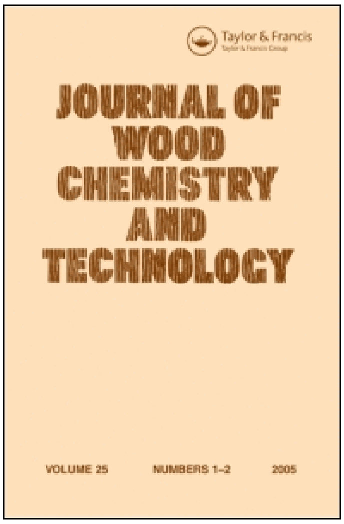

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Abstract: A pre-hydrolysis step to remove hemicelluloses from mixed hardwood chips consisting of maple, aspen, and birch with a ratio of 7:2:1 has been carried out. The effects of parameters on the pre-hydrolysis such as time, temperature, acetic acid addition, and raw material species, were determined. Different sugars, acetic acid, and furfural formation in the pre-hydrolysis liquor were quantified. The results showed that the pre-hydrolysis is a dynamic process, in which the removal of hemicelluloses increased with time while the conversion of extracted hemicelluloses to monosaccharides due to acid hydrolysis increased and part of the xylose was converted to furfural. The maximum temperature was the most critical parameter for hemicelluloses extraction and conversion, and a temperature of 170°C was the optimum for hemicelluloses extraction with relatively low conversion of xylose to furfural. About 11% of the xylan (in both monomeric and oligomeric forms) was removed at 170°C. Due to the presence of a high amount of xylan, birch produced the highest amount of xylose, followed by maple, and then aspen.

Keywords: Acetic acid, dissolving pulp production, furfural, hemicelluloses, mixed hardwood chips, pre-hydrolysis, xylan

INTRODUCTION

In the pre-hydrolysis kraft dissolving pulp production process, the wood chips are first pre-treated in a high-temperature pre-hydrolysis step to remove

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hemicelluloses. The hemicelluloses-depleted wood chips are then subjected to kraft pulping to remove lignin. The pulp is then bleached with the production of relatively pure cellulose as the dissolving pulp. During the downstream processes associated with dissolving pulp, hemicelluloses, such as xylans, can precipitate onto the cellulose micro-fibrils and cause operational and quality issues,[1] and therefore must be removed in the pulping process. A pre-hydrolysis step can serve the purpose of removing hemicelluloses from wood chips. Hemicelluloses removed can be a valuable source of hexose and pentose sugars,[2–5] and they can be further converted into value-added products such as ethanol, polymers, and other chemicals.[6] Therefore, the pre-hydrolysis kraft dissolving pulp production process naturally fits into the forest biorefinery concept.

Many studies on pre-hydrolysis of wood chips have been reported. Tunc and van Heiningen[7] made a systematic study on the dissolution profile of wood components: cellulose, hemicelluloses, and lignin from southern hardwood chips during the autohydrolysis at temperatures of 130 to 170°C in a modified accelerated solid pre-hydrolysis system (Dionex ASE-100). They found that xylo-oligomers were the predominant components in the extract at temperatures higher than 150°C, small amounts of furfural and hydroxymethylfurfural were produced at temperatures higher than 160°C, and most of the arabinan and galactan were removed from the wood at 160°C.[7] Casebier et al.[8] found that the pre-hydrolysis of southern pine chips by water at 170°C can essentially dissolve all of the arabino-galactan, some arabinoxylan, some galactoglucomannan, and some glucomannan while mannose- and xylose-containing polymers became significant when the reaction temperature was higher. Garrote et al.[9, 10] reported the results on autohydrolysis of *Eucalyptus*, and found that up to 90.4% of the initial xylan was removed in the pre-hydrolysis while the removal of cellulose was negligible. The autohydrolysis conditions can affect the process and the sugar composition significantly.[11] A post-hydrolysis with acid-catalyst at a low reaction temperature produced a xylose stream with a low inhibitor content for further fermentation.[12]

Hardwood species are important fiber resources, not only in Canada, but also in other countries.[13] In this article, we determined the characteristics of the pre-hydrolysis step of mixed hardwood species, which is the feed stock to an Eastern Canadian mill in the production of dissolving pulp based on the pre-hydrolysis kraft pulping process.

EXPERIMENTAL

Material

Maple, poplar, and birch wood chips were all supplied by a mill in Eastern Canada. The wood chips were classified in a chip classifier with 8 mm bar screen, 12.7 mm (1/2 inch) round screen. The bar screen is to control the chip thickness while the round screen is to control the chip width. The wood chips passing 8 mm bar screen and retaining on the 12.7 mm (1/2 inch) round screen were used. The mixed chips were used with a ratio of 7:2:1 for maple, poplar, and birch, respectively, in the study except for the experimental program on the effect of chip species, where the single wood species was used.

Pre-Hydrolysis

Wood chips were pretreated in water under vacuum overnight to remove air before the pre-hydrolysis experiments. Equivalent to 150 g wood chips and the required amount of water were added into a Parr reactor (Parr Instrument Company, Moline, Illinois, USA) with a circulation pump. The wood-to-liquid ratio was 1:4. The system was pre-warmed to 80°C, then heated to the maximum temperature in one hour, and then kept at the maximum temperature for a required duration. After that, it was cooled down to about 80°C. The pre-hydrolysis liquor was taken out and filtered by a cloth.

The maximum temperature used was 170°C except for the section on the effect of maximum temperature where the maximum temperature varied from 150, 170, 190, and 210°C. The time at the maximum temperature was 60 min. except for the program on the effect of pre-hydrolysis time, where the time varied from 30, 60, 90, and 120 min.

The repeatability of the pre-hydrolysis experiments was determined at the beginning of this project, and it was within 5%, and was supported by the verification experiments.

Post Acid Hydrolysis of the Pre-Hydrolysis Liquor

To hydrolyze the oligomers in the pre-hydrolysis liquor into monomeric sugars, a vial containing 1 mL of the pre-hydrolysis liquor and 20 ml 4% sulfuric acid was sealed in an autoclave before the autoclave was put in an oil bath (Neslab Instruments, Inc., Portsmouth, N.H., USA). The autoclave was kept in the oil bath at 121°C for one hour. This post acid hydrolysate was used to determine the total saccharides in the pre-hydrolysis liquor.

Sugar Analysis

The monomeric sugar contents in the pre-hydrolysis liquor and the acid hydrolysate were determined by using an Ion Chromatography[14] with a Pulse Amperometric Detector and CarboPac^{TM} PA1 column (Dionex-300, Dionex Corporation, Canada). De-ionized water was used as eluant with a flow rate of 1 mL/min, 0.2 N NaOH was used as the regeneration agent with 1 mL/min flow rate and 0.5 N NaOH was used as the supporting electrolyte with 1 mL/min flow rate. The samples were filtered and diluted prior to analysis. The experimental error for the sugar analysis was within 6%. The monomeric sugar contents in the post acid hydrolysate stood for the total saccharides in the pre-hydrolysis liquor. The sugar contents in oligomer form in the pre-hydrolysis liquor were calculated from the difference of the monomeric sugar contents with and without the post acid hydrolysis.

For sugar composition in the raw material, equivalent to 50 mg of wood meal was weighed into a vial that contained 1 mL 72% sulfuric acid. This strong acid hydrolysis was performed at room temperature for 1 hour on a shaker. Subsequently the sample in the vial was diluted by 17 mL water, sealed and transferred to an autoclave for further hydrolysis at 120°C for 1 hour. The same sugar analysis procedure mentioned earlier was then followed.

Acetic Acid and Furfural Analysis

The contents of acetic acid and furfural were determined by following an nuclear magnetic resonance (NMR) method.[15, 16] Both the pre-hydrolysis liquor and the post acid hydrolysate were analyzed for the acetic acid content. The acetic acid content in the pre-hydrolysis liquor represents the true amount of acetic acid in the pre-hydrolysis step, while that of the post acid hydrolysate is the sum of free acetic acid and acetyl groups bound to oligomers in the pre-hydrolysis liquor. The difference between them represented the acetyl groups bounded to oligomers in the pre-hydrolysis liquor. The repeatability of the acetic acid and furfural results was within 3%.

RESULTS AND DISCUSSION

Characterization of Raw Material

Wood meals of poplar, maple, and birch were hydrolyzed and the hydrolysates were subjected to sugar analysis. The results were shown in Table 1. It can be seen that xylan is the major hemicelluloses in these species and the contents are 19.74%, 19.96% and 25.46% for poplar, maple, and birch, respectively.

Table 1. Chemical composition of the raw materials (based on wood,%)

Wood species	Arabinose +Rhamnose	Galactose	Glucose	Xylose	Mannose	Acetyl
Poplar	0.66	0.64	61.86	19.74	0.23	4.48
Maple	0.97	0.88	56.20	19.96	2.66	4.90
Birch	0.79	1.01	51.89	25.46	1.50	5.66
Mixed*	0.89	0.85	56.90	20.47	2.06	4.89

*maple:poplar:birch = 7:2:1.

The acetyl group contents are 4.48%, 4.90%, and 5.66% for poplar, maple, and birch, respectively, and birch has the highest acetyl group content, which is in good agreement with the reported results in the literature (3.7%–5.65% for birch[17]). Hardwoods have a high proportion of xylose units and more acetyl groups than softwoods, indicating that when hardwoods are used as the feed stock more xylose and acetic acid will be generated during the pre-hydrolysis process.

Effect of Pre-Hydrolysis Time

We first investigated the effect of pre-hydrolysis time on the removal of hemicelluloses during the pre-hydrolysis step. The results were shown in Table 2. It is evident that sugars are present in the pre-hydrolysis liquor in both monomeric form and oligomeric form. The pre-hydrolysis is a dynamic process, in which the breakage of hemicelluloses, dissolution of oligomers, and the further hydrolysis of oligomers happen at the same time, while simultaneously acetic acid, which is the acid source for hydrolysis and dissolution of hemicelluloses, is generated.

It can also be found in Table 1 that the arabinose and rhamnose contents in the mixed chips is 0.89%. Based on the results in Table 2, we can find that arabinose and rhamnose were present in both monomeric and oligomeric forms

Table 2. Chemical composition of pre-hydrolysis liquors with different pre-hydrolysis time (based on wood,%)

Time*/min	30	60	90	120
Arabinose				
monomeric	0.25	0.28	0.28	0.22
oligomeric	—	0.02	0.04	0.00
Rhamnose				
monomeric	0.16	0.13	0.19	0.19
oligomeric	—	0.14	0.13	0.04
Galactose				
monomeric	0.19	0.16	0.24	0.27
oligomeric	0.02	0.30	0.37	0.21
Glucose				
monomeric	0.08	0.11	0.15	0.24
oligomeric	0.25	0.63	0.74	0.65
Mannose				
monomeric	0.04	0.08	0.17	0.27
oligomeric	0.36	0.71	0.93	0.75
Furfural	0.12	0.37	0.86	1.31

*Time: pre-hydrolysis time at the maximum temperature.

although the majority of arabinose is in the monomeric form. The presence of rhamnose and arabinose was also reported by others[18, 19] during the pre-hydrolysis step of other wood chips from the removal of xylan. Tunc and van Heiningen[7] reported that during the pre-extraction of mixed southern hardwood chips, the maximum arabinose content in the hydrolysate was 0.38%, while the arabinose content in the raw material was 0.52%. Arabinose units linked to the xylan backbone are highly labile to hydrolysis and the monomeric sugars can be further converted to furfural.[20] Table 2 showed that the total contents of arabinose and rhamnose saccharides reached the maximum at 90 min; subsequently it decreased due to the fact that monomeric arabinose underwent further dehydration to form furfural.

Galactose, glucose, and mannose were present in the pre-hydrolysis liquor in both monomeric and oligomeric forms, although the oliogmeric sugars are dominant (Table 2). Extending the pre-hydrolysis time from 90 to 120 min resulted in decreases of hexose contents in the oligomeric form while the monomeric contents exhibited some increases, indicating that further hydrolysis of the dissolved oligomeric sugars did occur. The sum of monomeric and oligomeric galactose showed a small decrease when the pre-hydrolysis time was extended from 90 to 120 min, which may be explained by the further conversion of monomeric galactose to other chemicals (e.g., hydroxymethyl furfural (HMF)). Tunc and van Heiningen reported that the pre-hydrolysis of mixed southern hardwood chips at 170°C for 100 min produced some HMF, although not significant.[21]

In Figure 1 xylose in monomeric/oligomeric form and total xylose saccharides contents in the pre-hydrolysis liquor were shown. The monomeric

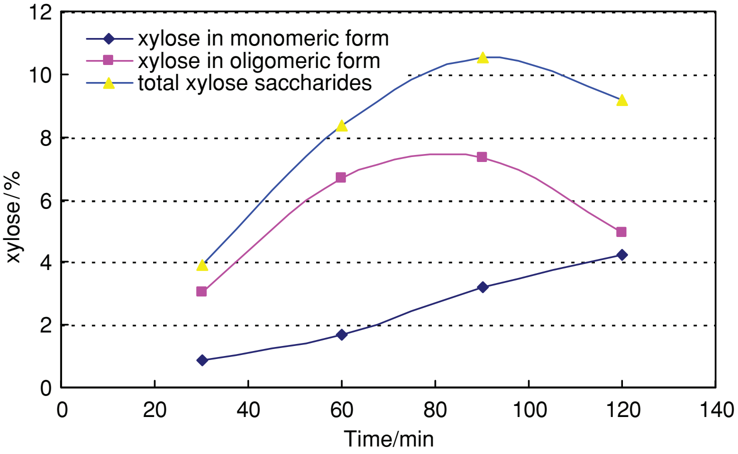

Figure 1. Xylose of different forms in the pre-hydrolysis liquor. Figure available in color online.

xylose content increased rapidly; after 120 min under the conditions specified, about 4.3% xylose in oligomeric form was present in the pre-hydrolysis liquor. The xylose in oligomer form reached a maximum at 90 min. Extending the pre-hydrolysis time can cause further hydrolysis of xylose oligomer into monomeric xylose, some of which was further dehydrated to produce furfural, resulting in the increase of furfural concentration in the pre-hydrolysis liquor. The presence of xylose in both monomeric and oligomeric form was also noted in an earlier study by Tunc and van Heiningen.[21]

The total xylose saccharides content in the mixed wood species was 20.47% (expressed as xylose). At the maximum of 10.54% obtained at 90 min, one can calculate that about 51.49% of the xylose sacharides removed from the wood chips during the pre-hydrolysis under the conditions studied, 30.55% of which was in the monomeric form while the remainder was in the oligomeric form. The implication of these results is that further hydrolysis, either hydrolytic or enzymatic, to break down the oligomers is needed prior to down-stream processing.

In Figure 2 the results on the amounts of acid and acetyl group bounded to oligomers in the pre-hydrolysis liquor were shown. The amount of acetic acid increased with the extension of the pre-hydrolysis time, while the acetyl group bounded to oligomers increased to the maximum at 90 min and then decreased at 120 min. The total acetyl group, expressed as acetic acid, in the pre-hydrolysis liquor reached the maximum of 3.76% at 90 min. The ratio of total acetyl group to the total xylose saccharides was 0.615, 0.338, 0.357, and 0.411 at the pre-hydrolysis time of 30, 60, 90, and 120 min, respectively.

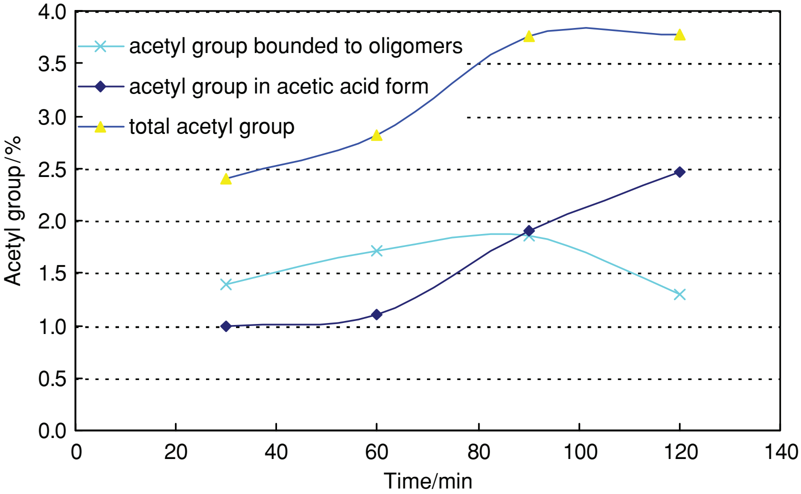

Figure 2. Acetyl group in acid acid form and acetyl group bounded to oligomers in the pre-hydrolysis liquor. Figure available in color online.

These results support the conclusion that the removal rate of acetyl groups was higher than that of xylose saccharides from the wood at the initial phase of the hydrolysis while the opposite was true in the latter phase of the process. Amidon and Liu[4] reported the concentrations of acetic acid and acetyl groups associated with polysaccharides in the wood extract as functions of hot-water extraction time.

Effect of Maximum Temperature

The effect of maximum temperature on the hemicelluloses pre-hydrolysis was determined at different maximum temperatures. The results were shown in Table 3. It can be seen that the maximum temperature is the key parameter that determines the sugar composition in the pre-hydrolysis liquor. It was also reported earlier[22] that the temperature, instead of the acid concentration, can significantly affect the hydrolytic pretreatment of poplar.

Table 3. Chemical composition of pre-hydrolysis liquors at different maximum temperatures (based on wood,%)

Max. temperature/°C	150	170	190	210
Arabinose				
monomeric	0.15	0.28	0.09	0.00
oligomeric	0.15	0.02	0.02	0.00
Rhamnose				
monomeric	0.02	0.13	0.10	0.01
oligomeric	0.07	0.14	0.04	—
Galactose				
monomeric	0.02	0.16	0.23	0.52
oligomeric	0.11	0.30	0.06	—
Glucose				
monomeric	0.02	0.11	0.38	0.03
oligomeric	0.22	0.63	0.35	0.66
Xylose				
monomeric	0.05	1.68	3.20	0.03
oligomeric	0.93	6.66	0.72	0.02
Mannose				
monomeric	0.00	0.08	0.42	0.06
oligomeric	0.25	0.71	0.34	—
Acetyl removed				
HAc form	0.32	1.10	3.33	4.97
bounded to oligomers	0.28	1.72	1.08	0.07
Furfural	0.01	0.37	2.99	3.65

Only a small amount of hemicelluloses was extracted at 150°C and the total xylose saccharides was only 0.98%. At 170°C the total xylose saccharides produced was 8.34% with the majority (6.66%) in the oligomeric form. At 190°C, the total xylose saccharides decreased significantly (3.20% in the monomeric form and 0.72% in the oligomeric form). At 210°C the presence of xylose saccharides were negligible. The decreased xylose saccharides was certainly due to their further conversion to others, such as furfural. For the purpose of utilization of xylose saccharides from the pre-hydrolysis liquor, a 170°C temperature appears to be ideal in such a process.

When the maximum temperature was increased to 190°C, a significant amount of furfural was produced in the pre-hydrolysis liquor (2.99%). The mass balance indicated that the amount of furfural generated could not account for the loss of five-carbon sugars, indicating that other chemicals including furfural-based polymers,[23, 24] could be formed during the course of reactions. The total acetyl group was further increased to 4.41%, 1.08% of which was still bounded to oligomers. Although we did not quantitatively determine the amount of HMF in the pre-hydrolysis liquor, the NMR spectrum showed that some HMF was produced. The amounts of glucose and mannose were almost unchanged, but one can find that at a higher temperature, more were in the monomeric form.

When the maximum temperature was increased to 210°C, almost all of the five-carbon sugars were consumed, which caused a great increase in the amount of furfural in the pre-hydrolysis liquor (3.65%). The amount of monomeric galactose was increased. The total acetyl group was 5.04%, which was higher than the original acetyl content of 4.89% in the raw material. Takeuchi et al.[25] proposed the decomposition of six carbon sugars to levulinic acid or HMF and their further degradation into acetic acid. Even at 210°C, the sum of monomeric and oligomeric glucose remained at a low level, which is consistent with those reported by Garrote et al.[20]

Effect of Acetic Acid Addition

Acetic acid is generated in the pre-hydrolysis process, and it can catalyze the hemicelluloses hydrolysis.[26–28] In reality, due to the recycling/re-use of weak pre-hydrolysis liquor, acetic acid may be present at the beginning of the pre-hydrolysis process. We studied the effect of acetic acid addition on the pre-hydrolysis process. Experimental conditions were the same as those in Table 2 except that an equivalent to 6g $\cdot$ L^{-1} acetic acid was added into the pre-hydrolysis system. The results were shown in Table 4. When comparing those in Table 2, we found that the time needed to reach the maximum total xylose saccharides yield was shortened by the addition of acetic acid, while the xylose in monomeric form at the pre-hydrolysis time of 60–90 min were also increased. These results support the conclusion that the addition of acetic

Table 4. Effect of acetic acid addition on the composition of pre-hydrolysis liquors (based on wood,%)

Pre-hydrolysis time at max. temperature/min	30	60	90	120
Arabinose				
monomeric	0.36	0.29	0.27	0.21
oligomeric	0.00	0.02	0.00	0.01
Rhamnose				
monomeric	0.10	0.15	0.18	0.19
oligomeric	0.11	0.13	0.11	0.04
Galactose				
monomeric	0.13	0.20	0.24	0.28
oligomeric	0.26	0.32	0.27	0.16
Glucose				
monomeric	0.07	0.11	0.18	0.23
oligomeric	0.56	0.70	0.65	0.52
Xylose				
monomeric	0.72	2.02	3.35	4.03
oligomeric	6.59	7.78	6.25	3.94
Mannose				
monomeric	0.04	0.11	0.20	0.28
oligomeric	0.77	0.86	0.85	0.65
Acetyl removed				
HAc form	2.67	3.22	3.70	4.43
bounded to oligomers	2.04	1.78	1.75	1.38
Furfural	0.11	0.50	0.80	1.49

acid can speed up: (i) the degradation of hemicelluloses into oligomers; (ii) the conversion of oligomers into monomeric sugars.

Effect of Chip Species

Different wood species have different hemicelluloses contents and their responses to the pre-hydrolysis were different. We studied maple, birch, and poplar wood chips separately. The results were shown in Table 5. We can see that the total xylose saccharides contents were 7.99%, 8.57%, and 10.98% for poplar, maple, and birch, respectively, representing about 40.5%, 42.9%, and 43.1% xylan removal.

The total acetyl group removed were 2.91%, 2.94%, and 3.66% for poplar, maple, and birch, respectively (Table 5), which corresponded to 65.0%, 60.0%, and 64.7% removal from the raw materials. Evidently, birch can produce the

Table 5. Chemical composition of pre-hydrolysis liquors with different wood species at 170°C (based on wood,%)

Wood species	Poplar	Maple	Birch
Arabinose			
monomeric	0.21	0.41	0.25
oligomeric	0.00	—	—
Rhamnose			
monomeric	0.11	0.14	0.15
oligomeric	0.12	0.13	0.12
Galactose			
monomeric	0.11	0.16	0.17
oligomeric	0.23	0.27	0.38
Glucose			
monomeric	0.05	0.08	0.05
oligomeric	0.33	0.62	0.33
Xylose			
monomeric	1.17	1.38	2.11
oligomeric	6.82	7.19	8.87
Mannose			
monomeric	0.04	0.08	0.05
oligomeric	0.53	0.82	0.49
Acetyl removed			
HAc form	1.26	1.02	1.25
bounded to oligomers	1.65	1.92	2.41
Furfural	0.36	0.29	0.36

highest amount of acetic acid and acetyl groups bounded to oligomers in the pre-hydrolysis liquor.

CONCLUSIONS

Oligomeric and monomeric sugars, acetic acid, and furfural co-existed in the pre-hydrolysis liquor. The process of pre-hydrolysis is a complex dynamic system that consists of: (1) the formation of acetic acid, (2) breakage of hemicelluloses and dissolution of oligomers, (3) degradation of oligomeric sugars to monomeric sugars, (4) decomposition of monomeric sugars to HMF and furfural, and (5) further reactions related to HMF and furfural. Increasing the pre-hydrolysis time and the maximum temperature resulted in: (1) the formation of more acetic acid; (2) the conversion of more oligomeric sugars to monomeric sugars. For the mixed chips, 10.54% of the total xylose saccharides content in the liquor was reached when the pre-hydrolysis was performed at 170 (°C and 90 min. The pre-hydrolysis condition, such as time, temperature should be controlled in order to produce the targeted final products (e.g., oligomeric sugars, monomeric sugars, furfural). For the purpose of hemicelluloses utilization from the pre-hydrolysis liquor, a pre-hydrolysis temperature of 170 (°C was optimum.

Acetic acid can speed up the hemicelluloses pre-hydrolysis and conversion. Therefore, by adding acetic acid, and/or recycling the pre-hydrolysis liquor, the hemicellulose pre-hydrolysis time of the pre-hydrolysis kraft dissolving pulp production process can be shortened; as a result, the throughput of the process can be increased.

Among the species studied, birch was the best species for xylose production, maple the second, and poplar the third. The total xylose saccharides content reached to 10.98% and the acetyl group removal was 3.66% at 170°C for birch.

REFERENCES

1. Sixta, H. *Handbook of Pulp*; WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2006.
2. Linko, M.; Vikari, L.; Suihko, M-L. Hydrolysis of xylan and fermentation of xylose to ethanol. Biotech Advs., **1984**, *2*, 233–252.
3. Amidon, T.E.; Christopher, D.W.; Shupe, A.M.; Wang, Y.; Graves, M.; Liu, S. Biorefinery: Conversion of woody biomass to chemicals, energy and materials. J. Biobased Materials Bioenergy., **2008**, *2* (2), 100–120.
4. Amidon, T.E.; Liu, S. Water-based woody biorefinery. Biotechnology Advances., **2009**, *27* (5), 542–550.
5. Chambost, V.; Mcnutt, J.; Stuart, P.R. Guided tour: Implementing the forest biorefinery (FBR) at existing pulp and paper mills. Pulp and Paper Canada., **2008**, *109* (7), 1–9.
6. van Heiningen, A.R.P.; Tunc, M.S.; MacEwan, K. Prehydrolysis of hemicellulose from mixed southern hardwood using hot water prehydrolysis. AIChE Annual Meeting, Conference Proceedings, 05 AIChE: 2005 AIChE Annual Meeting and Fall Showcase, Conference Proceedings, 9527, 2005.
7. Tunc, M.S.; van Heiningen, A.R.P. Hydrothermal dissolution of mixed southern hardwoods. Holzforschung., **2008**, *62* (5), 539–545.
8. Casebier, R.L.; Hamilton, J.K.; Hegrert, H.L.G. Chemistry and mechanism of water prehydrolysis on southern pine wood. Tappi J., **1969**, *52* (12), 2369–2377.
9. Garrote, G.; Dominguez, H.; Parajö, J.C. Mild autohydrolysis: An environmentally friendly technology for xylooligosaccharide production from wood. J. Chem. Technol. Biotechnol., **1999**, *74*, 1101–1109.
10. Garrote, G.; Parajö, J.C. Non-isothermal autohydrolysis of eucalyptus wood. Wood Sci. Technol., **2002**, *36*, 111–123.
11. Garrote, G.; Cruz, J.M.; Dominguez, H.; Parajö, J.C. Valorisation of waste fractions from autohydrolysis of selected lignocellulosic materials. J. Chem. Technol. Biotechnol., **2003**, *78*, 392–398.

12. Garrote, G.; Dominguez, H.; Parajö, J.C. Generation of xylose solutions from eucalyptus globules wood by autohydrolysis-posthydrolysis processes: Posthydrolysis kinetics. Bioresource Technology., **2001**, *79*, 155–164.
13. Yang, S.; Lu, L.; Ni, Y. Cloned poplar as a new fiber resource for the Chinese Pulp and Paper Industry. Pulp Paper Canada., **2006**, *107* (2), 34–37.
14. Davis, M.W. A rapid modified method for compositional carbohydrate analysis of lignocellulosics by high pH anion-exchange chromatography with pulsed amperometric detection (HPAEC/PAD). J. Wood Chem. Technol., **1998**, *18* (2), 235–252.
15. Ni, Y.; Kang, G.J.; van Heiningen, A.R.P. Are hydroxyl radicals responsible for degradation of carbohydrates during ozone bleaching of chemical pulp? J. Pulp and Paper Sci., **1996**, *22* (2), 53–57.
16. Ni, Y.; Kang, G. Formation of peracetic acid during peroxide bleaching of mechanical pulp. Appita J., **2007**, *60* (1), 70–73.
17. Fengel, D.; Wegener, G. *Wood Chemistry, Ultrastructure, Reactions*. Paperback Edition, Walter de Gruyter, Berlin, 1989.
18. Mittal, A.; Scott, G.M.; Amidon, T.E., et al. Quantitative analysis of sugars in wood hydrolyzates with ^{1}H NMR during the auto-hydrolysis of hardwoods. Bioresource Techonol., **2009**, *100*, 6398–6406.
19. Liu, S. A kinetic mode on autocatalytic reactions in woody biomass hydrolysis. J. Biobased Mater. Bioenergy., **2008**, *2* (2), 135–147.
20. Garrote, G.; Dominguez, H.; Parajö, J.C. Production of substituted oligosaccharides by hydrolytic processing of barley husks. Ind. Eng. Chem. Res., **2004**, *43* (7), 1608–1614.
21. Tunc, M.S.; van Heiningen, A.R.P. Lignin carbohydrate complexes (LCC) in the autohydrolysis extract of hardwoods. 94th Annual Meeting, Pulp and Paper Technical Association of Canada, B451–B456, **2008**.
22. Alireza, E.; Andrew, G.H.; John, J.F., et al. Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass. Bioresource Technol., **1997**, *59*, 129–136.
23. Shin, S.; Cho, N. Conversion factors for carbohydrate analysis by hydrolysis and ^{1}H-NMR spectroscopy. Cellulose., **2008**, *15*, 255–260.
24. Root, D.F.; Saeman, J.F.; Harris, J.F. Kinetics of the acid-catalyzed conversion of xylose to furfural. Forest Products J., **1959**, *9*, 158–165.
25. Takeuchi, Y.; Jin, F.; Tohji, K., et al. Acid catalytic hydrothermal conversion of carbohydrate biomass into useful substances. J. Mater. Sci., **2008**, *43*, 2472–2475.
26. Goyal, G.C.; Lora, J.H.; Pye, E.K. Autocatalyzed organosolv pulping of hardwoods. Tappi J., **1992**, *75* (2), 110.
27. Ni, Y.; Hu, Q. ALCELL® lignin solubility in ethanol-water mixtures. J. of Appl. Polymer Science, **1995**, *57*, 1441.
28. Ni, Y.; van Heiningen, A.R.P.; Lora, J.; Magdzinski, L.; Pye, E.K. A novel ozone bleaching technology for the ALCELL® process. J. Wood Chem. and Technol., **1996**, *16* (4), 367–380.