BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 63 (67), Numărul 3, 2017
Secţia
CHIMIE şi INGINERIE CHIMICĂ

OPPORTUNITY TO APPLY THERMAL DECOMPOSITION OF SPRUCE BARK AFTER EXTRACTIVES RECOVERY

BY

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Received: July 15, 2017
Accepted for publication: September 2, 2017

Abstract. The work explores the possibility to use the thermal decomposition of spruce bark (*Picea Abies*) in a second biorefinery flow sheet. Spruce bark was characterised and humidity, ash, hemicelluloses, cellulose and lignin content were determined. For the recovery of extractives two procedures were applied: the biomass was extracted with toluene-ethanol mixture using a conventional extraction and a 70% ethanol solution was used in an ultrasound assisted extraction process. In both cases the solid waste was subjected to pyrolysis conducted at 550°C under relatively low heating rate of 10°C/min. The aqueous phase was analysed by GC-MS. Similarities and some differences are highlighted by the GC-chromatograms and NP-gram characterisation, depending on the extraction procedures applied.

Keywords: biomass; extractives; pyrolysis; GC-MS; NP-gram.

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1. Introduction

Biomass is currently the largest renewable source in Romania and accounts for approximately half of total consumption of renewable energy in the EU. The socio-economic importance of biomass is high but often underestimated (Gonzalez-García *et al.*, 2014).

The global distribution of biomass highlights huge amounts yet unexploited (about 89%), with forest waste, agricultural, industrial and urban (Popa, 2014). The waste wood is completely untapped (used as a fuel in a considerable amount (about 50%) for local energy demand and only in rarely situation is converted to valuable chemicals or extractives) (Popa, 2014). The bark from forest species resulted as a solid waste in wood processing represents an important feedstock that can be subjected to a biorefinery process (Bujor *et al*., 2015).

Lignocellulosic biomass is composed of cellulose (25–50 wt%), hemicelluloses (15–40 wt%), lignin (10–40 wt%), extractives (0–15 wt%), and generally a small fraction of inorganic mineral matter (Strezov, 2014). The separation of extractives before processing is an interesting option for bark valorisation (Feng *et al*., 2013). There are known several compounds that could be extracted from lignocellulosic biomass in sequence using appropriate solvents (Table 1).

Table 1
Extractives from Bark

Solvent	Typical compounds removed in whole or part	References
Ethyl acetate	Phenolic acids, flavonoids, anthocyanins	Russell *et al.*, 2009
Methanol, methanol/water (50-90% v/v)	Anthocyanins, phenolic acids, catechins, cumarine, flavones, flavonoids, rutin, quercitine	Bleve *et al.*, 2008; Ross *et al.*, 2009
Ethanol, ethanol/water (10-90% v/v)	Anthocyanins, flavones, phenolic acids, tannins	Altiok *et al.*, 2008; Bleve *et al.*, 2008; Corrales *et al.*, 2009; Ross *et al.*, 2009
Ethanol 70% v/v	Total polyphenols	Talmaciu *et al.*, 2015 ; Ghitescu *et al.*, 2015; Lazar *et al.*, 2016
Chloroform	Flavonoids, free phenolic acids	Sharififar *et al.*, 2009
Dietil eter	Flavonoids, phenolic acids, cumarine	Ross *et al.*, 2009; Sharififar *et al.*, 2009
Hot water 80-100ºC	Proantocyanidines, phenolic acids, cumarine	Diouf *et al.*, 2009

Table 1
Continuation

Solvent	Typical compounds removed in whole or part	References
NaOH (2N-10N)	Tannins, phenolic acids bounds	Popa *et al.*, 2008; Ross *et.al.*, 2009
Petroleum ether	Phenolic acids, flavones, cumarine	Zhang *et al.*, 2009
Acetone/water (10-90% v/v)	Flavonols, hydroxycinamic acids, cumarine, xanthones	Altiok *et al.*, 2008; Sharififar *et al.*, 2009
n-hexan, isooctane, ethyl acetate	Flavonols, hydroxycinamic acids, anthocyanins	Alonso *et al.*, 2004
Acetone, acetone/water (10-90% v/v)	oleuropein, rutin, quercitine, flavanols, hydroxycinamic acids	Altiok *et al.*, 2008
Methanol/water (70% v/v)	Flavonols, quercitine, hydroxicinamic acids, hydroxybenzoic acid	Caridi *et al.*, 2007
Ethanol-toluene mixture	Waxes, fats, resins, and oils, plus tannins and certain other ether-insoluble components	Standard Test Method for Ethanol Toluene Solubility of Wood, 2001

But after extraction with various solvents a large amounts of residue remain. Pyrolysis represents an important process to valorise this residue. Many kinds of biomass species have been subjected to pyrolysis conditions to produce fuels, solvents and chemicals (Sonobe and Worasuwannarak, 2008), but the challenge is the economical separation of products for the chemicals and the liquid fuels markets.

Pyrolysis represents the thermal decomposition of biomass in the absence of oxygen (Le Roux, *et al.*, 2015). The products resulted in biomass pyrolysis include solid residue, oil and gases (carbon monoxide, methane, hydrogen, carbon dioxide) (Kan *et al*., 2016).

Depending on the final temperature and thermal environment pyrolysis will yield mainly solid residue at low temperatures, less than 450°C, when the heating rate is quite slow, and mainly gases at high temperatures, greater than 800°C, with rapid heating rates (Bridgwater, 2012). At an intermediate temperature and under relatively heating rates, the main product is oil (Parparita *et al*., 2014).

Pyrolysis temperature significantly influences the distribution and composition of products (Garcia-Perez *et al*., 2008; Westerhof *et al*., 2010). Generally, the oil yields reach their peak at temperatures between 400 and 550°C, and then decline after proceeding with heating. At temperatures higher

than 600°C, the oils and solid residue products are converted into gas due to the dominant secondary cracking reactions (Li *et al.*, 2007).

GC-MS analysis provides important information on the composition of pyrolysis products, due to good chromatographic separation and qualitative identification of compounds (Czégény *et al.*, 2012).

2. Experimental

2.1. Materials

Picea abies bark was obtained as waste from a wood processing company. Before extraction, bark was dried at room temperature, under normal aeration conditions. After drying, the spruce bark was milled in a GrindoMix GM 2000 equipment and passed through five successive sieves (by 0.25 - 1.25 mm diameters), for the particle size (d) distribution characterisation. For all experiments, the bark was used as a mixture of: 55% particles with a size between 0.25 and 1 mm, 30% particles of size smaller than 0.25 mm and 15% particles of size between 1 and 2 mm.

The specific solvents (ethanol and toluene) and chemicals have been provided by Sigma-Aldrich and Fluka companies.

2.2. Methods

Characterization of biomass

All methods applied for characterisation of bark (humidity, ash, hemicellulose, cellulose and lignin content) were performed following NREL Laboratory Analytical Procedures for standard biomass analysis.

The determination of hemicelluloses was performed using 1 g of spruce bark and 50 mL 2% H_2SO_4. The cellulose content was found applying the nitro-alcohol method using 1 g of spruce bark and 25 mL mixture (1 vol. HNO_3 and 4 vol. ethanol). The lignin content was determinate applying Klason-Komarov method using 1 g of bark and 15 mL 72% H_2SO_4.

Extraction procedures

Extraction with toluene-ethanol mixture was performed in a Soxhlet apparatus using 300 mL toluene-ethanol mixture in a liquid/liquid (L/L) ratio of 2/1 solvent and approximate 5 g of spruce bark. The ultrasound assisted extraction followed the protocol described by Lazar *et al.* (2016). 5 g of spruce bark and 50 mL ethanol-water (70% v/v) in a solid/liquid (S/L) 1:10 g sample mL^{-1} solvent were used.

For convenience the following abbreviations were used: SB – for unextracted spruce bark; SB-TolEtOH – for spruce bark extracted with toluene-

ethanol mixture; SB-UsEtOH – for spruce bark extracted with ethanol-water using a green ultrasound assisted extraction technique.

Pyrolysis of spruce bark

The pyrolysis experiments were performed under self-generated atmosphere in a glass reactor with an internal diameter of 30 mm and a total length of 350 mm. In each pyrolysis experiment 10 g of sample was placed inside reactor. Initial temperature was room temperature. Rate of the heating was 10°C/min, up to the final degradation temperature of 550°C, which was maintained for a final time of 15 min.

The pyrolysis products coṇsisted of volatile non-condensable compounds in the form of gases, volatile condensable compounds in form of an aqueous phase and an organic fraction (oil) and solid residue remained at the bottom of reactor. Cooling of volatile pyrolysis products was realised with a water-ice trap, which contained a test-tube for collection of liquid products, and a condenser cooled by a refrigerated bath at -15°C, to avoid lighter pyrolysis products to escape into gases.

Aqueous phase was separated by oil fraction for characterisation in details by gas chromatography. Diethyl ether was used as solvent for extraction of most part of organic compounds from the aqueous phase and for collection of oil fraction from the cold parts of reactor. Diethyl ether was evaporated as much as possible from the aqueous/oil fractions prior to GC analysis. Characterisation of pyrolysis aqueous fraction will be presented in this paper, while study of the pyrolysis oils and biochar will be subject of a future work.

Gas chromatography (GC)

A very easy method to characterise liquid products of the pyrolysis is gas chromatography (GC). The GC analysis of the aqueous phase was performed on an Agilent 6890N coupled with a 5975 inert XL MS detector. An HP5-MS capillary column was used, with 30 m length, 0.25 mm diameter and film thickness of 0.25 μm. A volume of 0.2 μL was injected by an automatic injector, using a split ratio of 10:1. Carrier gas was helium at a flow rate of 1.0 mL min^{-1}, to ensure the transport of the compounds through the column. The oven temperature was controlled according to the pre-set temperature program. For these experiments oven temperature was programmed from 40°C (2 min) to 300°C at a heating rate of 10°C min^{-1}. The final temperature of 300°C was held for 7 min. The injector and detector temperatures were maintained at 230°C. Compounds in liquid samples were identified according to the NIST database library.

3. Results and Discussion

A proximate analysis of spruce bark (Table 2) reveals a valuable composition suitable for a biorefinery approach.

Table 2
Analysis of Spruce Bark

	Humidity	Ash content	Hemicelluloses	Cellulose	Lignin
Percentage, [%]	8.8	1.8	39.3	29.3	42.4

Comparing with data reported in literature (Strezov, 2014), the spruce bark is a feedstock rich in hemicelluloses and lignin.

3.1. Pyrolysis Results

After the pyrolysis procedure, mass balance for the three samples is presented in Table 3:

Table 3
Pyrolysis Yield for Unextracted and Extracted Spruce Bark

	Gas, [%]	Aqueous phase, [%]	Oil, [%]	Solid residue, [%]
SB	19.5	25.7	18.2	36.6
SB-TolEtOH	19.4	27.3	15.6	37.7
SB-UsEtOH	14.6	27.4	21.3	36.7

The pyrolysis of spruce bark at 550°C gave about 20 wt% gases, 20-27 wt% aqueous fraction, 16-24 wt% oil and 37 wt% solid residue. Of the products resulted from pyrolysis, the highest amount was for solid residue. Between samples, pyrolysis doesn't give significant differences regarding quantity of the products.

3.2. GC Chromatograms

The GC-chromatograms of the aqueous phase (Fig. 1) show that many organic compounds formed by thermal degradation of spruce bark structure are soluble in the pyrolysis water. These are polar compounds such as acids, alcohols, aldehydes and ketones, formed mainly from the sugar fraction of the biomass. The aqueous phases have a similar distribution of compounds, with very small differences in the relative intensities of the peaks. The large peak in the 1.6 - 2.4 min range of retention time represents water and the spike at ~ 1.95 min stands for traces of diethyl ether from the separation of aqueous and oil fractions.

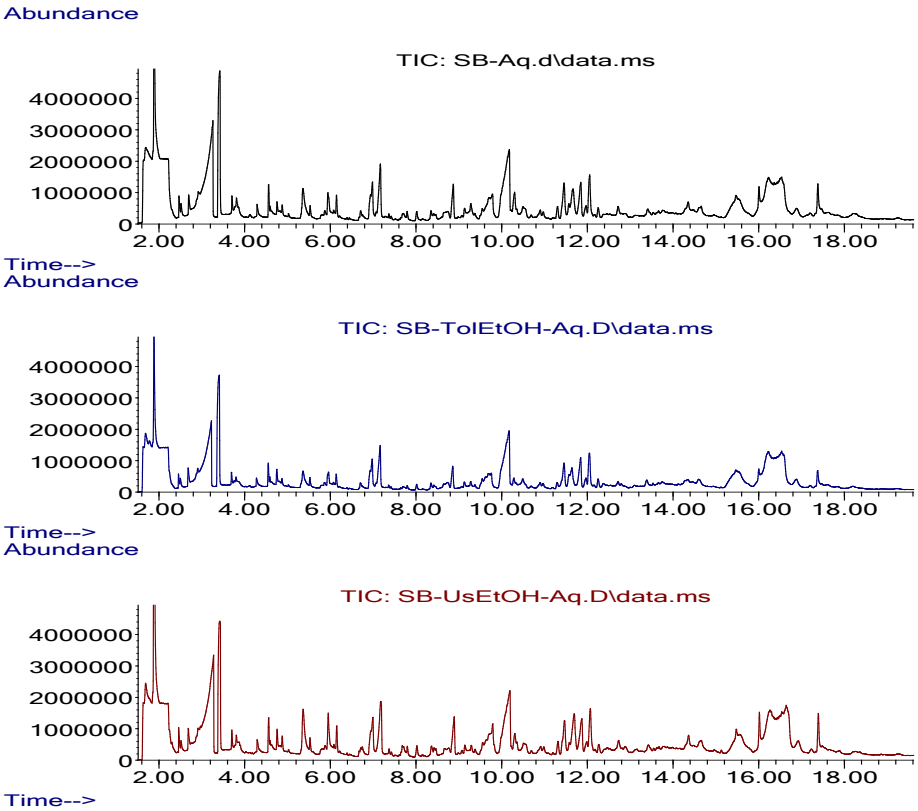

Fig. 1 – Total ion chromatograms for spruce bark pyrolysis aqueous phase.

Next studies will perform detailed analysis of the chromatograms to identify most significant compounds in pyrolysis aqueous phases.

3.3. Global Characterisation of Pyrolysis Liquids by NP Grams

The distribution of compounds in pyrolysis aqueous phase is described by the NP-gram curves (NP stands for normal paraffins) drawn in Fig. 2. NP-gram curves are calculated based on the GC chromatograms shown in Fig. 1. For drawing the NP-grams a preliminary GC analysis of a standard is needed. This standard should cover the entire retention time range of the sample chromatogram.

Polyethylene (PE) pyrolysis oil is generally used as standard because it contains homologue series of saturated and unsaturated normal paraffins, from pentane (C_5H_{12}) or lighter to triacontane ($C_{30}H_{62}$) or heavier, depending on the pyrolysis conditions. The chromatogram of PE oil obtained on a non-polar column gives a series of peak pairs corresponding to unsaturated and saturated

normal paraffins, in order of increasing number of containing carbon atoms. The retention times of the saturated normal paraffins are established and used as reference for the retention times of the compounds in sample chromatogram. Basically the chromatogram of the sample is compared with that of the PE oil (Kan *et al.*, 2016). All compounds in the sample that appear in the retention time range of two consecutive normal paraffins are considered to have the carbon number (n-C) equal to the number of carbon atoms of the higher parrafin. For example, all compounds in the sample appearing in the chromatogram after the retention time of hexane but before the retention time of heptane are considered to have the carbon number of seven (n-C_7). The sum of percentage areas for all peaks in a carbon number range is represented versus the corresponding carbon number. Considering the previous discussion on the first zones in the chromatograms (before 2.1 min for oils and before 2.4 min for aqueous fractions), in which water and diethyl ether are the main compounds, this area was not included in drawing the NP-grams.

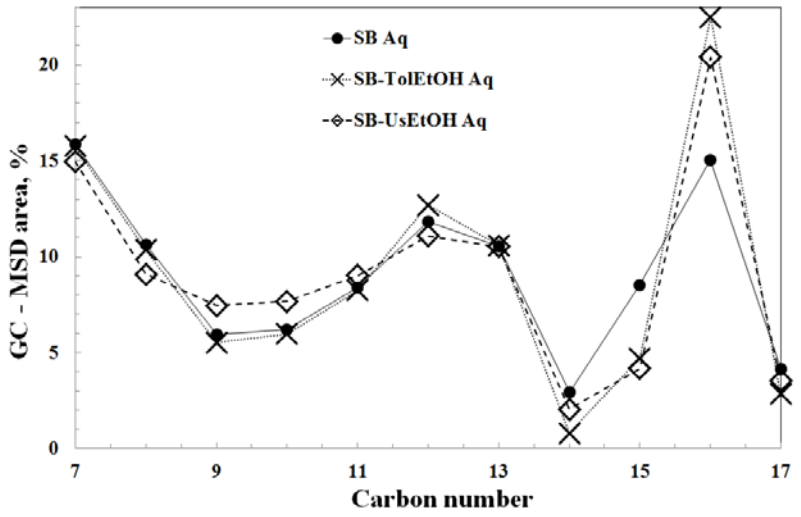

Fig. 2 – NP grams of pyrolysis aqueous phase

NP grams of pyrolysis aqueous phase (Fig. 2) show similar composition of fractions, with only few differences in the relative quantities of compounds between samples. There is a relatively narrow distribution of organic compounds soluble in pyrolyis water, from n-C7 to n-C17. Three major peaks were observed in NP-grams, at n-C7, n-C12 and n-C16. The composition of aqueous fraction from the pyrolysis of spruce bark extracted with toluene/ethanol mixture was similar with that of the unextracted sample in the n-C7 – n-C13 range of carbon number and with that of the sample extracted with ultrasounds/ethanol in the n-C14 – n-C17 range of carbon number.

4. Conclusion

Pyrolysis offers a flexible and attractive way of converting solid biomass into some easily stored and transported products, which can be successfully used for the production of heat, power and chemicals.

Pyrolysis aqueous fraction consists of pyrolysis water in which polar compounds such as acids, alcohols, aldehydes and ketones, formed mainly from the sugar fraction of the biomass are soluble. Advanced extraction or chemical reactions in water phase would be necessary for further utilisation of this fraction.

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POSIBILITATEA DE A UTILIZA DESCOMPUNEREA TERMICĂ PENTRU COAJA DE MOLID DUPĂ RECUPERAREA EXTRACTIVELOR

(Rezumat)

Lucrarea prezintă posibilitatea de a utiliza degradarea termică (piroliza) în etapa de biorafinare secundară a cojii de molid (*Picea Abies)*. Materia primă vegetală a fost caracterizată şi s-au determinat umiditatea, cenuşa şi conţinuturile de hemiceluloză, celuloză şi lignină. În etapa primară de biorafinare s-a urmărit separarea extractibilelor. Pentru aceasta au fost aplicate două procedee: extracţia convenţională (Soxhlet) cu amestec toluen-etanol şi extracţia asistată de ultrasunete cu o soluţie apoasă de etanol 70%. În ambele cazuri, materialul solid rezultat după separarea extractibilelor a fost supus degradării termice. Piroliza s-a realizat la presiune atmosferică, la o temperatură intermediară de 550ºC, la viteze relativ mici de încălzire. Fracţiile apoase au fost analizate prin GC-MS. Cromatogramele obţinute au evidenţiat asemănări şi diferenţe compoziţionale ce sunt determinate substanţial de procedeele de extracţie aplicate în etapa primară de separare a extractibilelor.