CHEMICAL AND SPECTRAL CHARACTERIZATION OF PREHYDROLYSATES OBTINED BY VEGETAL BIOMASS HYDROLYSIS

CARACTERIZAREA CHIMICĂ ŞI SPECTRALĂ A PREHIDROLIZATELOR OBȚINUTE PRIN HIDROLIZA BIOMASEI VEGETALE

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Abstract. *In this paper we studied the effect of temperature on yields reducing substances and yields on dry matter obtained under prehydrolysis batch of rapeseed stalks and beech sawdust function as catalyst. Also we studied the optical characteristics prehydrolysates obtained by hydrolytic treatments. Treatments were performed in the presence of three types of catalysts (demineralized water, 0.5 % sulfuric acid solution and 3 % solution of aluminum sulphate) depending on contact time and temperature. The results showed that in batch mode in the presence of 0.5 %* H_2SO_4 *solution, yield reaches a maximum at 170 °C (15.2 %) after which it decreases with increasing temperature from 5.94 % (180 °C). The explanation for this, can be given by the expense of decreasing content of carbohydrates, especially due to hemicelluloses hydrolysis that are decomposed at temperatures higher than 170 °C.*
Keywords: *prehydrolysis, batch processes, vegetal materials, fluorescence and UV-VIS spectroscopy.*

Rezumat. *În această lucrare s-a studiat efectul temperaturii asupra randamentelor în substanțe reducătoare şi a randamentelor în substanță uscată obținute prin prehidroliză în regim discontinuu a tulpinilor de rapiță şi rumeguşului de fag funcție de catalizator. S-a studiat de asemenea şi caracteristicile optice ale prehidrolizatelor obținute în urma tratamentelor hidrolitice. Tratamentele au fost efectuate în prezența a trei tipuri de catalizatori (apă demineralizată, soluție 0,5 % acid sulfuric şi soluție de 3 % sulfat de aluminiu) în funcție de durata de reacție şi temperatură. Rezultatele au arătat că în regim discontinuu, în prezența soluției de 0,5 %* H_2SO_4*, randamentul atinge un maxim la 170 °C (15,21 %) după care acesta scade odată cu creşterea temperaturii la 5,94 % (180 °C). Explicția acestui fapt se datorează micşorării conținutului de hidrați de carbon, mai ales pe seama hidrolizei hemicelulozelor care sunt descompuse la temperatură mai mare 170 °C.*
Cuvinte cheie: *prehidroliza, regim discontinuu, materiale vegetale, spectroscopia de fluorescență şi UV-VIS.*

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INTRODUCTION

Increasing price of conventional materials (oil, natural gas and coal) requires finding new resources, such as biomass, a renewable resource, in order both energy production (biodiesel, ethanol, gas and biogas) and to obtain micro- and macromolecular compounds with potential applications in biological and other chemical synthesis (Cazacu et. al., 2010).

The hydrolysis technology prefers a complex valorization of all chemical components of vegetal material: hemicelluloses in obtaining furfural and celollignin in manufacture of glucose, ethanol or feed yeast (Măluțan, 2008).

Rapeseed crop is an attractive feedstock for bioenergy production. Its seeds can be used to produce biodiesel while the rapeseed straw is good for bioethanol and biohydrogen production (Karakashev et al., 2007).

Rapeseed straw, an agricultural residue in the process of bio-oil extraction, is an abundant and low-cost lignocellulosic material in many European and Asian countries. Utilization of the rapeseed straw gives an added value for this material and a solution for the removal of this abundant waste, solving a problem of the bio-oil industry and increasing the economical yield of the process. Therefore, a double effect is obtained, economic and ecologic (Jeong et al., 2010).

Hydrothermal pre-treatment can be effectively used for releasing sugars from rapeseed straw, needing no chemical others than water (Diaz et. al., 2010).

In batch reactors were used frequently in kinetic investigations of cellulose hydrolysis with acid. Application of high temperature, although in theory would increase efficiency, is simply not possible because of operational difficulties arising from rapid response speed (Rozmarin et al., 1994).

MATERIAL AND METHOD

Obtaining of the prehydrolysate

The batch hydrolysis treatment of rapeseed stalks and beech sawdust was performed with demineralizated water at a range temperature of 150-190 ^{0}C for 120 minutes, using a reactor equipped with a temperature controller and an HPLC pump. The stainless steel digester was heated to the desired temperature and then placed in a sand bath (Liu et al., 2004). After hydrolysis, the prehydrolysate was separated from the biomass treated through filtration in order to establish the content of the reducing substances and the separated fractions (UV-VIS and fluorescence spectroscopy).

Methods of spectral analysis

1. UV-VIS Spectroscopy

The UV-VIS spectra of prehydrolysates were recorded on a spectrophotometer type JASCO 550V, the absorption region in 200÷900 nm, scan speed 200 nm/min and 1 nm resolution.

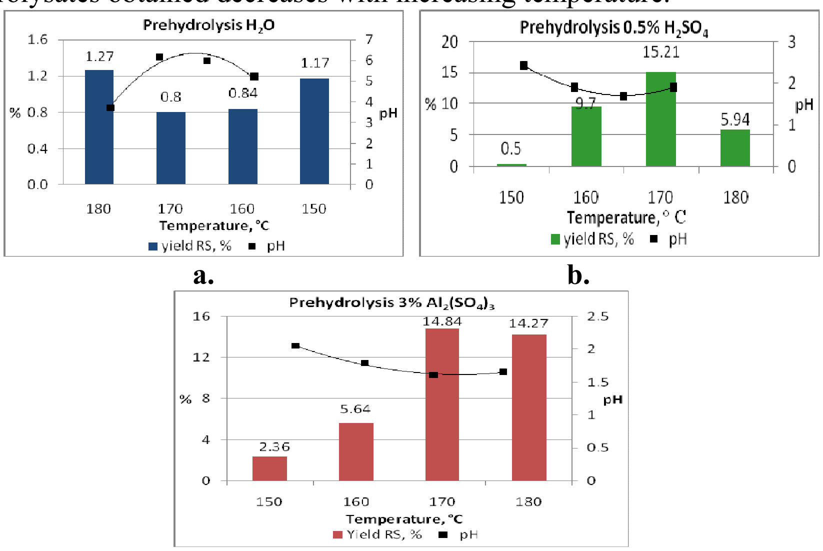
***2.* Fluorescence Spectroscopy**

The fluorescence emissions of prehydrolysates were registered on a luminiscence spectrometer Perking Elmer LS 50B, at wavelength excitation of 350 nm, the absorbtions being evaluated in the 400÷600 nm region, emission slit was 20 nm, scanning speed 500 nm/min.

RESULTS AND DISCUSSION

Effect of hydrolysis temperature on the yields of total reducing substance in the prehydrolysates

In batch mode in the presence of 0.5% H_2SO_4 solution, RS yield reaches a maximum at 170 ˚C (15.21%) after which it decreases with increasing temperature from 5.94% (180 ˚C). The explanation for this, can be given by the expense of decreasing content of carbohydrates, especially due to hemicelluloses hydrolysis that are decomposed at temperatures higher than 170 ˚C. Another observation is that in all three hydrolysis processes carried out in batch mode, the pH prehydrolysates obtained decreases with increasing temperature.



a. b.

c.

Fig.1 - Yields in RS (reported at oven dried material) and pH of hydrolysates of rapeseed stalks depending on temperature

Experiments on beech sawdust in the autohydrolysis with raising temperature to 140, 150 ˚C under moderate pressure batch (400 atm) yield increases of about 5 times and if not using water pressure increase yield is only 4 times. Criterion values hydrolysis in batch mode for the three types of processes are presented in Tables 1and 4.

Table 1.

Severity factor obtained prehydrolysates of rapeseed stalks in the presence of H_2O

Temperature 150 ˚C		Temperature 160 ˚C		Temperature 170 ˚C		Temperature 180 ˚C	
Time (min)	R_0	Time (min)	R_0	Time (min)	R_0	Time (min)	R_0
130	3856	120	7011	150	13236	120	27207

Table 2.

Severity factor obtained prehydrolysates of rapeseed stalks in the presence of 0.5% H_2SO_4 solution

Temperature 150 °C		**Temperature 160 °C**		**Temperature 170 °C**		**Temperature 180 °C**	
Time (min) = 114		Time(min) = 130		Time (min) = 110		Time (min) = 70	
R_0	CS	R_0	CS	R_0	CS	R_0	CS
3114	1.08	7596	1.99	14962	2.5	15871	2.29

Table 3.

Severity factor obtained prehydrolysates of rapeseed stalks in the presence of 3% $Al_2(S0_4)_3$ solution

Temperature 150 °C		**Temperature 160 °C**		**Temperature 170 °C**		**Temperature 180 °C**	
Time (min) = 110		Time (min) = 110		Time (min) = 110		Time (min) = 130	
R_0	CS	R_0	CS	R_0	CS	R_0	CS
3263	1.46	6427	2.02	12661	2.49	34008	2.87

Table 4.

Severity factor obtained prehydrolysates of beech sawdust in the presence of 0.5 % H_2SO_4 solution

Temperature 150 °C		**Temperature 160 °C**		**Temperature 170 °C**		**Temperature 180 °C**	
Time (min) = 110		Time (min) = 110		Time (min) = 110		Time (min) = 115	
R_0	CS	R_0	CS	R_0	CS	R_0	CS
3263	2.10	6427	2.32	12661	2.67	26073	3.00

Optical analysis of prehydrolysates

Absorption spectra in the UV-VIS and fluorescence recorded for prehydrolysates of rapeseed stalks obtained by prehydrolysis in regime batch are shown in Table 5. These are used to estimate the number of functional groups in particular compounds of lignin structure. Following analyzes of absorption signals were detected at 280 nm, thus confirming the presence of lignin fractions in prehydrolysates.

Table 5

The optical characteristics of the prehydrolysates of rapeseed stalks obtained in batch hydrolysis

Treatment	**Temperature (°C)**	**$\lambda_{emission\ (fluorescence)}$ $\lambda_{excitation}$ = 350 nm**	**λ, UV-VIS (nm)**
Demineralized water	150	410	281
	160	425	280
	170	424	279
	180	423	278

0.5% H_2SO_4 solution	150	430	203 / 282
	160	416	209 / 278
	170	415	204 / 279
	180	417	205 / 273
3 % $Al_2(SO_4)_3$ solution	150	408	214 / 276 / 348
	160	413	206 / 277 / 365
	170	410	206 / 231 / 277 / 372
	180	427	209 / 229 / 278 / 371

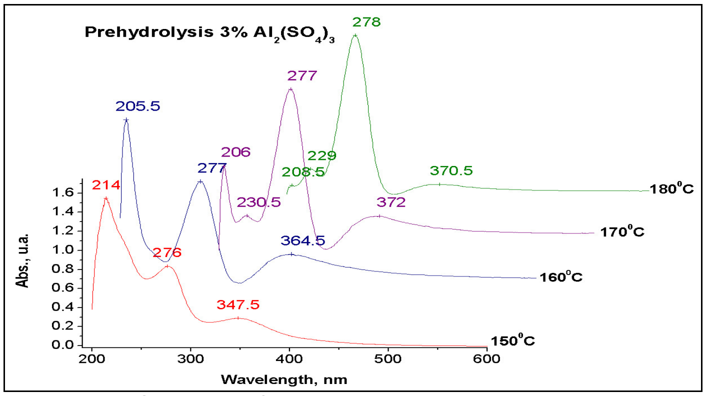


Fig.2 - UV-VIS spectra of rapeseed stalks prehydrolysates obtained by prehydrolysis in regime batch with 3% $Al_2(S0_4)_3$ solution

Recorded fluorescence emission wavelength decreases emission if hydrolysis with 3% $Al_2(SO_4)_3$ solution, and if additional UV-VIS absorption bands appear at 206-229 and 348-372, which is explained by absorption of degradation of compounds different from yields of 0.5% H_2SO_4 solution or water. UV-VIS spectra confirmation may be noticed in HPLC chromatograms. Absorbances when using beech sawdust can be obsevate in Table 6:

Table 6

Optical characteristics of sawdust beech prehydrolysates obtained by prehydrolysis with demineralized water

Temperature (°C)	Treatment	$\lambda_{emission\ (fluorescențce)}$ $\lambda_{excitation}$ = 350nm	λ, UV-VIS (nm)
140	hydrolysis of pentosans in batch mode (pressure=400 atm)	431	278
150	hydrolysis of pentosans in discontinuous mode	430	280
150	hydrolysis of pentosans in batch mode (pressure=400 atm)	459	278

If the beech sawdust prehydrolysates, UV-VIS spectra analysis of recorded if the sawdust beech prehydrolysate it shows characteristic bands at 278 nm and 280 nm highlighting the following molecular lignin fractions recorded in solution, alongside sugar degradation compounds (furfural). By analyzing the fluorescence spectra observed a shift of emission maxima at 431 nm (140 ˚C) to

459 nm (150 ˚C). By analyzing the fluorescence spectra observed a displacement of emission maxima at 431 nm (140 ˚C) to 459 nm (150 ˚C).

CONCLUSIONS

1. The behavior vegetal biomass, especially in the hydrolysis of polysaccharides was studied by batch hydrolysis process at different temperature levels.

2. Following UV-VIS spectral analysis and fluorescence we can say that the more accentuated modifications are observed at the prehydrolysates obtained by prehydrolysis with 3 % $Al_2(SO_4)_3$ solution of rapeseed stalks. These modifications are attributed to the presence of sugars at 220 nm and lignin fractions at 280 nm.

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