Research Concerning Formation, Characterization and Recovery of Lignin Polymeric Deposits in order to Get Some Lignin - phenol-formaldehyde Resins

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The paper shows a series of data concerning the formation and lignin nature of polymeric deposits built up at the beechwood pre-hydrolysis. By means of elemental compostion, data limit formulas (empiric) of deposits have been calculated also emphasizing the special influence of hidromodule over the structure of deposits. The second part of the paper shows aspects related to the recovery of lignin polymeric deposits in order to synthetize a lignin-phenol-formladehyde resin, useful to the wood processing sector as well as the energy sector.

Keywords: pre-hydrolysis, beech, limit formulas (empiric), lignin-phenol-formaldehyde resins

In the chemical pulp making process (threads, fibers, esters, ethers, foils, resins) beechwood chips before being subjected to kraft cooking (cooking with a sodium hydroxide solution and sodium sulphure), they are subject to a water (or steam) hydrolytic treatment called pre-hydrolysis or self-hydrolysis whose aim is to remove hemicelluloses (1-6). During this process, removal of hemicelluloses in a proportion of 80-85% took place. Pre-hydrolysis is carried out based on a certain chart (fig.1) at a maximum temperature of 170-175°C and a hidromodule of 1:3.5 (ratio between absolutely dry wood: water). In the beechwood, the most important polyose is glucuronoxylan acetate (29%). As a result of temperature, the following reactions took place during pre-hydrolysis:

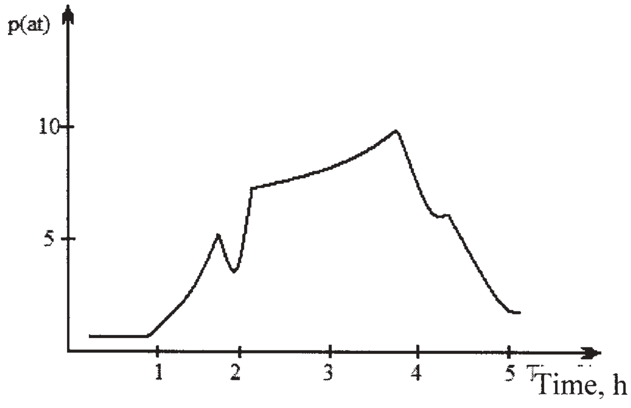

Fig. 1. Chart of beechwood pre-hydrolysis

-formation of acetic acid and formic acid by splitting the acetyl and formyl groups;

-decarboxilation of glucoronic acid and formation of methanol by splitting of metoxyl groups;

-hydrolysis of starch, some tannins and existing wood gums, with formation of glucose and other simple sugars;

-hydrolysis of pentosanes with formation of pentoses and dehydration of pentose up to furfural.

-hydrolysis of the other hemicelluloses with formation of suitable sugars.During pre-hydrolysis, apart hemicelluloses, other components such as tannins, colour substances, pectines dissolve in a rather high amount.

Some reactions that took place during pre-hydrolysis are summarized in Table 1.

After pre-hydrolysis, the recovery of prehydrolysate mainly containing products resulted from hemicellulose transformation took place. The pre-hydrolysate resulted after pre-hydrolysis, is shown as a brown-reddish solution with a smell of furfural and acetic acid, with a complex composition comprising monoses and oligosaccharides, furfural and its derivatives, organic acids (acetic acid, formic acid), methanol, acetone etc.

Due to its complex composition, the pre-hydrolysate is a convenient raw material for chemical and biochemical processing.

In the composition of pre-hydrolysate, the presence of some colloid substances is noticed. These substances deposit and cause a lot of difficulties in its chemical and biochemical processes (8). The literature does not provide information concerning the nature and possibility to exploit the deposits built up at beechwood pre-hydrolysis.

Experimental part

Pre-hydrolysate and deposits of pre-hydrolysate resulted from water pre-hydrolysis of beechwood, at a hidromodule of 1:3:5, pre-hydrolysis temperature is 175°C and the time, 110 min.

The presence of some harmful components in pre-hydrolysate (formic acid, methanol, acetone) was emphasized by chromatography, in the gas phase (chromatographic column, V2A, 1-2 m, CHROMOSORB W80-100 holder, stationary phase): digliceroles, supporting gas flow: 100 ml/min, detector temperature 110°C.

Concentration of colloids was determined by the method of activated carbon adsorption method and elution with ethanol and sodium hydroxide (8), and their nature was acknowledged by IR spectroscopy, and by elemental analysis (combustion method).

The content of metoxyl groups was determined by the Morgan-Zeisell method (10). The deposit was calcinated at a temperature of 800°C, and ash was analysed by atomic absorption spectroscopy.

In order to determine the nature of deposits built up in the pre-hydrolysis process, they were analysed by IR spectroscopy and by means of elemental analysis. Based on elemental composition, data limit formulas (empiric) of pre-hydrolysis deposits were determined (10).

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Table 1
MAIN REACTIONS TAKING PLACE DURING PRE-HYDROLYSIS

Components	Primary reaction products	Secondary reaction products
4-0-glucuronoxylan	Arabinose, xylan	Xylose
Arabino-galactan	Arabinose, galactose	-
Galactoglucomanan	Arabinose	Furfural, polyfuran
Glucomanan	Xylose, galactose, glucose, mannose	-
Lignin, tannins	Phenols	Humic substances

Results and discussions

Beechwood pre-hydrolysate has a typical composition having a high content of pentoses (77%), the major component being xylose, free furfural (3.5 g/L), harmful substances (formic acid-0.04%, acetone - 0.07%, methanol-0.15%) and colloidal materials (9.2 g/L), table 2.

Figure 2 shows the IR spectrum of the deposits from beechwood pre-hydrolysis and table 3 shows the interpretation of the main absorption bands of the spectrum.

Table 2
CHARACTERISTICS OF BEECHWOOD PRE-HYDROLYSATE

Characteristics	Values
Dry substance, g/l	57.5
Content of organic substances expressed in % in relation to dry substance	95.95
Total reducing substances, g/l	37.0
Chemical composition, %	Pentoses: 77 Hexoses: 23
Volatile acidity, expressed in acetic acid, g/l	1.85
Formic acid, %	0.04
Acetone, %	0.07
Methanol, g/l	0.15
Colloid substances, g/l	9.2
pH	3.5

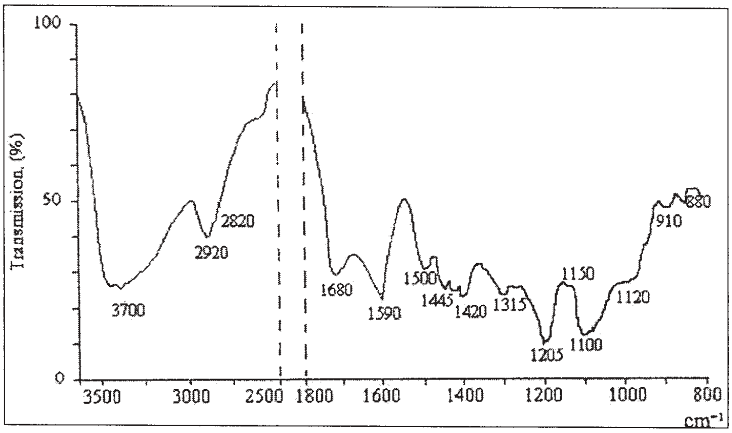

Fig. 2. IR spectrometer of deposits resulted from beechwood pre-hydrolysis

Table 3
THE MAIN ABSORPTION BANDS OF DEPOSITS RESULTED FROM BEECHWOOD PRE-HYDROLYSIS

Item	Absorption bands (cm^{-1})	Type of vibrations and functional group responsible for this vibration
1	2950	Valence vibration in C-H
2	2850	Valence vibration in C-H
3	1710	Valence vibration in C=O
4	1680	Valence vibration in C=O
5	1610	Valence vibration in C-C in ring
6	1550	Valence vibration in C-C in ring
7	1470	Deformation vibration of CH_2 group
8	1430	Deformation vibration of CH and CH_2 groups
9	1330	Deformation vibration of OH group
10	1220	Valence vibration of C=O group
11	1175	Valence vibration of C-O-C group
12	1150	Valence vibration of C-O-C group
13	1120	Valence vibration of C-O-C group
14	1040	Valence vibration of C-O-C group
15	940	Valence vibration in C=O
16	885	Vibration typical to glucosidic bound pyranosic ring

Table 4
ELEMENTAL ANALYSIS AND LIMIT FORMULAS (EMPIRIC) OF PRE-HYDROLYSIS DEPOSITS

Type of deposit	Content of:				Limit formula (empiric)
	C%	H%	O%	CCH_3 %	
Deposits at beechwood pre-hydrolysis (H=1:1,2, T=170 °C)	59.7	5.0	34.65	12.53	$C_gH_{7.35}O_3HH\ (OCH_3)_{0.78}$
Deposits at beechwood pre-hydrolysis (H=1:3.5, T=170 °C	54.4	4.9	37.60	15.80	$C_gH_{7.47}O_{4.1}\ (OCH_3)_{1.11}$
Bjorkman lignin in beech	60.33	6.27	33.35	21.39	$C_gH_{8.61}O_{2.35}(OCH_3)_{1.12}$

Table 5
ANALYSIS OF INORGANIC COMPONENT OF DEPOSITS FROM PRE-HYDROLYSIS

Component	Values %
Ash	2.6
Potassium	Lower than 0.1
Sodium	0.12
Magnesium	0.03
Calcium	0.08
Aluminium	Lower than 0.01
Iron	Lower than 0.01
Silicon	0.01

Table 6
SOLUBILIZATION OF DEPOSITS AT PRE-HYDROLYSIS

Concentration of NaOH %	Temperature °C	Dissolved %, at a time of			
		15 min.	30 min.	45 min.	60 min.
4	20	99.64	99.67	99.77	99.83
4	40	99.72	99.78	99.80	99.92
6	20	99.67	99.83	99.88	99.92
6	40	99.75	99.84	99.89	99.89

Analysing the deposits from pre-hydrolysis by means of IR spectroscopy and comparing this spectrum with the native lignin spectra, an uniformity of spectra is noticed, confirming the identical (aromatic) nature of investigated preparations.

Deposits made during pre-hydrolysis show an IR spectrum whose general aspect is typical to aromatic products (bands ranged between 1550 cm^{-1} and 1610 cm^{-1}).

It is also noticed the presence of the band from 1330 cm^{-1}, band typical for hardwood lignin due to the OCH_3 group. The lignin nature of deposits was also confirmed by means of elemental analysis (high carbon content of 54-59%, table 4).

Compared to cellulose, lignin is a polymer with a high carbon content and a low oxygen and hydrogen content, fact that indicates its aromatic nature. Based on the elemental composition data, the limit formulas (empiric) of deposits from prehydrolisis noticing different formulas according to the hidromodule used at pre-hydrolysis (table 4).

Deposits from pre-hydrolysis have a low content of ash (important feature for the chemical value of deposits), table 5.

The lignin nature of deposits is also sustained by the fact they are soluble in NaOH solutions having different concentrations at different temperatures (20-40°C), table 6.

As the table 6 shows an almost 100% solubilization can be carried out of deposits from pre-hydrolysis, by using NaOH with a 4-6% concentration, even at ambient temperature and a minimum time of 15 min.

To separate deposits, a 24 h-sedimentation (cold or hot) or a centrifugation at a temperature of 75°C and removal of deposits are recommended. A method of preventing deposits consists of charging lignosulphonic mash (dispersing effect) into the water from pre-hydrolysis (0.04-0.05%) or in pre-hydrolysate (0.02-0.2%).

We cannot talk about a complete removal of deposit formation during pre-hydrolysis because of hydrolysis and polycondensation reactions of lignin with furfural and its by-products.

Deposit formation is in close relation with furfural formation and is driven by polycondensation reactions between lignin destruction compounds and phenolic compounds with furfural based on a mechanism similar with condensation of phenolic substances with formaldehyde (fig. 3) [11].

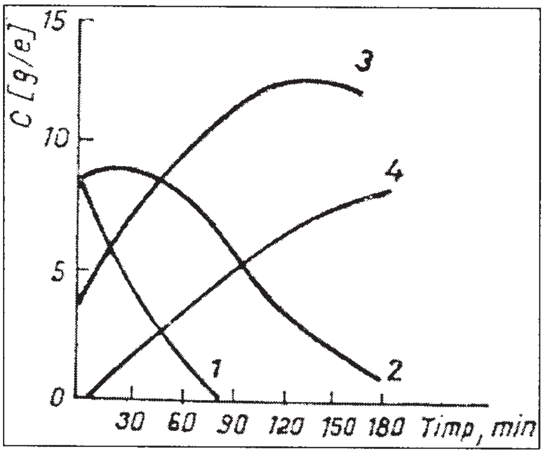

Fig. 3. Development of beechwood pre-hydrolysate (T= 170 °C, H= 1:3.5) according to time: 1-oligoxylans; 2-xylose; 3-furfural; 4- condensation products

Limitation of furfural condensation reactions has a positive effect over the furfural production, too. Considering the lignin nature of deposits, they were used in the preparation of some lignin-phenol-formaldehyde resins dedicated to the manufacture of fibreboards [18].

As they show a good chemical, mechanical and thermal strength, resins are regularly used in other industrial branches as well as for household products.

During precondensation, 50 parts of phenol, 25 parts of formaldehyde (37%) and 0.75 parts of oxalic acid are warmed up for 90 min. at 85-90°C.

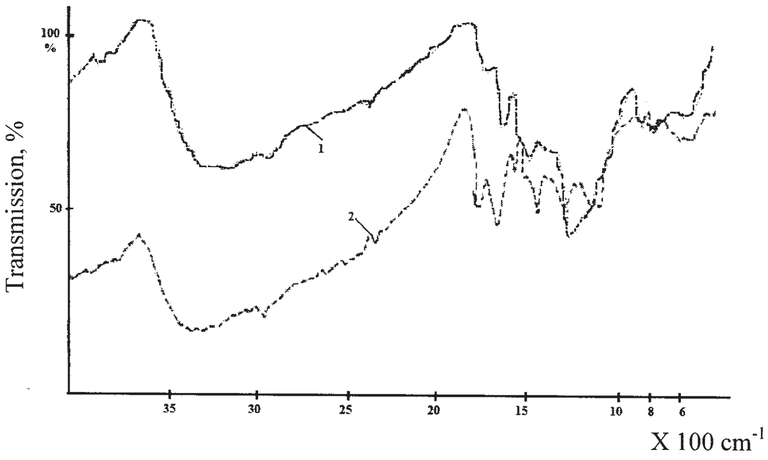

Fig. 4. IR spectrum of ligno-phenol-fomaldehyde resin compared to spectra of pre-hydrolysis deposits and dry substance in pre-hydrolysis: 1- deposits from pre-hydrolysis; 2- lignin-phenol-formaldehyde resin

Table 7

HEATING VALUE OF DEPOSISTS FROM PRE - HYDROLISYS COMPARED TO SOME COALS

Name	Heating value, Kcal/kg
Deposits from pre-hydrolisis	6050
Anthracite	6097
Brown coal	3071
Washed pit coal for semicoke	5052

In the main condensation phase, 25 parts of lignin deposits, 50 parts phenol and 1.5 mL sulphuric acid (d=1.84) are introduced.

The main reaction takes place at 140°C for 60 min. Following reactions, a resin containing 67% active substance is obtained, insoluble, soluble in organic solvents, that between 60-100°C are shown as plastics and below 60°C, they can be processed as powder.

To identify the main changes that occur at the condensed product, this was analysed by IR spectroscopy. Figure 4 shows the IR spectrum of the resin obtained compared to the IR spectrum of deposits from pre-hydrolysis.

In the resin spectrum, high bands of 690, 750, 1505, 1590 cm^{-1}, characteristics of aromatic rings and band from 1335 cm^{-1} representing the variation of syrilinge ring and carbonyl groups are noticed.

The resin synthesis reaction is fostered by the high lignin content (deposits used have a lignin content of 93.73% and ash 0.51%).

Lignin shows improved adhesive properties in its copolymers both with phenols and aldehydes.

With the resin obtained in laboratory, production tests were carried out with fibreboard using 50 parts sawdust, 10 ml Urelit (40% active substance) and 40 parts resin.

The mixture was homogenized, pressed and kept in the oven for 8 h resulting a plate with good strength characteristics (over 10% higher, and the plate did not disintegrate in water at 20°C). As advantages, the higher unifornmity of plates is noticed as well as the possibility of pressing thicker plates.

Another way to use the deposits from pre-hydrolysis is burning thanks to the high heating value (table 7).

Conclusions

Polymeric deposits are a special problem for the chemical and biochemical use of pre-hydrolysate. These deposits are of lignin nature being the result of the polycondensation reactions between phenolic compounds, furfural and its by-products. Pre-hydrolysate from the beech prehydrolysis contains more furfural than softwood pre-hydrolysate and that is why, polymeric lignin deposits are built up more intensively in case of hardwood pre-hydrolysate (around 10.5 kg deposits/ton of hardwood compared to around 4-5 kg deposits/ton of softwood).

The amount of polymeric deposits depends on the species of wood and pre-hydrolysis conditions.

Due to their chemical nature, polymeric lignin deposits were used in order to get lignin-phenol-formaldehyde resins.

The chemical use of these deposits or their burning represent an original contribution to the complex use of pre-hydrolysate and the reduction of environmental pollution.

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