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COMPARATIVE STUDY OF PREHYDROLYSIS METHODS FOR VEGETAL MATERIALS

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Abstract

This paper presents the results obtained using the prehydrolysis treatments of rapeseed stalks depending on regime and the catalyst. The vegetal materials were subjected under different temperature conditions and then characterized for the yield reducing substances. The differences between samples have been established by using FTIR and depend on the successive hydrolytic treatments of dynamic and static regime in the presence of various catalysts. The experimental data show that the hydrolysis reaction induces the modification of cellolignin functionality.

Key words: dynamic regime, FTIR, prehydrolysis, rapeseed stalks, static regime

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1. Introduction

Production of biofuels and “green chemical” from renewable resources is of great interest as an alternative to fuels and fossil chemicals usual. A possible solution to fill the lack of energy in the world is the use of biomass as a sustainable alternative source of energy used to produce chemicals and biofuels with high added value (Xu et al., 2013).

Biomass residues resulting from agricultural crops (such as rapeseed stalks, wheat straw, barley, corn, sugar cane etc.) and wood waste (softwoods, hardwoods) are a significant source of raw materials, untapped properly and present in high quantities. These materials contain polysaccharides (cellulose and hemicellulose), which can be released by hydrolysis for the production of bioethanol and green chemicals. Interest for the use of biomass as a potential source of energy and chemical intermediates increased in recent years (Saxena et al., 2009), because the vegetal materials are biodegradable, not expensive and can be converted to

valuable products with numerous applications in various industrial fields

Thus, we are witnessing currently studies performed for bio-fuels production of second generation in which cellulosic materials play a key role as secondary resources from agriculture or forestry, in particular energy crops on lands without the agricultural value.

The rapeseed stalks (*Brassica napus*) represent an attractive feedstock for several specific applications: production of bioenergy, production of energy with thermal applications, such as pyrolysis (Jeong et al., 2010); production of biodiesel (Šimáček et al., 2009), production of bioethanol due its high content of carbohydrates (more than 60%) (Lu et al., 2009); production of fermentable sugars (Kang et al., 2012); production of chemical compounds, such as glucose, xylose, acetic acid, furfural and 5-hydroxymethylfurfural (Jeong et al., 2010).

These applications involves a step of pretreatment, classified according to catalyst, operating temperature, method of energy supply, hydrodynamic regime, methods for the introduction

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of reactants and evacuation of products, while not all were sufficiently well developed to become feasible in the application processes are carried out on an industrial scale (Kusch and Morar, 2009).

Most frequently applied methods implies, e.g. the use of water vapors (Cara et al., 2008) or explosions by carbon dioxide (Zheng et al., 1998); hot water treatment (Mosier et al., 2005), chemical processes that involves acidic (Lloyd and Wyman, 2005) or alkaline treatments (Kaar and Holtzapfle, 2000) or the organosolv pretreatment. Thus, at present, vegetal biomass pretreatment methods are divided into physical, chemical, physico-chemical (Zhao et al., 2009) and biological (Kusch and Morar, 2009) processes.

The present paper was performed in order to establish optimal working conditions at the prehydrolysis of the studied vegetal material, namely rapeseed stalks, in the two operating regimes: dynamic, static and moderate pressure.

2. Materials and methods

2.1. Raw materials

Samples of rapeseed stalks were collected from different fields after harvest.

The FTIR analysis were performed using cellolignins obtained after hydrolytic treatments in static and dynamic regime, denoted as: CL_S1-cellolignin obtained by hydrolysis with 3% solution of $\text{Al}_2(\text{SO}_4)_3$ and CL_S2-cellolignin obtained by hydrolysis with 0.5% solution of H_2SO_4 .

2.2. Hydrolysis of the vegetal materials

The prehydrolysis process is preferred for the complex and integral recovery of chemical components of vegetal materials: the polysaccharides towards obtaining the glucose and further bioethanol and lignin as a source of aromatic compounds with added value. In order to evaluate the hydrolytic potential of the vegetal material represented by rapeseed stalks, we performed the prehydrolysis in two operating regimes, namely under dynamic

conditions (reactive flow of 2mL/min at predefined temperature) and static conditions (predefined temperature and time) with 3% $\text{Al}_2(\text{SO}_4)_3$ solution (S1) and 0.5% H_2SO_4 solution (S2) (Liu and Wyman, 2003, 2004). The schematic representation of the hydrolytic conversion during the pretreatment of the vegetal material is shown in Fig. 1 (Panzariu, 2013).

The pretreatment resulted in two fractions: a solid one (cellolignin), and a liquid one, containing oligosaccharides, monosaccharides, decomposition products of sugars, fractions of lignin with low molecular weight. The liquid fractions obtained from these prehydrolytic treatments were analyzed for the content of total reducing substances (TRS).

2.3. Sample analysis

2.3.1. Concentration of the total reducing substances (TRS)

The total reducing substances were determined by the method with dinitrosalicylic acid (DNS) using a JASCO V-550 spectrophotometer at a wavelength of 540 nm.

Prior to determining the total reducing substances the posthydrolysis of the hydrolysates was conducted using NREL standard method No 002 (Adney and Baker, 1996), with 4%(w/w) H_2SO_4 solution, at 120°C and for 60 min residence time.

2.3.2. FTIR spectroscopy

The FTIR spectra of cellolignins were recorded, in a KBr pellet, with a DIGILAB-SCIMITAR FTS 2000 spectrometer, in the 4000-400 cm^{-1} range, with a resolution of 4 cm^{-1} , 32 scans.

3. Results and discussion

3.1. Raw material composition

The raw material used was rapeseed stalks with the following chemical composition: ethanol-benzene extractives=2.43%; cellulose=45.94%; lignin=26.56%; easily hydrolyzable polysaccharides (PUH)=36.28%; slow hydrolyzable polysaccharides (PGH)=36.06% (Panzariu and Malutan, 2012a).

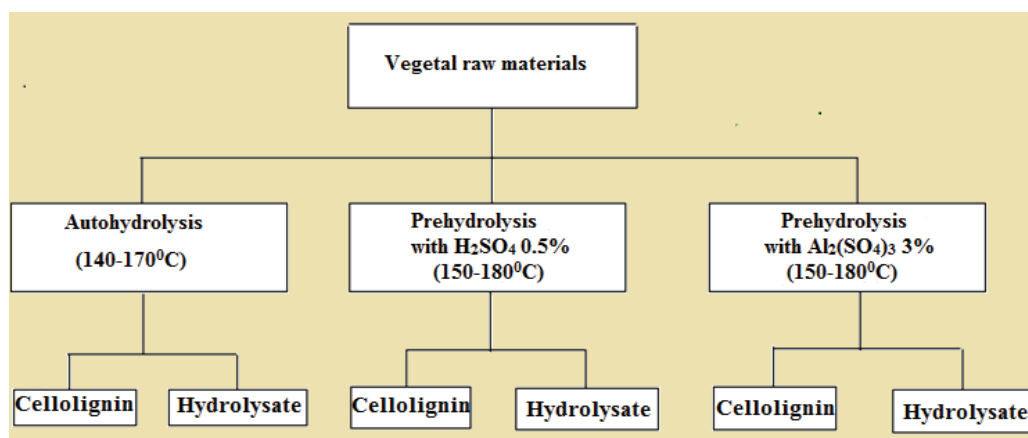


Fig. 1. Schematic representation prehydrolysis of processes

The cellulose, lignin, PUH and PGH contents were determined according to the classic methods of analysis (the cellulose through the nitro-alcoholic method, the lignin through the Klason-Komarov method) (Rozmarin et al., 1984).

3.2. Yield of total reducing substances (TRS)

The prehydrolysis is a preliminary treatment of vegetal material, which may be performed using water or acidic regime, at high temperatures (150°C-160°C). For prehydrolysis different chemicals may be used (mineral acids, organic acids, sulfite solutions etc.), but the most used agent of prehydrolysis is water.

Rogalinski et al. (2008) have achieved a pretreatment of rye straw with hot water in a continuous feeding reactor. The degree of solubilization of the vegetal material was high, the yield of the undesired degradation products increased with increasing with the severity of pretreatment. Ingram et al. (2009) studied the pretreatment of rye straw with hot water in a semi-continuous reactor and concluded that a temperature range between 170°C and 230°C would be optimal.

The experimental data obtained in the autohydrolysis, at the prehydrolysis with acid catalysts and the prehydrolysis with salt of rapeseed stalks are shown in Fig. 2 (a-b). These data are compared, as histograms and show the influence of nature and the addition of the catalyst on the yields of reducing substances in the prehydrolysis, depending on the temperature and prehydrolysis regime applied.

Comparing with other substances reducing yields of prehydrolysate (reported at oven dried material) obtainable from prehydrolysis with three types of catalysts, it is found that, when the temperature rises, this results in increasing yields of reducing substances. It can be observed that, when using dynamic regime, lower values of the reducing substance was obtained in the presence of 3% $\text{Al}_2(\text{SO}_4)_3$ solution, instead using the static regime with saline catalyst to obtain the best performance at 170°C. In the dynamic mode, the yields of reducing substances at autohydrolysis may reach values of up to 11% sugars (reported at the relative content of hemicellulose), which imposes the use of a specific catalyst. Low yields obtained in this case would be due to the high percentage of ash of vegetal material, which plays an important role in catalyst deactivation.

Varying the pH of prehydrolysate within the limits 4-4.5 is insufficiently for a significant depth hydrolysis (Panzariu, 2013). By using a solution of 0.5% H_2SO_4 at prehydrolysis of rapeseed stalks, yields of sugar reach the maximum values of 42%-45% related to hemicellulose at the temperature of 150-160°C. In static regime, at prehydrolysis of rapeseed stalks with 3% solution of $\text{Al}_2(\text{SO}_4)_3$ the yields of sugars can reach a maximum of 44%

reported to hemicelluloses, for temperatures of 170°C.

The treatment of vegetal material with hot water, as well as with hot water under pressure can result in improved yields of pentoses and reduced amounts of by-products.

3.3. FTIR analysis

The following ratios of the relative absorbance for different groups were defined (Malutan et al., 2008):

- Mean value of OH groups = average (A_{3430} , A_{1370} , A_{1165} , A_{1043})/ $A_{1510(1600)}$

- Mean value of phenolic OH groups = $A_{1370}/A_{1510(1600)}$

- Mean value of OCH₃ groups = average (A_{2890} , A_{1460} , A_{1420})/ $A_{1510(1600)}$

- Mean value of C=O groups = $A_{1720}/A_{1510(1600)}$

- Mean value of aromatic ring = average (A_{1510} , A_{1600} , A_{844})

- Ratio of aliphatic to aromatic signals = $A_{2936}/A_{1510(1600)}$

- S/G ratio A_{1330}/A_{1269}

The analysis of the FT-IR absorption spectra of the obtained celollignins shows that the OH total groups relative to the phenylpropane units increase from 0.68 to 2.27 (Table 1), with any increasing of operating temperature between 150-170°C, when using $\text{Al}_2(\text{SO}_4)_3$ as catalyst. At the temperature of 160°C the number of OH alcoholic groups is constant, around 1. Methoxy groups recorded an increase from 0.68 to 1.05 with temperature increasing from 150-170°C. Also the C=O groups vary from 0.72 to 1.54 (a doubling of the C=O). These increases of the number of functional groups are the results of functionalization reactions taking place during continuous hydrolytic treatments in the presence of 3% $\text{Al}_2(\text{SO}_4)_3$ solution.

In the operating temperature range of 160°-180°C it is observed that total OH groups increase significantly at 170°C. The alcoholic OH groups show a decrease from 1.14 to 1.00 (Table 2) with increasing temperature. Methoxyl groups is decreasing at 170°C and the same is carried and C=O groups. These changes are due to functionalization reactions that occur throughout discontinuous hydrolytic treatments in H_2SO_4 solution. By analyzing the data obtained during discontinuous hydrolytic treatments in the presence of $\text{Al}_2(\text{SO}_4)_3$, it is found that the number of Ar-OH groups increases from 1.42 to 2.95 with increasing the operating temperature from 160°C to 180°C (Table 3). In the opposite direction, the number of alcoholic OH groups decreases when the temperature rises. The same is valid for methoxyl groups when the temperature rises there is a gradual decrease in their number. The number of C=O groups show an increase from 0.81 to 4.01 (Table 4). When the temperature rises from 170°C at 180°C there is a

large increase of C=O groups number due to the functionalization reactions, throughout the discontinuous hydrolytic treatments in the presence of Al₂(SO₄)₃.

We observed that the number of total OH groups, related to phenyl propane units increases from 1.38 to 2.71 (Table 4) with increasing the operating temperature between 150-170°C, when using H₂SO₄ catalyst. The alcoholic OH-groups occurs an increase low at 160°C compared to other temperatures. The C=O groups show a decrease from

1.67 to 0.78, all these changes being due to functionalization reactions, during the discontinuous hydrolytic treatments in the presence of H₂SO₄ catalyst.

From the analysis of FTIR spectra obtained for cellulignins there are observed these maximum intensity characteristic bands of the valence vibration, ν(C-O) from 1059 to 1034 cm⁻¹ and ν(O-H) at 3414-3428 cm⁻¹. The maximum decreases in intensity with increasing temperature from 150°C to 170°C (Panzariu and Malutan, 2012b).

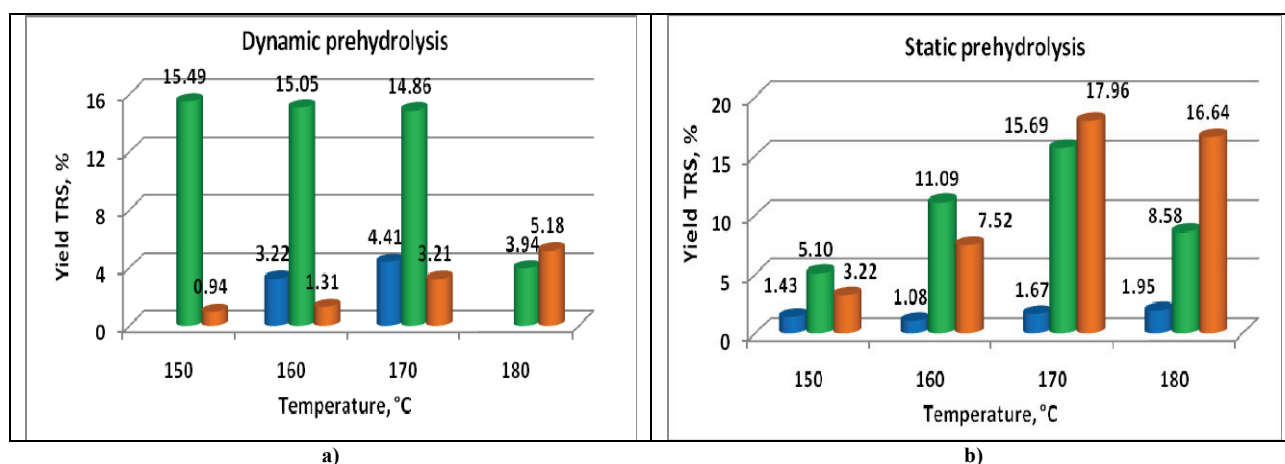


Fig. 2. Yield of total sugars obtained from the prehydrolysis of rapeseed stalks depending on the temperature and the catalyst (a) dynamic regime (b) static regime demineralized H₂O; 0.5% H₂SO₄ solution; 3% Al₂(SO₄)₃ solution

Table 1. Values of the characteristic parameters for cellulignins obtained of dynamic hydrolysis of 3% Al₂(SO₄)₃ solution (S1)

Sample	OH total groups	OH alcohol groups	OCH ₃ groups	C=O groups
CL 150 S1	0.68	0.57	0.68	0.72
CL 160 S1	1.45	1.03	0.80	0.83
CL 170 S1	2.27	0.91	1.05	1.54

Table 2. Values of the characteristic parameters for cellulignins obtained of dynamic hydrolysis of 0.5% H₂SO₄ solution (S2)

Sample	OH total groups	OH alcohol groups	OCH ₃ groups	C=O groups
CL 160 S2	2.58	1.14	1.08	1.11
CL 170 S2	2.71	1.13	1.02	0.78
CL 180 S2	2.30	1.00	1.12	1.63

Table 3. Values of the characteristic parameters for cellulignins obtained of static hydrolysis of 3% Al₂(SO₄)₃ solution (S1)

Sample	OH total groups	OH alcohol groups	OCH ₃ groups	C=O groups
CL 160 S1	1.42	1.08	1.06	0.81
CL 170 S1	1.47	0.76	0.94	1.10
CL 180 S1	2.95	0.70	0.80	4.01

Table 4. Values of the characteristic parameters for cellulignins obtained of static hydrolysis of 0.5% H₂SO₄ solution (S2)

Sample	OH total groups	OH alcohol groups	OCH ₃ groups	C=O groups
CL 150 S2	1.38	1.00	0.81	1.67
CL 160 S2	2.58	1.14	1.08	1.11
CL 170 S2	2.71	1.13	1.02	0.78

4. Conclusions

The experiments were performed in order to establish the working conditions at the prehydrolysis of the rapeseed stalks, in dynamic and static operating conditions, and moderate pressure.

The ratios of the relative absorbance for different groups were modified during the hydrolysis, probably because due to functionalization reactions which occur throughout hydrolytic treatments.

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