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Problems with the biodegrability assessment of biomass materials for combustion

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Abstract: *Problems with the biodegrability assessment of biomass materials for combustion.* The presented work includes research on different types of biomass: woody biomass, agricultural biomass, waste biomass, mixture of woody biomass with plastics. The aim of the study was the evaluation of the standardized biodegradability assessment method of the biomass materials for combustion and its suitability for use in laboratory practice.

Keywords: biomass, solid biofuels, biomass content, biodegrability

INTRODUCTION

Among the many possibilities of energy generation, apart from conventional fuels, biomass combustion seems to be the most rational solution. In Poland, the most serious sources of this renewable material are the wastes from agricultural plant production and wood wastes. The main aspect of biomass use is the fact that the combustion of solid biofuels (for economic reasons) allow to fulfill Poland's international obligations in the field of electricity and heat from renewable sources. Activities, which are aimed at obtaining new renewable raw materials that can be processed into biofuel, are compatible with the provisions of the Polish Energy Policy until 2030 [1], adopted by the Council of Ministers in 2009. The effect of the policy was to implement a series of laws designed to support the production of energy from renewable sources. An example is the Regulation of the Minister of Economy of 23 August 2010, which defines biomass as follows: "Biomass - solid or liquid substances of plant or animal origin, which are biodegradable, derived from the products, waste and residues from agriculture, forestry and related industries, as well as parts of other wastes that are biodegradable and grains with non-compliant quality (…)" [2]. Unfortunately, the relevant legislation does not contain a definition of the biodegradation process, as well as the description of an appropriate assessment methods and the boundary parameters. Due to the industry and government demands, it was proposed to use the analytical procedure contained in the EN 15440:2011 [3] in order to determine the biodegradability. The basis for this decision was the assumption that biomass is a natural biodegradable material. Therefore the biomass content in the evaluated material can be the basis for its classification as the biodegradable materials. The adoption of method, which is so difficult to accept due to its merits, was caused by the belief that there were no other rapid methods for determining this factor.

The cited standard [3] is used to determine the biomass content in the mixture of waste (mainly municipal) providing a basis for qualification of a part of generated energy as renewable energy. In practice, it is the method of assessing differences in solubility of the various components of biomass fuel. This method and its use as an indicator of the biomass fuels biodegradability is very controversial. This is related to the accepted analytical procedures and the assumption that the portion of a sample marked as non-biomass is not biodegradable. However, the use of the method in practice became a fact recognized by the Energy Regulatory Office (URE). Because of the inflow of inquiries from industry, as well as requests for the opinion on the results obtained, the Laboratory of Bioenergy in the Wood

Technology Institute has undertaken the work in this subject, in order to learn practical adopted procedures.

The aim of this study was the evaluation of the biodegradability assessment method of the biomass materials for combustion – the standardized method of selective dissolution – and its suitability for use in laboratory practice. The specific objective of this study was to determine the possibility of adapting the analytical procedures which are recommended for use in solid recovered fuels (by selective dissolution) as a method for assessing the biodegradability of solid fuels derived from biomass.

MATERIALS AND METHODS

The scope of the research included an analytical work based on the requirements of EN 15440:2011 [3] for determination of biomass content in the studied biomass materials. The presented studies included four groups of biomass:

- woody biomass: spruce (*Picea abies* Karst.), pine (*Pinus sylvestris* L.),
- agricultural (fruit) biomass: oil palm kernel shells (PKS) (*Elaeis guineensis* Jacq.),
- waste biomass from the chemical processing of wood – lignocellulosic waste after the hydrolysis process (lignocellulose),
- mixture of woody biomass with plastics: spruce with polypropylene (PP) in a weight ratio of 1:1; spruce with polypropylene in a weight ratio of 9:1; spruce with polystyrene (PS) in a weight ratio of 1:1; spruce with polystyrene in a weight ratio of 9:1.

The proposed selection of samples was dictated by several important (from the viewpoint of industrial practice) factors:

- wood species commonly used in domestic industry (woody biomass),
- waste from food and agricultural industry - currently used for energy production (fruit biomass),
- chemical wastes from wood processing, currently used for the production of energy (waste woody biomass),
- biomass impurities - plastics (e.g. residual packaging).

The preparation of the samples was conducted according to the requirements of the appropriate standards [4,5]. Pre-ground material was disintegrated in a knife-mill into grains of the desired size of 1.0 mm.

The determination of biomass and non-biomass content was conducted according to EN 15440:2011 [3]. Biomass content was expressed in a percentage by weight using the selective dissolution method, which involved the treatment with the concentrated sulphuric acid (VI) topped with hydrogen peroxide. The biomass in the solid fuel was selectively dissolved and the "non-biomass" was remained in the residue. The biomass content was corrected for the carbonates by measuring the ash content before and after dissolution.

The ash content was determined in the temperature of (550±10)°C according to the appropriate standards [6,7] for each type of material. The determinations were conducted in three parallel trials.

RESULTS AND DISCUSSION

The results of the studies on the content of ash, biomass, and non-biomass are shown in Table 1.

After assessment of the data in the Table, it can be concluded that in the samples of pure spruce wood biomass content (according to the used procedure) was at a level close to 100%. In the case of pine wood, this value was 95%. Such a state can be explained by the participation of extractives, which include fatty acids, resin acids, terpenes and terpenoides.

These compounds – naturally occurring in softwood – are more resistant to concentrated acid dissolution [8], which is reflected in the results obtained.

The biomass content in the studied lignocellulose material was at a level of 68.9%, which in this case, is a very low value. This material - the waste from the furfural production - is a mixture of lignin and cellulose in the proportions difficult to determine [9]. It seems that a high proportion of lignin in a studied material could have had a significant impact for the results obtained. Lignin, which is a natural polymer with phenolic character, hardly subjects to digestion (dissolution) in an acidic medium, even at high concentrations of acid used [8]. Also, a period of lignocellulose wastes residence on landfill was unknown, which could significantly affect the ratio of lignin to cellulose in the evaluated material, as well as the physic-chemical state of these substances. In addition, the tested material could be subjected to natural degradation processes under the influence of atmospheric and biological impacts. As a result of the above mentioned processes, the evaluated material could be substantially different from the known properties of lignocellulose obtained directly from the hydrolysis process. In the authors' opinion, most of the components shown in the lignocellulose analysis as non-biomass are a part of the lignin with a high degree of polymerization.

Tab. 1 Ash content, biomass and non-biomass content in woody biomass, agricultural biomass, waste biomass and mixtures of woody biomass with plastics.

Material	Ash wt.%$_d$	Biomass content wt.%$_d$	Non-biomass content wt.%$_d$
Spruce *Picea abies* Karst.	0.2	99.8	0
Pine *Pinus sylvestris* L.	0.2	95.3	4.4
PKS *Elaeis guineensis* Jacq.	3.8	89.4	6.7
Lignocellulose	21.7	69.0	9.4
Spruce : PP 1:1	0.2	76.2	23.6
Spruce : PP 9:1	0.3	99.5	0.2
Spruce : PS 1:1	1.1	51.4	47.5
Spruce : PS 9:1	0.5	89.8	9.7

d: dry

The biomass content, according to the used procedure, in the agricultural (fruit) biomass – PKS – was at a level of 89%. As the sample was originated from the fruits characterized by a high share of fatty substances, it is believed that these substances were responsible for the high content of "non-biomass". As previously explained, fatty acids contained in the sample are more resistant to the concentrated sulfuric acid (VI), which results in a relatively high proportion of so-called non-biomass substances.

The next stage of the study was to evaluate the procedure used for the mixtures of biomass and waste plastics. According to the information given in EN 15440:2011 [3], the procedure is used to assess exactly this type of material. The study involved a mixture made of spruce (having the highest share of "biomass") and selected waste materials - polypropylene and polystyrene. The data in Table 1 show that only the mixture of spruce with PS correspond to the actual content of biomass in the prepared sample.

The mixture of spruce wood with PP obtained significantly higher results than the expected. In the mixture of 10% of the polypropylene the assay of the biomass was 99%, while in the mixture with 50% of PP the result was 76% of the biomass. This situation could be explained by the low resistance of polypropylene to the concentrated acids.

CONCLUSIONS

The determinations of the biomass content in the different biomass materials, conducted in accordance with the procedure described in EN 15440:2011 [3], made possible to assess the biomass fraction content expressed as a weight percentage. It is concluded that this method is characterized by a good accuracy only for certain types of biomass. The correct results were obtained for one species of treated wood (spruce) as well as for the mixture of wood biomass with polystyrene.

In case of the fruit biomass (PKS), the results of analyses differed significantly from the expected value – the calculated content of biomass was at the level of below 95%, despite the absence of impurities of non-biomass character. In the authors' opinion, most of the components shown in the analysis as "non-biomass" are part of the lignin with a high degree of polymerization.

The assessed method has not worked for analysis of lignocellulose waste after the hydrolysis process. This material, constituting the biomass within the meaning of the relevant provisions [2,10], showed a significant difference from the expected value. The content of "non-biomass" was above 5%, which also may be associated with a high content of lignin with a high degree of polymerization.

Strongly negative assay results were obtained for the mixture of woody biomass and synthetic additives (spruce wood and PP), where the calculated values deviate significantly from the true (model). In this case, the action of strong oxidants caused the depreciation of polypropylene to a higher degree than it was resulted from the information contained in the standard [3].

The research made possible to acquire the knowledge and experience to enable critical evaluation of the analytical method, which should be used to rapidly assess the "biodegradability" of biomass for combustion.

Based on the research, as well as on the knowledge and experience of the Wood Technology Institute, the assumption that biomass determined by the selective dissolution method is synonymous to biodegradable biomass seems to be a wrong statement.

Unfortunately, the lack of other rapid methods resulted in the dissemination of it into practice. In addition, the Energy Regulatory Office (URE) accepted this method as a support in the case law with reference to biomass (issuing certificates of origin - the so-called "Green certificates"). Many controversies over qualification of energy generated from renewable sources, caused by the URE decisions, make it necessary to perform the interdisciplinary research. There is a need to compare the recommended classical methods of materials biodegradability assessment, for example, in the documents of the Organization for Economic Co-operation and Development (OECD) [11] or in literature [12,13] with the methods used in industrial practice (selective dissolution method, the method of analysis of carbon C^{14}, et al.).

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Streszczenie: *Problemy z oceną biodegradowalności materiałów biomasowych przeznaczonych do energetycznego spalania.* Celem pracy była ocena przydatności do użytku w praktyce laboratoryjnej jednego ze sposobów oceny biodegradowalności materiałów biomasowych przeznaczonych do energetycznego spalania – znormalizowanej metody selektywnego rozpuszczania. Badania przeprowadzono na czterech grupach biomasy: biomasa drzewna (świerk, sosna), biomasa owocowa (łupiny pestek olejowca gwinejskiego), biomasa drzewna - odpadowa (ligninoceluloza pohydrolityczna), mieszanina biomasy drzewnej (świerk) z polipropylenem i polistyrenem. Przeprowadzone badania pozwoliły stwierdzić, że jest to metoda charakteryzująca się dobrą precyzją jedynie dla niektórych rodzajów biomasy. Poprawne wyniki, w stosunku do wartości oczekiwanych, uzyskano dla drewna świerka, a także dla mieszaniny drewna świerka z polistyrenem. W przypadku biomasy owocowej rezultaty analiz znacznie odbiegały od spodziewanych wartości (wartości poniżej 95%). Zdecydowanie niekorzystne wyniki oznaczeń uzyskano również dla mieszaniny biomasy drzewnej z polipropylen, gdzie wyliczone wartości znacznie odbiegały od rzeczywistych (modelowych). Oceniana metoda nie sprawdziła się także w przypadku analiz zawartości ligninocelulozy pohydrolitycznej.

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