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ASSESSEMENT OF CRUDE LIQUID PHASE RESULTED IN HYDROTHERMAL CARBONZIATION OF SPRUCE BARK WASTES

BY

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Abstract. This work aims to investigate the influence of process parameters on chemical composition of liquid phase resulted from hydrothermal carbonization of spruce bark (*Picea abies*). The thermal conversion of biomass was carried out at 200 and 240°C with a residence time of 2.5 and 5 h and a solid to liquid ratio of 1:10. Chemical characterization of liquid phase showed a presence of an important content of polyphenols and carbohydrates. The process parameters had a significant influence on chemical composition. Thus, an increase in temperature and residence time leads to a decrease of total polyphenols content and carbohydrates as well.

Keywords: bio-crude liquid; hydrothermal carbonization process; total polyphenols content; total reducing sugars content; spruce bark biomass.

1. Introduction

In recent years, biomass showed an attractive and important interest in order to obtain fine chemicals and bio-fuels, due to the fact that it is a renewable

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and sustainable resource. Also, biomass leads to reduction of consume of fossil fuel and to decrease of environmental pollution (Huang *et al.*, 2021).

Biomass can be converted into high value-added products through biochemical, thermochemical, mechanical and physical processes. Several methods for thermal conversion of biomass were well known: pyrolysis, torrefaction, gasification, hydrothermal carbonization (Volf *et al.*, 2020).

Hydrothermal carbonization process (HTC) is considered one of the most important thermochemical conversion method due to the following reasons: the possibility of using wet biomass, an easy operation with mild process parameters, an eco-friendly process (Bejenari *et al.*, 2021; Kojić *et al.*, 2021).

The distillate water or deionized water are usually used solvents in the HTC process. Water provides the necessary reaction medium, and in the same time, is able to catalyse reactions such hydrolysis, dehydration and decarboxylation (Drabold *et al.*, 2020).

Thermal conversion of biomass leads to formation of a high carbon solid product with a wide range of applications: soil amendment, solid fuel, capacitor, cost efficient adsorbent, medical applications (Fang *et al.*, 2018; Hu *et al.*, 2010), as well as a bio-crude liquid, whose composition depends directly on feedstock chemical composition (Gimenez *et al.*, 2020).

In this research, the hydrothermal carbonization was done by varying the temperature, residence time and biomass to liquid ratio after which different yields and conversion degrees were achieved. The temperature of 200 and 240°C and residence time of 2.5 and 5 h were varied while solid to liquid ratio was 1:10. The main objectives of this work are: i) to obtain a bio-crude liquid by hydrothermal carbonization of spruce bark, ii) to investigate the influence of process parameters on chemical composition of bio-crude liquid, iii) to assess the physical and chemical characteristics of liquid phase.

2. Materials and Methods

2.1. Material

The spruce bark (SB) used in this work was collected from Vatra Dornei area and was supplied from the forestry and wood processing industry. SB was cleaned from sand, dust and other impurities and a soft drying process was applied in order to eliminate the humidity. When the SB achieved a constant weight the material was milled and a powder with 0.5-2 mm particle size was obtained.

2.2. Methods

2.2.1. *Hydrothermal Carbonization*

The hydrothermal carbonization process (HTC) was carried out in a stainless-steel autoclave with a 0.2 L glass vessel inside. A mixture of 5 g of feedstock and 50 mL of distillate water were immersed in reactor. The mixture was allowed to stand 2 hours for a better dispersion of biomass in water. The process parameters were varied in order to analyse the influence of HTC process on final products. The experiments were performed at 200 and 240°C, with a residence time at 2.5 and 5 h. After each experiment, the reactor was cooled down to room temperature and a filtration process was applied in order to separate the solid (hydrochar) and liquid phase (bio-crude liquid). Hydrochar was washed with distillate water until the yellow colour of the wash water could no longer be observed. Bio-crude liquid and wash water were collected and refrigerated for next characterization while hydrochar was dried at 105°C and kept dry for further characterization.

The yield in hydrochar and the conversion degree were determined following the equations:

$$Yield = \frac{weight_{\ hydrochar}}{weight_{\ spruce\ bark}} \times 100, \% \tag{1}$$

$$Conversion\ degree = \frac{weight_{\ spruce\ bark} - weight_{\ hydrochar}}{weight_{\ spruce\ bark}} \times 100, \% \tag{2}$$

2.2.2. *pH Determination*

The bio-crude liquid and wash water pH value were determined using a Multi 305i pH-meter. Before the measurements, the pH-meter was calibrated using two buffer solutions with known pH (in this case 4 and 10). For each experiments the bulb was washed with distilled water and carefully cleaned with paper to remove any traces of previous used solution.

2.2.3. *Total Polyphenol Content*

Total polyphenolic content (TPC) was determined using the Folin-Ciocalteu (F-C) method (Ignat *et al.*, 2011), following the same protocol described by Lazar and co-authors (Lazăr *et al*., 2016). In short, an aliquot (bio crude liquid and wash water) was mixed with distillate water, sodium carbonate solution and Folin-Ciocalteu reagent, and the resulted mixture was allowed to stand for 1.5 h at room temperature, protected from light. In order to determine the TPC, the absorbance of mixture was read at 765 nm using a Cintra 101 GBC spectrophotometer. Previously the calibration curve for Gallic acid as standard was performed. TPC is expressed in mg Gallic acid equivalents (GAE) per g spruce bark dry weight. All experiments were performed in triplicate and the average was considered.

2.2.4. *Total Reducing Sugars Content*

The total reducing carbohydrates content was determined using the dinitrosalicylic acid method (DNS), following the protocol described by Miller (Miller, 1959). Thus, the samples (bio-crude liquid and wash water) were mixed with 3-5, dinitrosalicylic acid (DNS) reagent. The final mixture was kept on a bath water at 95°C for 15 min, after which it was cooled at room temperature. Using a UV-VIS Cintra 101 GBC spectrophotometer, the absorbance at 540 nm was evaluated. The calibration curve with glucose as standard was previously performed. Total reducing carbohydrates content is expressed in mg per g spruce bark dry weight. All measurement were performed in triplicate and average was considerate.

3. Results and Discussion

3.1. Hydrothermal Carbonization Process

The main advantage of HTC process is the possibility of using wet biomass. While a pre-drying process is no more necessary, the conversion is cost-efficient. The HTC process is applied at mild temperature (180-300°C) with self-generated pressure and residence time for several hours (1-16 h).

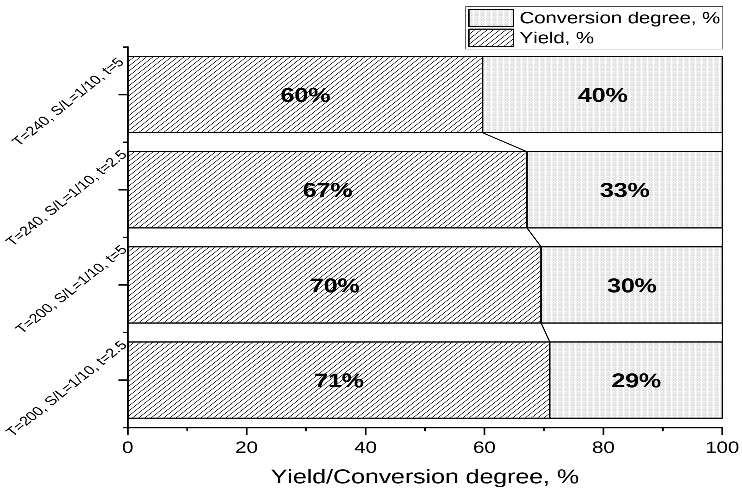

Fig. 1 – Yield of hydrochar and conversion degree of SB during HTC process, where T – temperature, S/L – solid to liquid ration, t – time.

In Fig. 1 are presented the yields of hydrochar and the conversion degree obtained after spruce bark HTC at 200 and 240°C with residence time at 2.5 and 5 h, and solid to liquid ratio 1:10. It can be seen that both parameters, temperature and time have a significant influence on yield and conversion degree. Thus, with increase of temperature a decrease of yield and consequently an increase of conversion degree was observed. The residence time showed similar. The literature reported analogous data yield: for hydrochar between 50-80%, while for liquid phase the values obtained were between 5-20% (Funke and Ziegler, 2010; Qambrani *et al.*, 2017)

3.2. pH Determination

The Fig. 2 highlights the pH value of the liquid phase and wash water. The pH values indicate an acid character of both samples. The acidity of the samples is due to the products resulting from the decomposition of the main compounds of lignocellulosic biomass and their transition to the liquid phase. Small differences in the pH values were identified with the increase of temperature and time. Thus, the increase of temperature leads to a reduced increase in pH, while increase in reaction time leads to a small decrease in the pH profiles.

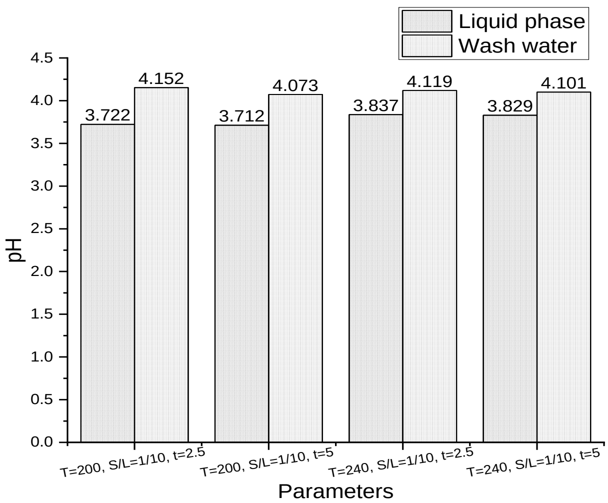

Fig. 2 – pH value of liquid phase and wash water,
where T – temperature, S/L – solid to liquid ratio, t – time.

Nakason and co-workers reported a similar behaviour for the liquid phase obtained in HTC process of the cassava rhizome. The decrease in pH is due to the hydrolysis reaction and the decomposition of the compounds in the cassava rhizome and their transition into the liquid phase in the form of sugars, organic acids such as acetic, lactic, propionic, levulinic and formic acids, while increasing the pH value is due to polymerization and condensation reactions of degraded biomass products (Nakason *et al.*, 2018).

Xu and co-workers reported in their research that the acidic or alkaline character of liquid phase depends on the type of biomass. Thus, the acidic character of bio-crude liquid is characteristic for samples which resulted from HTC process of lignocellulosic biomass, due to the formation of a variety fatty acids. The alkaline character is characteristic for liquids resulted from HTC process of protein-rich biomass (Xu *et al*., 2020).

3.3. Total Phenol Content

The total polyphenols content in the liquid phase and the wash water were determined following the same procedure applied by Lazăr and co-authors (Lazăr *et al*., 2016). From the experimental data presented in table 1 it is observed that the liquid phase has a higher polyphenols content compared to the wash waters. It was noted that the increase of temperature and of residence time did not significantly influence the total polyphenols content.

Table 1
Total Polyphenols Content

Working parameters	TPC (mg GAE/g spruce bark)	
	Liquid phase	Wash water
T=200°C, t=2.5, S/L=1/10	12.1602	7.7047
T=200°C, t=5, S/L=1/10	10.0978	7.0122
T=240°C, t=2.5, S/L=1/10	10.8786	8.5029
T=240°C, t=5, S/L=1/10	12.7524	8.3414

A very recent study on HTC applied to coffee grounds reported 22.45 mg GAE/g coffee grounds in liquid phase using as process parameters 180°C for 30 min (Massaya *et al*., 2021). The total polyphenols content in liquid phase depends heavily on the biomass subjected to HTC.

3.4. Total Reducing Sugars Content

The method using dinitrosalicylic acid (DNS) is a conventional one but simple, wide available and suitable for determining the concentration of carbohydrates in liquid samples (Wood *et al*., 2012), respectively in the crude liquid and wash water resulted from HTC process.

After the conversion of spruce bark using HTC and process parameters presented in Table 2, a relatively low concentration of carbohydrates was observed in crude liquid and in wash waters as well. The increase of temperature and time leads to a decrease in the concentration of reducing carbohydrates.

Table 2
Total Reducing Carbohydrates Content

Process parameters	Total reducing sugars content (mg/g spruce bark)	
	Liquid phase	Wash water
T=200°C, t=2.5, S/L=1/10	5.1153	3.1928
T=200°C, t=5, S/L=1/10	4.8821	2.5124
T=240°C, t=2.5, S/L=1/10	4.6974	1.9698
T=240°C, t=5, S/L=1/10	2.5696	1.9129

Xiao and co-authors obtained a concentration of 0.48 mg/mL of sugars in the liquid phase resulted from the hydrothermal conversion process of spirulina at 200°C, and for higher temperatures a decrease in reducing sugar content (Xiao *et al.*, 2019).

Nakason and co-workers reported that, the reducing sugars found in the liquid phase resulting from the hydrothermal carbonization process of cassava rhizome are: xylose, glucose, galactose, arabinose and mannose (Nakason *et al.*, 2018).

3.5. Dry Matter Determination

As the liquid phase and the wash water can be kept for a relatively short period of time and a degradation of both samples were observed after one week, it was necessary to find a way to preserve the samples longer. A better preservation of bio-crude liquid and wash water could be: samples concentration, drying, lyophilisation. In all this procedures information on dry matter content are useful. Thus, both samples obtained after spruce bark hydrothermal conversion were placed on a bath water at 105°C until a total evaporation of water was observed. The dry matter was evaluated and the results are presented in Table 3.

Table 3
Dry Matter Content

Process parameters	Dry matter content (g dry matter/100 g spruce bark)	
	Liquid phase	Wash water
T=200°C, t=2.5, S/L=1/10	9.1291	4.9996
T=200°C, t=5, S/L=1/10	5.6197	3.9997
T=240°C, t=2.5, S/L=1/10	5.4193	4.1995
T=240°C, t=5, S/L=1/10	4.6735	3.3997

4. Conclusions

There are two distinct phases resulted after spruce bark hydrothermal carbonization process of spruce bark. The most relevant is the hydrochar, a value-added product obtained with a yield of 60-70%. However, interest have to be attributed also to liquid phase that still presented an important chemical composition. Due to the decompositions of the main components presented in biomass (hemicelluloses, cellulose and lignin), a significant content of polyphenols (10-12 mg GAE/g spruce bark) and carbohydrates (2-5 mg/g spruce bark) were identified in liquid phase. In addition, the bio-crude liquid have an acid character. The decrease in pH is due to the hydrolysis reaction and the decomposition of the compounds and their transition into the liquid phase in the form of sugars and organic acids such as acetic, lactic, propionic, levulinic and formic acids.

Considering the chemical composition of bio-crude liquid obtained after spruce bark thermal decomposition some application have to be investigated in order to consider this secondary product as a resource.

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EVALUAREA CARACTERISTICILOR FIZICO-CHIMICE
A FAZEI LICHIDE OBȚINUTE ÎN PROCESUL DE HIDROTERMOLIZĂ A
COJII DE MOLID

(Rezumat)

Lucrarea prezintă analiza influenței parametrilor de proces asupra compoziției chimice a fazei lichide rezultate din procesul de hidrotermoliză a cojii de molid (*Picea abies*). Conversia termică a biomasei a fost realizată la 200 și 240°C în intervalul de timp de 2,5 și 5 h, iar raport solid: lichid de 1:10. Caracterizarea chimică a fazei lichide a arătat prezența unui concentraţii importante de polifenoli și carbohidrați. Parametrii de proces au o influență majoră asupra compoziției chimice a produselor rezultate. Astfel, o creștere a temperaturii și a timpului de conversie conduce la o scădere a conținutului total de polifenoli și a conținutului de carbohidrați în fracţia lichidă rezultată.