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Influence of the raw material properties on the liquefied wood chemical composition

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Abstract: *Influence of the raw material properties on the liquefied wood chemical composition.* The subject of the studies was to investigate the effect of raw material used for the liquefaction process on the liquefied wood chemical composition. Various types of post-industrial wood waste including mixed hardwood/softwood powder, bark, pine, and beech sawdust were liquefied according to the procedure previously described by the authors. The raw wood materials were characterized in terms of their fraction composition, buffer capacity, formaldehyde content and bulk density, among others. Fourier Transform Near Infrared Spectroscopy (FT-NIR) was applied for characterization of both the raw materials used for liquefaction treatment as well as of their liquefaction products. Spectra were qualitatively evaluated by means of Principal Component Analysis (PCA). The results obtained indicate that all raw materials investigated can be easily discriminated before liquefaction, however after the transformation process the same products become more homogenous from the spectroscopic point of view. It was concluded therefore, that any sort of investigated wood wastes might be used as a primary material for liquefaction.

Keywords: liquefied wood, raw material, wood waste, FT-NIR spectroscopy, PCA analysis

INTRODUCTION

Processes associated with the logging, exploitation or processing of timber result in generation of various wastes and by-products. Although small-sized and post-consumer wood waste are considered as a burden on the various industrial processes, it may also be seen as a valuable source of raw material. Taking this fact into account, the wood waste management becomes an important issue for sustainable management of resources and economic aspects of related industries.

Numerous studies confirm the possibility of wood wastes transformation, including wood packaging waste [Yuan et al. 2013], cork dust [Dos Santos et al. 2016], bark [Janiszewska et al. 2016], by means of liquefaction. In this work four types of post-industrial wastes were selected for the liquefaction process. Both, raw materials used for preparation of liquefied wood as well as liquefied wood products were characterized using Fourier Transform Near Infrared Spectroscopy (FT-NIR). FT-NIR is a technique capable of fast and non-destructive characterization of organic materials. While infrared spectroscopy in the mid-range was previously used for characterization of liquefied wood [Li et al. 2015], the sample preparation procedure is more complex when compared to that required by NIR spectroscopy. Another important advantage of FT-NIR is its ability to distinguish various hydroxyl groups, highly affecting the hygroscopic properties of investigated materials. Therefore, FT-NIR has been selected as an alternative to the standard methods. The aim of this study was to investigate the effect of the raw material used for the liquefaction process on the chemical composition of the liquefied products.

MATERIALS AND METHODS

The raw wood material consisted of mixed hardwood/softwood powder, bark, pine, and beech sawdust originated from wood processing industry. All these resources were carefully characterized in terms of their fraction composition, pH, buffer capacity, formaldehyde content and bulk density.

Determination of the fraction composition of particles was carried out using a Fritsch screening machine with a set of screens with mesh diameters of 8,0; 4,0; 2,0; 1,0; 0,50; 0,25 in the case of pine and beech sawdust. The set of meshes for wood powder and bark included fractions of 0,8; 0,5; 0,4; 0,315; 0,25; 0,125; 0,08 mm. Approximately 200 g of raw material (60 g in the case of wood powder) was taken from each batch using the quartering method. The sieving time was 15 minutes. The bulk density was calculated as the mass to volume (2L) ratio. The acid and alkaline buffer capacity was determined at 20°C and 100°C. Aqueous extracts of wood waste (0,5<0,25 mm fraction), previously dried to a constant weight, were prepared at a ratio of 25 g wood waste per 250 cm^3 of water. The wood waste was kept in water (20°C) for 30 minutes and boiled under reflux for 30 minutes, then separated from the extracts on a Büchner funnel with filter paper using a vacuum pump. 50 cm^3 of the extract was transferred by pipette to a 100 cm^3 beaker. Next, potentiometric titration was performed using 0.025 N sulphuric acid as a titrant, achieving pH 3,0 in the case of alkaline buffer capacity and 0.025 N sodium hydroxide as a titrant, achieving pH 7.0 for acid buffer capacity. Before the test pH of the aqueous extracts at 20°C was determined. Two aqueous extracts within each portion of raw material were prepared. Determinations were carried out three times and the results were averaged. Determination of formaldehyde content in raw material was performed by the perforator method according to PN EN 120:1994 standard.

The formaldehyde content was tested at 1% moisture content. The mass of the sample was reduced to 100 g.

The raw material samples were then processed by liquefaction according to the procedure described previously by Janiszewska et al. [2016]. Both, the products of liquefaction and raw materials used for liquefaction treatment were then characterized using the Fourier Transform Near Infrared spectroscopy (FT-NIR). VECTOR 22-N FT-NIR produced by Bruker Optics GmBH was used for spectral measurements in the range between 4000 cm^{-1} and 12000 cm^{-1} with the resolution of 8 cm^{-1}. The spectra pre-processing included computation of derivatives and vector normalization. Derivatives were calculated according to the Savitzky-Golay algorithm (2nd polynomial order, 17 smoothing points). Principal Component Analysis (PCA) was used for spectral data evaluation. OPUS 7.0 software package (Bruker Optics GmBH) was used for data processing and mining.

DISCUSSION

In order to characterize the raw wood waste materials, the determination of the fraction composition was carried out. The results of the sieve analysis are presented below.

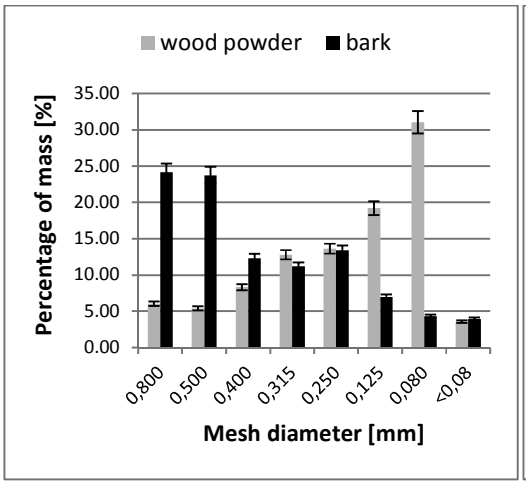

Fig. 1. Fraction composition of wood waste (wood powder and bark)

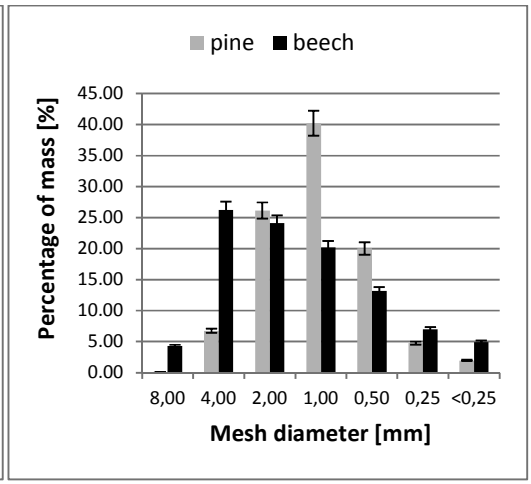

Fig. 2. Fraction composition of wood waste (pine and beech sawdust)

The screen analysis of particles indicated a great dispersion of the fractions depending on the type of waste. In case of bark 85% of the samples were belonging to the fractions ≤0,8 mm to ≥0,25 mm (Fig. 1). Similarly, around 90% of pine sawdust were fitting to the fraction ≤2 mm and ≥0,25 mm (Fig. 2). In case of beech sawdust same fraction (≤2 mm to ≥0,25 mm) amounted to 65% of the overall samples. Bigger fraction ≤8 mm to ≥4 mm constituted over 30% (Fig.2). Wood powder was characterised by a relatively high content of tiny fraction (≤0,125 mm to ≥0,08 mm) and accounted for over 50% (Fig.1). Considering the most optimal form, fraction ≤0,5 mm to ≥0,25 mm was selected as that usable for the liquefaction experiments. The summary of raw wood material properties (bulk density, formaldehyde content and pH) are presented in table 1.

Table 1. Characteristic of raw material for liquefaction treatment

Tested property	Measurement unit	Type of raw material			
		bark	pine sawdust	beech sawdust	wood powder
Bulk density	kg/m^3	218	57	62	96
Formaldehyde content	mg/100 g total dry mass	0.3	0.7	0.3	0.7
pH, tested in 20°C	-	3.7	4.3	4.7	4.3

The next stage was to test the acid and alkaline buffer capacity of wood waste used for liquefaction process. The influence of the type of wood waste on the buffer capacity is presented in Fig. 3 and 4. The results confirmed fact that the buffer capacity of the hardwoods is higher than in case of softwoods [Frąckowiak 1999].

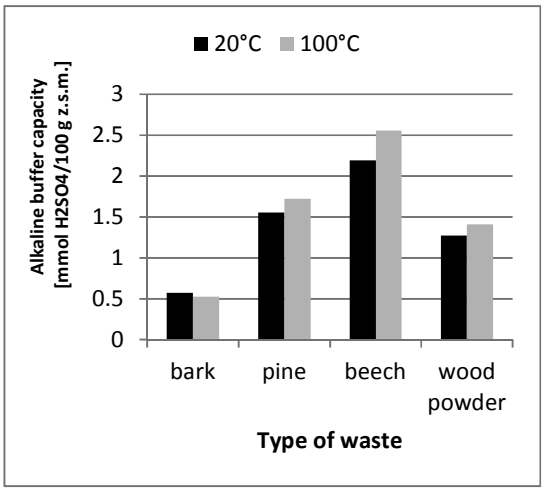

Fig. 3. Influence of waste type on the alkaline buffer capacity

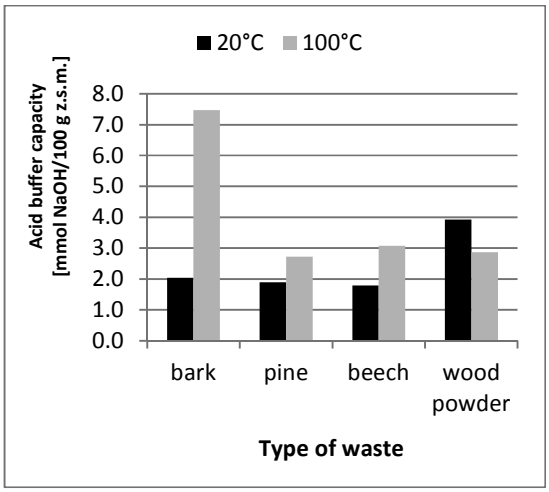

Fig. 4. Influence of waste type on the acid buffer capacity

Change of the pH value in comparison to change of buffer capacity is relatively small. Both pine and beech sawdust as well as wood powder have weak acid pH (Table 1). Bark waste pH were lower. In case of bark, pine sawdust and wood powder acid buffer capacity increased in comparison to the alkaline buffer capacity. It might have important influence on the mechanical properties, as well as formaldehyde content, in case of future use of the liquified wood as additive in the panels production. It was previously reported that the drop of mechanical properties and increase of formaldehyde content is observed with growth of acid buffer capacity [Frąckowiak 2005].

The spectral analysis in the NIR range was measured to screen for the chemical composition. Multivariate data analysis was performed in addition to standard spectra interpretation. Principal Component Analysis (PCA) was performed on spectra of raw materials and liquefied wood products (Figure 5 right). PCA searches for unique properties of spectra and separates sets of input data into groups of unique similarities allowing visualization of natural clustering of the data. The measure of the geometrical overlap of modeled groups is the selectivity coefficient *S*. The value of $S < 1$ indicates that groups are overlapping, $S = 1$ when two clusters are in contact, and $S > 1$ in case of two separated sets [Sandak J. et al. 2016]. It is expected that *S* should be >1 between all classes if the assurance of the unambiguous model is required. In fact, in case of raw resources the selectivity index for all investigated cases is >1 (ranging 1.3 to 4.7 as shown in Figure 5 left). However, in a case of liquefied products *S* value is lower than 1 in all cases ($0.2 < S < 0.7$). It is evident that all the raw materials can be easily distinguished before liquefaction, even that after the transformation process the same products become more homogenous (from the spectroscopic point of view). This suggests that the type of wood waste used for liquefaction has relatively little effect on the resulting products. Thus, it is assumed that any kind of investigated lingocellulosic wood waste might be used as a primary resource for liquefaction.

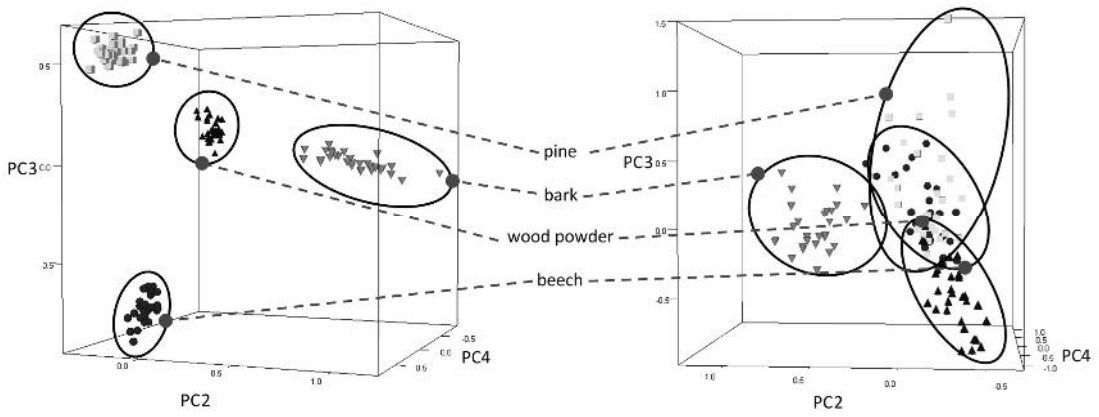

Fig.5. PCA of raw materials used for liquefaction treatment (pre-processing: 2nd derivative +VN, range: 11920-4050cm^{-1}) and liquefied wood product (pre-processing: 2nd derivative +VN, range: 10600-4130cm^{-1})

CONCLUSIONS

Liquefied wood can be considered as an alternative feedstock for various polymer materials and possess a great potential for practical implementations into several bio-resources converting industries. The results showed that all tested raw materials can be easily distinguished before liquefaction, however after the transformation process the same products become more homogenous from the spectroscopic point of view. This suggests that the type of wood waste used for liquefaction has relatively little effect on the resulting product and any kind of investigated wood waste might be used as a primary material for liquefaction.
Application of NIR spectroscopy in the research on liquefied wood proved to have a great potential for quality evaluation of both raw resources and products of their liquefaction. This technique allows non-destructive characterization of various material properties in relatively short time and at a low cost. Moreover, recent development in field of optics and electronics open new possibility for direct implementation of spectroscopy for on-line process monitoring. Accordingly, results of the presented research conducted by means of FT-NIR are currently confronted with equivalent tests scrutinized by means of miniaturized portable NIR equipment.

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Streszczenie: *Wpływ surowca drzewnego na skład chemiczny upłynnionego drewna.* Przedmiotem badań była ocena wpływu surowca drzewnego stosowanego podczas procesu upłynniania na skład chemiczny upłynnionego drewna. Upłynnieniu poddano różne typy odpadów drzewnych, w tym trociny sosnowe, trociny bukowe, mieszany (liściasto-iglasty) pył drzewny oraz korę, zgodnie z metodyką opisaną wcześniej przez autorów. Zbadano skład frakcyjny, pojemność buforową, pH, zawartość formaldehydu oraz gęstość nasypową surowca przeznaczonego do upłynnienia. Zarówno surowiec jak i produkty upłynnienia scharakteryzowano za pomocą spektroskopii w bliskiej podczerwieni. W celu jakościowej interpretacji widm wykorzystano analizę głównych składowych (PCA). Wykazano, że surowiec drzewny przed upłynnieniem jest łatwo rozróżnialny pod względem spektroskopowym, natomiast produkty powstałe po procesie upłynnienia mają skład chemiczny bardziej zbliżony. Wydaje sie zatem, że typ materiału poddanego upłynnianiu nie jest ograniczeniem do przeprowadzania procesu.

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