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**Review of the doctoral dissertation of Komal d/o Aziz Gill, MSc, entitled "Application of isotope methods for determination of bio-based content in solid materials" prepared at the request of the Chairperson of the Discipline Council for Earth Sciences and Environment, Natalia Piotrowska, PhD, Professor at SUT**

Increasing amounts of generated waste is an extremely important problem on a global scale, which causes enormous environmental pollution. Hence, there is not only an urgent need to recover valuable substances from this waste, but also to recycle it as much as possible, especially using renewable materials. As it is well known, new products are usually created in the process of recycling. However, during their production, additional quantities of hydrocarbons are often consumed, which may originate both from fossil raw materials and from so-called bio-components. In the modern world, in connection with the necessary protection of the atmosphere, it is particularly important to minimise greenhouse gas emissions from fossil fuels and, consequently, to make greater use of biofuels, not only for energy purposes, but also in production processes and in recycling of various materials. In view of various legal conditions concerning, among other things, the taxation of production, there is also a need to control to what extent coal and fossil hydrocarbon resources have been used in the production of various goods, and to what extent modern biocomponents have been used, too.

The doctoral dissertation of Komal Aziz Gill, MSc, prepared under the supervision of Danuta Michczyńska, PhD, Professor at SUT aims to increasingly promote green energy and green recycling and the possibility of controlling the use of biocomponents in the production of various goods.

The doctoral dissertation by Komal Aziz Gill submitted for the review consists of:

* an introductory text, presented in both English and Polish, which is in fact an extended summary of the co-authored scientific articles comprising the dissertation, of which the Doctoral Student is the first author and also the corresponding author;
* an original co-authored scientific article entitled "Study of bio-based carbon fractions in tires and their pyrolysis products" (13 pp.), published in 2022 in the renowned Radiocarbon journal (5-year IF - 4.6);
* an original co-authored article entitled "Technical carbon black and green technology" (7 pp.), published in 2023 in the Geochronometry journal (5-year IF - 1,O);
* an original co-authored article, entitled "Monitoring of modern carbon fraction in disposable packaging" (10 pp.), published in 2024 in the journal Radiocarbon (5-year IF - 4 6);
* a co-authored chapter in the monograph entitled "Bio-carbon content determination in disposable packaging by liquid scintillation counting" (14 pp.), published in the monograph published by the Silesian University of Technology Publishing House in 2024 under the editorship of Sebastian Werle and Joanna Ferdyn-Grygierek entitled " Ochrona klimatu i środowiska, nowoczesna energetyka — wybrana problematyka” [Climate and environmental protection, modern energy sector - selected problems];
* declarations and description of the co-authors' own contribution to the creation of individual articles and a chapter in the monograph, which shows that the Doctoral Student's contribution to their creation was very significant and was at the level of 45%, 65%, 70% and 70% respectively.

Particularly noteworthy is the fact that the PhD student undertook an ambitious, and - at the same time - novel research problem, aiming at the use of measurements of the concentration of a radioisotope of carbon in order to determine the proportion of biobased carbon in comparison with fossil carbon in samples of selected products and wastes constituting a significant burden for the environment. Thus, the main objective of the research undertaken was to determine the concentration of modern carbon in materials such as (1) tyre rubber and its pyrolysis products, (2) carbon black and (3) disposable packaging often used in recycling.

The specific objectives of the undertaken research were both methodological and purely utilitarian. In the methodological sphere, the problem was to develop a preliminary preparation of the studied materials, as well as an effective method for the determination of 14C concentration in the analysed solid materials. On the other hand, utilitarian objectives included the determination of biobased carbon content on the basis of the results obtained from measurements of 14C concentration in the studied materials.

Methodological problems and the specific results of the study of bio-based carbon content in tyre rubber samples and their pyrolysis products (samples of recovered carbon black and pyrolysis oil) are presented in a co-authored paper entitled “**Study of bio-based carbon fractions in tyres and their pyrolysis products**”. This paper presents a detailed methodology for determining the concentration of the radiocarbon isotope (14 C) in tyres and their pyrolysis products. Samples were taken from truck and passenger car tyres in the form of shredded rubber, pyrolysis oil and recovered soot. Measurements of radiocarbon content were performed both using the accelerator mass spectrometry technique (ASM – the National Laboratory of Age Determination in Trondheim), after prior graphitisation of the samples, and the liquid scintillation technique (LSC – 14 C and Mass Spectrometry Laboratory in Gliwice) in which LSC was preceded by the synthesis of benzene from the samples. The results obtained with these two methods are consistent. It was also found that the concentration of radiocarbon in rubber is highly variable due to its complex structure and composition in tyres (e.g. due to the different proportion of natural rubber in the studied samples). It was also documented that 14C concentration values were higher in pyrolysis oil compared to rubber and higher in truck tyres compared to tyres from passenger cars.

The article “**Technical carbon black and green technology**” addresses the concentration of biocarbon in technical carbon black used in the production of tyres, various rubber products and cable sheathing. It is worth mentioning that the production of technical carbon black (TCB) itself, which can be produced by thermal decomposition of both fossil coals and biomass in an anaerobic environment, can produce significant CO2 emissions of various origins. Hence, the production of carbon black raises sustainability concerns due to the significant dependence on fossil raw materials. The research undertaken by the Doctoral Student was conducted to monitor the renewability of technical carbon black samples by determining the 14C isotope concentration. Both liquid scintillation (LSC) and accelerator mass spectrometry (AMS) techniques were used to measure the concentration of this isotope. Examination of four different carbon black samples provided by Contec S.A. Poland revealed that they contained extremely low concentrations of 14C, reaching <1% of modern carbon, indicating that the four differently graded carbon black samples were either not produced from renewable sources or were produced with their minimal contribution.

The article “Monitoring of modern carbon fraction in disposable packaging” addresses the presence of 14C in various disposable packaging made from bio-based raw materials. The amount of 14C in the samples reflects the amount of biocarbon used in their production. Common types of disposable packaging such as cups, plates, straws, cutlery and baking paper were included in the study. The analysed samples were made of materials such as paper, wheat bran, sugar cane and wood. The average concentration of the 14C isotope, as measured by accelerator mass spectrometry (AMS) is greater than 100 pMC in all tested samples, indicating that the samples are modern. The relatively high 14C concentration values in the waterproof layer of the sample indicate that bioplastic, rather than plastic, was used in the production of the sample. The highest 14C isotope concentration values were measured for samples that used the oldest biomass (wood and paper) and the lowest for products from current crops (sugar cane and wheat bran), which is consistent with the trend of changing 14C concentrations in the biosphere. The study also addressed the problem of heterogeneity and representativeness of the subsamples.

In the co-authored chapter entitled "**Bio-carbon content determination in disposable packaging by liquid scintillation counting**", the concentration of 14C and - at the same time - the amount of bio-carbon in samples of disposable packaging was determined using a scintillation technique, with the same samples analysed as those previously measured by accelerator mass spectrometry (AMS). A comparison of the measurements performed by the two methods showed that in some cases there were significant differences in the concentration of 14C, which is mainly related to the difference in mass size of the analysed samples.

The analysis of the presented articles that constitute the reviewed achievement allows us to conclude the significant contribution of the Doctoral Student to the implementation of the methodology for the determination of the concentration of 14C in various materials and products related to their recycling as well as in a variety of waste and disposable packaging, Ms Komal Aziz Gill, MSc, has fully met the established aim of research, achieving specific results that provide evidence of the proportions of biobased carbon used during the recycling of various wastes, as well as in the manufacturing process of some disposable products and packaging.

Given that the results of Ms Komal Aziz Gill's research, which constitutes her PhD achievement, have been published in reputable scientific journals with a high IF and have therefore gone through a system of careful review by experts in isotope chemistry. I raise no formal comments.

However, when analysing this achievement from a substantive point of view, it seems important to ask which of the applied concentration determination techniques has the potential to be used in routine, utilitarian applications aiming to determine the proportion of biobased carbon in different products and wastes, especially considering the mass of samples analysed and analytical costs.

In conclusion, it should be emphasised that the PhD achievement of Ms Komal Aziz Gill, MSc, is an excellent example of the use, adaptation and implementation of familiar techniques of radiocarbon quantification, so far used mainly in geochronological research, for monitoring and supporting the pro-ecological production of selected commodities, in order to reduce CO2 emissions from fossil fuels. It is also worth noting that the Doctoral Student has taken care to disseminate her research results in the form of valuable publications, as well as presentations at international and national scientific conferences. She is also a co-author of 5 publications not related to the research included in the PhD achievement. This demonstrates the scientific maturity of Ms Komal Aziz Gill, MSc, and the ability to conduct scientific research independently.

Considering the above, I conclude that the reviewed doctoral achievement more than fulfils the conditions set out in Article 13(1) of the Act of 13.03.2003 on scientific degrees and academic title and degrees and title in art. Thus, I request that Ms Komal Aziz Gill be admitted to the further stages of the doctoral dissertation procedure. At the same time, I address a motion to the Discipline Council for Earth and Environmental Sciences of the Silesian University of Technology in Gliwice to consider granting an appropriate scientific award to the doctoral student.

Szczecin, 28 December 2024