27 pMC. Given the combined uncertainty, both measurement results were reproducible and agreed with each other.

For blend-20, the two subsamples measured by LSC and AMS gave 20.62 ± 0.29 pMC and 21.06 ± 0.17 pMC, respectively. The difference was 0.44 ± 0.34 pMC, and the expected value of the uncertified biocarbon content was 20%. The difference was satisfactory, and the values agreed with each other, given the combined uncertainty.

Similarly, the radiocarbon content for blend-30 using the LSC method was 30.67 ± 0.36 pMC. This measurement result was reproducible and in fair agreement with the 31.33 ± 0.19 pMC (with 0.66 ± 0.41 pMC difference) obtained using the AMS method and expected uncertified biocontents (30%).

The consistency of the results for blend-15 using both LSC and AMS methods was also verified. The results were 14.03 ± 0.22 pMC and 15.27 ± 0.16 pMC for LSC and AMS, respectively. The combined uncertainty was ± 0.27. However, compared to the other samples, the difference (1.24 pMC) between the methods increased. To confirm the results of the LSC measurement for this blend-15, the same experiment was repeated. Surprisingly, the resulting value of 13.46 ± 0.19 pMC was slightly lower compared to the previous value. The calculated mean was 13.75 ± 0.21 pMC. At present, there is not enough information about the possible factors that might have affected the ^{14}C measurements of this sample, as it was kept for 30 days in a laboratory freezer before measurement. Also, blend-15 sample was used for AMS reproducibility test, giving very similar results (see Table 3 and Figure 3).

The results of the radiocarbon content for all the samples are reported in Figure 1 versus the HVO content. The results showed good reproducibility between LSC and AMS. All the values were within the range of 2-sigma uncertainty bars, which showed that both the sample preparation methods and the subsequent radiocarbon measurements produced reliable results. As the ^{14}C content in HVO is ca. 100 pMC, the results for all other fuel blends follow a linear trend.

As shown in Figure 2, the results for the six fuel blends using both LSC and AMS were also compared using a regression plot. The linear regression equation ($y = ax + b$; $a = 1.022 \pm 0.025$, $b = 0.07 \pm 0.43$) with $R^2 = 0.9975$ showed a good correlation between the LSC and AMS measurement results. From Figure 2, the distribution of the measured values of radiocarbon content in relation to the regression line indicated a good reproducibility between the AMS and LSC results due to the observed linearity, with only one exception of blend-15, where the measurement results for the two methods were distributed further apart compared to other samples.

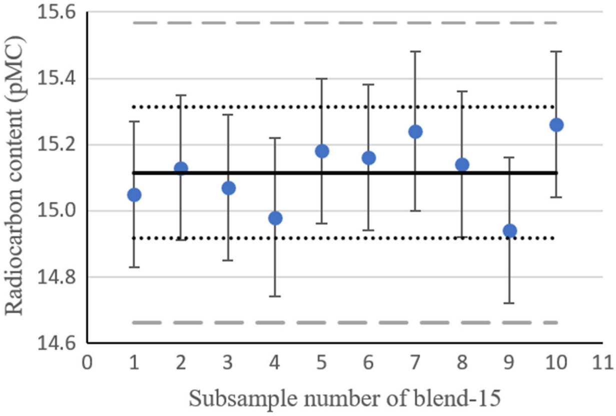

Figure 3. *Graphical presentation of the radiocarbon content for the reproducibility test from the MICADAS system in our laboratory. Error bars show 2-sigma uncertainties. Solid line shows the average, dotted lines show the double standard deviation from the average, and the dashed line shows the 3% acceptability limits as provided by ASTM D6866-22 standard.*

Additionally, the measured results of radiocarbon concentration in 10 subsamples of blend-15 with the same volume (2 µl) are listed in Table 3.

The major purpose of conducting additional measurements was to investigate the reproducibility of the MICADAS system in the Gliwice laboratory. The calculated mean of the 10 results showed 15.12 ± 0.10 pMC. Compared to the previous measurement of the radiocarbon content in blend-15 (15.27 ± 0.16), both results were reproducible, given the calculated uncertainty (difference 0.15 ± 0.19 pMC). The results of the reproducibility test are also presented in Figure 3. They were within a 2-sigma range, which proved that from the sample preparation using a tin capsule for liquids, through the sealing procedure and the combustion in the elemental analyzer, to the graphitization by AGE, reproducible results were shown from the MICADAS system in our laboratory. To confirm the reproducibility of the measurement results by MICADAS, a chi-square (χ^2) statistical test was performed, and the results are reported in Table 3. The computed χ^2 value was 7.72, and the critical value (CV) was 21.67 (with a confidence level, $\alpha = 0.01$). Therefore, due to the χ^2 value being less than the CV, there was no significant difference between the reported results for all 10 aliquots, meaning all the results were reproducible and agreed with each other.

Conclusions

The main purpose of this study was to test the best sample preparation and measurement methods in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. Using LSC and AMS methods, the preparation of fuel blend samples was tested. The measurement results from both methods showed good reproducibility for sample processing as shown in Figure 1. The minor differences between AMS and LSC may result from the different carbon conversion efficiency during the benzene production, although the corrections were made for fractionation effect. However, due to the increase of observed change for blend-15 during the reproducibility test using the LSC method, this sample will be subjected to further studies for sample preparation and measurement in the future to deduce appropriate explanations for this small change. For AMS, the sample preparation using a tin capsule for liquids and a sealing press was effective. The experimental results of the radiocarbon content were corrected for isotope fractionation processes ($^{13}C/^{12}C$ ratio measured by IRMS) that occurred during the preparation and measurement. Furthermore, the investigation of the reproducibility test for blend-15 using the AMS method showed that the results for the radiocarbon content measured by the MICADAS accelerator were reliable.

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References

Alves JCL and Poppi RJ (2016) Quantification of conventional and advanced biofuels contents in diesel fuel blends using near-infrared spectroscopy and multivariate calibration. *Fuel* **165**, 379–388. doi: 10.1016/j.fuel.2015.10.079.

Anyaoha KE and Zhang L (2021) Renewable energy for environmental protection: Life cycle inventory of Nigeria's palm oil production. *Resources, Conservation and Recycling* **174**(April):105797. doi: 10.1016/j.resconrec.2021.105797.

Baranyika JB, Piotrowska N, Kłusek M, Michczyński A and Pawlyta J (2022) Testing the Methods for Determination of Radiocarbon Content in Liquid Fuels in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. *Radiocarbon* **64**(6), 1447–1456. doi: 10.1017/rdc.2022.35.

BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML (2008) Evaluation of measurement data-Guide to the expression of uncertainty in measurement JCGM100:2008:1–134. https://www.bipm.org/documents/20126/2071204/JCGM_100_2008_E.pdf/cb0ef43f-baa5-11cf-3f85-4dcd86f77bd6.

Casau M, Dias MF and Matias CO (2022) Residual biomass : A comprehensive review on the importance, uses and potential in a circular bioeconomy approach. *Resouces* **11**(4), 1–16.

Castillo PAC, Castro PM and Mahalec V (2017) Global optimization of nonlinear blend-scheduling problems. *Engineering* **3**(2), 188–201. doi: 10.1016/J.ENG.2017.02.005.

Coplen TB, Brand WA, Gehre M, Gro M, Meijer HAJ, Toman B, Verkouteren RM, Survey USG, Biogeochemistry M and Box PO, et al 2006. New guidelines for δ^{13}C measurements. *Analytical Chemistry* **78**(7), 2439–2441.

Culp R (2017). Radiocarbon analysis for biofuel quantification in fuel blends. *Encyclopedia of Analytical Chemistry*, 1–13. doi: 10.1002/9780470027318.a9587.

Culp R, Cherkinsky A, Ravi Prasad GV (2014) Comparison of radiocarbon techniques for the assessment of biobase content in fuels. *Applied Radiation and Isotopes* **93**, 106–109. doi: 10.1016/j.apradiso.2014.01.007.

Dijs IJ, van der Windt E, Kaihola L and van der Borg K (2006) Quantitative determination by ^{14}C analysis of the biological component in fuels. *Radiocarbon* **48**(3), 315–323. doi: 10.1017/S0033822200038777.

Directive 2009/30/EC (2009) Directive 2009/30/EC of the European Parliament and of the Council of 23 April 2009 amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and amend. https://eur lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0088:0113:EN:PDF.

Dobrzyńska E, Szewczyńska M, Pośniak M, Szczotka A, Puchałka B and Woodburn J (2020) Exhaust emissions from diesel engines fueled by different blends with the addition of nanomodifiers and hydrotreated vegetable oil HVO. *Environmental Pollution* **259**. doi: 10.1016/j.envpol.2019.113772.

Doll CG, Plymale AE, Cooper A, Kutnyakov I, Swita M, Lemmon T, Olarte MV and Wang H (2021) Determination of low-level biogenic gasoline, jet fuel, and diesel in blends using the direct liquid scintillation counting method for ^{14}C content. *Fuel* **291** (November 2020), 120084. doi: 10.1016/j.fuel.2020.120084.

Fahrni SM, Southon JR, Santos GM, Palstra SWL, Meijer HAJ and Xu X (2017) Reassessment of the ^{13}C/^{12}C and ^{14}C/^{12}C isotopic fractionation ratio and its impact on high-precision radiocarbon dating. *Geochimica et Cosmochimica Acta* **213**, 330–345. doi: 10.1016/j.gca.2017.05.038.

Gill K, Michczyński D, Michczyńska A, Piotrowska N, Kłusek M, Końska K, Wróblewski K, Nadeau M-J and Seiler M (2022) Study of bio-based carbon fractions in tires and their pyrolysis products. *Radiocarbon* **64**(6), 5–9. doi: 10.1017/RDC.2022.88.

Guo X, Liang C, Umar M and Mirza N (2022) The impact of fossil fuel divestments and energy transitions on mutual funds performance. *Technological Forecasting and Social Change* **176**(December 2021), 121429. doi: 10.1016/j.techfore.2021.121429.

Hajdas I, Ascough P, Garnett MH, Fallon SJ, Pearson CL, Quarta G, Spalding KL, Yamaguchi H and Yoneda M (2021) Radiocarbon dating. *Nature Reviews and Primers* **1**(62), 689–702. doi: 10.1038/s43586-021-00058-7.

Haverly MR, Fenwick SR, Patterson FPK and Slade DA (2019) Biobased carbon content quantification through AMS radiocarbon analysis of liquid fuels. *Fuel* **237**(October 2018), 1108–1111. doi: 10.1016/j.fuel.2018.10.081

Horvatinčić N, Barešić J, Bronić IK and Obelić B (2004) Measurement of low ^{14}C activities in a liquid scintillation counter in the Zagreb Radiocarbon Laboratory. *Radiocarbon* **46**(1), 105–116. doi: 10.1017/S0033822200039412.

Howaniec N and Smoliński A (2014) Effect of fuel blend composition on the efficiency of hydrogen-rich gas production in co-gasification of coal and biomass. *Fuel* **128**, 442–450. doi: 10.1016/j.fuel.2014.03.036.

ICPP (Intergovernmental Panel on Climate Change) (2013) Climate change 2013: the physical science basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge and New York, 1–1535.

Idoeta R, Pérez E, Herranz M and Legarda F (2014) Characteristic parameters in the measurement of ^{14}C of biobased diesel fuels by liquid scintillation. *Applied Radiation and Isotopes* **93**, 110–113. doi: 10.1016/j.apradiso.2014.01.019.

Krajcar Bronić I, Barešić J, Horvatinčić N and Sironić A (2017) Determination of biogenic component in liquid fuels by the ^{14}C direct LSC method by using quenching properties of modern liquids for calibration. *Radiation Physics and Chemistry* **137**, 248–253. doi: 10.1016/j.radphyschem.2016.01.041.

Krištof R and Kožar Logar J (2013) Direct LSC method for measurements of biofuels in fuel. *Talanta* **111**, 183–188. doi: 10.1016/j.talanta.2013.03.009.

Liaquat AM, Masjuki HH, Kalam MA, Varman M, Hazrat MA, Shahabuddin M and Mofijur M (2012) Application of blend fuels in a diesel engine. *Energy Procedia* **14**, 1124–1133. doi: 10.1016/j.egypro.2011.12.1065.

Libby WF (1961) Radiocarbon dating. *Science in the News* **133**(Mar. 3, 1961), 621–629.

Mann WB (1983) An international reference material for radiocarbon dating. *Radiocarbon* **25**(2), 519–527.

Maruccio L, Quarta G, Braione E and Calcagnile L (2017) Measuring stable carbon and nitrogen isotopes by IRMS and ^{14}C by AMS on samples with masses in the microgram range: Performances of the system installed at CEDAD-University of Salento. *International Journal of Mass Spectrometry* **421**, 1–7. doi: 10.1016/j.ijms.2017.05.014.

Morone P and D'Amato D (2019) The role of sustainability standards in the uptake of bio-based chemicals. *Current Opinion in Green and Sustainable Chemistry* **19**, 45–49. doi: 10.1016/j.cogsc.2019.05.003.

Němec M, Wacker L and Gäggeler H (2010) Optimization of the graphitization process AT AGE-1. *Radiocarbon* **52**(3), 1380–1393. doi: 10.1017/S0033822200046464.

Norton GA, Cline AM and Thompson GC (2012) Use of radiocarbon analyses for determining levels of biodiesel in fuel blends – Comparison with ASTM Method D7371 for FAME. *Fuel* **96**, 284–290. doi: 10.1016/j.fuel.2012.01.026.

Oinonen M, Hakanpää-Laitinen H, Hämäläinen K, Kaskela A and Jungner H (2010) Biofuel proportions in fuels by AMS radiocarbon method. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* **268**(7–8), 1117–1119. doi: 10.1016/j.nimb.2009.10.113.

Pazdur A, Fogtman M, Michczyński A and Pawlyta J (2003) Precision of ^{14}C dating in Gliwice radiocarbon laboratory. FIRI programme. *Geochronometria* **22**(September 1999):27–40.

Pimentel D and Patzek TW (2005) Ethanol production using corn, switchgrass, and wood; Biodiesel production using soybean and sunflower. *Natural Resources Research* **14**(1), 65–76. doi: 10.1007/s11053-005-4679-8.

Prasad GVR, Culp R and Cherkinsky A (2019) δ^{13}C correction to AMS data: Values derived from AMS vs IRMS values. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* 455(January 2018), 244–249. doi: 10.1016/j.nimb.2019.01.034.

Schuurman Y, Fogassy G and Mirodatos C (2013) Tomorrow's biofuels: Hybrid biogasoline by co-processing in FCC Units. *The Role of Catalysis for the Sustainable Production of Bio-Fuels and Bio-Chemicals* **2013**, 321–349. doi: 10.1016/B978-0-444-56330-9.00010-3.

Serrano-Ruiz JC and Dumesic JA (2011) Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuels. *Energy and Environmental Science* **4**(1), 83–99. doi: 10.1039/c0ee00436g.

De Souza JE, Scherer MD, Cáceres JAS, Caires ARL and M'Peko JC (2013) A close dielectric spectroscopic analysis of diesel/biodiesel blends and potential dielectric approaches for biodiesel content assessment. *Fuel* **105**, 705–710. doi: 10.1016/j.fuel.2012.09.032.

Stenström KE, Skog G, Georgiadou E, Genberg J and Johansson A (2011) A guide to radiocarbon units and calculations Lund University, Department of Physics, Division of Nuclear Physics.(LUNFD6(NFFR-3111)/1-17/(2011)). Lund University, Nuclear Physics.

Stuiver M (1983) International agreements and the use of the new oxalic acid standard. *Radiocarbon* **25**(2), 793–795.

Stuiver M and Polach HA (1977) Reporting of ^{14}C data. *Radiocarbon* **19**(3), 355–363.

Sulek MW, Kulczycki A and Malysa A (2010) Assessment of lubricity of compositions of fuel oil with biocomponents derived from rape-seed. *Wear* **268**(1), 104–108. doi: 10.1016/j.wear.2009.07.004.

Synal HA, Stocker M and Suter M (2007) MICADAS: A new compact radiocarbon AMS system. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* **259**(1), 7–13. doi: 10.1016/j.nimb.2007.01.138.

Türck J, Singer A, Lichtinger A, Almaddad M, Türck R, Jakob M, Garbe T, Ruck W and Krahl J (2021) Solketal as a renewable fuel component in ternary blends with biodiesel and diesel fuel or HVO and the impact on physical and chemical properties. *Fuel* **310**(PC), 122463. doi: 10.1016/j.fuel.2021.122463.

Urzędowska W and Stępień Z (2016) Prediction of threats caused by high FAME diesel fuel blend stability for engine injector operation. *Fuel Processing Technology* **142**, 403–410. doi: 10.1016/j.fuproc.2015.11.001.

Verger T, Azimov U and Adeniyi O (2022) Biomass-based fuel blends as an alternative for the future heavy-duty transport: A review. *Renewable and Sustainable Energy Reviews* **161**(March), 112391. doi: 10.1016/j.rser.2022.112391.

Vrtiška D and Šimáček P (2016) Prediction of HVO content in HVO/diesel blends using FTIR and chemometric methods. *Fuel* **174**, 225–234. doi: 10.1016/j.fuel.2016.02.010.

Wacker L, Synal HA and Marcus C (2010) Bats: A new tool for AMS data reduction. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* **268**(7–8), 976–979. doi: 10.1016/j.nimb.2009.10.078.

Zhang Z, Deng Y, Pham MH, Zuo W, Peng Q and Yin Z (2018) Effects of fatty acid methyl esters proportion on combustion and emission characteristics of a biodiesel fueled marine diesel engine. *Energy Conversion and Management* **159**(December 2017), 244–253. doi: 10.1016/j.enconman.2017.12.098.

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Gliwice, 07th July 2024

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Authorship statement

I hereby declare that my contribution to the paper that I first-authored:

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My contribution included: Sample selection and preparation of benzene and graphite for LSC and AMS analysis, preparation of CO_2 for IRMS analysis, calculations of carbon content based on EA results, ^{14}C and ^{13}C measurements; writing of text, preparation of all figures and tables, paper submission in journal, responding to reviewers' comments.

My participation to the work (Baranyika et al. 2024) was 80 %

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Mój wkład obejmował: selekcję próbek i przygotowanie benzenu i grafitu do analiz LSC i AMS, przygotowanie CO_2 do analiz IRMS, obliczenia zawartości węgla na podstawie wyników EA, pomiary ^{14}C i ^{13}C; napisanie tekstu, przygotowanie wszystkich rycin i tabel, złożenie artykułu w czasopiśmie, odpowiadanie na komentarze recenzentów.

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My contribution was as follows: Supervision of PhD research, supervision of AMS analysis, calculations of ^{14}C content from AMS and assistance in paper revision

My participation to the work was 10 %.

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Mój wkład był następujący: nadzór nad badaniami doktoranckimi, nadzór nad analizą AMS, obliczenia zawartości ^{14}C z AMS i pomoc w poprawkach artykułu

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My contribution was as follows: Supervision of LSC measurements, calculations of ^{14}C content from LSC and assistance in paper revision

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Mój wkład był następujący: nadzór nad pomiarami LSC, obliczenia zawartości ^{14}C z LSC oraz pomoc w redagowaniu publikacji

Mój udział w powstaniu pracy wynosił 10 %.

Podpis