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Review of the doctoral dissertation entitled "Application of isotope methods for determination of biocomponents in liquid fuels"

by Jean Baptiste Baranyika, MSc

The basis for the preparation of this review is the invitation letter from the Chairman of the Council of the Discipline of Earth and Environmental Sciences of the Silesian University of Technology, Natalia Piotrowska, PhD, DSc, Eng, Prof. in SUT, dated 8th November 2024. The dissertation's supervisor is Natalia Piotrowska, PhD, DSc. Eng., Prof. in SUT.

1. Topic of the doctoral dissertation and the relevance of its selection

In light of the European Union's dedication to achieving climate neutrality, member states are required to gradually eliminate the use of fossil fuels. The European Green Deal serves as a blueprint for the EU's transition towards achieving climate neutrality by 2050. To accomplish this, the EC has introduced the European Climate Law which establishes goals for decreasing greenhouse gas emissions, including a minimum 55% reduction by 2030 (compared to 1990 levels). This will involve the development of alternative energy sources such as biomass,

photovoltaics, wind farms, wave, and nuclear energy. All these efforts are aimed at significantly reducing CO_2 emissions.

Globally, the use of liquid fuels derived from renewable sources that are environmentally friendly has been widely implemented in an effort to decrease CO_2 emissions into the atmosphere. One popular type of fuel produced from biomass is known as bio-oil, which is considered to be a carbon-neutral fuel. This is due to the fact that the CO_2 emitted in bio-oil combustion is offset by the CO_2 captured from the air during the growth of the biomass. Additionally, combustion of bio-oil does not produce sulfur oxides (SO_x) and reduces nitrogen oxide (NO_x) emissions by approximately 50% when compared to the emissions from biodiesel combustion in gas turbines.

This lining forms the basis of fuel blending strategies aimed at reducing the net flux of carbon into the atmosphere and the use of fossil fuels. This could be achieved through the use of blends containing biofuels derived from renewable resources, such as crops or biodiesel from vegetable oil. Unfortunately, the cost of producing energy from these renewable resources is higher than that of fossil fuels. The EU has prepared a financial mechanism to make the use of renewable fuels more attractive by reducing taxes on bio-components. The key is to control the quality of the liquid fuels. This is done by measuring the carbon isotope ^{14}C in the fuel. Fossil fuels do not contain this isotope because of their age. On the other hand, biofuels and fuel blends containing bio-components, known as bio-components, contain a relatively high proportion of radiocarbon.

Global research efforts are focused on developing effective techniques for measuring and identifying the biocomponents in fossil fuels. Traditional analytical methods may not be directly suitable for biofuels due to their complex chemical composition. It is crucial to create sensitive, reliable, and cost-efficient methods for detecting the biocomponents of biofuels. Moreover, standardized analytical procedures are necessary to comply with quality standards and environmental regulations governing the production and utilization of biofuels. However, the lack of uniformity in existing methods may result in inconsistent results, impeding the widespread acceptance and commercialization of biofuels.

The PhD thesis is focused on adapting the methodology for determining the content of biocarbon using isotope methods in the Gliwice Radiocarbon and Mass Spectrometry Laboratory and verifying the accuracy of this methodology. However, this is a utilitarian rather than a scientific objective. As a scientific objective, however, the analysis of uncertainties in

radiocarbon dating caused by various factors, such as sample preparation and measurement procedures should be highlighted. In his work, MSc Baranyika has not only shown that these parameters affect the uncertainty of the results, but more importantly has shown how to obtain accurate and realistic results, which are crucial for informed decision-making in environmental and climate sciences. 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.

In summary, I believe that the topic and scope of the PhD thesis proposed by MSc Jean Baptiste Baranyika are undoubtedly in the area of important problems related to the development of an effective technique to determine the content of biocarbon using isotope methods. The topic of the PhD thesis should be considered as fully justified.

2. General characteristics of the PhD dissertation

The PhD dissertation was presented as a single-topic series of three multi-authored publications with a total value of 350 Points of the Ministry of Education and Science and 17,4 Impact Factor points. The papers included in the dissertation were published between 2022 and 2024. These papers, listed below, were discussed in the form of a report (prepared in both English and Polish), with the common title 'Application of isotope methods for determination of biocomponents in liquid fuels':

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. 66(3):437-447. doi:10.1017/RDC.2024.51.

The report is 30 pages long and consists of 6 chapters, 7 figures, 6 tables and only 44 references.

Unfortunately, in the first part of the report, where the research topic is described, the state of the world's methods for determining biocomponents in liquid fuels are presented in a very laconic way. In addition, MSc Baranyika has rightly shown that the implementation of fuel blending strategy contributes to the reduction of net carbon flux to the atmosphere and to the reduction of dependence on fossil fuels, but it is not clear how this is achieved in Poland. This requires additional comment during the public defence. The development of a suitable procedure for the preparation of samples to measure the biobased carbon content in various substances is necessary to guarantee the reliability of the results. The end of the PhD candidate's research topic description correctly identifies the main challenge in using traditional analytical methods to characterise the biocomponents in fossil fuels. Often the classical analytical methods are not appropriate due to biofuels' complex matrices and chemical composition. Anyway, additional comments are needed why "the existing methods often lack harmonization, which may lead to inconsistency of results, hindering the widespread adoption and commercialization of biofuels".

At the end of the description of the laconic state-of-the-art, a short, synthetic summary of the theoretical part of the work is missing. This summary should justify the purpose of the research conducted and provide a reference to the main part of the dissertation presented in the form of three research papers, which presents the methodology and research.

The first paper, entitled "Testing the methods for determination of radiocarbon content in liquid fuels in the Gliwice Radiocarbon and Mass Spectrometry Laboratory", published in Radiocarbon, presented the testing and validation of methods for determination of radiocarbon (^{14}C) content in liquid fuels in the Gliwice Radiocarbon and Mass Spectrometry Laboratory. MSc Baranyika, together with other authors, studied two techniques such as Accelerator Mass Spectrometry (AMS) and Liquid Scintillation Counting (LSC). The researchers used several samples, including a ^{14}C-free fuel and hydrotreated vegetable oil (HVO), to investigate the effectiveness of each method in measuring biocomponents in fuels. Sample preparation for AMS involved elemental analysis (EA) combustion followed by graphitisation, while LSC required conversion of liquid fuels to benzene to measure radioactivity. The study showed that both AMS and LSC gave reliable results for ^{14}C content. However, challenges such as isotopic fractionation and the potential for radon contamination were addressed, highlighting the need for careful sample handling and preparation. The results demonstrated the importance of refining sample preparation techniques to improve the accuracy and reproducibility of radiocarbon measurements.

In Fig. 1 radiocarbon (^{14}C) contents of tested liquid fuels grouped according to different methods of sample preparation are presented. However additional comment is required regarding the statement in the report that '*...no resublimation experiments were conducted on B37 and diesel-BP samples in this study. These differences for the three samples with 14C 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.*"

MSc Baranyika's contribution to the first paper was 75% and included sample selection and preparation of benzene and graphite for LSC and AMS analysis, preparation of CO_2 for IRMS analysis, calculation of carbon content based on EA results, ^{14}C and $\delta^{13}C$ measurements, as well as writing the text, preparing all figures and tables, and editing and responding to reviewers' comments.

In the second paper, the determination of radiocarbon (^{14}C) content in bio-oil samples using a compact modern accelerator mass spectrometry system known as the Mini Carbon Dating System (MICADAS) at the Gliwice Radiocarbon and Mass Spectrometry Laboratory was made. PhD candidate prepared bio-oil samples and a reference biomass sample (pistachio shells) to analyze the ^{14}C content. Why that kind of biomass sample was chosen as a reference? Results indicated that one bio-oil was not derived from the reference biomass, while the others were found to be blends of bio- and fossil components. The ^{14}C measurements demonstrated reproducibility and reliability, confirming the effectiveness of the sample preparation technique and the sensitivity of the MICADAS system.

MSc Baranyika's contribution to the above paper was 80% and included sample selection and preparation of graphite for AMS analysis, calculation of carbon content based on EA results as well as ^{14}C measurements and data reduction, writing of text and presentation of graphical and tabular results, and preparation of responses to reviewer comments.

In the third paper, entitled "Determination of radiocarbon content in liquid fuel blends by accelerator mass spectrometry and liquid scintillation counting in the Gliwice Radiocarbon and Mass Spectrometry Laboratory", MSc Baranyika and other authors investigated the determination of radiocarbon (^{14}C) content in various liquid fuel blends using two primary methods, i.e. accelerator mass spectrometry (AMS) and liquid scintillation counting (LSC). The study aimed to improve the accuracy of the measurement of biocomponents in fuels, which is becoming increasingly important in the context of reducing CO_2 emissions. In the paper,

existing sample preparation techniques were used to accurately assess the biocarbon content in blends of hydrotreated vegetable oil (HVO) and a 14C-free petrodiesel sample. The strong correlation between the AMS and LSC results was demonstrated, indicating high reproducibility.

In the last part of the PhD report MSc Baranyika presented short summary of his contribution to the "PhD project" (it should be rather PhD dissertation) as well as the general conclusions from the research studies.

Editing and technical remarks

- The SI units should be used in the entire PhD dissertation (e.g. temperature should be presented in K, etc);
- Minor spelling mistakes were found in the text (i.e. at p.10 is "….bio-oil samples by MIni Carbon…" should be "….bio-oil samples by Mini Carbon…";
- All symbols used in the formulas should be defined (i.e. formula for calculation the biogenic carbon content at p.17).

Summary and conclusions

I conclude that the doctoral dissertation of Jean Baptiste Baranyika, MSc, represents an original solution to a scientific problem. Based on the research and analysis carried out, the PhD candidate has achieved the stated objectives of the thesis.

The results obtained are of high scientific and cognitive value. The candidate has demonstrated a good ability to formulate scientific problems, conduct research and analyze the results. The doctoral thesis submitted for review is in the scientific discipline of Earth and Environmental Sciences.

I find that the doctoral thesis of Jean Baptiste Baranyika, MSc, entitled "Application of isotope methods for determination of biocomponents in liquid fuels" fully complies with the conditions of the Law of 20th July 2018 on Higher Education and Science. I hereby present to the Board of the Discipline of Earth and Environmental Sciences of the Silesian University of Technology the recommendation for admission of the PhD candidate, Jean Baptiste Baranyika, MSc, to PhD defence.

Adam Marcin Smoliński

Elektronicznie podpisany przez Adam Marcin Smoliński
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