Aqueous Thermomechanical Pretreatment of Aspen in a Batch Reactor System
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AQUEOUS THERMOMECHANICAL PRETREATMENT
OF ASPEN IN A BATCH REACTOR SYSTEM

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ABSTRACT

The fractionation of wood consists of the separation of the fibrous material into its constitutive polymers (i.e. extractives, hemicellulose, cellulose and lignin) in a sequential and selective way. The thermochemical or biochemical upgrading of each fraction leads to the production of common and fine chemicals. The first step of the fractionation process is the pretreatment which permits the solubilization of extractives and hemicellulose. The residue thus obtained is more accessible to chemicals and enzymes. The goal of this paper is to prove that a thermomechanical pretreatment in aqueous phase (without adding any chemical) may solubilize, in a relatively selective way, the hemicellulose. This process consists of the following steps: 1) Steeping of aspen sawdust (0.25-0.50 mm) in water at 7% consistency for 16 h; 2) Cooking at 165-235°C; 3) Rapid discharge (i.e explosion) at $\Delta p = 6.9$ MPa; 4) Quenching. The extent (i.e conversion) and selectivity (i.e. hemicellulose removal vs delignification) of wood solubilization have been studied as a function of cooking temperature in a batch reactor system.

INTRODUCTION

Cellulose, the earth's most abundant organic compound and a renewable resource, has incited researchers to work in the development of new production technologies for fuels, chemicals and food. Chemical treatments of lignocellulosics with NaOH, NH_3, SO_2, H_2SO_4 as well as impregnation and delignification agents have been studied in processes such as chemical and chemimechanical pulping and acid hydrolysis. Their effectiveness depends on cellulose swelling as well as on lignin softening and/or removal. On the other hand, physical treatments, such as crushing and grinding, steaming, and irradiation, have proven to be effective in creating accessibility to chemicals and enzymes[1,2].

Since the energy crisis of the early seventies, several studies have been undertaken which deal with thermochemical processes for biomass conversion, such as gasification, integral liquefaction and pyrolysis[3]. These treatments occur under severe thermal conditions (T=250-1000°C). Liquids obtained from pyrolysis and integral liquefaction are heterogeneous and as a whole can be used only for combustion. More than 250 compounds have been identified in oils resulting from vacuum pyrolysis of wood. In order to isolate these products, it is necessary to use separation technologies (i.e. obtain bulk fractions by solvent extraction followed by a fine separation of each resulting fraction with the use of membranes). In order to avoid these mixtures containing many compounds of different chemical nature, fractionation process has been suggested as an alternative leading to the separation of biomass into its constitutive polymers (i.e. extractives, hemicellulose, cellulose and lignin) in a sequential and selective way. The thermochemical or biochemical upgrading of each fraction leads to the production of separated chemicals

such as xylitol, furfural or protein from hemicellulose, sugars, ethanol or ruminant feed from cellulose and phenols or fuels from lignin[4]. Obviously, this approach differs from the preceding three because fractionation separates before upgrading.

The first step of the fractionation process is the pretreatment (T=150-240°C). This step is important because it allows: a) The solubilization of extractives and hemicellulose; b) The attack of the lignocellulosic complex, which improves the substrate accessibility to further solvolytic, hydrolytic or enzymatic action[1,5]. Since hardwoods are abundant and less used in pulping processes, they have been considered as model substrates for pretreatment studies.

The pretreatment processes can be classified according to the physical state of the solvent:
a) Steam processes. The lignocellulosic substrate is steam-treated at temperatures ranging from 140 to 240°C for 1-2 min followed by a rapid pressure release (i.e. explosion) through a discharge valve. Batch processes use a Masonite gun[6] and continuous processes , like the Stake system[7], are conducted in a horizontal pressurized digester being fed continuously by means of a coaxial reciprocating screw. These steam explosion processes have succeeded in separating lignocellulosic material into individual fibres. This effect has been combined with chemical impregnation to produce new ultra-high-yield chemimechanical pulps which require less refining energy than conventional processes[8,9]. Although the steam explosion processes have been identified as physical processes, they are rather physicochemical processes because two phenomena are present in this pretreatment: a) mechanical action caused by the rapid pressure release; b) chemical action resulting from

autohydrolysis[10] (i.e. hydrolytic attack achieved by the acetic acid formed during the steaming). It has been reported that physicochemical steam explosion pretreatments improve digestion of the resulting residues[11] and shred the fibres into many individual fragments[12].

b) Liquid-phase processes, such as solvolytic delignification in an aqueous solution of phenol (Battelle), explosive expansion with ammonia (Afex), thermolysis in aqueous phase at high temperatures[13], dilute-acid prehydrolysis[14] and thermomechanical pretreatment in aqueous phase[15,16]. In the latter process, an aqueous slurry of lignocellulosic materials flows through a capillary or a homogenization valve with further explosion.

In all cases, the pretreatment is responsible for the structural modification of the lignocellulosic complex which becomes more accessible to reactants and enzymes. It should be remembered that defibration is due to softening and partial dissolution of the compound middle lamella, which is rich in lignin. During pretreatment, the hemicellulose is depolymerized and subsequently solubilized. Moreover, a fraction of the lignin is partially depolymerized and carried into solution. Furthermore, the cellulose undergoes a change in its crystallinity and can also partially depolymerize, depending on operating conditions.

The goal of this paper is to analyze the influence of cooking temperature on both the extent and selectivity of wood solubilization via a thermomechanical pretreatment of aspen in aqueous phase. The analysis of residues permits determination of the operating conditions leading to the hemicellulose solubilization and how much lignin is eventually put into solution.

EXPERIMENTAL

Raw materials

This study was conducted using debarked aspen (*Populus Tremuloides*), a prototype hardwood. Wood chips were ground in order to retain the fraction having a particle size of 0.25-0.50 mm. This size ensures an appropriate specific surface and avoids heat transfer and diffusion problems. It should be noted that grinding is a physical pretreatment which enhances the accessibility to the lignocellulosic complex. The composition of water extracted aspen, as determined by thermogravimetric analysis according to Chauvette et al.[17] method, was the following: hemicellulose: 28.9%, cellulose: 53.4% and lignin: 17.7%. The chemical composition of raw aspen was calculated by taken into consideration the water extractives content: hemicellulose: 26.2%; cellulose: 48.4%; lignin: 16.1% and hot water extractives: 9.3%. The aspen wood used in this work contains a high extractives percentage compared to commonly values found for this species. Inorganic matter (i.e. ash) was approximately 0.6%. The empirical formula of aspen used in this study is $C_6H_{9.03}O_{4.40}$.

Operation of the reactor system

A scheme of the reactor system used is shown in Figure 1. The first autoclave is a cooking digester and the second one acts as a quenching vessel to stop reactions. Both autoclaves were agitated with a Magnedrive device and were connected through an automatic valve.

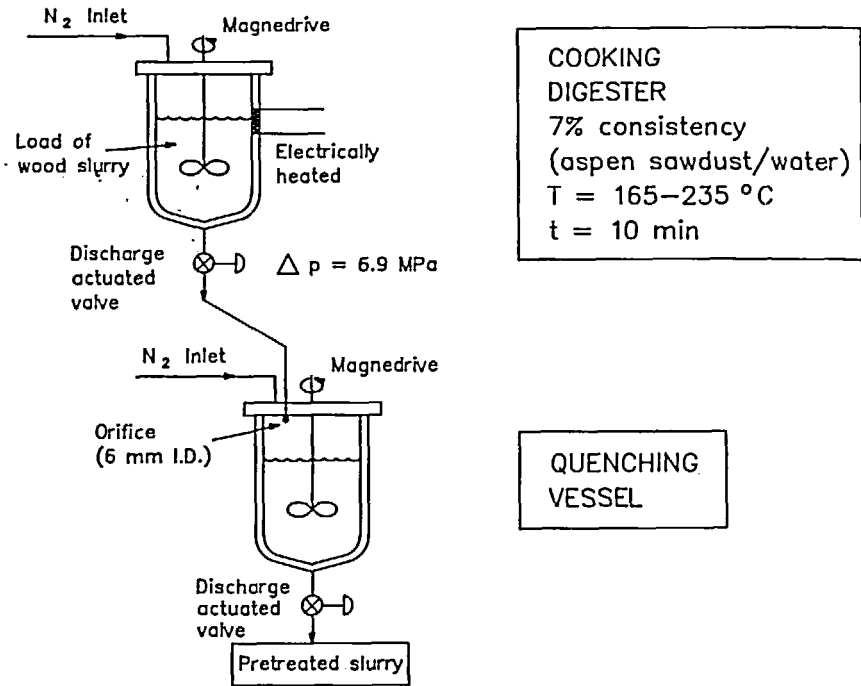The thermomechanical pretreatment experiments were carried out as follows:

N$_2$ Inlet   Magnedrive

COOKING
DIGESTER
7% consistency
(aspen sawdust/water)
T = 165−235 °C
t = 10 min

Load of
· wood slurry   Electrically
                                 heated

Discharge
actuated $\triangle$ p = 6.9 MPa
valve

N$_2$ Inlet   Magnedrive

Orifice
(6 mm I.D.)   QUENCHING
                                 VESSEL

Discharge
actuated
valve

Pretreated slurry

FIGURE 1:   Schematic diagram of batch reactor system.

- Steeping of aspen sawdust in water for 16 h. The consistency
of slurry was 7% wt/wt. Slurries at higher consistencies were
too viscous, resulting in an incorrect flow between autoclaves.
For example, at 10% consistency, 20-40% of initial slurry was
retained in the cooking digester after the discharge.

- Charging the cooking digester with 300-350 mL of wood
slurry, followed by N$_2$ purging.

- Heating up to the prescribed temperature. Long times were
required to preheat the slurry since the autoclave is
electrically heated.

- Pressurization of cooking digester with N$_2$ in order to obtain
a pressure difference between autoclaves of 6.9 MPa when the
slurry is discharged.

- High pressure cooking at a prescribed temperature ranging from 165 to 235°C.
- Discharge of slurry into the quenching vessel through a 6 mm diameter orifice by the opening of a pneumatically actuated automatic valve (i.e, explosion). The pressure gradient at the beginning of the discharge was 6.9 MPa.
- Rapid cooling of pretreated slurry.

Analytical procedure

After the flash discharge, the system was left to cool for a few minutes. Then, the quenching vessel was emptied and the resulting slurry was vacuum filtered and extracted with boiling water in a soxhlet at atmospheric pressure. The residue thus produced was oven-dried at 60°C and preserved for further analysis. It has to be remembered that the pretreatment is performed in aqueous phase. Thus, the residues obtained from the process must be washed with boiling water to recover the soluble substances remaining adhered to the solid substrate. In order to be able to evaluate the net effect of the pretreatment, it is necessary to compare the percentages of constitutive polymers present in the wood to that remaining in the residue, once both have been washed with boiling water. The following analyses (details on apparatus and procedure are available elsewhere[18]) were achieved:
- Thermogravimetric analysis. The characterization of polymers can be done according to two methods: Humid analysis or thermogravimetric analysis. The latter method was chosen for the following reasons: i) The operation is performed in solid phase and consequently no solutions need to be prepared nor reagents to be used; ii) Analysis requires short times (ca. 1 h); iii) Results are reproducible.
- Gas chromatography of sugars obtained by acid hydrolysis. This determination allows the study of the variation of specific
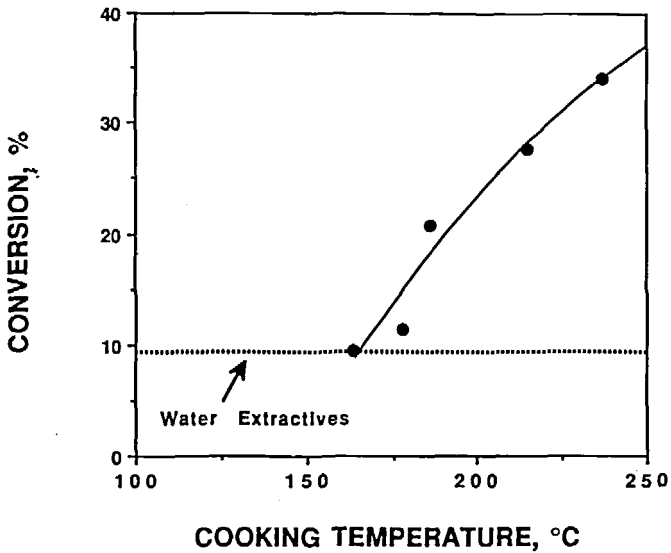
FIGURE 2:   Extent of aspen solubilization as a function of
cooking temperature (conversion is expressed as g
of solubilized matter /100 g of o.d. raw aspen).

markers, such as xylose, mannose and galactose as indicators
of the hemicellulose content in the residues.

RESULTS AND DISCUSSION

We have studied the influence of reaction temperature on both
the extent and selectivity of aspen solubilization by means of a
thermomechanical pretreatment in aqueous phase.

Figure 2 shows the extent of aspen solubilization (i.e.
conversion: g of dissolved matter after hot water extraction /
100 of initial o.d. wood) according to the cooking temperature.

The point at the lowest temperature represents water extracted aspen. It is remarkable that at cooking temperatures below 150°C, the conversion corresponds to the hot water extractives content. Therefore, the pretreatment is ineffective at low thermal severity, probably due to the absence of autohydrolytic reactions in these operating conditions. At higher temperatures, the conversion increases almost linearly with temperature in the range that was studied (4%/10°C and varies from 17 to 38% when temperature rises from 190 to 240°C). The pretreatment leading to the hemicellulose solubilization must dissolve the extractives as well as the lignin present in the compound middle lamella, which accounts for 20-25% of the total lignin[19]. Furthermore, amorphous, low molecular weight cellulose is readily hydrolyzed and is solubilized at about the same rate as hemicellulose. The maximum value is 5-10% of the total cellulose[20-22]. Moreover, complete removal of hemicellulose is not obtainable since to reach levels higher than 90% requires severe conditions[14]. Therefore, the conversion needed to remove 90% of hemicellulose would be around 38.5%. This hypothetical result will be confirmed later when considering the selectivity of the pretreatment.

The conversion is a variable which can easily be evaluated because no chemical analyses are required. However, this macroscopic value gives no information about which substances are solubilized. Consequently, conversion cannot be used to determine the pretreatment selectivity when several reactions occur simultaneously, as when solubilizing wood.

The selectivity of the pretreatment was found by analyzing the residues (i.e. identification and quantitative determination of constitutive polymers in residue). The results reported in Figure 3 represents the mass of holocellulose remaining in the residue after the pretreatment of 100 g of raw o.d. aspen.
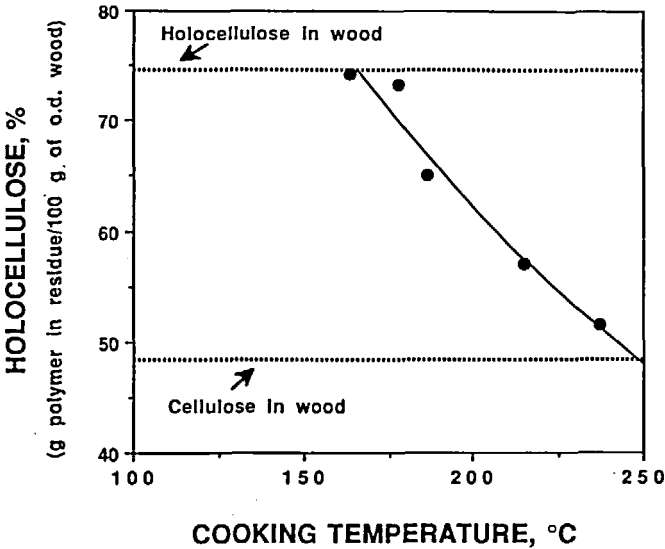
FIGURE 3: Reduction of residual holocellulose content with increasing cooking temperature. The ordinate is expressed as g of holocellulose in the water extracted residue / 100 g of o.d. raw aspen.

These values were calculated by multiplying the percentage of holocellulose remaining in the residue by (1 - conversion). It is observed that there is no holocellulose removal at temperature below 150°C. The removal of 90% of hemicellulose + amorphous cellulose should produce a residue having almost 48.6% of residual holocellulose. This result corresponds to a cooking temperature of about 240°C, at which the conversion is equal to 35%. This agrees with results previously obtained from conversion profiles.

Table 1 gives the content of residual lignin as a function of cooking temperature. Lignin content (expressed as g of lignin / 100 g of hot water extracted residue) stays approximately constant below 180°C. Since conversion increases with

TABLE 1

Extent of   lignin solubilization as a function
of cooking temperature

Cooking Temperature (°C)	Conversion g/100 g o.d. wood (%)	Lignin g/100 g w.e. resid. (%)	Lignin g/100 g o.d. wood (%)
Water Extracted Wood	9.3	17.7	16.1
164	9.5	17.3	15.7
178	11.4	17.3	15.3
186	20.8	18.1	14.3
215	27.7	20.2	14.6
237	34.1	21.2	13.9

temperature, it results in a simultaneous lignin and carbohydrate solubilization. However, at temperatures higher than 180°C, the residue is lignin-enriched due to the increasing carbohydrate dissolution. On the other hand, the lignin content (expressed as g of lignin/100 g of o.d. wood) decreases gradually with temperature, but undergoes little variation at temperatures higher than 185°C. At 237°C, 15% of the initial lignin has been solubilized. This value is below that of 20-25% reported by Sjöström[19]. A fraction of the lignin in the middle lamella could be dissolved during the water extraction of the initial wood, thus reducing the percentage of lignin dissolved during pretreatment when compared to the water extracted wood. There is no evidence in this work of lignin recondensation reactions, because there is no increase in apparent lignin content at high temperatures. However, these reactions were suspected in other works due to the repolymerization between soluble lignin and degradation products[4,23].
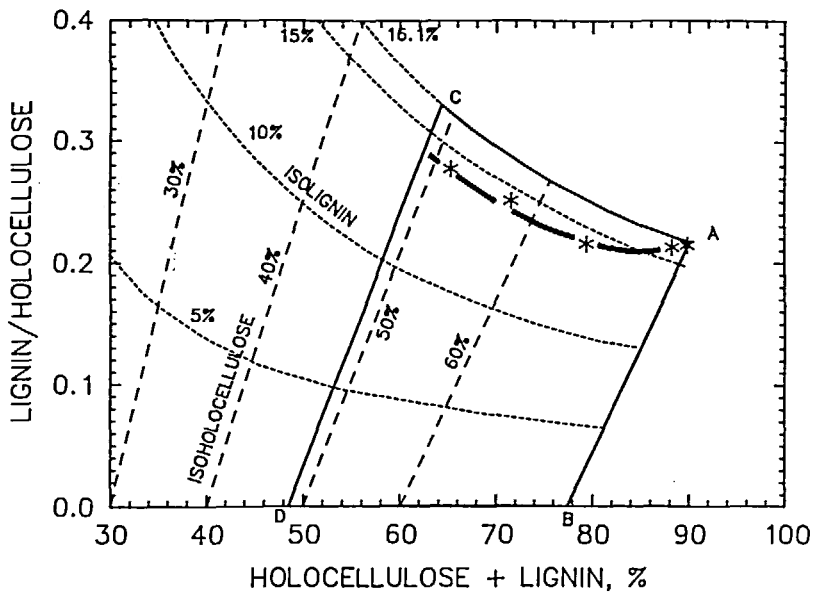
FIGURE 4: Ross diagram for the thermomechanical pretreatment of aspen wood. Holocellulose and lignin are expressed as g of polymer in the water extracted residue / 100 g of raw o.d. aspen.

The Ross diagram is a graphical method representing the evolution of different extractive processes and has been used in pulp and paper industries[24]. This diagram may describe the selectivity of the thermomechanical pretreatment of aspen, as depicted in Figure 4. Ideal extractive processes must follow the quadrilateral lines: A->C: Hemicellulose removal from wood; A->B: Delignification of wood; C->D: Delignification of hemicellulose-free wood; B->D: Hemicellulose removal from holocellulose. Therefore, ideal pretreatment (i.e. removal of hemicellulose) should follow the line A->C. The Ross diagram for the thermomechanical pretreatment of aspen shows that it is not respected because of the simultaneous removal of a fraction of lignin. On the other hand, as expected, an increase in temperature results in an increasing aspen solubilization. At

low temperatures (i.e. high values of holocellulose+lignin), the lignin/holocellulose ratio remains approximately invariable. It means that lignin and carbohydrates are simultaneously solubilized. However, at temperatures higher than 185°C (i.e. holocellulose+lignin lower than 75%), the solubilization of aspen follows an - isolignin line of 14%, thus indicating that carbohydrates are preferentially dissolved. The solubilization line intersects the line CD (i.e. total removal of hemicellulose) at a value of holocellulose+lignin equal to 62.7%. Thus, the solubilization of 90% of hemicellulose is reached at conversion of 34.7%. This value confirms the results evaluated by calculation from both conversion and residual holocellulose profiles.

As reported in Table 2, the main sugar present in hemicellulose is xylose. Therefore, this monosaccharide may be considered as an indicator of the hemicellulose solubilization. As observed, the xylose content decreases with rising cooking temperature. At 237°C, the residue contains mainly glucose with a small amount of xylose (probably corresponding to slowly-hydrolyzable xylose), thus indicating that hemicellulose has been put into solution in these conditions.

The simultaneous solubilization of most of the hemicellulosic carbohydrates and a fraction of lignin occurs in initially neutral aqueous medium. This dissolution may be explained by the following phenomena: i) Thermochemical reactions, such as hydrolytic reactions (i.e. dissociation of water and autohydrolysis) and lignin repolymerization reactions. The latter appears not to be significant in this work. On the other hand, it has been shown that H_3O^+ species coming from water dissociation are not comparable to that resulting from acetic acid dissociation below 300°C[23]. Therefore, autohydrolysis must be considered the main thermochemical mechanism leading to the solubilization/depolymerization of hemicellulose. ii) Sudden decompression. When the slurry is

TABLE 2

Monosaccharides content of aspen residues
as a function of cooking temperature

Cooking Temperature (°C)	Monosaccharide g/100 g carbohydrate in residue (%)			
	Xylose	Mannose	Galactose	Glucose
164	16.1	3.4	0.4	79.6
186	9.9	1.8	0.7	87.6
215	5.6	1.9	1.0	91.5
237	2.3	0.7	0.7	96.3

rapidly decompressed, vapor bubbles are formed from liquid water, thus producing an expansion of the lignocellulosic matrix leading to defibration.

CONCLUSIONS

This study has shown that the thermomechanical pretreatment of aspen in a batch reactor system is possible in aqueous phase and in the absence of chemicals. The solubilization of wood may be studied by means of a macroscopic variable: the conversion. The pretreatment is ineffective at low thermal severity since at temperatures lower than 150°C, conversion remains invariable and is equal to the water extractives content. The removal of almost all the hemicellulose is accomplished at

about 240°C. Under these conditions, 35% of initial aspen is dissolved. This conversion is higher than the (water extractives + hemicellulose) content because the thermomechanical pretreatment puts into solution other substances, such as 15% of the initial lignin and probably 5-10% of the initial cellulose (i.e. easy-hydrolyzable cellulose). The softening of the middle lamella at high temperature leads to a partial dissolution of the lignin contained between the fibres. This fact indicates that ideal pretreatment is not achieved by this one-stage process in aqueous phase. Therefore, it is necessary to add swelling chemicals in order to protect lignin. However, it would be possible to obtain almost pure hemicellulose in aqueous medium without the addition of chemicals by means of a two-stage process. 1) Pretreatment at 180-185°C. Water extractives as well as most of the soluble lignin are solubilized. A small fraction of hemicellulose is inevitably also put into solution. 2) Pretreatment of residue at 240°C. In this step, the hemicellulose is preferentially solubilized.

Autohydrolytic reactions and mechanical effects due to the rapid pressure release (i.e explosion) are responsible for yielding a more accessible residue, which may be subsequently converted into chemicals by fractionation routes following the thermomechanical pretreatment (i.e. solvolytic extraction of lignin with dioxane or NaOH and/or acid hydrolysis of the modified cellulose).

It has been shown that the Ross diagram describes correctly the selectivity of aspen solubilization and permits evaluation of the operating conditions at which hemicellulose is entirely removed from wood.

ACKNOWLEDGEMENTS

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