CELLULOSE CHEMISTRY AND TECHNOLOGY

SOME ASPECTS OF THE CHANGES IN BIRCH WOOD IN THE MILD ACIDIC HYDROLYSIS PROCESS AND ITS EFFECT ON THE SUCCEEDING PYROLYSIS PROCESS

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Pre-treatment of wood is a substantially important stage to make its components more accessible for conversion to valuable products. The goal of this study was to investigate the mild hydrolysis pre-treatment of birch (*Betula pendula*) wood for improving the cellulosic part accessible to pyrolysis for obtaining anhydrosugars. Lignocellulose (LC) was obtained after separating hemicelluloses from birch wood chips by treating them with 3% sulphuric acid from the wood oven dry mass, followed by acid hydrolysis with steam at 100-180 °C during 60 min. Electron paramagnetic resonance (EPR) spectroscopy data showed the formation of polyconjugated systems in the LC structure, starting from a pre-treatment temperature of 130 °C, which, coupled with the decreasing degree of polymerisation (DP), was not favourable for the formation of levoglucosan. The optimal pre-treatment temperature can be considered to range from 120 to 130 °C.

Keywords: lignocellulose, hydrolysis, pyrolysis, levoglucosan

INTRODUCTION

Despite the extensive research on biomass, including wood, it is still insufficiently utilised as a source for obtaining basic substances for chemicals and fuels. Pre-treatment of wood is a substantially important stage to make the structure of its components, mainly cellulose, more accessible for conversion to valuable products and fuels by the biochemical or thermochemical way.[1,2] Cellulose, as the most widespread natural polymer, is an interesting raw material as a source for chemicals, especially levoglucosan (1,6-anhydro-β-D-glucopyranose), as one of the main final thermal degradation products.[3] To avoid the formation of a complex mixture of side products, it is preferable to remove hemicelluloses, and partly soluble extractives and lignin.[4] Up to 50-90% of cellulose is bound with hydrogen bonds and forms a crystalline structure, but the remaining structure is less ordered, and amorphous cellulose is formed. These two structural forms of cellulose have different behaviour in the hydrolysis process and the following pyrolysis process.

As a result of acidic mild hydrolysis, the hemicellulosic part of wood breaks down to monomers and has an effect on the amorphous cellulose fraction, partly or completely converting to monomers, with the following degradation to hydroxymethyl furfural, levulinic acid and other compounds,[5] as a result increasing the remaining crystallinity accordingly. However, lignin is more resistant to steam treatment than hemicelluloses, while some components of lignin are gradually degraded or modified in the process. For bioethanol processing from lignocellulosic raw materials, it is necessary to obtain monomeric sugars, but in the case of obtaining levoglucosan, the best results of the levoglucosan yield from cellulose are reported to be up to 60%; however, the use of glucose as a raw material leads to a low yield[6] of products with levoglucosan and its isomer 1,6-anhydro-β-D-glucofuranose, i.e. 40% and 19%, respectively.[7]

Regardless of the reported high yields of levoglucosan in the laboratory, even pilot scale problems embrace the lack of a cheap, simple, reliable and efficient method[8] for separation, as well as the scalability of the laboratory experiments. The degradation of levoglucosan, substantially hampered in the presence of aromatic compounds, is reported.[9]

The goal of the present study was to investigate the effect of the mild hydrolysis pre-treatment of birch wood on improving the cellulosic part accessible to pyrolysis for obtaining sugars and especially levoglucosan.

EXPERIMENTAL

Raw material

Lignocellulose (LC) samples were obtained from birch (*Betula pendula*) wood chips from veneer production shorts with average dimensions of 100 x 10 x 4.5 mm and a moisture content of 30%, and ground to a particle size < 2 mm.

Hydrolysis

The material was treated with 3% H_2SO_4 from the wood oven dry mass in the form of a 30% water solution, sprayed in a paddle mixer with the mixing time of 10 min. Then followed acidic hydrolysis with steam in a temperature range of 100-180 °C during 60 min and subsequent aqueous washing of LC residues till a pH of 4.5 was reached.

Analysis

In the obtained LC, the content of holocellulose was detected by the Wise method,[10] and the degree of polymerisation (DP) was determined with viscosimetric measurements, performed in a cadoxen (cadmium-oxide ethylenediamine) solution according to the procedure described by Brown and Wikstrom.[11] The content of α-cellulose was determined using holocellulose by extraction with 17.5% NaOH, and the α-, β- and γ-cellulose content according to the TAPPI standard.[12] All chemical analyses were carried out in triplicate.

Electron paramagnetic resonance (EPR) spectra were recorded at room temperature with a Bruker EMX spectrometer (Germany) operating at 9.6 GHz and a 50 kHz magnetic field modulation. The central magnetic field was 345 mT – a resonance field corresponding to organic free radicals, including lignin-related radicals. Spectra were recorded at microwave power of 1mW and modulation amplitude of 0.02 mT; the scan range was 10-20 mT. The spectra were obtained as the first derivative of absorption, and the spin quantifications of the EPR signals were determined by double integration of the first derivative of the spectra relative to the spectrum of the DPPH• standard. Before EPR measurements, the samples were annealed at 120 °C under high vacuum (ca. $1x10^{-4}$ Torr) to remove free radicals, non-inherent in polyconjugated systems. The mass of a sample probe (residual moisture content < 1%) was 10.0-20.0 mg. Spectroscopy parameters, such as line width, line intensity and *g*-factor, were determined directly from the spectrum, and the amount of paramagnetic centres (PMC) and extent of conjugation units *n* were calculated according to T. Dizhbite *et al.*[13]

Thermogravimetric analyses were carried out with a METTLER TOLEDO STAR System TGA/SDTA851 in an inert nitrogen atmosphere with a flow rate of 20 mL/min at a heating rate of 10 °C/min.

The Py-GC/MS analysis was performed using a Frontier Lab Micro Double-shot Pyrolyser Py-2020iD (pyrolysis temperature 500 °C, heating rate 600 °C/s), directly coupled with a Shimadzu GC/MS-QP-2010 gas chromatograph with a capillary column RTX-1701 (60 m × 0.25 mm) with 0.25 µm stationary phase film (injector temperature 250 °C, ion source 250 °C with EI of 70 eV, the MS scan range *m/z* 15–350, carrier gas helium at a flow rate of 1 mL/min and a split ratio of 1:30). The weight of the sample probe was 1.00-2.00 mg. The oven programme was 1 min isothermal at 60 °C, then a linear temperature increase of 6 °C/min to 270 °C, and finally 10 min at 270 °C. The apparatus was modified by the installation of the splitter of the carrier gas flow Vitreous Silica Outled Splitter (VSOS) in order to perform analysis, simultaneously using FID and MS detectors. As a result of the modification, the volatile products released during pyrolysis can be identified (MS detector) and quantified (FID detector) simultaneously. The mass spectrometer was operated in the electron impact mode using the electron energy of 70 eV. The identification of individual compounds was performed on the basis of a GC/MS chromatogram using the Library MS NIST 147.L113, whereas the relative area of the peaks of individual compounds was calculated using the Shimadzu software on the basis of GC/FID data. The summary molar areas of the relevant peaks were normalised to 100%, the data for five repetitive pyrolysis experiments were averaged and the relative error of measurement was less than ± 5%.

RESULTS AND DISCUSSION

As expected, depending on the conditions of birch wood mild hydrolysis, the LC yield remarkably decreased with increasing hydrolysis temperature, as shown in Table 1, but the cellulose content rose up to a temperature of 120 °C, reaching 95.5% from the whole amount of holocelluloses. Then, the content started declining, which could be explained by the formation of very short chain oligomers detected as γ-cellulose (Fig. 1), as well as the possible interaction with lignin and formation of pseudo-lignin.[14] However, at hydrolysis temperatures above 150 °C, supposedly because dramatic condensation reactions occurred between lignin and cellulose, conventional component detection methods were not suitable any more.

Judging from the results of the thermogravimetric analysis, at a hydrolysis temperature of 100 °C, the effect of pre-treatment on the thermal degradation of LC was minimal.

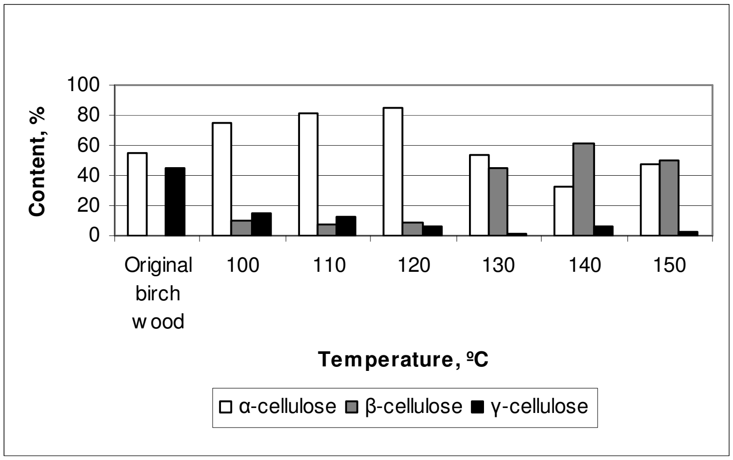

Figure 1: Content of α-, β- and γ- cellulose in holocellulose depending on the pre-treatment temperature

Table 1
LC yield and composition depending on the hydrolysis temperature

Temperature (°C)	Yield (mass %)		
	LC	Holocellulose	Cellulose
100	78.9	70.6	60.1
110	74.2	67.1	63.5
120	64.9	66.6	63.8
130	63.9	64.7	62.1
140	62.6	59.8	50.1
150	53.2	57.2	47.9
160	51.7	n.d.	n.d
180	46.3	n.d	n.d

Table 2
Results of LC thermogravimetric analysis

Temperature (°C)		Yield (mass %)	
Hydrolysis	DTG max	Volatiles, at DTG max	Residue at 800 °C
100	333	50.3	2.4
110	356	56.0	13.2
120	350	50.5	13.1
140	350	48.7	17.7
150	350	41.1	23.8
160	350	25.9	37.1
180	385	23.5	28.5

However, the increase in the hydrolysis temperature above 100° by only 10° changed the hydrolysis conditions (pressure of superheated steam) and, obviously, led to a more complete removal of hemicelluloses and partial amorphisation of cellulose. As a result, the temperature of the maximum of the main degradation (DTG) grew from 333 to 356 °C, and the amount of volatile products at this stage increased by 5.7% (Table 2).

The effect of the hydrolysis temperature in the range of 120-160 °C on the properties of LC manifested itself in an increase in the temperatures of the main thermal degradation (from 333 to 350 °C), as well as a decrease in the amount of volatile products at this stage (from 50.5 to 41.1%). In this case, the temperature of the maximum after the hydrolytic treatment at 120-160 °C did not change. Probably, at this temperature, depolymerisation of the crystalline regions of cellulose occurred, the share of which, in accordance with the decline in the share of volatile products at this stage, decreased with increasing temperature. It should be mentioned here that, with increasing temperature of LC hydrolysis from 110 to 160 °C, the yield of solid carbonaceous residue at 800 °C increased from 13.2 to 37.1%, respectively.

Under the conditions of hydrolytic treatment at a temperature of 180 °C, considerable changes in LC occurred, governed by the components' polycondensation reactions. In accordance with the changes in the chemical structure and the formation of more stable bonds, the temperature of the main degradation grew up to 385 °C and the amount of volatile products at this stage decreased to 23.5%. However, with the subsequent increase in the thermal treatment temperature up to 800 °C, reactions of the further degradation with the formation of volatile products occurred. As a result, the yield of the solid residue at 800 °C decreased, compared to that for the sample subjected to hydrolysis at 160 °C, and was equal to 28.5%.

After different studies on cellulose, Shafizadeh[15] and Piskorz[4] established that lowered DTG peak temperatures correspond with increased volatiles and maximum levoglucosan production. In our case, this relationship is not fulfilled completely, because pre-treatment in the temperature region 120-140 °C gives practically equal DTG maxima for LC, but levoglucosan yield is different. The maximum of DTG for α-celluloses (Table 3), isolated from the LC obtained at hydrolysis temperatures of 100-140 °C, was recorded at the same temperature, i.e. 352 °C. The amount of the volatile products formed at this temperature practically did not change. The solid carbonaceous residue at 800 °C decreased (from 15.6 to 11.2%) upon the destruction of α-celluloses, with elevating temperature of wood hydrolysis. The increase in the amount of volatile products indicated a decline in the thermal stability at the stage above the polymer depolymerisation temperature.

The destruction of α-cellulose, obtained from LC after hydrolysis at 150 °C, proceeded with the maximal rate at a temperature that was lower by 30 °C, compared to that of other samples; in this case, the amount of products at this stage increased by 17%. The yield of the solid residue of α-cellulose, obtained from the LC treated at 150 °C, considerably increased at 800 °C. This testified that the formation of volatile products developed mainly at low temperatures.

In contrast to α-cellulose, the thermal destruction of β-celluloses, isolated from the LC obtained at different temperatures of hydrolysis, proceeded without any change in the temperature of the main degradation and in the amount of volatile products at this stage, and at 800 °C. In this case, in comparison with α-cellulose, an increase of volatile products at the stage of the main degradation and up to 800 °C occurred. Obviously, the transformation of cellulose upon the increase in the hydrolysis temperature, resulting in a decline in the strictly oriented regions of cellulose and, as a consequence, an increase in the formation of β-celluloses, proceeded, with the formation of a homogeneous polymer structure with weakened intermolecular bonds and a low DP.

Important information about the changes promoted by the hydrolysis in the LC chemical structure was gained from EPR, which showed changes in the spectral parameters of organic free radicals (Table 4). The EPR spectra of LC, obtained by hydrolysis at different temperatures (100-180 °C) and time, are characterised by the presence of stable PMC with a narrow (line width of 0.5-0.9 mT) single line spectrum. Taking into account the hydrolysis conditions, the registered PMC are assigned to the stable free radicals of polyconjugated systems (PCS), which can be evaluated by the amount and sizes of conjugation sub-structures or clusters. With increasing hydrolysis temperature, the value of the *g*-factor gradually decreases from the values, typical for the localisation of PMC on oxygen atoms (for example, for the phenoxyl radicals of the untreated wood lignin), to the values typical for PCS. The parameter *n* of EPR spectra, corresponding to the average number of the CH fragments included in the region of the delocalisation of the non-conjugated electron of PMC, characterises the size of the conjugation units and the mean extent of conjugation.

In the case of increasing wood hydrolysis temperature, the *n* value increases, beginning with the temperature 130 °C, showing the progress of the processes of condensation and aromatisation in the lignin structure, especially markedly at 160-

180 °C. The amount of conjugation units, taking into account the complexity of the structure of the natural polymer containing polyconjugated systems, approximately corresponds to the content of stable PMC of LC. The systems, developing the processes of condensation in the LC structure, are indicated by an increase in the content of PMC and, correspondingly, the regions of conjugation substructures and clusters. With increasing hydrolysis temperature above 130 °C, the formed polyconjugated systems of LC are evenly distributed throughout the volume of the organic matrix, changing the nature of the subsequent thermal degradation. It can be seen from the results (Table 4 and Fig. 2) that the optimal pre-treatment temperature interval for the formation of levoglucosan is 110-130 °C, characterized with relatively little changes in the *n* and DP values. These results can be associated with three kinetics regions in acidic hydrolysis related to amorphous, mesamorphous or transition and crystalline cellulose.[16]

Without cellulose isolated with 17.5% sodium hydroxide usually called α-cellulose,[17] holocellulose contains cellulose molecules with decreasing chain lengths formed in the cleavage of the α-cellulose, and it is possible to divide β- and γ-cellulose after acidation with acetic acid. The content of α-, β- and γ-cellulose in the isolated holocelluloses from LC strongly depended on the pre-treatment temperature (Fig. 1) and α-cellulose content increased up to a temperature of 120 °C, but then decreased, and the increased content of β-cellulose indicated the starting depolymerisation of the more stable crystalline cellulose macromolecules.

Analytical pyrolysis was carried out with LC, as well as isolated α- and β-celluloses, and the relative yield of levoglucosan is shown in Figure 2. Pyrolysis results testified that β-cellulose, obtained from the LC at a temperature of 100 °C, showed a four times lower relative yield of levoglucosan, compared to the case of α-cellulose, with a relatively high content of amorphous cellulose, which decreased with increasing pre-treatment temperature, because it was subjected to hydrolysis easier.[5]

Table 3
Results of thermogravimetric analysis on isolated α- and β-celluloses

Temperature			Yield (mass %)			
Hydrolysis	DTG max		Volatiles at DTG max		Residue at 800 °C	
	α	β	α	β	α	β
100	352	320	45.2	49.7	15.6	24.8
110	352	326	44.8	50.4	14.9	23.6
120	352	325	44.5	54.2	14.0	24.0
130	352	329	44.8	54.6	13.7	24.1
140	352	334	44.6	54.5	11.2	23.7
150	323	324	62.0	52.5	30.6	23.9

Table 4
Changes in the LC depending on hydrolysis temperature

Hydrolysis temperature (°C)	*g*-factor	n	DP
Birch wood	2.00458	8.65	553
100	2.00414	9.93	436
110	2.00427	9.28	359
120	2.00409	9.94	342
130	2.00418	10.67	304
140	2.00395	12.13	260
150	2.00377	13.94	170
160	2.00356	15.82	n.d
180	2.00337	17.31	n.d

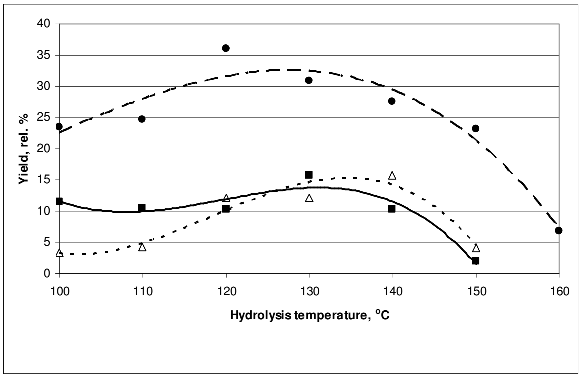

Figure 2: Levoglucosan yield depending on the pre-treatment temperature and material: ● - lignocellulose; ■ - α-cellulose; Δ - β-cellulose

Comparing with levoglucosan yields from original LC, it can be seen that samples of α- and β-celluloses gave a twice lower yield, but it should be taken into account that the isolation of α- and β-celluloses proceeded with alkaline solution, and the laboratory results of this study demonstrated that the effect of alkali pre-treatment altered the materials and gave reduced yields of levoglucosan. In this case, the analytical pyrolysis results are considered to illustrate the general tendencies of the pyrolysis process. It can be concluded to a certain extent that cellulose decomposition to levoglucosan favoured the high content of α-celluloses, accompanied with no more than 50% changes in the DP average value. Further decrease of the DP increased the content of β-celluloses and the char yield, which is shown in Table 4, but did not increase the levoglucosan yield. It is interesting that, from the TG results, the char yield from β-cellulose was higher than that from α-cellulose in the temperature range, favourable for levoglucosan formation, practically remained the same and had little effect in general. Bash and Levin[18] established the fact that for pure cellulose dehydration proceeds mainly in the less ordered regions, partially due to thermal cross-linking, which is favourable to char formation for β-celluloses, but in crystalline regions depolymerization occurs, explaining the lowest char yield and the highest volatiles and levoglucosan yield from α-cellulose. At temperatures above 130 °C, β-cellulose content in the LC exceeds α-cellulose content and the yield of levoglucosan continues to decrease. This evidences that the cellulose fine structure changes impact on the formation of levoglucosan, and the essential challenge is to elucidate pre-treatment parameters in order to obtain the maximum yield.

CONCLUSION

The temperature of birch wood mild acidic pre-treatment has a significant effect on the quantity of α-, β- and γ-cellulose and DP, i.e. with increasing hydrolysis temperature, the LC yield and α-cellulose content decrease. At the same time, EPR spectroscopy data show the formation of polyconjugated systems in the LC structure, starting from a pre-treatment temperature of 130 °C, which, coupled with decreasing of DP, is not favourable for the formation of levoglucosan. The optimal pre-treatment temperature for obtaining levoglucosan can be considered to range from 120 to 130 °C.

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