Integrated Forest Products Refinery (IFPR)

FINAL REPORT

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EXECUTIVE SUMMARY

Managed forests in the US have enormous potential as sources of bioenergy and biomaterials. Realizing this potential requires an approach that integrates new separation and conversion technologies with existing forest products procurement, production and delivery infrastructure.

US chemical pulp mills receive more than 100 million dry tons of wood each year. The objective of this project is to evolve existing chemical pulp and wood product mills into Integrated Forest Products Refineries (IFPRs) that produce new biomaterials and export renewable energy while continuing to meet the demand for pulp and paper products. The transition to IFPRs will be enabled by economic returns from ongoing pulp and paper production, while producing additional biomaterials and renewable energy.

In an IFPR it is most cost effective to use trees principally for solid wood production, while the residual wood fiber and biomass (bark) are used for pulp and power production respectively. The dominant kraft pulping process is then used to release the highest quality fiber for pulp production from essentially all hardwood and softwood species with minimal environmental impact. The kraft pulp yield is only about 50% because most of the hemicelluloses and almost all the lignin dissolve in the spent pulping stream, called black liquor. The black liquor is combusted for steam and electricity generation, while the dissolved inorganic cooking chemicals are recovered and recycled for pulping. Since the heating value of the carbohydrates is much less than that of lignin, the combustion of dissolved hemicelluloses does not constitute optimal economical use of this resource. Therefore, in the present studied IFPR concept, a significant amount of the hemicelluloses are extracted from the wood chips prior to pulping. The dissolved hemicelluloses are then partially adsorbed on the kraft fibers to increase pulp yield and final paper quality. The hemicelluloses in the extract could also be used as feedstock for sugar based polymers, chemicals and/or liquid transportation fuels.

The objective of the present project is to develop the following processes and products:
1. Extraction of Hemicelluloses from Wood Chips and its Integration in the Pulp Production.
2. Development of Renewable Materials using Extracted Hemicelluloses or Cellulosic Fibers.

Task 1 was performed by PI, Adriaan van Heiningen, in collaboration with International Paper. Task 2 was performed by co-PI, Douglas Gardner. Both PI and co-PI are professors at the University of Maine.

In the original proposal Task 1 was to use alkaline liquors for pre-extraction of hardwood chips and use autohydrolysis for softwood chips, followed in both cases by modified kraft cooking to produce bleachable grade pulp. The objective was to obtain pre-extracted kraft pulp yields and paper properties comparable to that of the corresponding conventional kraft pulps and paper respectively. Then the pre-extracted wood solution would be used to increase the yield and properties of the kraft pulps made from the pre-extracted wood by adsorption of the dissolved hemicelluloses. In task 2 the dissolved wood extract solids are used for the production of Sheet Molding Compounds (SMCs). The sub projects of Task 1 are: Exploratory pre-extraction–kraft studies of hardwoods (Chapter 4.1.1), Fundamental studies of autohydrolysis of hardwoods (Chapter 4.1.2), Pre-extraction – kraft studies of softwoods (Chapter 4.1.3), Green liquor pre-extraction – kraft cooking of hardwoods (Chapter 4.1.4) and Green liquor pre-extraction – kraft cooking of softwoods (Chapter 4.1.5). The adsorption of GL hardwood extract liquor onto hardwood and softwood kraft pulp to increase the total yield is reported in Chapter 4.2, while in chapter 4.3 it is explored whether the wood solids in a hot water extract of maple wood strands could be used to substitute for polystyrene in the production of SMC.

Task 1

The pre-extraction–kraft studies of hardwoods showed that when extracting about 10% of the wood, the final kraft pulp yield and physical properties could only be maintained at a level similar to that of regular kraft pulp when the final extract pH was close to neutral. This so-called "near neutral" pre-extraction condition at a level of 10% wood dissolution was achieved by contacting the wood chips with green liquor (GL) at a charge of about 3% (as Na_2O on wood) at 160 °C for almost 2 hours (or an H-factor of about 800 hrs.). During subsequent kraft cooking of the pre-extracted hardwood chips the effective alkali charge could be reduced by about 3% (as Na_2O on wood) and the cooking time shortened relative to that during regular kraft cooking, while still producing the same bleachable grade kappa number as the kraft control pulp. For softwood, no extraction conditions were discovered in the present investigation whereby both the final kraft pulp yield and physical properties could be maintained at a level similar to that of regular softwood kraft pulp. **Therefore for hardwoods the "near- neutral green liquor pre-extraction conditions do meet the requirements of the IFPR concept, while for softwood, no extraction conditions were discovered which do meet these requirements.**

Application of simulated industrial GL at an extraction H-factor of about 800 hrs and 3% GL charge in a recirculating digester produced an hardwood extract containing 4.4% (on wood) of total anhydro-sugars, 2% of acetic acid, and 1.3% of lignin. Xylan comprised of 80% of the sugars of which about 85% is oligomeric. Since only polymeric hemicelluloses and lignin may be adsorbed on pulp (produced at a yield of about 50% from the original wood), the maximum theoretical yield increase due to adsorption may be estimated as 10% on pulp (or 5% on wood). However, direct application of raw GL hardwood extract for hemicelluloses adsorption onto hardwood kraft pulp led to a yield increase of only about 1% (on pulp). By using the wet-end retention aid guar gum during the adsorption process at a charge of 0.5% on pulp the yield gain may be increased to about 5%. Unfortunately, most of this yield increase is lost during subsequent alkaline treatments in the pulp bleach plant. It was found that by performing the adsorption at alkaline conditions the adsorption loss during alkaline treatment in the bleach plant is mostly avoided. Thus a permanent adsorption yield of about 3 and 1.5% (on pulp) was obtained with addition of guar gum at a charge of 0.5 and 0.1% respectively during adsorption of GL hardwood extract on pre-extracted kraft pulp at optimal conditions of pH 11.5, 90 C for 60 minutes at 5% consistency. The beatability of the adsorbed kraft pulps was improved. Also, significant physical strength improvements were achieved. **Further study is needed to determine whether the improvements in pulp yield and paper properties make this an economic IFPR concept.**

Task 2

Application of the wood solids of a hot water extract of *Acer rubrum* wood strands as a substitute for polystyrene used for production of SMC maintained the water adsorption properties of the final product. Further work on the physical properties of the hemicellulose containing SMCs need to be completed to determine the potential of wood extracts for the production of partially renewable SMCs.

Impact of the research

The discovery of the "near-neutral" green liquor extraction process for hardwood was filed as a US patent application called: "Treating a lignocellulosic material", U.S. 2008142176 (2008). The inventors are: Adriaan Reinhard Pieter van Heiningen, Sung-Hoon Yoon, Haixuan Zou, Jianer Jiang and Gopal C. Goyal, i.e. the PI and two co-workers, and collaborators of International Paper (J. Jiang and G. Goyal). The discovery formed the basis for a commercial Integrated Biorefinery that will extract hemicelluloses from wood chips to make biofuels and other specialty chemicals. The pulp production process will be maintained as is proposed in the present researched IFBR concept. This Integrated Biorefinery will be constructed by Red Shield Acquisition LLC (RSA) at the Old Town kraft pulp mill in Maine. RSA in collaboration with the University of Maine will develop and commercialize the hemicellulose extraction process, the conversion of the hemicellulose sugars into butanol by fermentation, and the separation of specialty chemicals such as acetic acid from the extract. When operating the facility will produce 1.5 million gallons per year of butanol and create 16 new "green collar" jobs. The successful project will demonstrate the technical and economical feasibility to convert lignocellulosic extract to biofuel that will form the basis for a series of commercial scale biorefineries. RSA received a 30 million dollar award from DOE in January 2010 to assist RSA with the demonstration of the Integrated Biorefinery at the Old Town mill. Previously, a spare pulp digester was converted to a new extractor, and in 2009 it was demonstrated that a good hemicellulose extract could be produced, while simultaneously producing market pulp. Since then more than 250 hours of operational experience has been acquired by the mill generating a hemicellulose extract while simultaneously producing market pulp at a scale of 1000 tonnes (OD)/day of mixed northern hardwood chips.

Publications in refereed journals and patent applications resulting from the IFPR research

In total 18 refereed papers were published and 3 patent applications were filed resulting from this IFPR research.

ACKNOWLEDGEMENT and DISCLAIMER

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1. INTRODUCTION

Lignocellulosics are considered as feed stock for transportation fuels and chemicals because they are abundant, can be grown on relatively poor soil using low energy and nutrient inputs, and do not compete with food production. Wood has additional advantages related to its higher density, year-round harvesting and low silicate content compared to agricultural lignocellulosics. The collection and processing of wood at centralized facilities is already practiced by the forest products industry. Therefore, the production of biofuels and chemicals besides traditional products such as paper, tissue, board and wood products presents a great opportunity to the forest products industry to improve its profitability. It also addresses the strong public interest to use renewable and “carbon-neutral” lignocellulosic biomass for production of transportation fuels and bio-based chemicals to address two pressing global issues; climate change and “peak oil”. In this so called Integrated Forest BioRefinery (IFBR) tree stems are processed to traditional forest products, while intermediate process streams and forest and agricultural biomass are converted into biofuels, biomaterials, chemicals and electricity.

The amount of sustainably removable biomass which could be produced on forestland has been estimated at about 368 million dry tons [1]. Together with agricultural biomass, giving a total of more than 1.3 billion dry tons, this could potentially meet more than one-third of the 2004 US demand for transportation fuel [1]. US chemical pulp mills receive more than 100 million dry tons of wood each year. The objective of the present project was to investigate two technologies which would allow an existing chemical pulp to produce new biomaterials while continuing to meet the demand and maintain the quality of pulp and paper products. The projects are:

1. Extraction of Hemicelluloses from Wood Chips and its Integration in the Pulp Production.
2. Development of Renewable Materials using Extracted Hemicelluloses or Cellulosic Fibers.

In an IFPR it is most cost effective to use trees principally for solid wood production, while the residual wood fiber and biomass (bark) are used for pulp and power production respectively. The dominant alkaline pulping process is then generally used to release the highest quality fiber for pulp production from essentially all hardwood and softwood species with minimal environmental impact. The pulp yield is only about 50% because most of the hemicelluloses and almost all the lignin end up in the spent pulping stream, called black liquor. The black liquor is combusted for steam and electricity generation, while the dissolved inorganic cooking chemicals are recovered and recycled for pulping. Since the heating value of hemicelluloses is significantly lower than that of lignin (HHV of 17.6 versus 23.3-26.6 MJ/kg [2]), the combustion of dissolved hemicelluloses does not constitute optimal economical use of this resource. Therefore, in an IFPR a significant amount of the hemicelluloses may be extracted from the residual wood chips prior to pulping. The hemicellulose sugars in the extract could then be used as a feedstock for the production of ethanol, chemicals or polymers. The hemicellulose oligomers in the extract could also partly be adsorbed on delignified fibers to increase pulp yield and quality. Alternatively the oligomers may be used to replace fossil fuel based chemicals and resins in wood composites for the development of bio-composite materials. The waste streams of the new conversion processes will be combined with black liquor to recover the heat value, and recycle sodium and/or sulfur.

The projects of the original approved proposal were:

1. Extraction of Hemicelluloses from Wood Chips and its Integration in Pulp Production.
2. Development of Bio-Composite Materials using the Hemicellulose-Based Polymeric Materials.
3. Conversion of the Hemicellulose Extract into Chemicals and Polymers.

The funding for the last project, which was scheduled to be performed by Dr. Joseph Bozell at NREL, Golden, CO., was withdrawn by DOE after initial approval of the original proposal due to US Government budget cuts. Projects 1 and 2 were performed at the University of Maine under the guidance of Dr. Adriaan van Heiningen and Dr. Douglas Gardner respectively. International Paper collaborated with Dr. van Heiningen on project 1, and provided part of the funding for the project. Dr. van Heiningen had the overall responsibility for the entire project.

The economic, energy and environmental benefits of the project were originally estimated based on a pulp yield increase of 2% compared to conventional alkaline pulping, and implementation of the hemicellulose extraction technology in 50% of the chemical pulp mills in the US. The higher pulp yield leads to an extra pulp production of 1 million tons at a value of about $500 million ($500/ton pulp assumed). The incremental pulp production is equivalent to an additional income of about $20/ton pulp produced. In addition it was assumed that 10% of the wood could be extracted before pulping at 50% of the mills, and that the wood solids in the extract would be converted at 40% mass yield to 2 million tons of sugar-based chemicals and resins. At a price of $1000/ton this represents an additional revenue stream of $2000 million/year or $80/ton pulp produced. Overall the benefits of the IFPR are: enhanced economic competitiveness of the domestic forest products industry; increased domestic supply of renewable energy and bio-based products; reduced greenhouse gas emissions, and preserving and creating jobs in rural communities.

2. BACKGROUND

2.1 Forest Biorefinery Concept

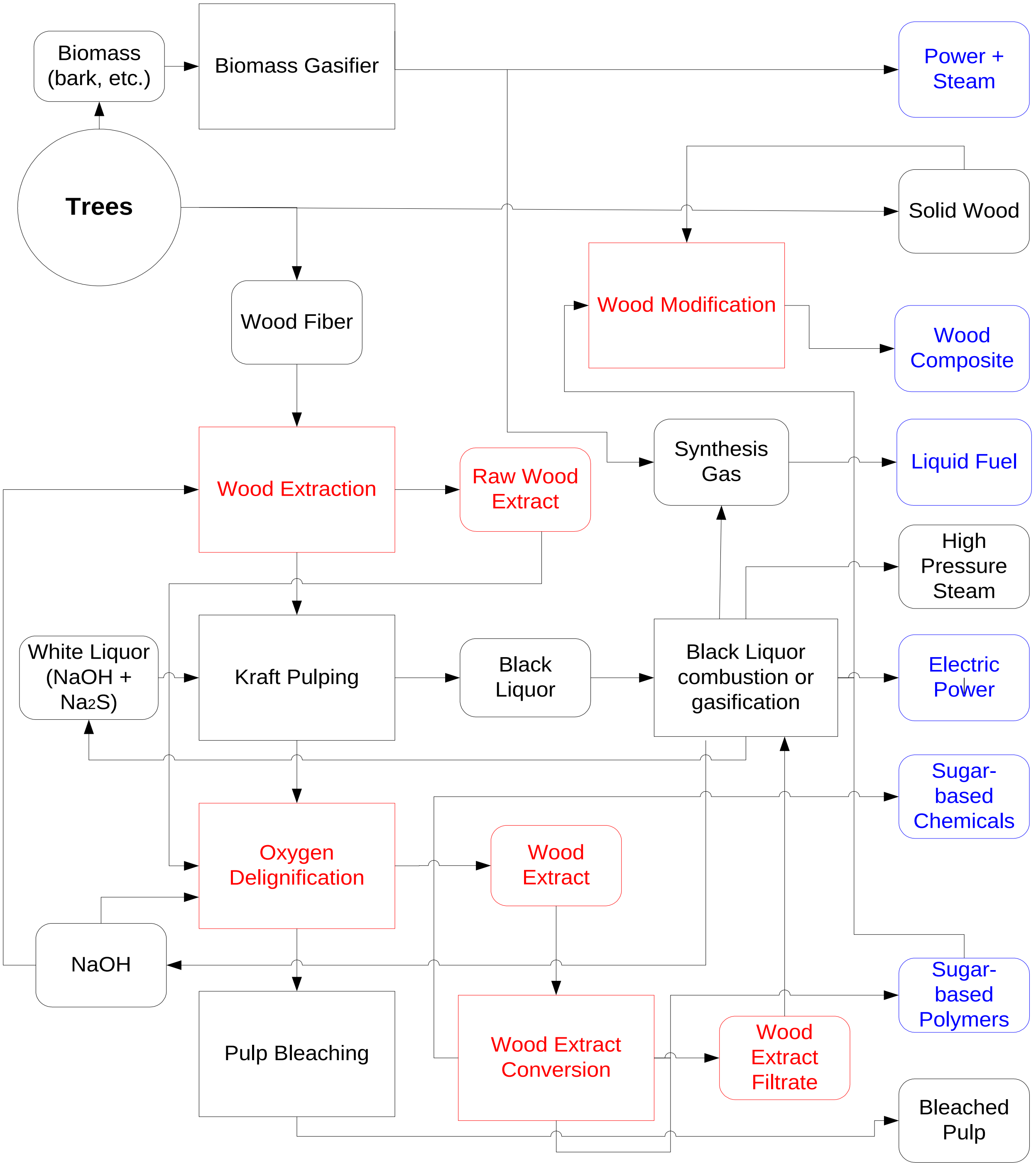
Our original technology vision of an “Integrated Forest Products Refinery (IFPR)” is shown in Figure 1. The block diagram describes the integration of hemicellulose pre-extraction and production of hemicellulose-based products in a pulp and solid wood production facility. The new products indicated in blue on the right hand side of the diagram are: electric power, new wood composite materials, liquid fuel, chemicals and polymers. The traditional pulp and paper products are indicated in black. The red boxes represent new processes and process streams which were to be studied as part of the original proposal. Because the contribution of NREL dealing with the wood extract conversion to sugar-based polymers was eliminated by DOE due to budget restrictions, this subproject was not investigated. The square black boxes are processes which already exist or are under development (for example black liquor gasifiers) in an IFPR.

In an IFPR it is most cost effective to use trees principally for solid wood production, while the residual wood fiber and biomass (bark) are used for pulp and power production respectively. The dominant alkaline pulping process is then used to release the highest quality fiber for pulp production from essentially all hardwood and softwood species with minimal environmental impact. The pulp yield is only about 50% because most of the hemicelluloses and almost all the lignin end up in the spent pulping stream, called black liquor. The black liquor is combusted for steam and electricity generation, while the dissolved inorganic cooking chemicals are recovered and recycled for pulping. Since the heating value of hemicelluloses is significantly lower than that of lignin (HHV of 17.6 versus 23.3-26.6 MJ/kg [2]), the combustion of dissolved hemicelluloses does not constitute optimal economical use of this resource. Therefore, in the proposed IFPR a practical amount of the hemicelluloses are extracted from the residual wood chips prior to pulping. The hemicellulose sugars in the extract could then be used as a feedstock for the production of ethanol, chemicals or polymers. The hemicellulose oligomers in the extract could also partly be adsorbed on delignified fibers to increase pulp yield and quality. Alternatively the oligomers may be used to replace fossil fuel based chemicals and resins in wood composites for the development of bio-composite materials. The technology to gasify black liquor is an integral part of the IFPR. However, this emerging technology is not part of the present proposal.

2.2 State of the Art

While performing the hemicellulose extraction research we discovered [3] that about 10% of hard wood chips could be dissolved in the pre-extraction stage, while maintaining the pulp yield and physical properties after subsequent kraft pulping. These conditions produced a “near-neutral” extract containing dissolved wood including hemicellulose oligomers and sodium acetate. Red Shield Acquisition LLC (RSA), doing business as Old Town Fuel & Fiber (OTFF), was awarded a $30 million grant from the U.S. Department of Energy in January 2010 to demonstrate and commercialize at their kraft pulp mill in Old Town, ME, to extract hemicelluloses from wood chips to make biofuels and speciality chemicals based on this process. When operating, the facility will produce 1.5 million gallons per year of butanol and 2.2 million gallons of acetic acid per year. Presently, more than 250 hours of operational experience have been obtained in mill trials at more than 1000 tonnes/day OD wood continuous operation.

Figure 1. Integrated Forest Products Refinery



3. LITERATURE REVIEW

3.1 Hemicellulose chemistry

Hemicelluloses comprise roughly one-fourth to one-third of the weight of wood, thus ranking second in abundance after cellulose. Unlike cellulose, hemicelluloses are branched hetero-polysaccharides, non-crystalline, and have a relative low degree of polymerization of about 80-200. There are two major classes of hemicelluloses; glucomannans and xylans. The two principal hemicelluloses in softwoods are acetyl-galactoglucomannan (AcGGM) at about 20 w/w % and about 5-10 w/w % of arabinoglucuronoxylan. Hardwood hemicelluloses consist mainly of glucoronoxylan (15–30 w/w %) with some (2–5 w/w %) glucomannans [4]. Removal of hemicelluloses in pure form from wood involves hydrolysis of covalent (ester and ether) bonds which link the hemicelluloses mostly to lignin. The ester bonds are easily cleaved by alkali, while the ether linkages (most probably at the α-carbon of lignin) are much more stable [5]. Without prior delignification, hardwood xylans can be extracted in considerable amounts from wood using aqueous alkaline solutions. However, softwood hemicelluloses may only be obtained after preceding delignification [6]. Galactoglucomannan in softwood and glucoronoxylan in hardwood contain acetyl groups at the C2 and C3 positions of the chain sugar units. Deacetylation occurs easily under alkaline conditions. This is important for extraction of hemicelluloses, since the solubility of deacetylated hemicelluloses is greatly reduced and its propensity to crystallize is improved [7]. As a result parts of the hemicelluloses are retained or redeposited on wood during pulping, and explains the retention of hemicelluloses by fibers after high temperature treatment.

Hemicelluloses behavior during kraft pulping

During the preheat phase (70 to 120 °C in about one hour) of kraft cooking of pine chips only about 10% of the original lignin is removed (Aurell and Hartler) [8]. However about 50% of the original glucomannan is removed mostly by the alkaline peeling reaction (see Figure 2a reproduced from Aurell and Hartler [8]). Evidence for this is that the addition of $NaBH_4$, which reduces the reactive aldehyde end group of glucomannan, diminishes the glucomannan removal to only about 20% (see Figure 2a). Further evidence was provided by Alen et al.[9] who found that after a similar preheat phase the hydroxyl monocarboxylic acids content in pine kraft black liquor accounted for about 4% on wood, of which half were glucoisosaccharinic acid, the major product of the peeling reaction. At the end of the kraft cook the glucomannan content of pine pulp stabilizes at about 25% of the original amount in wood because glucomannan crystallizes and remains adsorbed on the pulp after deacetylation and side-chain cleavage.

In Figure 2b it can be seen that only a small amount of xylan is removed below about 140 °C during kraft cooking of pine chips. This implies that the peeling reaction is of little importance for xylan during the preheat phase. This is further confirmed by the fact that addition of $NaBH_4$ leads to a small decrease rather than a large increase in xylan yield as was found for the glucomannan retention. The explanation is that more xylan is removed by simple dissolution of the xylan oligomers due to the higher alkali concentration in the pulping liquor with $NaBH_4$ addition. The higher alkali concentration is the result of less alkali consumption by glucomannan which is stabilized by $NaBH_4$. The comparative stability of xylan against the peeling reaction derives from the presence of the arabinose side chain at the C-3 position and the 4-O-methylglucuronic acid groups at the C-2 position of the xylan chain. [4].

○ , ● : 15.75 % EA , 0 % $NaBH_4$ ▲ : 25 % EA, 0 % $NaBH_4$
◊ , ♦ : 15.75 % EA, 0.5 % $NaBH_4$ ▼ : 25% EA, 0.5 % $NaBH_4$

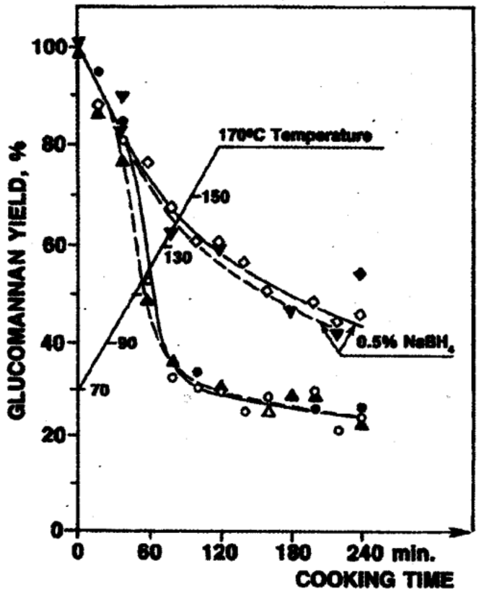


Figure 2a. Glucomannan removal during pine kraft cooks (reproduced from [8])

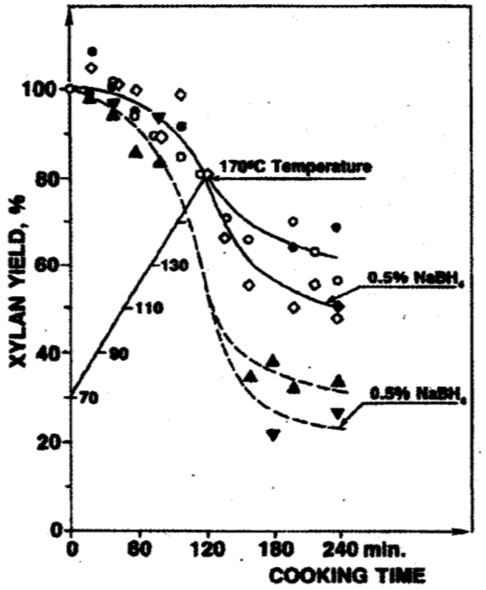


Figure 2b. Xylan removal during pine kraft cooks (reproduced from [8])

Hemicellulose behavior during acidic conditions

Based on the earlier review of the behavior of hemicelluloses during kraft cooking, it is clear that alkaline pretreatment of softwood chips will produce an extract containing only a small amount of polymeric xylan since galactoglucomannan will be degraded by the peeling reaction. Recently is has been found that up to 80% of the acetyl-galactoglucomannan may be extracted from ground softwood by heat treatment with water at very high temperatures of 190 -200 °C for a few (2 -5) minutes [10]. Although the DP was significantly lower than in wood (24 vs 150), the extracted glucomannans were still acetylated. The extracted glucomannan yield decreased to a low value of 2% accompanied by full deacetylation of the dissolved oligomers when NaOH was added to the wood meal during the heat treatment and the final pH of the solution was larger than 5.0. In a much earlier study [11] it was found that after treatment of spruce wood for 1.5hr at 125 °C with different pH solutions (pH ranging from 3.1 to 8.0) the extract yield was largest when the least amount of acetyl groups were removed from the wood. This occurred at a pH of 4.0 obtained by extraction with a solution of $NaHSO_3$ which removed only 31% of the acetyl groups in the original wood and dissolved 17% of the wood weight. Therefore it appears possible to extract polymeric AcGGM from softwood chips at mild acidic conditions. The acidic pre-extraction step is similar to that of the prehydrolysis kraft process, where the objective is to produce a dissolving pulp containing very small amounts of hemicelluloses [12]. However, the objective of pre-extraction within the IFBR concept is to remove the hemicelluloses in polymeric form with as little delignification as possible. Also a fundamental difference between the present IFPR concept and prehydrolysis-kraft is that in the IFPR the extract is contacted with the produced kraft pulp at alkaline conditions (needed for oxygen delignification) which favor deacetylation and thus redeposition on the fibers, resulting in a yield gain. The selection of the mild conditions is also important in order to minimize acid hydrolysis of cellulose and condensation of lignin. Lignin condensation will require harsher kraft cooking and pulp bleaching conditions to obtain fully bleached pulp.

In summary, during high temperature alkaline treatment of softwoods, about 50% of the glucomannan (or about 10% of the wood weight) is removed by peeling leading mostly to hydroxyl monocarboxylic acids dissolved in black liquor. On the other hand hardwood xylans can be extracted in considerable amounts as oligomers using aqueous alkaline solutions due to side chains at the C-2 and C-3 of xylan which provide relative stability against the peeling reaction. Extraction with pure water causes acidic conditions due to release of acetic acid from hemicellulose. The acidity may lead to degradation of cellulose by acid hydrolysis at high temperature, which is unwanted in an IFBR that produces pulp as one of its major products.

3.2 Integrated forest biorefinery studies

The concept of an Integrated Forest Products Biorefinery (IFBR) has been advanced by a number of investigators [13-16], who envision converting woody biomass, dedicated annual crops and municipal waste into bio-energy and basic chemicals. The subject of the present proposal which involves extracting hemicelluloses, which normally end up in the black liquor of Kraft pulp mills, prior to pulping and use the extract for the production of ethanol and acetic acid, has been described [17]. The extracted liquor undergoes hydrolysis to monomeric sugars, separation of lignin, acetic acid and furfural, and fermentation of the sugars to ethanol followed by distillation and other purification process. A technical economic evaluation of the near neutral hemicellulose extraction process which was considered based on experimental results of the present proposal was published by Mao and co-workers [18] assuming mixed southern hardwood chips as the feedstock and using 3% green liquor to extract the wood chips. In another recent study pre-extraction of poplar wood chips at strong alkaline conditions (1-2 Molar NaOH at L/W of 4kg/L) and relatively low temperatures (50 – 90^{o}C) was reported by Al-Dajani and Tschirner [19]. At these conditions about 40-50 kg of hemicellulose oligomeric sugars could be extracted per ton of wood without detrimental effect on overall pulp yield when the extracted wood was subjected to modified kraft pulping. In a simulation of this process [20], the extracted hemicellulose sugars were converted to ethanol and the economics of ethanol production integrated in a kraft pulp mill were determined. A minimum selling price for ethanol of $3.41/gallon for a wood feed rate of 2000 dry metric tonne/day was predicted. In this process the hemicelluloses are first separated from the caustic solution using nanofiltration and then hydrolysed into monosugars using 1.1% sulfuric acid at 190 °C for 2 minutes. Fermentation of wood pre-hydrolysates to ethanol are reported by Mendes et al. [21]. One of the few studies which used softwood as a feedstock for a forest biorefinery is that of Frederick et al. [22] who used a mild pre-treatment with sulfuric acid of Southern Pine.

3.3 Sorption of polymeric hemicelluloses on pulp

In order to deposit extracted hemicelluloses on pulp after kraft pulping as proposed in the present IFPR concept, it is important that a significant part of the dissolved hemicelluloses remain in polymeric form. It has been found that tetramers are the smallest polymers to adsorb onto cellulose surfaces [23]. The adsorption of dissolved xylan in pulping liquor on kraft pulp fibers was already studied in the fifties [24, 25]. It was subsequently shown that the higher yields of birch kraft pulp could be explained by the re-uptake of dissolved xylan during the later stage of cooking [26]. Also glucomannan could be adsorbed on cellulose fibers but at a different rate than xylan [27]. Different fiber types; cotton, hardwood pulp and softwood pulp, exhibited significant differences in adsorption yield [24]. It was found that the sorption rate process was controlled by diffusion transport of the hemicelluloses molecules from the liquor phase to the fiber surface [28]. A decrease in alkaline pH in the liquor phase increased the sorption. The alkalinity and temperature of the liquor showed the same influence on the rate of hemicelluloses adsorption [29]. The xylan structure also greatly affected the adsorption rate; complete removal of uronic acids accelerated the adsorption rate. The results indicated that high temperature and low uronic acid content gave maximum adsorption [30]. The hemicelluloses adsorption was thought to be of a physical adsorption nature, and the difference in rates was attributed to the inhibiting effect of uronic acid carboxyl groups [27]. The deposited xylan was located on the outer surface of cellulose fibers, and a large portion (about 50%) was resistant to alkali extraction at high temperatures [31]. The location and the charge of xylan had a considerable impact on the formation of inter-fiber bonds [32]. More recently Gatenholm and his group reported on the mechanism of xylan adsorption [33, 34]. They suggest that xylan adsorbs after forming aggregates in solution rather than being built up on the cellulose surfaces over time by multilayer adsorption of xylan.

3.4 Effect of hemicelluloses retention on pulp properties and yield

Although cellulose is the major component in pulp fibers, hemicelluloses also contribute significantly to pulp quality. Firstly, retention of hemicelluloses in pulp means a higher pulp yield, which is most important from an economic point of view. Secondly, hemicelluloses improve pulp beatability by shortening beating time to acquire the same freeness [35], and thirdly hemicelluloses improve pulp properties such as increased adsorption ability and enhancing pulp strength [36 – 40].

In the past, many efforts have been made to stabilize hemicelluloses during pulping. However, for the dominant kraft pulping technology the practical solutions to minimize hemicelluloses degradation and dissolution are still limited to the use of polysulfide and (PS) anthraquinone (AQ). These two additives stabilize the reducing end groups of the carbohydrates by oxidation leading to modest increases in yield of 1-4% for softwood [41].

3.5 Sheet molding compounds

Sheet molding compound (SMC) are used in automotive and transportation applications. The use of natural fibers and wood extracts in SMCs is of interest in order to reduce both cost and renewability by replacing the glass fibers and (oil-based) polyester resins presently used for the manufacture of SMCs [42-43]. However in order for these partially renewable SMC’s to be used in practice they have to comply with strength requirements, but especially have good resistance to water absorption and retain their mechanical performance during aging in humid environments [44-45].

4. RESULTS AND DISCUSSION

4.1 Pre-extraction studies

It was planned in the original proposal to use alkaline liquors for pre-extraction of hardwood chips and use autohydrolysis for softwood chips, followed in both cases by modified kraft cooking to produce bleachable grade pulp. The pulps would be compared to those produced by regular kraft pulping. The objective was to obtain pre-extracted kraft pulp yields and paper properties comparable to conventional kraft pulps and paper. If this was obtained, then the pre-extracted solution would be used for yield increase of the pre-extracted kraft pulps by adsorption of the dissolved hemicelluloses on the fibers and for use in the production of Sheet Molding Compounds (SMCs). The latter two topics are described in chapter 4.2 and 4.3 respectively. The sub projects of the pre-extraction studies in Chapter 4.1 are: Exploratory pre-extraction–kraft studies of hardwoods (4.1.1), Fundamental studies of autohydrolysis of hardwoods (4.1.2), Pre-extraction – kraft studies of softwoods (4.1.3), Green liquor pre-extraction – kraft cooking of hardwoods (4.1.4) and Green liquor pre-extraction – kraft cooking of softwoods (4.1.5)

4.1.1 EXPLORATORY PRE-EXTRACTION – KRAFT STUDIES OF HARDWOODS

4.1.1.1 Experimental

Fresh mixed southern hardwood chips (35% Gum (both sweet and black), 35% Southern Red Oak, 15% Red Maple, 12% Poplar and Sycamore and 3% Southern Magnolia) were obtained from International Paper. Extraction and cooking experiments were conducted using a profiled pilot digester equipped with an external heat exchanger and a forced liquor circulation system. The wood chips were subjected to pre-extraction at a liquor-to-wood ratio (L/W) of 4.5 L/kg using 0, 3, 10 and 20% NaOH (% as Na_2O) at various temperatures (125 - 160^oC) and time (45, 60 and 90 minutes), or 3% (as Na_2O) Na_2CO_3 at 140^oC for 90 minutes, or 3% (as Na_2O) green liquor (GL) + 0.05% AQ for 90 minutes at 140^oC, 60 minutes at 160^oC and 110 minutes at 160^oC. The green liquor sulfidity was 30% on a TTA basis. Wood weight loss was determined from the difference between the weight of fresh wood chips and that of thoroughly washed wood residue. The chemical composition of wood was determined by the procedure described in TAPPI Standards [46]. The monosugar contents were obtained by HPAEC analysis after double acid hydrolysis of extracted wood [47, 48]. The uronic anhydride content was determined using the chromophoric group analysis method of Scott [49]. The compositions of the extracts were determined by HPAEC (monosugars), HPLC (acetic acid) and UV (lignin) as described in detail by Tunc and van Heiningen [50]. After completion of pre-extraction, the liquor was drained from the chips (about 2/3 of the total liquor), and 30% sulfidity white liquor plus fresh water was added to obtain a L/W of 4.5 L/kg at the required effective alkali charge. The effective alkali charges were 12, 13 or 15% for pre-extraction kraft pulping and 15% (all as Na_2O) for the kraft control. The cooking time for both the kraft control and kraft cooks on pre-extracted chips was varied from 100 minutes to 240 minutes at the maximum cooking temperature of 160^oC. Pulps obtained were disintegrated in a laboratory pulper, passed through a pilot vibrating reject screen and thoroughly washed and collected on a 200-mesh screen with flowing tap water. The wet pulps were then placed in a refrigerator without air-drying for measurement of pulp yield, kappa number, reject contents, residual effective alkali concentration and intrinsic viscosity [ASTM Standard D 1795-62] using standard testing methods. The residual effective alkali concentration of black liquor was determined using a modified SCAN-N 33:94 Method [51, 52].

4.1.1.2 Results and discussion

Pre-extraction with NaOH

Southern hardwood chips were pre-extracted using 0, 3, 10 and 20% NaOH (on ODW as Na_2O). The extraction conditions, wood weight loss and residual pH of the extracts are summarized in Table 1. The wood weight loss during extraction increases from almost 3% at the mildest condition (pure water, 130^oC, 90 minutes) to about 40% at the most severe condition (20% NaOH, 150^oC, 90 minutes). The solids content of the water extracts were an order of magnitude smaller (0.16 - 1.6%) than those obtained with NaOH (5 - 15%). It should be noted that the solids content for the most severe NaOH extraction is similar to that of regular kraft black liquor. The final pH of alkaline extraction varied from acidic (with water), to near-neutral (at 3% NaOH) to alkaline (at 10 and 20% NaOH). The pH drop during mild alkaline or water extraction is caused mostly by acetic acid formed by hydrolysis of acetyl groups in the hemicelluloses.

Table 1. Water and alkaline extraction results of southern mixed hardwoods

ID	NaOH charge (% as Na_2O)	T_{max} (^oC)	Time at T_{max} (min)	H-Factor (hours)	Weight Loss (% on ODW)	Residual pH	Residual EA (% as Na_2O)
X-01	0	150	90	261	12.03	4.06	0.00
X-02	0	130	90	39	2.88	4.40	0.00
X-03	0	140	90	103	3.98	4.12	0.00
X-04	0	160	60	436	11.34	3.56	0.00
X-05	0	150	90	261	5.95	3.67	0.00
X-06	3	140	90	103	8.01	7.04	0.00
X-07	3	150	90	103	8.39	6.23	0.00
X-08	10	125	45	12	17.1	13.25	3.63
X-09	10	150	90	261	24.34	12.88	0.84
X-10	20	150	90	261	40.14	13.70	15.25

The wood weight loss data of Table 1 are plotted against H-factor during extraction in Figure 3. It can be seen that the weight loss increases with increasing H-factor both for water and alkaline extraction, while the wood dissolution also increases with increasing NaOH charge.

Table 2 shows the composition of the original wood and that of the extracted and well-washed wood after extraction at three different NaOH charges (0, 10 and 20%) for 90 minutes at 150^oC (H-factor: 261hrs). All percentages are based on original oven-dried wood. The carbohydrate composition (cellulose and hemicelluloses) was calculated from the monosugar analysis following the procedure described by van Heiningen *et al.* [53].

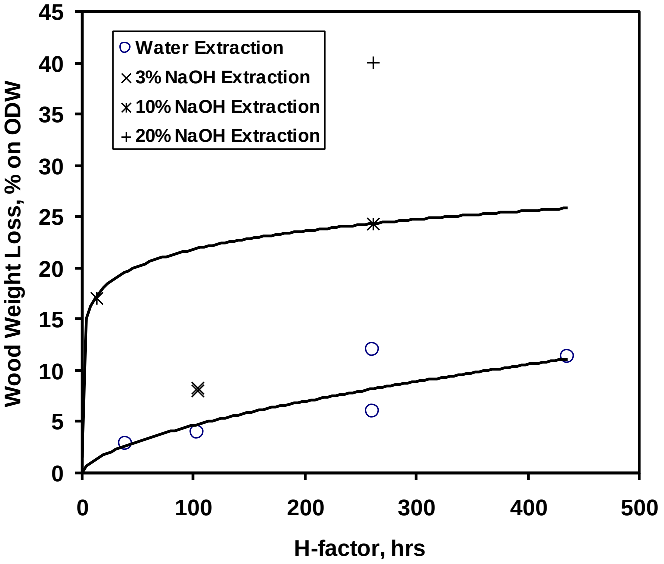


Figure 3. Wood Weight Loss vs. Extraction H-factor.

Table 2. Composition of original and extracted wood after NaOH extraction (percentages based on oven dry weight of the original wood)

ID	NaOH Charge (%)	T_{max} (°C)	Time at T_{max} (min)	Monosugars (% on ODW)					Cellulose (%)	Hemi-Cellulose (%)	Glucomannan (%)	Xylan (%)	Lignin (%)	Others		Total (%)
				Ara	Gal	Glu	Man	Xyl						Ash (%)	EtOH-Benzene Extracts (%)	
CTRL	Original Wood			0.50	1.04	44.19	2.36	16.74	42.80	26.83	4.76	22.04	29.43	0.52	0.42	100
X-01	0	150	90	0.13	0.59	41.76	1.73	12.77	40.74	18.97	3.35	15.63	26.96	0.28	1.02	87.97
X-08	10	125	45	0.34	0.46	38.68	0.56	11.85	38.35	16.11	1.35	14.76	27.15	1.19	0.11	82.91
X-09	10	150	90	0.29	0.28	37.63	0.38	10.81	37.40	13.93	0.88	13.04	22.95	1.24	0.14	75.66
X-10	20	150	90	0.18	0.18	37.14	0.53	7.72	36.83	9.70	1.03	8.68	12.79	0.48	0.06	59.86

The original southern mixed hardwood is identified as the control (CTRL). It can be seen that the original wood contains 22.0% xylan (which includes the 4-O-methylglucoronic acid groups), 4.8% glucomannan, 42.8% cellulose and 29.4% lignin. With increasing severity of extraction, i.e. for sample X-01 to X-10, more of the wood components were progressively removed. It can also be seen from the Table 2 that the lignin removal is modest (about 2%) when performing the extraction with pure water or 10% NaOH at 125°C for 45 minutes (X-08). However a significant amount of lignin is removed (6.5-16.6%) when using (10-20%) NaOH at 150°C for 90 minutes. Furthermore, it is interesting to note that amount of cellulose and glucomannan extracted with NaOH is roughly the same (4.5-6.0 and 3.4-3.9%) irrespective of extraction time, temperature and NaOH charge. However the removal of xylan increases continually with extraction severity. The total amount of organics, carbohydrates and lignin removed from wood chips during NaOH extraction are plotted against wood weight loss in Figure 4.

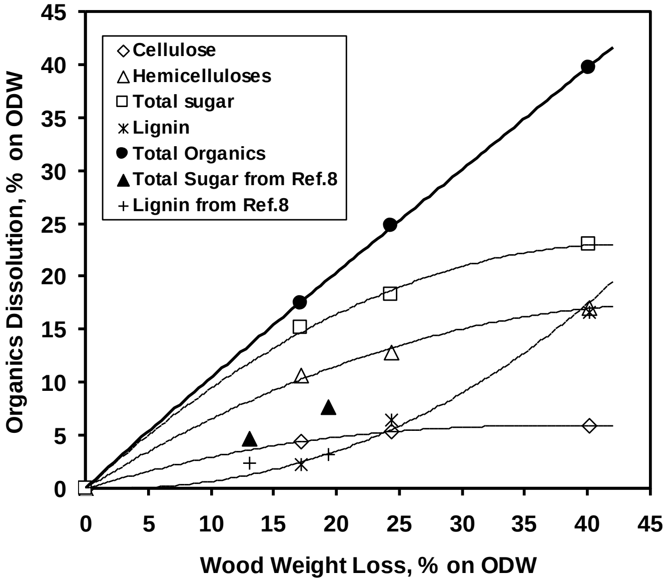


Figure 4. A material balance plot for wood organics dissolution vs. wood weight loss during NaOH extraction of southern mixed hardwoods.

The total sugar amount in Figure 4 represents the sum of cellulose and hemicelluloses removed at a given weight loss, and the total organics are the sum of total sugar and lignin removed. The slope of the line through the total organics removed is close to 1 which indicates that the measurements of the wood components are internally consistent. While the carbohydrate removal levels off as the wood weight loss increases, lignin removal shows an exponential increase with increasing wood weight loss. Al-Dajani et al [19] extracted hemicelluloses from aspen chips using two different mild alkaline solutions containing 2.08M (25.78% on ODW as Na_2O) and 1.67M (20.70% on ODW as Na_2O) of NaOH for 4 hours at 50°C and 90°C, respectively. Based on the data provided, it was calculated that 4.7% and 7.7% of total sugars and 2.4% and 3.3% of Klason lignin were removed at 13% and 19.3% weight loss extractions, respectively. For comparison, these data are also shown in Figure 4. There appears to be a good agreement in terms of lignin removal, but a significant lower sugar removal was observed from the data of reference [8] compared to the present results. This is likely due to the higher temperature used in the present experiments.

NaOH Pre-extraction Effects on Kraft Pulping

The results of 0, 3, 3.5 and 10% NaOH pre-extraction and subsequent kraft pulping are listed in Table 3. Also included in Table 3 is a control cook at 160°C, 15% EA charge, L/W of 4.5 L/kg and an H-factor of about 1,600 hrs which produced a pulp of 46.6 % total yield at 16 kappa number and Tappi viscosity of about 41 cp pulp. The data shows that for pure water extraction the total pulp yield decreases significantly below that of the control at extraction temperatures of 140°C or higher. At 150°C the total pulp yield is more than 5% lower than the control, and at 160°C the yield loss is almost 7%.

Table 3. Results of 0, 3, 3.5 and 10% NaOH pre-extraction and subsequent kraft pulping

ID	PROCESS 1 [Extraction(L/W=4.5)]					PROCESS 2 [Kraft Pulping(L/W=4.5)]								
	NaOH Charge (%)	$T_{max.}$ (^oC)	Time at T_{max} (min)	H-factor	Wood Yield (%)	EA Charge (%)	T_{max} (^oC)	H-factor	Total Yield (%)	Screen Reject (%)	Kappa No.	Intrinsic Viscosity (c.p)	Carbohydrates	
													Cellulose (%)	Hemi-celluloses (%)
Raw Wood	NA					NA							42.80	26.83
CTRL	NA					15.0	160	1617	46.57	0.07	16.5	40.6	35.78	9.36
X01-KP1	0	150	90	261	87.89	15.0	160	1777	40.53	0.01	12.6	-	-	-
X12-KP2						12.0	160	1499	41.50	1.45	20.3	98.0	35.30	4.69
X13-KP3						13.5	160	1500	41.19	0.59	16.2	92.3	35.14	4.81
X02-KP04	0	130	90	39	97.12	13.5	160	1500	46.59	0.12	-	-	-	-
X03-KP05	0	140	90	103	96.02	13.5	160	1500	44.79	0.17	-	-	-	-
X04-KP06	0	160	60	436	88.66	13.5	160	1496	38.71	0.16	13.1	69.8	34.89	2.86
X06-KP07	3	140	90	103	91.99	13.5	160	1500	45.27	0.02	-	-	-	-
X07-KP08	3	150	90	261	91.61	12.0	160	1500	45.64	0.08	-	-	-	-
X11-KP09	3.5	150	90	261	-	12.0	160	1500	45.84	0.05	-	-	-	-
X08-KP10	10.0	125	45	12	82.90	15.0	160	1588	40.80	0.02	10.5	16.0	33.16	6.83

The only exception is experiment X02-KP04, a water extraction at 130^{o}C for 90 minutes, which leads to the same total pulp yield. This pretreatment process is similar to very long pre-steaming, and leads only to a very small amount extracted as can be seen in Table 1 with wood weight loss of only 2.88%. Thus it appears that with pure water extraction it is not possible to extract a significant amount of organics from hardwood without causing also a sizable loss in yield of the final kraft pulp. Also when 10% NaOH is added to keep the extraction medium alkaline during 45 minutes extraction (leading to 17.4% wood substance removal, see experiment X08-KP10), the total pulp yield after cooking is 40.8%, i.e. similar to that obtained with pure water extraction 45 minutes at 150^{o}C. The reduction in total pulp yield after high temperature pure water extraction is mostly due to a loss of xylan as can be seen from the carbohydrate analysis shown in Table 2. It is also interesting to note that although pure water extraction at 150^{o}C leads to a loss of hemicellulose and cellulose in the kraft pulp relative to that of the control of 4.6% and 0.5% respectively, addition of 10% NaOH reduces the hemicellulose loss to about 2.0% while the cellulose loss increases to about 2.0%. The above results show that a final acidic extract (pH of about 4 due to release of acetic acid) or alkaline extract (pH of about 13) during high temperature extraction are detrimental with respect to the total pulp yield. Therefore three extractions and subsequent kraft cooks were performed with 3 or 3.5% NaOH (on ODW) during extraction to neutralize the acetic acid released in the extraction process (X06-KP07, X07-KP08 and X11-KP09). In all three cases about 8% of wood substance was removed during extraction and the total pulp yield was only about 1% lower than that of the control at about the same total alkali charge as the control. Thus it appears that the pH of the extract must be kept near neutral at high temperature treatment to avoid a significant loss in total pulp yield. This treatment will be called “near-neutral” pre-extraction.

The chemical composition changes of southern mixed hardwoods with 10% NaOH pre-extraction and subsequent kraft pulps are illustrated in Figure 5.

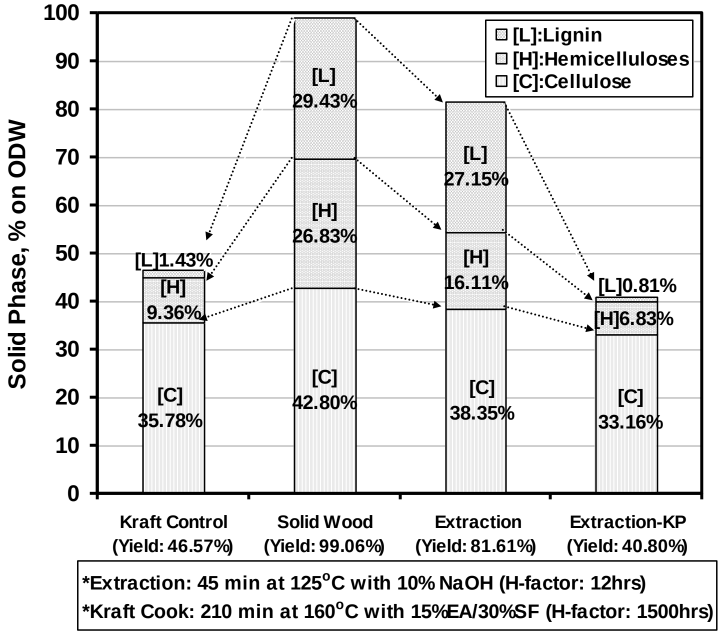


Figure 5. Effect of 10% NaOH pre-extraction on the chemical compositions of extracted wood and kraft pulps.

Figure 5 shows that approximately 4.5% cellulose, 10.7% hemicelluloses and 2.3% lignin (leading to about 17.5% wood substance removal) were removed from the original wood during 10% NaOH extraction. As the extracted wood chips were subjected to subsequent kraft cooking, additional amounts of 5.2% cellulose, 9.2% hemicelluloses and 26.3% lignin were removed from the extracted wood. This mass balance analysis on the pre-extraction and kraft cook indicates that approximately 15% of wood sugars could be pre-extracted for IFBR with only about 5% loss in carbohydrate yield of the pulp compared to kraft control. Viscosities of the pulps obtained with water extraction are all higher than that of the control (Table 3). This implies that the extraction leads to protection of the cellulose against alkaline hydrolysis in the subsequent cooking step.

4.1.1.3 Conclusion

The above results show that when an acidic (pH of about 4) extract is produced by pre-extraction with water at high temperature (160°C for 60 minutes) a final kraft pulp yield is obtained which is almost 7% lower than the control kraft cook. When the extract remains alkaline (pH about 13) by pre-extraction with 10% (on chips) NaOH, then the final kraft pulp has a hemicellulose and cellulose loss both of about 2.0% (on chips) relative to the kraft control pulp. However by keeping the final extract pH close to neutral by adding only 3 or 3.5% NaOH (on chips) the total pulp yield was only about 1% lower than that of the control, while still about 8% wood substance is extracted in the pre-extraction stage. Thus it appears that the pH of the extract must be kept near neutral at high temperature pretreatment to avoid a significant loss in total pulp yield. This treatment will be called “near-neutral” pre-extraction, and will be described in Chapter 4.1.4.

4.1.2 FUNDAMENTAL STUDIES OF AUTOHYDROLYSIS OF HARDWOODS

Simple pre-extraction of wood chips before pulping is presently already applied in practice in the form of the pre-hydrolysis kraft process to produce dissolving grade pulp and specialty cellulose. However, in this process the extracted hemicellulose are not recovered but are carried along with pre-extracted chips, and then become part of the kraft black liquor during the cooking stage. In the IFBR, on the other hand, the hemicellulose extract will be removed for conversion into higher value-added products. In order to better understand the effect of operating conditions during water pre-hydrolysis on the composition of the extract and that of the extracted wood, a series of hydrothermal pretreatments of a mixture of southern hardwoods were carried out at different temperatures of 130 ºC to 170 ºC for 100 minutes, and at different times at 170°C in an accelerated solid extraction system, namely a modified Dionex ASE-100 extractor. This type of extractor is commercially available and well suited for rapid laboratory extraction and pretreatment experiments at elevated temperatures and pressures. Cellulose, hemicelluloses, lignin, acetyl groups and uronic acid groups remaining in the wood were determined from analysis of the solids, while the content of oligosaccharides and monosaccharides, lignin, acetic acid, furfural and HMF were determined in the extract.

Wood hydrolysis with only water (or autohydrolysis is environmentally friendly and inexpensive compared to dilute mineral acid prehydrolysis [54]. Acetic acid released from the acetylated polysaccharides in wood at elevated temperatures during autohydrolysis lowers the pH of the extract to a range of 3 to 4, allowing the removal of hemicelluloses from the wood by autohydrolysis [55]. Two approaches have been described in literature to quantify the effect of operating conditions during water pre-hydrolysis on the composition of the extract and that of the extracted wood. Brasch and Free [56] introduced in 1965 the so-called prehydrolysis factor, which combines the effect of time and temperature in one parameter, similar to the H-factor for the Kraft cooking [57]. Lin [58] subsequently determined in 1978 the activation energy for the cleavage of glycosidic bonds of the carbohydrate material in the wood, and coined the term P-factor for the hydrolysis process. The P-factor is given by the following expression [59]:

$$P-factor = \int_0^t \frac{k(T)}{k_{100^oC}} dt = \int_o^t e^{40.48-\frac{15106}{T}} dt \qquad (1)$$

where t is reaction time in hours, T is temperature in Kelvin, k is the rate constant. The activation energy used in equation (1) is 125.6 kJ/mol (or 30 kcal/mol) which is only slightly smaller than the Kraft cooking activation energy of 134 kJ/mol (or 32 kcal/mol) used in the H-factor. Another but similar approach to combine the effect of time and temperature on the hydrolysis of lignocelluloses was later (1987) introduced by Overend and Chornet [60]. They defined the term severity-factor as:

$$R_O = t \cdot e^{\frac{T[^oC]-100}{14.75}} \qquad (2)$$

where t is reaction time in minutes and T is temperature of reaction in Celsius. This approach has since mostly been adopted in the biomass conversion field. However, because the P-factor is based on the concept of activation energy we will be using this approach in the present report.

4.1.2.1 Materials and methods

The same mixture of Southern hardwood chips as those used in the exploratory pre-extraction – kraft studies (Chapter 4.1.1) were used for the autohydrolysis experiments. The SHM chips were air dried, ground in a Wiley mill and the fraction passing 2 mm holes was stored in double plastic bags for later experimental use. The wood extractives were removed from the ground wood particles by dichloromethane extraction to eliminate interference of wood extractives on the analysis of carbohydrate and lignin in the extracted wood. The chemical composition of extractives-free SHM is summarized in Table 4. The amounts of cellulose, hemicelluloses, and lignin of the extractives-free SHM are 42.30±0.64, 28.72±0.64 and 28.61±0.19%, respectively. For the calculations of the major components from the anhydro-sugar analysis, see [61].

Table 4. Chemical composition extractives-free southern hardwood mixture (% on wood)

Chemical component	Amount (% by wt)		Chemical component	Amount (% by wt.)
Arabinose	0.52±0.01		Klason Lignin	25.78±0.20
Galactose	1.00±0.01		Acid Sol. Lignin	3.20±0.05
Glucose	43.66±0.61		Ash	0.34±0.07
Xylose	15.48±0.03		AcG	2.76±0.08
Mannose	2.18±0.05		UAG	4.83±0.10

Experimental procedures

Autohydrolysis was performed at 150 ºC for 15 to 500 minutes and for 100 min at 130 ºC to 170 ºC in a modified Dionex ASE-100 extractor. The time at temperature is corrected for heat-up time using the Dionex program of the modified ASE-100. The liquor to wood ratio (L/W) was approximately 3.7:1. The amount of water required to displace the extract in the cell after autohydrolysis in the ASE-100 was found to be 1.5 reactor volumes based on the observed outlet concentration profile. More details about the modified ASE-100 are given by Tunc and van Heiningen [61]. The experimental analysis scheme for the hemicellulose extraction of the SHM is summarized in figure 6.

Analysis of wood particles

The ash content of the wood was determined according to TAPPI standard method T211 om-85. The acid insoluble lignin content, Klason lignin, was determined according to a method by Effland [62], while the acid soluble lignin content is determined by Tappi method 250. The uronic anhydride content was determined using the method developed by Scott [49]. The monosugar content of hydrolysate produced by the two-step hydrolysis with 72 and 4% sulfuric acid [47] was determined by High Performance Anion Exchange Chromatography with Pulse Amperometric Detection (HPAEC-PAD). Acetic acid in the hydrolysate was determined by HPLC using a refractive index detector and BIO-RAD Aminex HPX-87H column. The mobile phase used was 5 mM H_2SO_4 with flow rate of 0.6 mL/min and the oven temperature was 60 ºC.

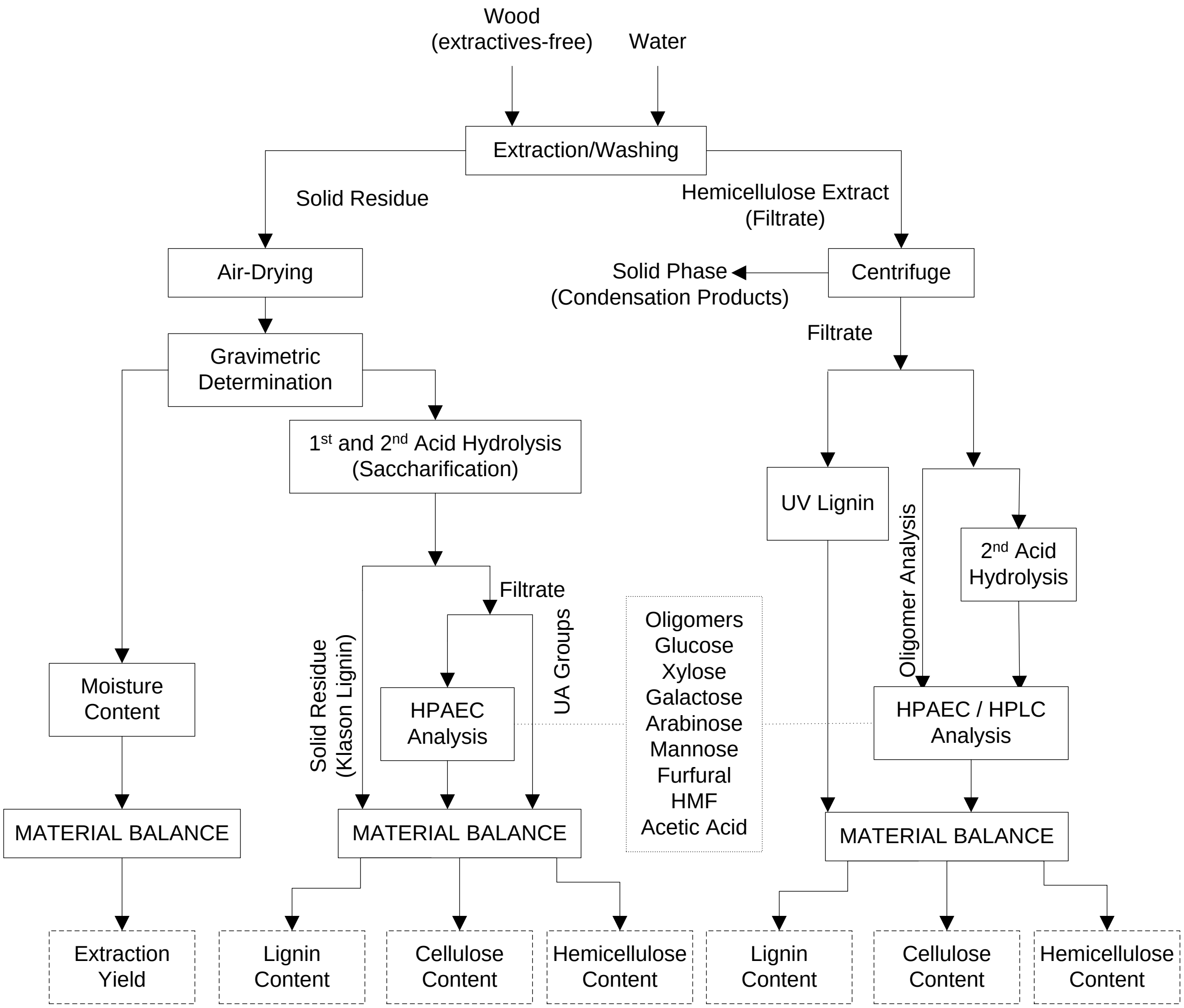


Figure 6. Experimental design for autohydrolysis of wood

Analysis of solid and liquid phases after autohydrolysis
The wood solids remaining after displacement washing were air dried and subjected to the same analysis applied to the original wood. The extraction yield was calculated from the difference in oven dry wood weight before and after autohydrolysis. The pH of the liquid phase, called hemicellulose extract, after autohydrolysis was recorded. The hemicellulose extract was analyzed for monosugar content using a Dionex HPAEC-PAD by direct injection of a sample and after one hour hydrolysis of the sample with 4% H_2SO_4 at 121 °C in an autoclave. The yield of oligomers was calculated from the increase in monosugar anhydride content due to acid hydrolysis. Furfural and HMF in the hemicellulose extract were determined using the HPLC system described previously. The lignin content of the hemicellulose extract was determined from the UV-Vis absorbance at 280 nm with extinction coefficient of 20.3 ($l\ g^{-1}cm^{-1}$) for hardwoods [63]. Pectins were not determined. However, that results in minor mass balance errors since the content of pectins in hardwoods is less than 1% [64].

4.1.2.2 Results and discussion

The autohydrolysis extraction yield is plotted against P-factor in figure 7. It is clear that the effect of time and temperature is represented by a single relationship described by the P-factor. This confirms that the activation energy of 125.6 kJ/mol correctly represents the wood dissolution during autohydrolysis. The extraction yield increases linearly with increasing P-factor from 1.5 % at an extrapolated P-factor of zero hrs. to obtain 22 % at P= 600 hrs. The wood dissolution slows down at higher P-factors. Since at the extrapolated P-factor the extraction yield is approximately 1.5%, it suggests that initially some low-molar mass cellulose readily diffuses out from the wood particles [65].

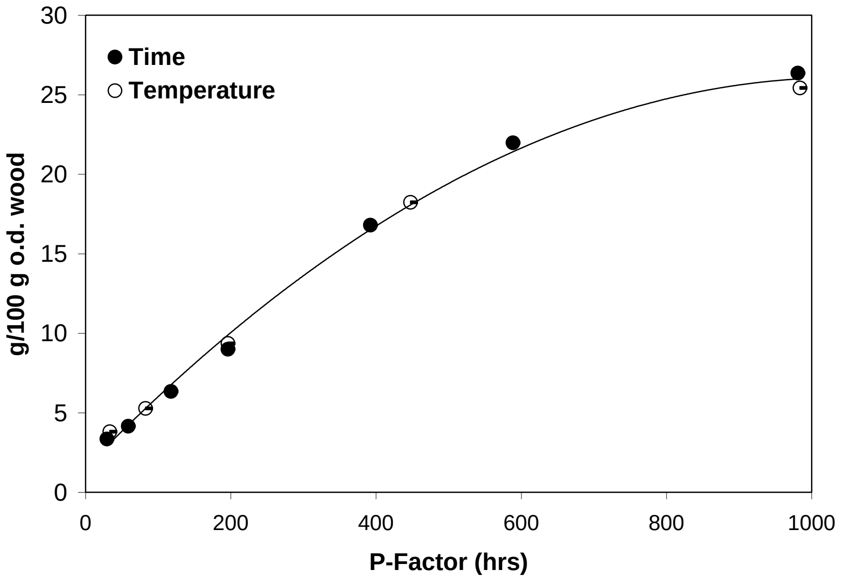


Figure 7. Extraction yield of southern hardwood mixture as a function of P-factor

The major wood components (cellulose, hemicellulose, lignin) remaining in the wood after autohydrolysis are depicted in figure 8. It is obvious that cellulose stays intact during dissolution due to its high molecular weight and crystalline nature, while a small amount of delignification takes place. The same behavior was observed by others [55, 66]. The majority of wood dissolution is due to hemicellulose removal. It is interesting to note that the P-factor concept works for all three major wood components suggesting that their removal during autohydrolysis is governed by the same activation energy of 125.6 kJ/mol.

The wood acids (acetic and uronic) remaining in the wood after autohydrolysis are depicted in figure 9 It is obvious that the effect of time and temperature on uronic acid groups remaining in the wood can be described by a single relationship as a function of P-factor, while that of the acetyl groups remaining in the wood cannot. The reason for these is that the initial acetyl groups in the original wood in both experimental sets (time and temperature) are not the same (2.76±0.08 and 3.30±0.05 for time and temperature effect respectively). It is clear from figure 9 that the amount of wood acids (uronic and acetic) remaining in wood decrease dramatically with increasing P-factor. Approximately 70 and 85% of initial acetyl groups and uronic acid groups respectively dissolve during autohydrolysis at the most severe conditions studied.

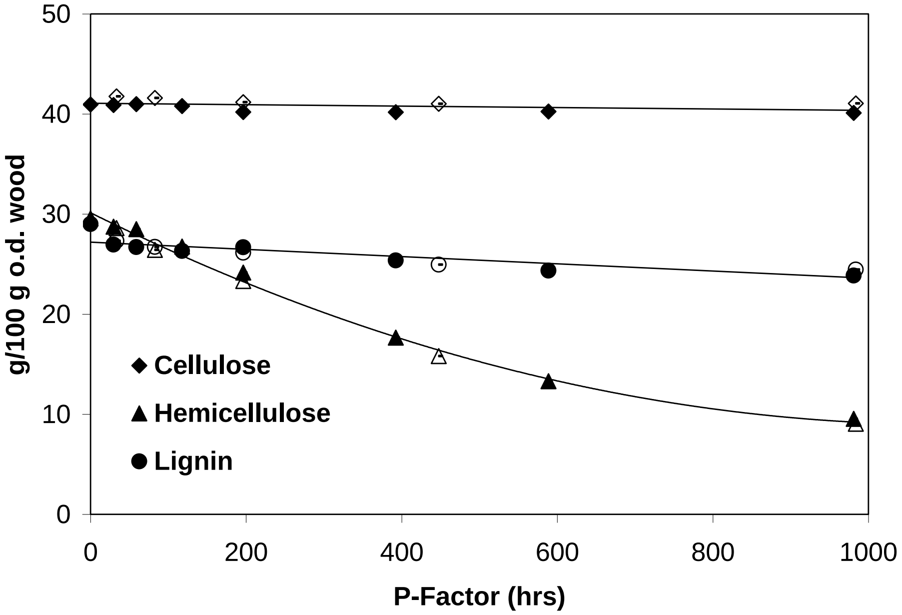


Figure 8. Wood components remaining in southern hardwood mixture (SHM) after autohydrolysis as a function of P-factor

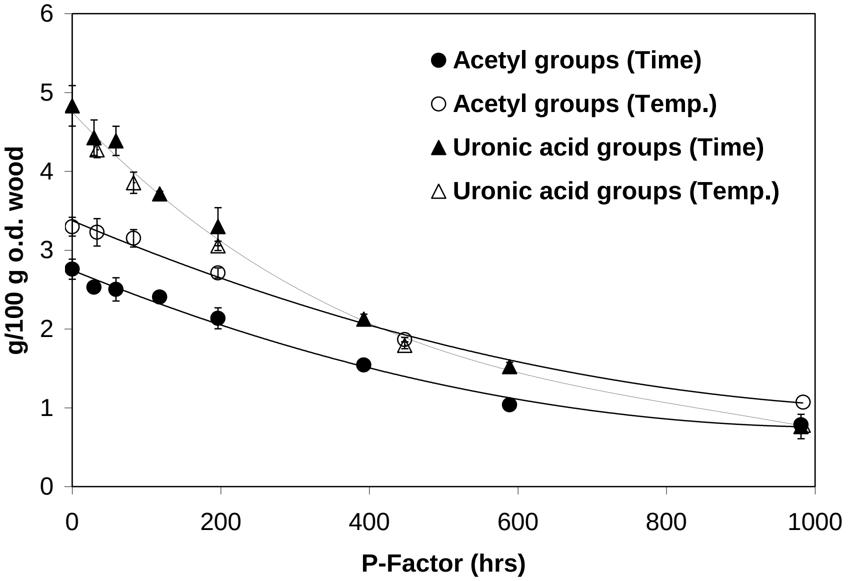


Figure 9. Wood acids (acetyl groups and uronic acid groups) remaining in southern hardwood mixture (SHM) after autohydrolysis as a function of P-factor

The extraction yield of the hardwood hemicelluloses (xylan and glucomannan) determined from analysis of the solid phase is depicted in figure 10. The S-shaped xylan extraction yield curve implies that the extraction rate of xylan is slow initially and reaches a maximum at about a P-factor of 800 hrs. The rate of xylan removal slows down significantly at the highest P-factor of almost 1000 hrs. used in this study. The rate of glucomannan removal shows the same general behavior as that of xylan, only at a level of about 5 times lower. The slow initial removal of xylan and glucomannan may be explained by the initially low acidity of the solution, and these polymers first need to be degraded before they become soluble.

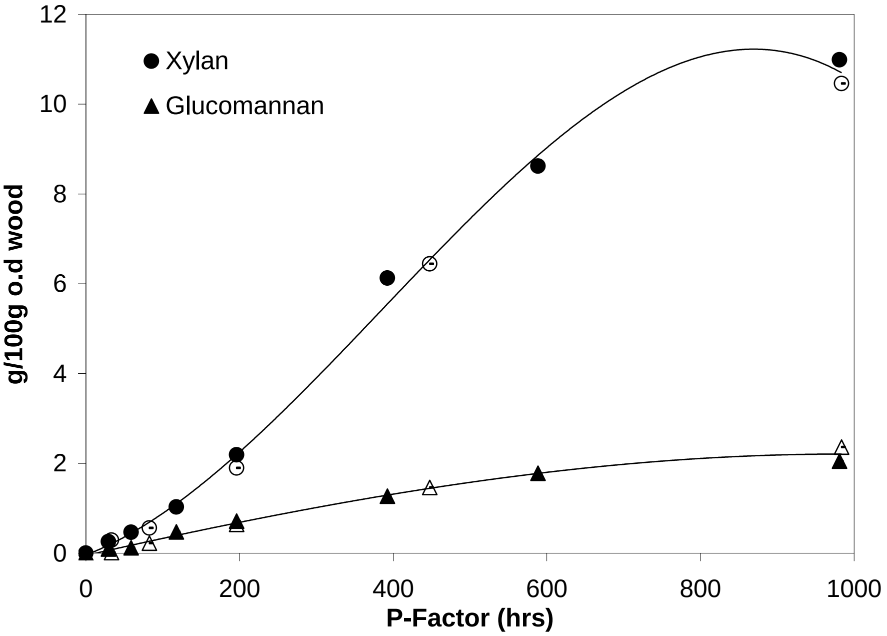


Figure 10. Extraction yield of xylan and glucomannan as a function of P-factor

Figure 11 depicts the ratio of the side groups relative to xylose in xylan remaining in the wood during autohydrolysis as a function of P-factor. It is clear from figure 11a that the ratios of both arabinose and galactose to xylose in xylan remaining in the wood decrease with increasing P-factor and reach a plateau at P-factor of 600 hrs. It is obvious from figure 11b that although the effect of time and temperature on the ratio of uronic acid groups to xylose in xylan remaining in the wood can be described in a single relationship as a function of P-factor. Again the ratio of acetyl groups relative to xylose can only be represented by two different relationships due to the fact that two wood samples with different initial amount of acetyl groups in the original wood were used. It is apparent from figure 9b that the ratio of uronic acid groups in xylan remaining in the wood during autohydrolysis slightly decreases with increasing P-factor, while the ratio of acetyl groups remaining in the wood is almost constant.

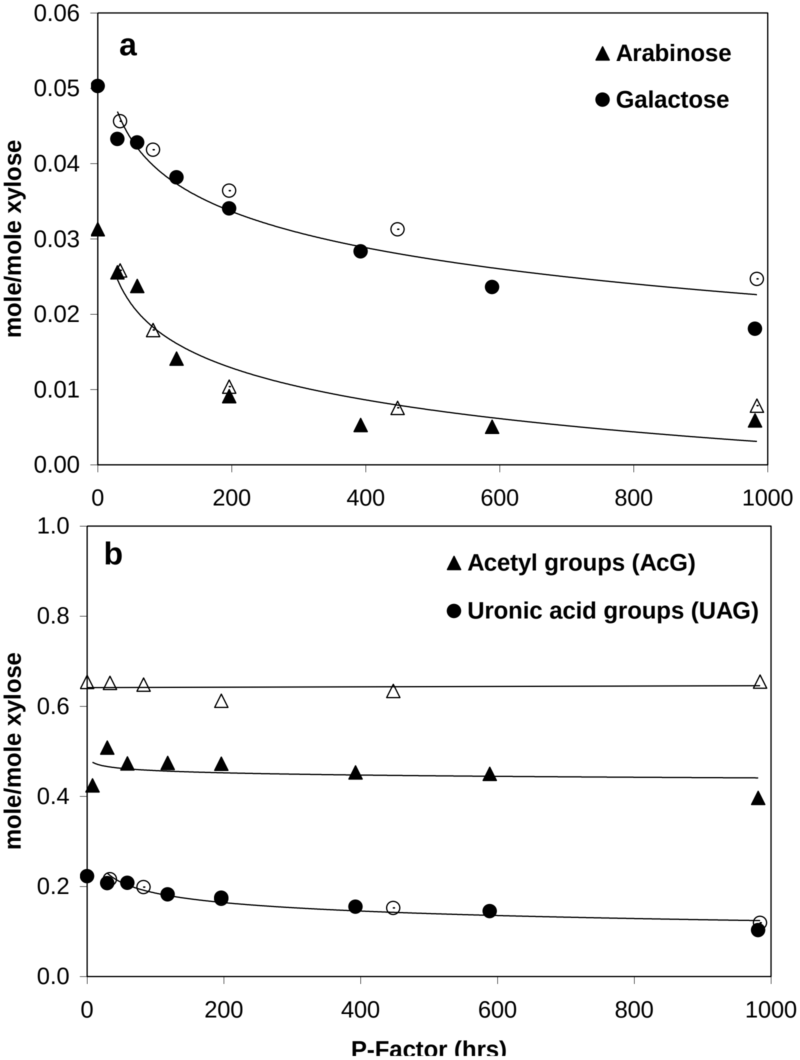


Figure 11. The ratio of the side groups relative to xylose in xylan remaining in the wood during autohydrolysis, a) Arabinose and galactose b) Acetyl groups and uronic acid groups

The xylose, xylo-oligosaccharide and furfural contents in the extract obtained from the extract analysis are presented in Figure 12. The mass balance loss (MBL) of xylan calculated from the xylan mass balance is also shown in figure 12. It shows that xylan dissolves mostly as oligosaccharides up to P-factor of 200 hrs. and at more severe conditions the oligosaccharides depolymerize to monomeric xylose by acid hydrolysis [54]. Further dehydration of xylose to furfural is insignificant up to a P-factor of 600 hrs. However, small amounts of furfural are observed at more severe conditions. Although the amount of xylose increases constantly, the amount of xylo-oligosaccharide reaches a plateau around P-factor of 800 hrs. It should be noted that no significant HMF generation was observed during autohydrolysis. At the most severe conditions (P-factor of 980 hrs.) the amount of HMF generated is 0.032% based on wood. It is clear from figure 12 that the mass balance loss (MBL) is approximately ±1% during autohydrolysis.

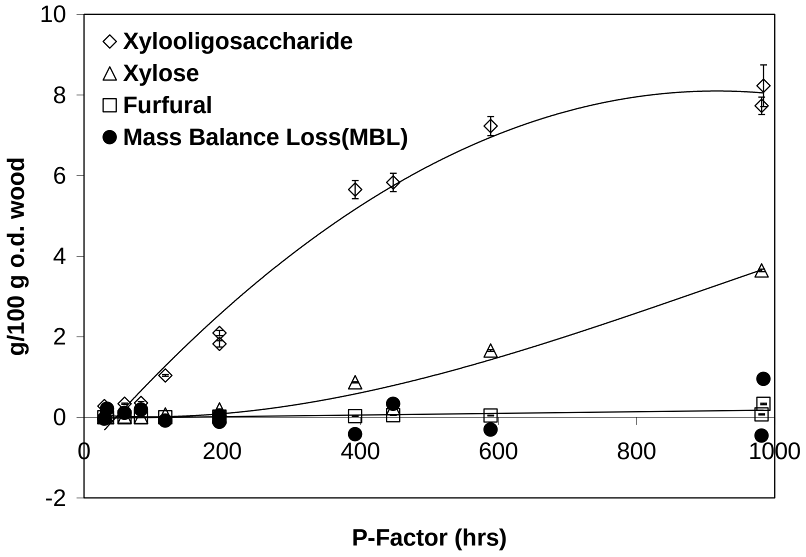


Figure 12. Xylose, xylo-oligosaccharide, furfural and MBL in hemicellulose extract as a function of P-factor

The final pH of the hemicellulose extract and [H^+] ion concentration after autohydrolysis are plotted against P-factor in figure 13. It shows that the effect of temperature and time on the pH of the autohydrolysis extract after autohydrolysis can be described by a single relationship as a function of P-factor. i.e.:

$$pH = 7.59 * P_{factor}^{-0.11} \qquad (3)$$

where P_{factor} is in hours. At a P-factor larger than about 50 hrs. the pH is less than 4.8, i.e. the point below which the released acetyl groups are mostly in the form of acetic acid (pKa = 4.8). The pH of the extract decreases from 5.5 to 3.6 over P-factor between 30 and 980 hrs. It is also clear from figure 13 that [H^+] concentration rapidly increases with increasing P-factor up to 400 hrs.; then it slows down.

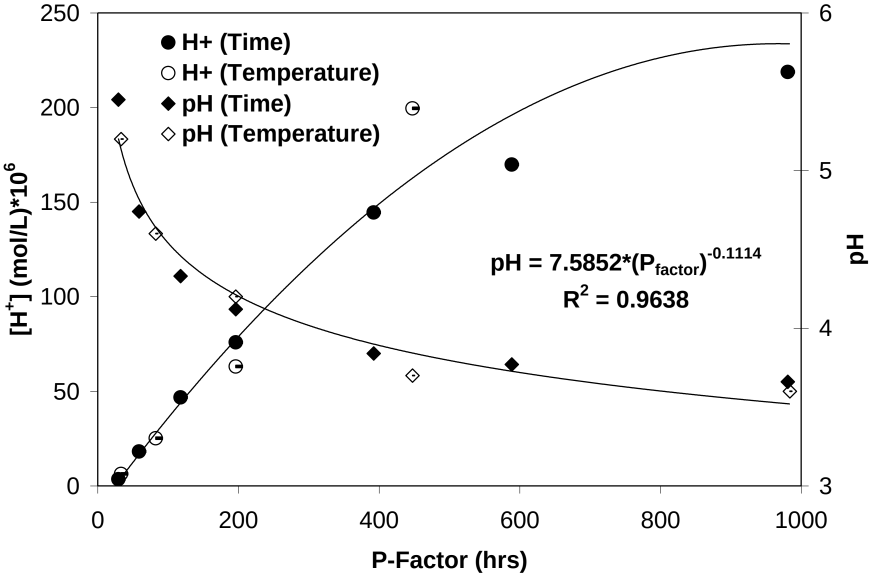


Figure 13. The final pH of the hemicellulose extract after autohydrolysis as a function of P-factor

4.1.2.3 Conclusion

It is shown that xylo-oligosaccharides can be removed from hardwood in high yield without extensive delignification and degradation of cellulose. The effect of time and temperature on the dissolution of different wood components of a southern hardwood chips mixture can be expressed by a single relationship involving the prehydrolysis factor or P-factor. Xylan is the most abundant species in the reaction medium at P-factor higher than 200 hrs. Xylan mainly dissolves in oligomeric form however significant hydrolysis to xylo-oligomer to xylose takes place at the highest P-factor of about 1000 hrs. studied. The extraction rate of xylan is initially slow and then it reaches a maximum at approximately a P-factor of 800 hrs. The rate of xylan dissolution slows down significantly at the highest P-factor of almost 1000 hrs. studied. The rate of glucomannan removal shows the same behavior as that of xylan, however it is almost five times lower than that of xylan. Approximately 70% of hemicelluloses in original wood are extracted during autohydrolysis at P-factor of about 1000 hrs. The ratio of both arabinose and galactose side groups relative to xylose in xylan remaining in the wood during autohydrolysis decreases with increasing P-factor and it reaches a plateau at a P-factor of about 600 hrs. The ratio of acetyl groups to xylose in xylan remaining in wood stays relatively constant, while that of uronic acid groups slightly decreases with increasing P-factor. The acidity of the hemicellulose extract increases with increasing P-factor and reaches a plateau around P-factor of 800 hrs in the present range of study. No significant amount of furfural and HMF was generated under the present extraction conditions. The results show that the modified ASE is a useful instrument to study autohydrolysis of lignocellulosic materials, and that xylan may be efficiently extracted from hardwood (SHM) without significant removal of cellulose and only a small amount of lignin.

4.1.3 WATER PRE-EXTRACTION – KRAFT PULPING OF LOBLOLLY PINE

During kraft pulping of softwoods about 15-20% of the wood weight as hemicellulose (25-30% in wood) end up in spent pulping liquor. Therefore the combined amount of softwood hemicelluloses removed in the pre-extraction process **and** subsequent pulping process should be similar or less than 15 – 20% (based on wood). In this chapter we explore whether this objective can be achieved with pure water pre-extraction and subsequent kraft cooking of Southern Pine chips. The effect of time and temperature of the hemicellulose extraction on the yield and properties of the pulp obtained after subsequent kraft pulping were investigated and the results were then compared to regular kraft pulps of the same kappa number.

4.1.3.1 Experimental

Wood Chip Preparation

Fresh Loblolly pine chips were obtained from International Paper. Chips with defects including barks, knots and decayed parts were removed prior to screening. The chips were then screened in a Weyerhaeuser classifier. The wood fraction passing 10 mm wide slots but collected on 7/8, 5/8 inch and 5mm round screens were used. All these fractions were well mixed and air-dried using a fan at room temperature. The air-dried wood chips were then put in plastic bags and their equilibrium moisture content was determined.

Water Extraction

Extraction experiments were conducted using eight 300 ml cylindrical bomb digesters placed inside a large rocking high pressure vessel filled with polyethylene glycol as heat transfer fluid. The rocking device rotates 180^{o} every 30 sec. Thirty grams (oven dried wood) of softwood chips in each bomb digester were subjected to pure water extraction a liquor-to-wood ratio of 4.5. The extraction temperature was ramped from room temperature to a preset maximum temperature of 160, 170, 180 or 190^{o}C at a rate of 2.13^{o}C per minute. Extraction times at the maximum temperature were varied from 10 to 90 minutes. Each bomb was then quenched in cold water. The liquor was separated from the pre-extracted chips, followed by washing of the chips on a 200-mesh screen with warm (tap) water and then oven-dried to measure the weight loss.

Kraft Cooking

The pre-extracted wood chips were subjected to conventional kraft cooking (30% sulfidity) using the same bomb digesters and rocking device as used for water pre-extraction. The liquor-to-wood ratio was 4, the final cooking temperature 170^{o}C, and the effective alkali (EA) charge was 15% for the extracted and 15 and 17% for the control cooks. Cooking times at 170^{o}C were varied to obtain different kappa numbers. Pulps obtained from each cook were disintegrated in a blender and thoroughly washed on a 200-mesh screen with warm tap water. The pulps were then air-dried for measurement of pulp yield, kappa number and intrinsic viscosity.

Extraction Liquor Analysis

Extraction liquor samples were analyzed for solids content (by freeze drying), pH, and lignin and sugar content. As before, the monomeric and polymeric sugar content was determined using HPAEC (High Pressure Anion Exchange Chromatography) analysis before and after acid hydrolysis of the samples. The lignin content was determined by UV analysis. The overall analytical procedure is shown in Figure 14.

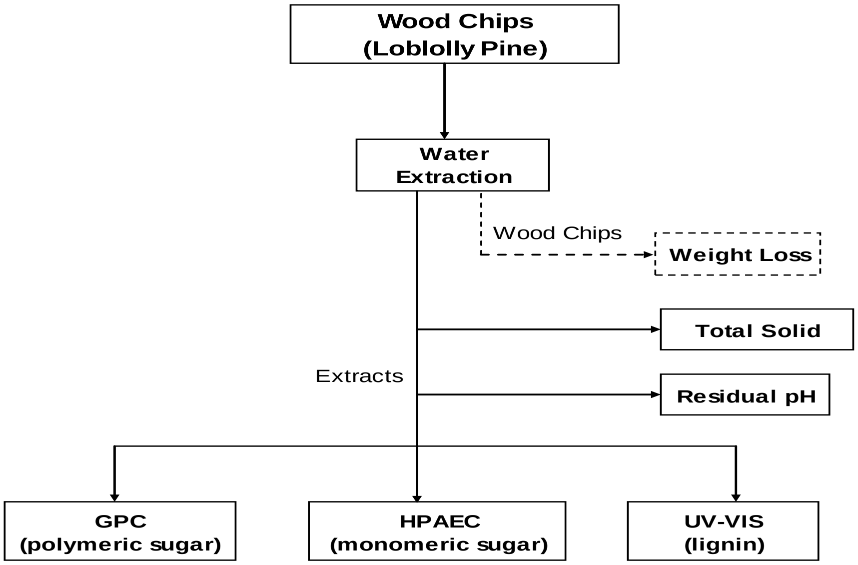


Figure 14. Analytical Procedure for Loblolly Pine Extracts.

4.1.2.2 Results and Discussion

Wood Chip Weight Loss

The weight loss data obtained after extraction of the Loblolly Pine chips are shown in Table 5. The weight loss increases from almost 2% at the mildest extraction condition (10 minutes at 160^{o}C) to 24% at the most severe condition (90 minutes at 190^{o}C). The weight loss is plotted against total extraction time (includes heat-up time) in Figure 15. It can be seen that the weight loss increases both with increasing extraction time and final temperature.

Table 5. Weight Loss Data after Hot Water Extraction of Loblolly Pine

Run	T_{max} (^{o}C)	Time at T_{max} (min)	H-Factor (hrs.)	Wt. Loss (%)
1	160	10	100	1.97
2	160	24	200	4.98
3	160	65	500	7.87
4	170	15	184	10.07
5	170	45	794	15.03
6	170	90	1487	17.68
7	180	15	934	16.68
8	180	15	934	16.13
9	180	15	934	16.62
10	180	45	2153	20.66
11	180	45	2153	19.62
12	180	90	3441	22.11
13	190	15	1777	18.10
14	190	45	4048	22.53
15	190	90	7250	24.03

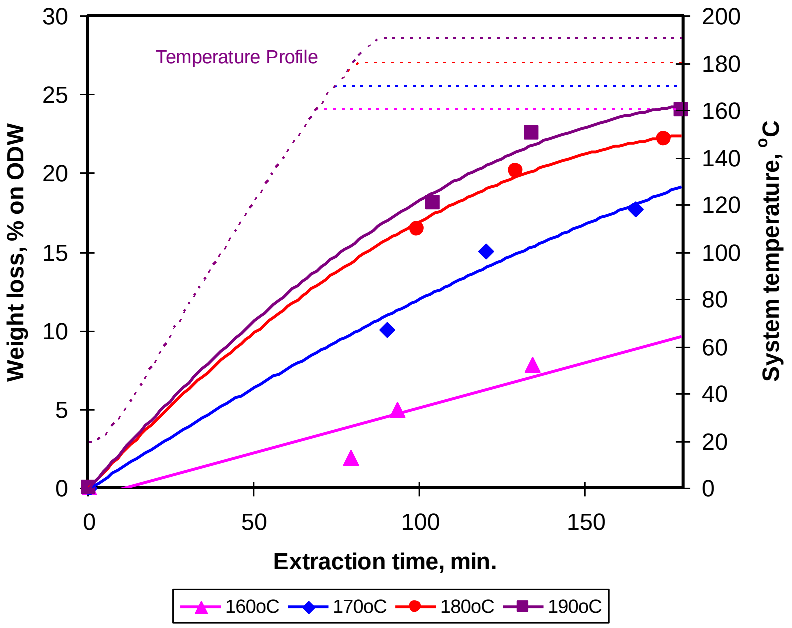


Figure 15. Weight Loss vs Total Extraction Time at Different Maximum Temperatures.

The weight loss data are plotted against H-factor in Figure 16. H-factor is a means of expressing reaction time and temperature as a single variable [57]. It can be seen in Figure 16 that regardless of extraction temperature, a single relationship between the extraction weight loss and H-factor is obtained. This indicates that the activation energy of the kinetics of wood dissolution during pure water extraction is the same as that of kraft cooking, i.e. 32 kcal/mol. The results in Figure 3 also show that the weight loss increases rapidly to 15% at an H-factor of about 1,000 hrs and then the increase levels off at higher H-factors.

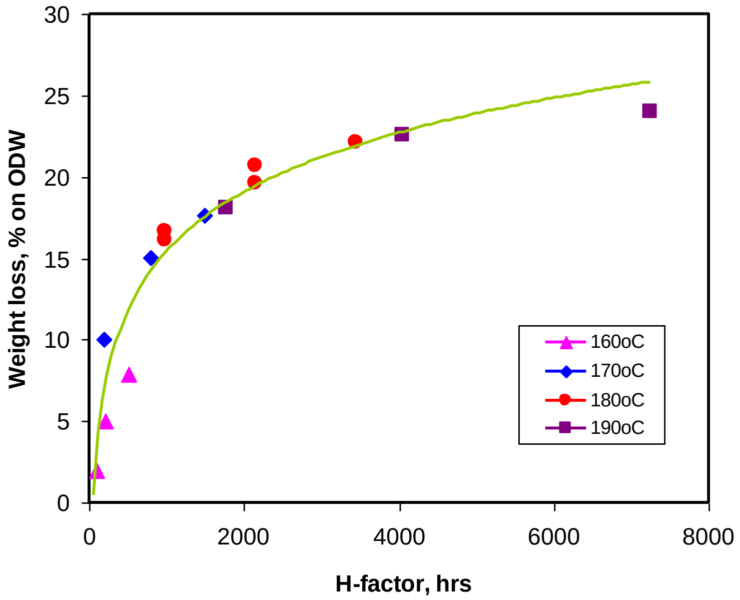


Figure 16. Extraction Weight Loss versus H - Factor.

Components of Water Extracts

The amounts of wood sugars in monomeric and polymeric form in the extracts were calculated from the content of monosugars (glucose (Glu), mannose (Man), arabinose (Ara), xylose (Xyl) and galactose (Gal)) determined by HPAEC analysis. The HPAEC analysis was performed both before and after hydrolysis of the extracts with 4% H_2SO_4 at 121 °C for one hour in an autoclave. The yield of cellulose and hemicellulose in polymeric form in the extract was calculated from the increase in monomeric sugar content caused by the acid hydrolysis. The concentrations of arabinose, galactose, glucose, xylose and mannose after acid hydrolysis expressed in mg/ml are shown in Table 6. The total amount of cellulose, C, and hemicelluloses, H, which led to these concentrations were then calculated using the following equations:

$$C = Glu * \left(\frac{162}{180}\right) - \frac{Man}{b} * \left(\frac{162}{180}\right) \tag{4}$$

with b = 4.15 (Average value for number of mannose units per glucose unit in hemicellulose of Pine/Spruce wood, based on Janson [67])

$$H = (Ara + Xyl) * \left(\frac{132}{150}\right) + (Gal + Glu + Man) * \left(\frac{162}{180}\right) - C \tag{5}$$

Table 6. HPAEC Sugar Analysis of Pure Water Extract of Loblolly Pine Chips

Extraction Temperature (T_{max}, ^oC)	Time at T_{max} (min)	Monosugars (mg/ml sample)					Total Cellulose, C (mg/ml)	Total Hemi-celluloses, H (mg/ml)
		Arabinose	Galactose	Glucose	Xylose	Mannose		
170	15	2.31	2.64	2.54	4.33	7.81	0.59	16.9
	45	1.84	3.77	3.78	6.04	11.91	0.82	23.7
	90	1.47	3.23	4.79	5.92	14.39	1.19	25.5
180	15	1.62	3.33	4.47	6.48	13.92	1.00	25.7
	45	0.88	3.08	5.03	4.58	14.04	1.48	23.6
	90	0.47	2.45	4.63	2.42	14.85	0.95	21.3
190	15	1.31	3.41	4.23	5.42	12.10	1.18	22.5
	45	0.49	2.06	4.69	2.52	10.42	1.96	16.1
	90	0.20	1.25	3.92	1.27	5.47	2.34	8.5

The concentrations of the monosugars in the fresh extract (i.e. before acid hydrolysis) expressed in mg/ml are shown in Table 7. Comparison of the data in Table 7 with that in Table 6 leads to the following observations. Most of the arabinose is removed as a monomer from (arabino-4-O-methylglucorono) xylan at the start of the hydrolysis process, and is continuously degraded in the extract at longer extraction times. A major fraction of galactose remains attached as a side chain to polymeric galactoglucomannan dissolved in the extract. At higher extraction severities most of the extracted xylan is in monomeric form; only the extracts at 170 ^oC for 15 and 45 minutes show xylan mostly in polymeric form. Glucomannan on the other hand remains mostly in polymeric form even at high severity extraction conditions. Most of the monomeric glucose in the extract originates from glucomannan, with the rest of glucose in the form of dissolved cellulose.

Table 7. HPAEC Sugar Analysis of Fresh Water Extract (i.e. without acid hydrolysis)

Extraction Temperature (T_{max}, °C)	Time at T_{max} (min)	Monosugars (mg/ml sample)				
		Arabinose	Galactose	Glucose	Xylose	Mannose
170	15	2.07	0.41	0.08	0.60	0.12
	45	1.90	1.03	0.23	2.66	0.73
180	15	1.68	1.25	0.37	4.00	1.63
	45	0.86	1.66	0.96	4.37	3.54
	90					
190	15	1.36	1.55	0.60	4.69	2.12
	45					
	90					

The total amounts of cellulose and hemicelluloses removed expressed in percent of original oven dry wood weight were calculated by multiplying respectively the values for C and H in Table 6 by 0.45, i.e. by the liquor-to-wood ratio (4.5 L/kg) divided by 10. The amounts of polymeric cellulose and polymeric hemicelluloses in the extract expressed in percent of original oven dry wood weight were obtained by subtracting the concentrations of arabinose, galactose, glucose, xylose and mannose in Table 7 from the corresponding sugars in Table 6, then using the equations for C and H respectively, and then multiplying the result by 0.45. All these components in the extract including total solids content and lignin content, expressed in percentage of original dry wood weight, are listed in Table 8.

Table 8. Components in Pure Water Extract of Loblolly Pine Chips in % on OD wood

Extraction Temperature (T_{max}, °C)	Time at T_{max} (min)	pH	Total Solids (%)	Polymeric Sugars (%)	Total Hemi-cellulose (%)	Polymeric Hemi-celluloses (%)	Total Cellulose (%)	Lignin (%)
170	15	3.64	15.72	6.6	7.6	6.3	0.27	0.47
	45	3.48	16.02	8.4	10.7	8.0	0.37	0.76
	90	3.48	18.45	7.4	11.5	6.9	0.54	1.25
180	15	3.48	17.51	8.4	11.6	7.9	0.45	1.33
	45	3.35	19.13	6.6	10.6	5.9	0.67	2.21
	90	2.80	17.51	-	9.6	-	0.43	3.38
190	15	3.33	18.05	7.2	10.1	6.7	0.53	1.53
	45	2.79	18.23	4.3	7.3	3.4	0.88	3.34
	90	2.71	14.13	3.4	3.8	2.3	1.05	5.11

The total sugar yield (total hemicellulose + total cellulose), polymeric sugar yield, hemicellulosic sugar yield, total cellulose yield and lignin yield in the extract are plotted against H-factor in Figure 17. It can be seen that the yield data obtained at different temperatures and times are each described by a single curve. The extracted amount of lignin and (polymeric) cellulose increase approximately linearly with H-factor, while the extracted amount of hemicellulose (sum of polymeric and monomeric forms) displays a maximum at an H-factor of about 1,500 hours. The total polysaccharide content in the extract (i.e. polymeric hemicellulose and cellulose) displays a maximum at an H- factor of about 500 hrs. The total sugar content in the extract, which is the sum of all monomeric and polymeric sugars, also reaches a maximum value at an H-factor of about 1500 hours because the sugar contribution is dominated by hemicelluloses. At an H-factor of about 500 hours the extract contains about 8 % of polymeric sugar (based on original dry wood weight) with a minor removal of 0.3% cellulose and 0.5% lignin. The explanation for the existence of a maximum for the polysaccharide yield is that the extracted oligomers are further hydrolyzed to monosugars due to the acidity of the extract created by the release of acetic acid from the hemicelluloses. The hemicellulose yield goes through a maximum because the monosugars are further degraded to furfural, hydroxyl-acids, and other degradation products.

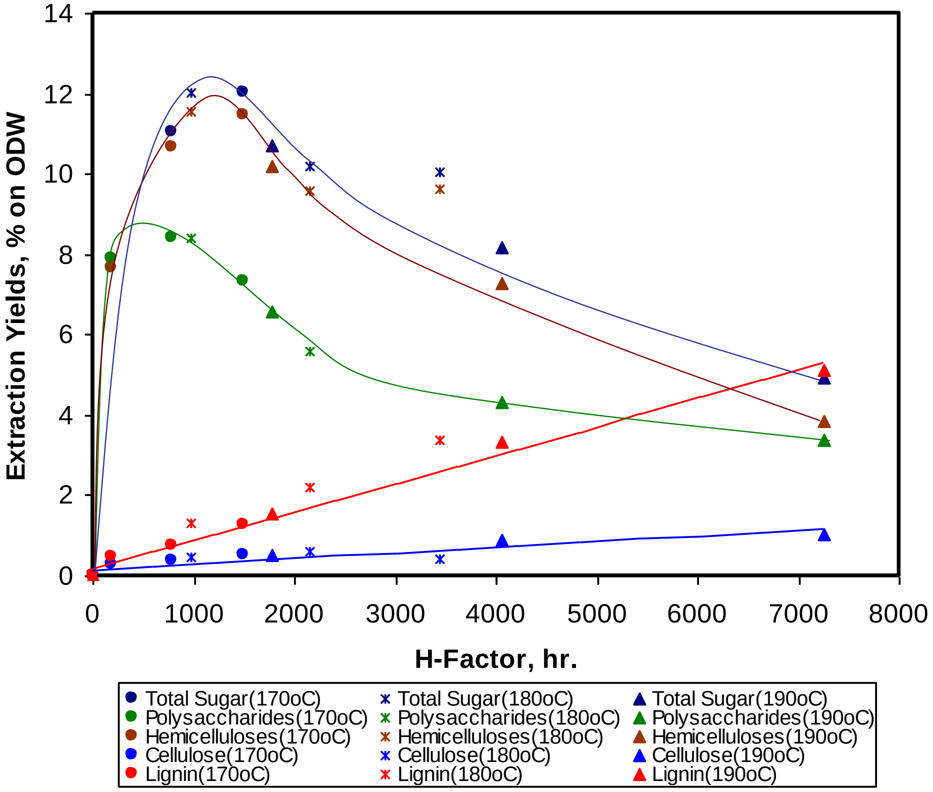


Figure 17. Extracted Wood Components versus H-factor.

Mass Balance Analysis

An overall mass balance analysis was performed to test the internal consistency of the data. The extraction yield may be calculated from the weight loss of the wood chips, from the total solid content of the extraction liquor, and from the sum of all the organic components in the extract. The organic components are the monomeric sugars, polymeric sugars and lignin. The results for the extractions at 170 °C are shown in Figure 18. It can be seen that the extraction yield calculated from the organic components is somewhat lower than that calculated from the wood chip weight loss or total solids content of the extract. This is expected because dissolved organic components such as acetic acid, methanol, 4-O-methyl glucuronic acid, as well as sugar degradation products such as furfural and others are not accounted for.

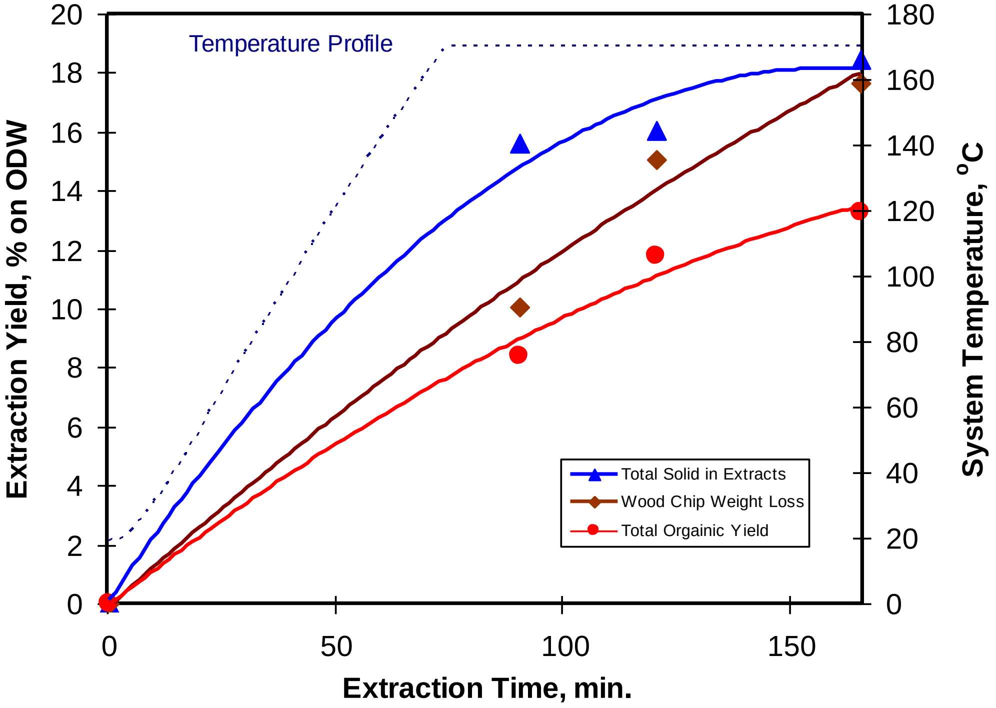


Figure 18. Mass Balance Analysis for Water Extraction of Loblolly Pine at 170°C.

pH of Extract

The total sugar and polymeric sugar yields are plotted against residual pH of the water extracts in Figure 19. It can be seen that both the total sugar and polymeric sugar yields increase sharply as the pH drops from the neutral to a level below about 4. Maximum yields are obtained at a pH of about 3.5. The yield then rapidly decreases as the pH drops below 3. This suggests that the extraction with water should be terminated before the pH drops below 3.5.

The residual pH of the water extracts is plotted as a function of H-factor in Figure 20. It shows a rapid drop from neutral to an acidic level of pH 4 in the very early stages of extraction up to an H-factor of about 100. At an H-factor level of about 500, the residual pH of the water extracts reaches 3.5 and then drops below pH 3 at H-factors larger than about 3000 hours. The pH drop during water extraction is caused by acetic acid formed by hydrolysis of acetyl groups in the hemicelluloses.

Kraft Pulping of Pre-extracted and Control Loblolly Pine Chips

In order to obtain a relatively high yield of polymeric hemicellulose in the extract, but at the same time minimize the degradation of cellulose, the Loblolly Pine chips were pre-extracted using pure water prior to kraft pulping at H-factors of about 500, 200 and 100 hours. The pre-extracted wood chips were then subjected to kraft pulping at 15% effective alkali charge and 30% sulfidity. The cooking results were compared with two reference controls (at 15% and 17% effective alkali charge and 30% sulfidity). The wood weight loss after pre-extraction of the loblolly pine chips was presented earlier in Table 5.

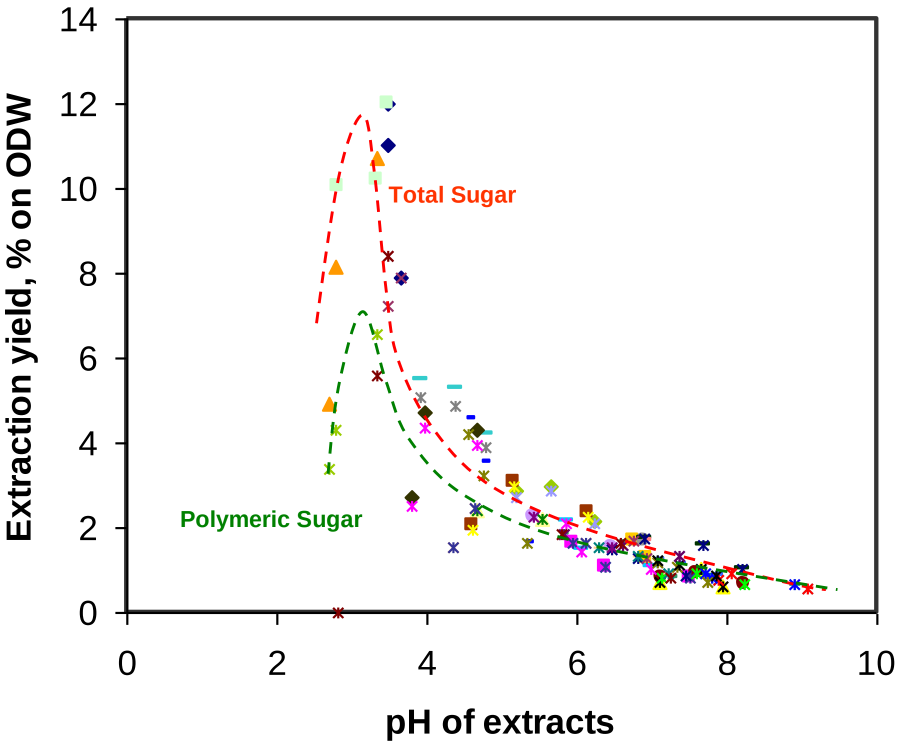


Figure 19. Total Sugar and Polymeric Sugar Yields versus Extract pH.

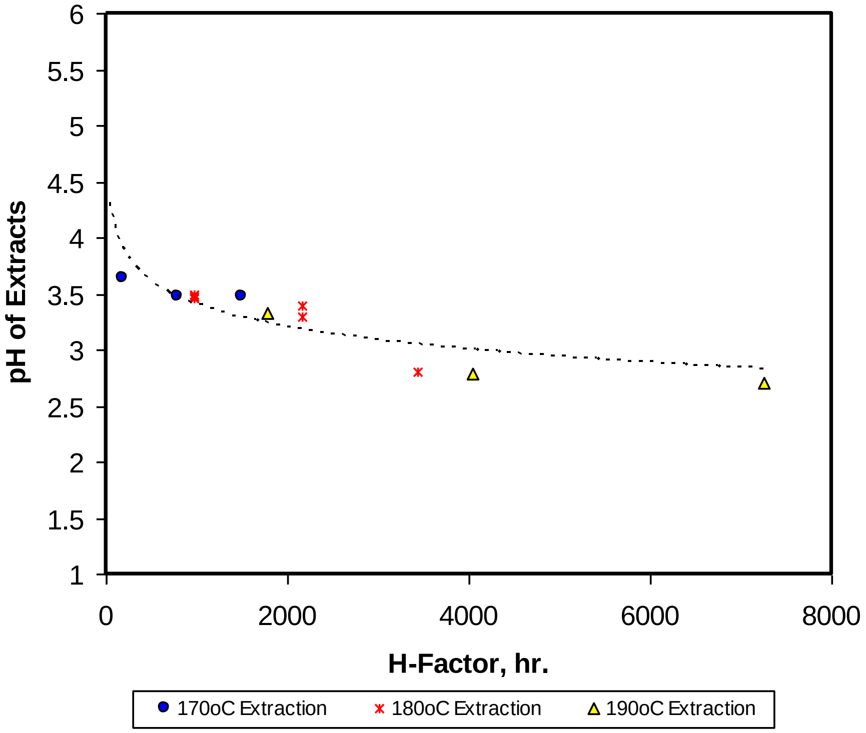


Figure 20. pH of Water Extract versus H-factor

Rate of Kraft delignification

The percentage of residual lignin (as % on wood), L_r, was calculated as:

$$L_r = 1.5\times10^{-3}\left[Kappa\right]\cdot\left[Yield\,(\%)\right] \qquad (6)$$

Figure 21 shows the residual lignin as a function of pulping time at 170°C for both the pre-extracted and control cooks. All the pre-extraction-kraft cooks showed significant higher delignification rates than the kraft control cooks. The improvement in delignification rate may be due to an increased accessibility of the cell wall and cleavage of lignin-carbohydrate covalent bonds during pre-extraction [68].

Assuming first order kinetics in residual lignin (as % on wood), L_r, the delignification rate can be expressed as:

$$\frac{dL_r}{dt} = kL_r \qquad (7)$$

where t is the time at maximum cooking temperature and k is the temperature-dependent delignification rate constant. Based on equation (7), the delignification rate constant, k, can be calculated from the slope of the regression lines through data plots of $\ln\left(L_r / L_{r,p}\right)$ against t. The delignification rate constants at 170°C for the pre-extracted and control kraft cooks are summarized in Table 9.

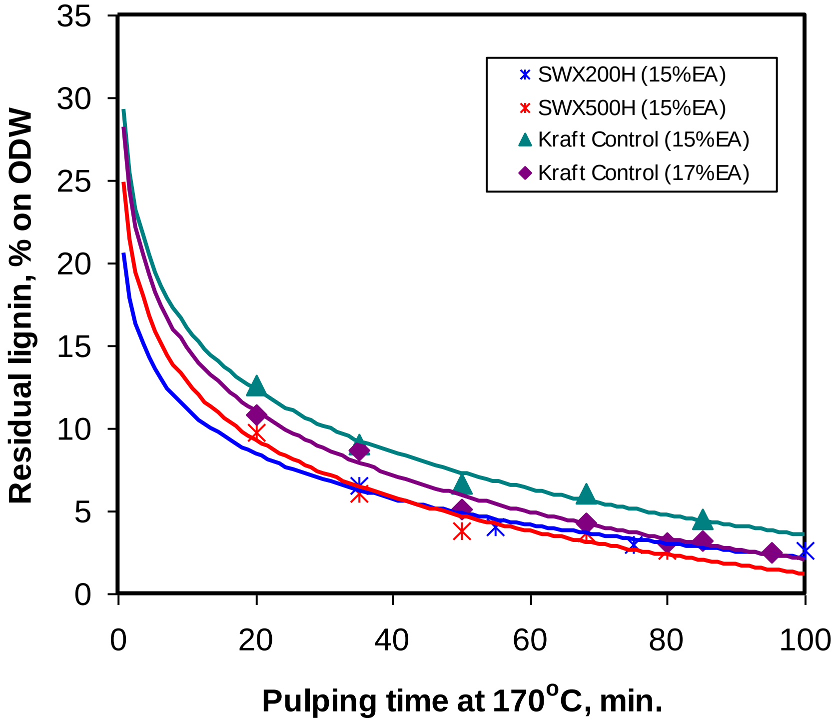


Figure 21. Residual Lignin (based on wood) versus Pulping Time at 170°C.

Table 9. Delignification Rate Constants for 170^{o}C Kraft Pulping of Loblolly Pine Chips.

Sample ID	Extraction		Cooking			Pulping Results	
	Media	H-factor	EA (%)	Sulfidity (%)	L/W	k , min^{-1}	Regression Coeff. (R^{2})
SXW-200H (15%EA)	Water	200	15	30	4	0.0227	0.99
SXW-500H (15%EA)	Water	500	15	30	4	0.0212	0.89
Control (15%EA)	-	0	15	30	4	0.0150	0.96
Control (17%EA)	-	0	17	30	4	0.0196	0.98

The delignification rate constants for 15% effective alkaline kraft cooking of water pre-extracted chips were 40 to 60% higher than the kraft control cooks at 15% effective alkaline charge. Compared to the 17% effective alkaline kraft control cooks, the 15% effective alkaline kraft cooks of water pre-extracted chips still showed a 10 to 20% higher k value. This improvement in delignification rate for water pre-extracted chips leads to a pulp production rate increase.

Total Pulp Yield

In order to evaluate the delignification selectivity of the water pre-extracted wood chip cooking, total pulp yields were plotted against pulp kappa numbers as shown in Figure 22.

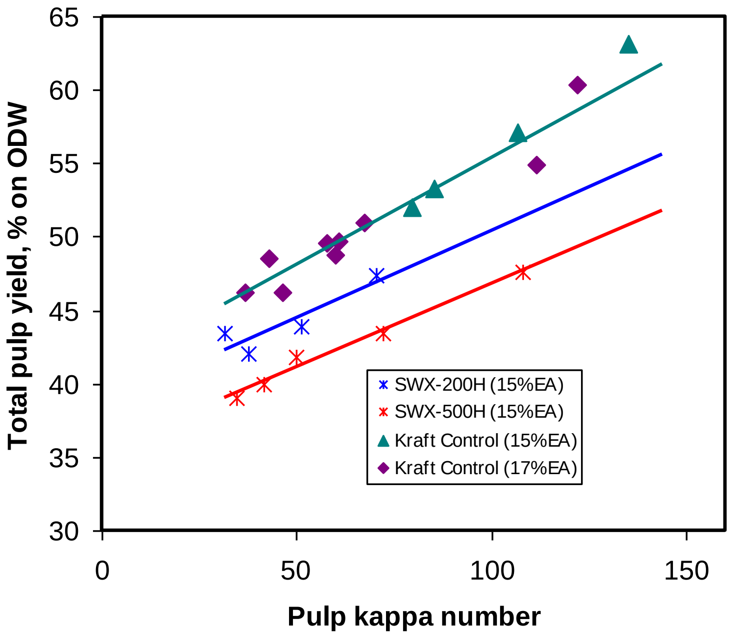


Figure 22. Total Pulp Yield (on wood basis) versus Pulp Kappa Number for 170^{o}C Kraft Pulping of Loblolly Pine Chips.

As expected, a linear relationship was observed between total pulp yields and pulp kappa number for the water pre-extracted kraft and kraft control cooks. Total pulp yield based on wood at the same kappa number decreases as the H-factor for water pre-extraction increases from 100 to 500hrs. A total pulp yield decrease at Kappa 30 of approximately 3% compared to the control cooks was observed for the 200 hour H-factor pre-extracted chips. For the 500 H factor pre-extracted chips the yield loss (based on wood) approximately doubles to 6%. These values compare to extraction yields (based on wood) of 4 and 8% respectively (see Table 5). Therefore these results show that additional wood sugars are removed during kraft pulping of pure water pre-extracted chips compared to those which end up in the black liquor during conventional kraft cooking to the same kappa number. More research is needed to better understand the mechanism for this additional wood sugar loss, so that operating procedures can be defined whereby this yield loss can be minimized to achieve viable conditions for a forest biorefinery which produces pulp besides other products as described in the Introduction of this paper.

Consumption of Effective Alkali

The development of residual effective alkali as cooking proceeds for the extracted chips and the control chips is shown in Figure 23. It shows that the alkali consumption during kraft cooking of both 200 and 500 H-factor the extracted chips is the same as that of the control cooks also performed at the same Effective Alkali charge of 15% on wood.

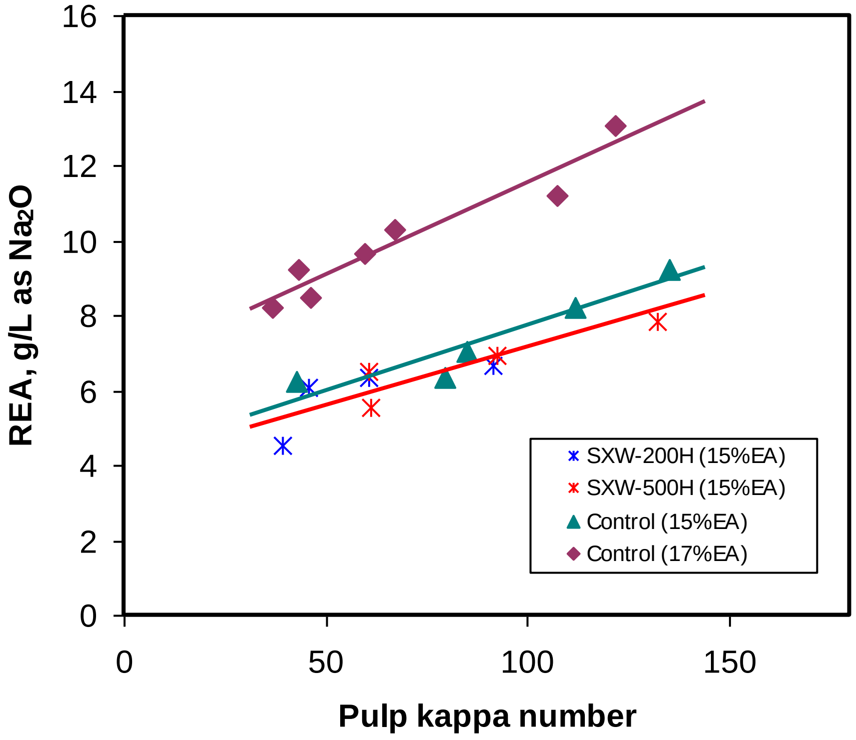


Figure 23. Residual Effective Alkali versus Pulp Kappa Number for 170°C Kraft Pulping of Loblolly Pine Chips.

This result implies that the alkali consumption savings during kraft pulping due to pre-extraction of sugars are compensated by additional alkali consumption due to additional carbohydrate removal during kraft cooking. Thus it appears that pre-extraction leads to additional peeling of wood sugars which are retained in the control pulp. Again, the mechanism underlying this additional consumption of alkali should be studied in order to define operating conditions which would lead to savings in effective alkali consumption during kraft cooking after pre-extraction.

Pulp Viscosity

The intrinsic viscosity of the pulps versus Kappa number is shown in Figure 24. It shows that the cellulose – lignin selectivity during kraft pulping is not affected by mild pre-extraction with pure water at 200 and 500 H-factor. This means that these pre-extraction conditions are mild enough that acid hydrolysis of cellulose during extraction is minimal. It also suggests that the strength properties of paper made from the pre-extracted kraft pulps will be similar to that of the control kraft pulps. Further physical testing of the pulps beaten to different freeness values is needed for conformation.

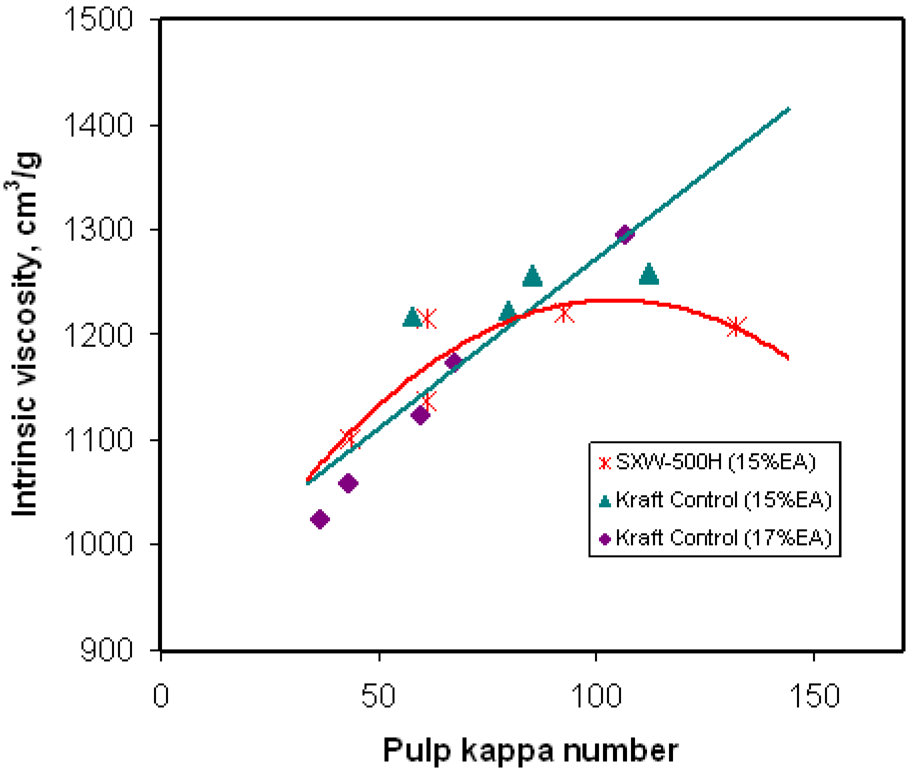


Figure 24. Intrinsic Viscosity versus Pulp Kappa Number for 170°C Kraft Pulping of Loblolly Pine Chips.

Refining Response

The PFI mill refining responses of pulps obtained after kraft cooking of hot-water pre-extracted wood chips and those by conventional kraft cooking are shown in Figure 25.

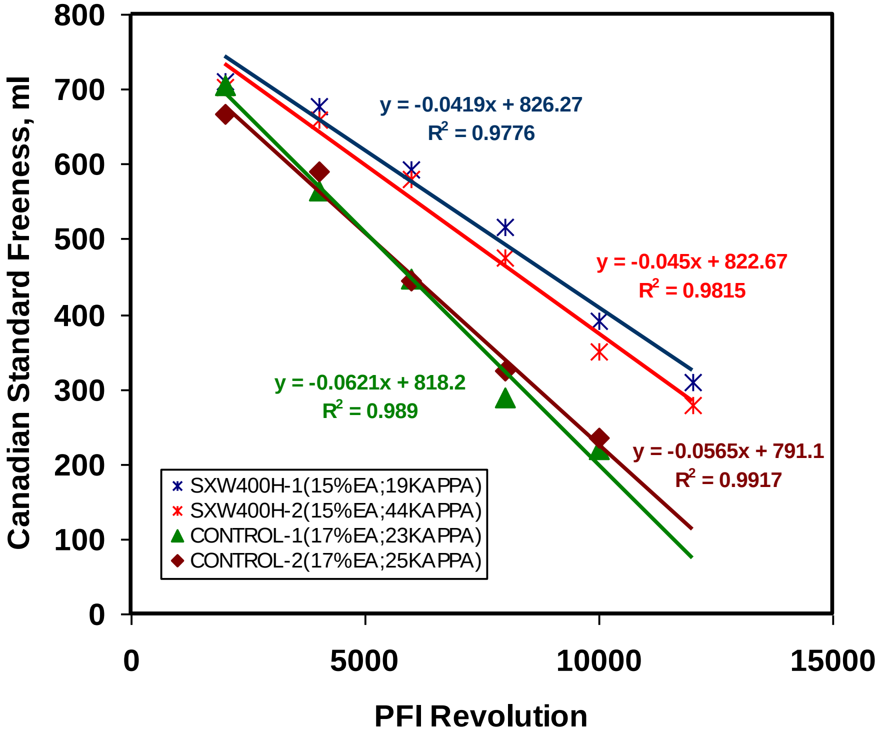


Figure 25. A plot of pulp freeness (CSF) versus PFI mill revolution for hot-water extraction kraft cooks and controls.

The refinability of a pulp is the ease with which the pulp fibers can be fibrillated internally and externally and shortened to some extent in water under a mechanical action. The pulp freeness (CSF) indicates the ease with which water drains away from the papermaking fibers while they are being formed into a wet mat on the drainage plate of the Canadian standard freeness tester. As expected, pulp freeness decreased as PFI mill revolution increased in each pulp type. A fairly linear relationship was observed between pulp freeness and degree of refining as can be seen in Figure 25. The hot-water pre-extraction kraft pulps appeared to need much longer beating time to attain the same level of freeness and this is likely related to the lower percentage of hemicelluloses. Generally, pulps which are low in hemicelluloses are very resistant to refining and have poor strength characteristics, whereas pulps which contain a high percentage of hemicelluloses beat very quickly and produce strong sheets [69]. Brauns *et. al.* [70] reported that when a wood pulp is purified by alkali extraction to the point where it contains about 99% alpha cellulose, it cannot be refined at all and will not make satisfactory paper, inasmuch as the fibers do not swell in water and remain in a shrunken condition. Clark [71] reported that the hemicellulose most responsible for the swelling or the increase in the plasticity of cellulose with refining was glucomannan. Thus the poor refining characteristics of the extracted kraft pulps are consistent with their lower hemicellulose content.

Handsheet Strength

The tensile strength of the handsheets are plotted versus CSF for each pulp in Figure 26.

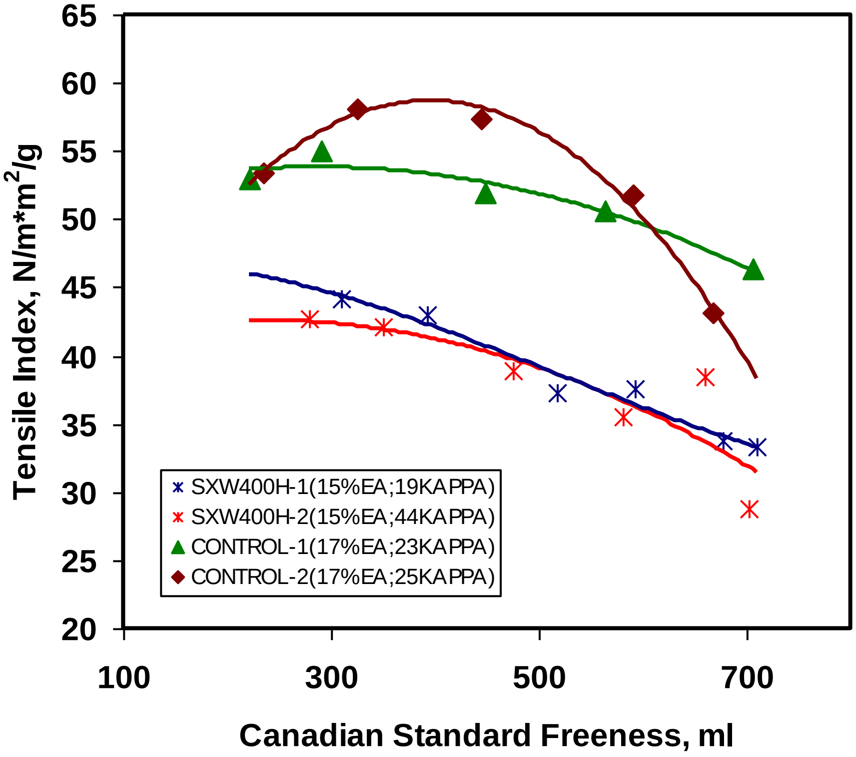


Figure 26. A plot of tensile index of handsheets for water pre-extraction kraft pulps versus pulp freeness.

A significantly loss in tensile strength was observed in handsheets prepared from the water pre-extraction kraft pulps compared to control at a given freeness level. The negative effects of pre-extraction on the tensile strength of kraft pulps is likely caused by the low interfiber bonding ability of the hemicellulose-poor pulps at the same degree of refining. It has been generally accepted that glucomannan in softwood pulp are more effective in fiber bonding than xylan in hardwood pulp because of their primary hydroxyl group [72].

Figure 27 shows the wet zero-span tensile strengths of handsheets plotted as a function of CSF. No significant difference was observed in zero-span tensile strength between water pre-extraction kraft pulps and the control. The zero-span tensile strength is an index of the average ultimate strength of randomly oriented fibers, and is useful for measuring the loss in individual fiber strength caused by overcooking, high acidity, or other degrading effects. Therefore, the result shown in Figure 27 indicates that the pre-extraction of wood chips with water prior or to kraft pulping does not significantly deteriorate the strength of individual fibers obtained from the kraft pulping. This result clearly shows a good agreement to the results obtained from the intrinsic viscosity analysis in Figure 24.

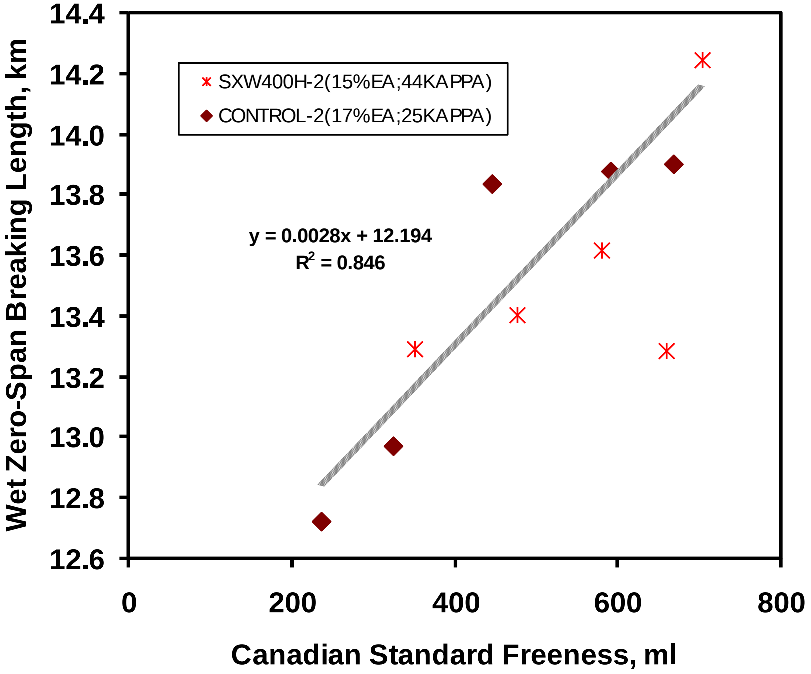


Figure 27. A plot of wet zero-span breaking length as a function of CSF of pulps.

Figure 28 shows a plot of tear resistance versus tensile strength of handsheets obtained from water pre-extraction and control kraft cooks.

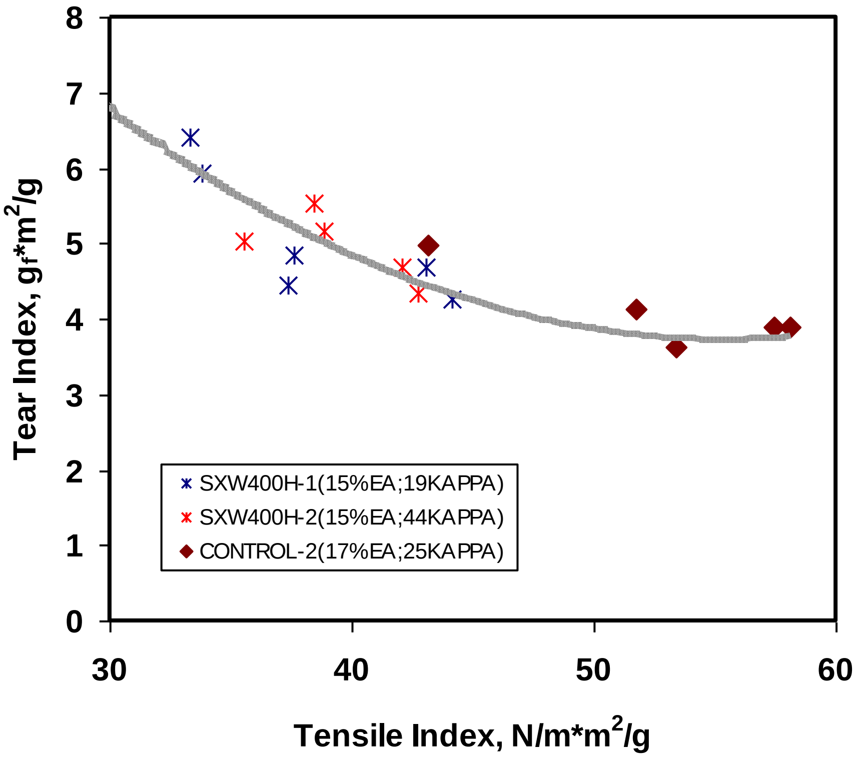


Figure 28. A plot of tear index as a function of tensile index of handsheets.

No significant difference in tear resistance was observed between kraft pulps obtained from hot-water pre-extraction followed by kraft pulping and control handsheets. Tearing resistance is known to be dependent on three properties: total number of fibers participating in the sheet rupture, fiber length, and number and strength of the fiber-to-fiber bonds [73]. Since the fiber bond strength is lower for the pre-extracted kraft pulps (see Figure 26), the good tear strength observed for these handsheets might be due to the increase in the number of fibers per basis weight resulting from the low yield of the pre-extracted kraft pulps.

4.1.3.3 Conclusion

The pre-extraction effectiveness of Southern Pine with pure water and subsequent kraft pulping behavior of the extracted wood chips was studied. The effect of time and temperature during pure water extraction on wood weight loss and wood component removal may be described by a single parameter, the H-factor. This suggests that the activation energy of the kinetics of wood dissolution during pure water extraction is the same as that of kraft cooking. The total polymeric sugar content in the extract reaches a maximum of about 8% at an H- factor of about 500 hrs with a minor removal of 0.3% cellulose and 0.5% lignin. The sum of all monomeric and polymeric sugars reaches a maximum of about 12% at an H-factor of about 1500 hours. The maxima in polymeric and total sugar content in the extract are caused by acid hydrolysis due to acetic acid released from the hemicelluloses. This suggests that the extraction with water should be terminated before the pH drops below about 3.5. The delignification rate constants for kraft cooking of water pre-extracted chips are 40 to 60% higher than corresponding kraft control cooks performed at 15% effective alkaline charge and 30% sulfidity. Unfortunately the total pulp yield based on the original wood at kappa 30 is 3 and 6% lower than the control at pre-extracting H-factors of 200 and 500 hours respectively, while the alkali consumption is the same as the control. The water pre-extraction kraft pulps are more difficult to refine and have a lower tensile strength due to their lower hemicellulose content compared to the control. The intrinsic fiber strength is the same as that of the control as seen by comparable pulp viscosity, wet zero-span tensile strength and tear resistance. More research is needed to understand the mechanism underlying the lower pulp yield based on original dry wood after water pre-extraction.

4.1.4 GREEN LIQUOR PRE-EXTRACTION – KRAFT COOKING OF HARDWOODS

4.1.4.1 Experimental

In chapter 4.1.1 it was shown that the pH of the extract must be kept near neutral after about 10% wood substance removal during high temperature pre-extraction to avoid a significant loss in total kraft pulp yield as compared to the control kraft cook. Practical implementation of this "near-neutral" pre-extraction treatment would favor the use of mill-available alkali sources such as green liquor or Na_2CO_3. Therefore a new set of pre-extraction experiments were performed with green liquor (GL)+AQ. The alkali charge during pre-extraction was 3% on wood as Na_2O, while the AQ charge was 0.05% on OD wood. No AQ was added during cooking, including the control kraft cooks. The sulfidity of the green liquor was 30% on a TTA basis. For other experimental details, see Chapter 4.1.1.

4.1.4.2 Results and Discussion

Pre-extraction with 3% GL (as Na_2O)+0.05%AQ pre-extraction for 90 minutes at 140^oC, 60 minutes at 160^oC and 110 minutes at 160^oC (L/W=4.5 L/kg) led to the removal of about 4.5%, 8.3% and 9.6% of wood substance respectively. The 4.5% weight loss value obtained with 3% GL (+AQ) at 140^oC is lower than that with 3% NaOH (8.0%) at 140^oC.

The residual pH of the 3% GL (+AQ) extraction liquor is plotted as a function of extraction H-factor in Figure 29. It shows a rapid drop from alkaline to a near-neutral level of pH around 6.5 in the very early stage of extraction up to an H-factor of about 100 hours. At an H-factor of about 400 hours, the residual pH of the 3% GL (+AQ) extraction reaches 5.9 and then steadily drops below pH 5.5 at H-factors larger than about 800 hours. The pH drop is mostly caused by continued dissolution of acetic acid formed by hydrolysis of acetyl groups in hemicellulose.

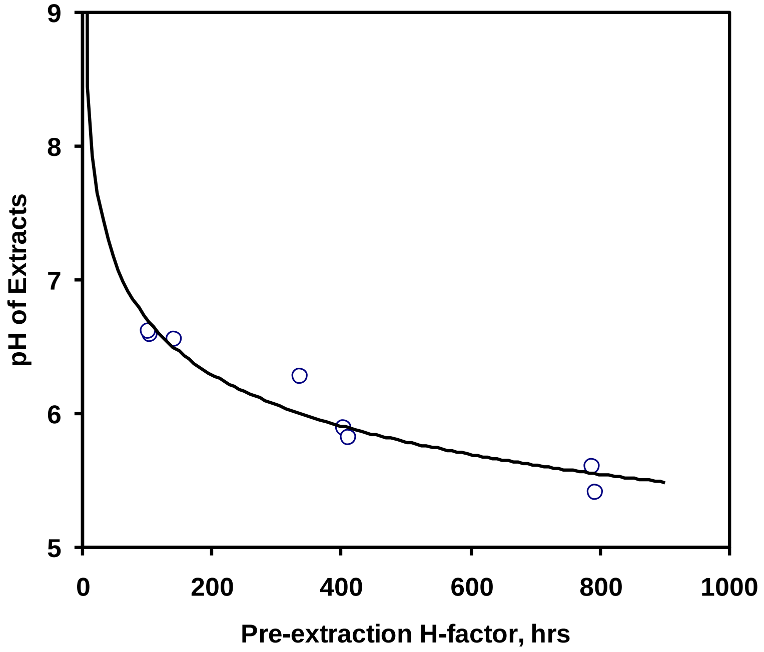


Figure 29. pH of 3% GL (+AQ) extracts versus pre-extraction H-factor.

The composition of near-neutral extracts using 3% GL (+AQ) at three different H-factor conditions (106, 403 and 792 hrs) is given in Table 10. In all three cases, acetate is the largest organic component in the extract followed by lignin. Xylan increases strongly with increasing H-factor and reaches 1.45 (on oven dry wood) at H=792 hrs. It should be noted that the identified organics in the extract represent 58-64% of the wood weight loss. This means that 34-42% of the dissolved wood was not identified. This may be related to degradation of hemicellulose sugars during high temperature treatment at the initially slightly alkaline conditions. Additionally, the amount of dissolved xylan may be underestimated because xylan is quantified as xylose by HPAEC analysis after acid hydrolysis, and this treatment cleaves only a smaller fraction of the bond between the glucuronic acid group which dissolves together with xylan [74, 75].

Table 10. Composition of extraction with 3% GL (+AQ) of southern mixed hardwood chips for 90 minutes at 140^{o}C and 60 and 90 minutes at 160^{o}C

Composition of Extract	% on ODW		
	90min-140^{o}C (H-factor 106)	60min-160^{o}C (H-factor 403)	110min-160^{o}C (H-factor 792)
Wood Weight Loss	4.45	8.30	9.62
Xylan	0.26	0.70	1.40
Glucan	0.11	0.19	0.35
Mannan	0.05	0.05	0.08
Arabinan	0.03	0.06	0.10
Galactan	0.08	0.12	0.20
4-O-MGA	0.11	0.18	0.37
Acetate	1.45	2.04	2.08
Lignin	0.83	1.51	1.60
Total sugars	2.09	3.34	4.58
Dissolved organics	2.92	4.85	6.18

In order to evaluate the delignification rate of kraft cooking of 3% GL (+AQ) pre-extracted southern mixed hardwood chips, kappa numbers were plotted as a function of kraft pulping H-factor in Figure 30. All kraft cooks with pre-extraction showed higher delignification rates than the kraft control cooks. The significant improvement in delignification rate may be due to increased accessibility of the cell wall as well as cleavage of lignin-carbohydrate covalent bonds during pre-extraction [65]. There appears to be no significant difference in delignification behavior among kraft cooks of the three different H-factor pre-extracted wood chips.

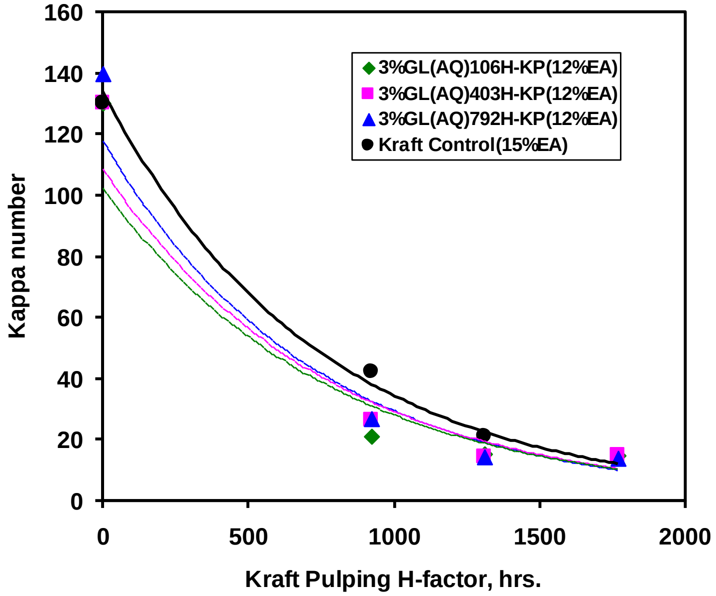


Figure 30. Kappa number versus kraft pulping H-factor

In order to evaluate the delignification selectivity of kraft cooking of hardwoods after 3% GL (+AQ) pre-extraction, the total pulp yield was plotted against kappa number in Figure 31.

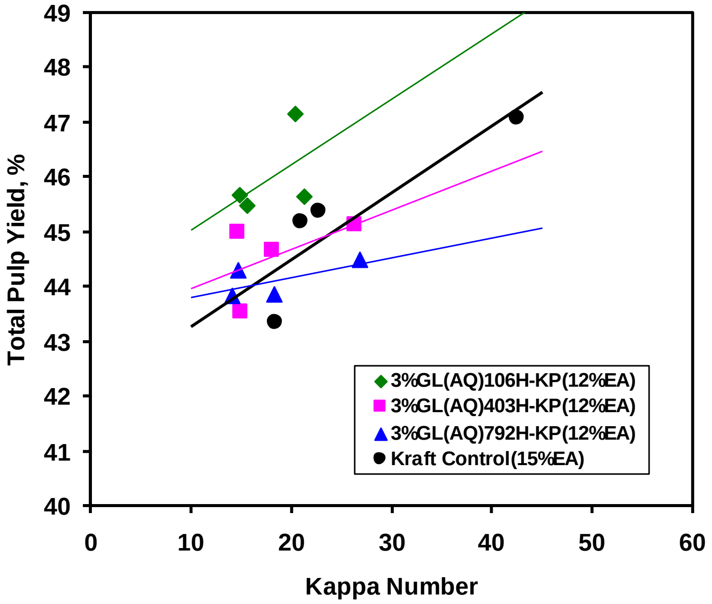


Figure 31. Total pulp yield versus kappa number for kraft pulps obtained from kraft cooks with 3% GL (+AQ) pre-extracted wood chips and for conventional kraft pulps

Even though the result shows somewhat scattered data and linear regressions with R^2 of 0.33 - 0.79, it clearly shows that the total pulp yield for the kraft cooks with near-neutral pre-extraction is as good as or slightly higher than that of the control kraft pulps. The kraft cooks of 3% GL (+AQ) pre-extracted hardwood chips with 107 hour extraction H-factor shows about 1-1.5% yield gains compared to control. No significant difference in total pulp yields was observed between the cooks of 3% GL (+AQ) pre-extracted chips at 403 and 792 hours extraction H-factor and kraft control at the kappa number range of bleachable grade. The residual effective alkali (REA) concentration was plotted as a function of pulp kappa number in Figure 32.

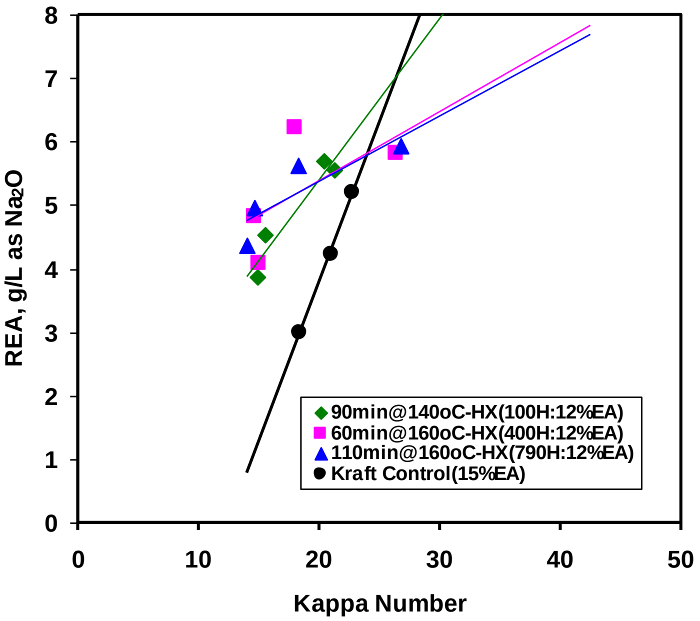


Figure 32. Plots of residual effective alkali versus kappa number.

Even though 3% lower initial effective alkali was charged to the kraft cooks of the 3% GL(+AQ) pre-extracted wood chips, the final residual effective alkali concentration in the black liquor samples was higher than that of the kraft control. The kraft cooks after pre-extraction with 3% GL (+AQ) consumed about 2.5 - 3% less effective alkali during the subsequent kraft cooks than kraft cooks of the same kappa number in the bleachable grade range. This result implies that the alkali requirements for pre-extraction are balanced by alkali consumption savings during subsequent kraft pulping.

Papermaking Properties of Kraft Pulps with Mild Alkaline Pre-extraction

Three fundamental properties of papermaking such as refining response, tensile strength and tear resistance were evaluated for pulps prepared from kraft pulps with 3% GL (+AQ) pre-extraction at 400 H-factor and for conventional kraft pulps without pre-extraction. The PFI mill refining responses of the pulps are shown in Figure 33. The refinability of a pulp is the ease with which the pulp fibers can be fibrillated internally and externally and shortened to some extent in water under a mechanical action. A fairly linear relationship was observed between freeness and PFI mill revolution (degree of refining). The pre-extracted kraft pulps appeared to need slightly more beating to attain the same level of freeness, most likely due to the lower percentage of hemicelluloses. As a broad generalization, pulps that are low in hemicelluloses are very resistant to refining and have reduced strength characteristics, whereas pulps that contain a high percentage of hemicelluloses beat quickly and produce stronger sheets. It was reported [71] that the hemicellulose most responsible for the swelling or the increase in the plasticity of cellulose with refining was glucomannan. However, handsheets prepared from 3% GL (+AQ) at 400 hour H-factor pre-extracted kraft pulps exhibited a tensile strength as good as or only slightly lower than the kraft control pulps (Figure 34). Figure 35 shows a plot of tear resistance versus tensile strength of handsheets of the pre-extracted pulps. About 5-10% higher tear resistance was observed for the "near-neutral" pre-extracted pulps compared to the control pulps. Tearing resistance is known to depend on total number of fibers participating in the sheet rupture, fiber length, and number and strength of the fiber-to-fiber bonds [73].

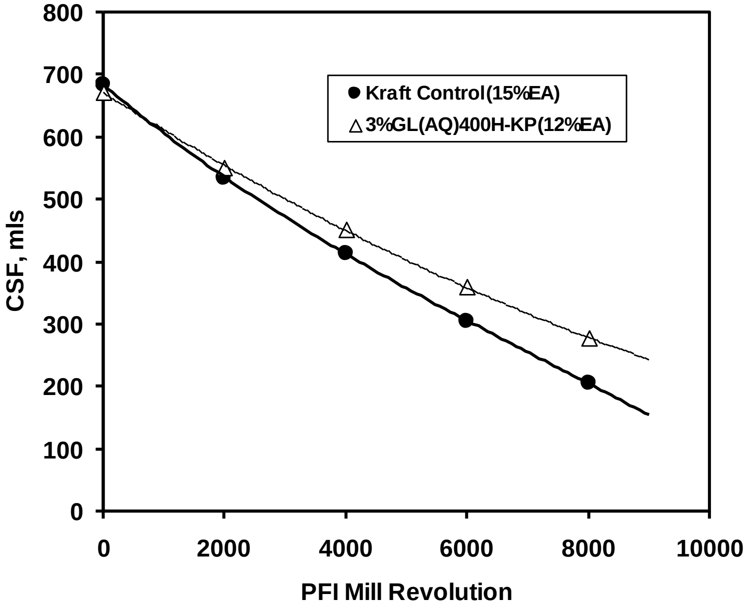


Figure 33. Plot of pulp freeness (CSF) versus PFI mill revolution for 3% GL (+AQ) 400H pre-extracted kraft pulps and control kraft pulps.

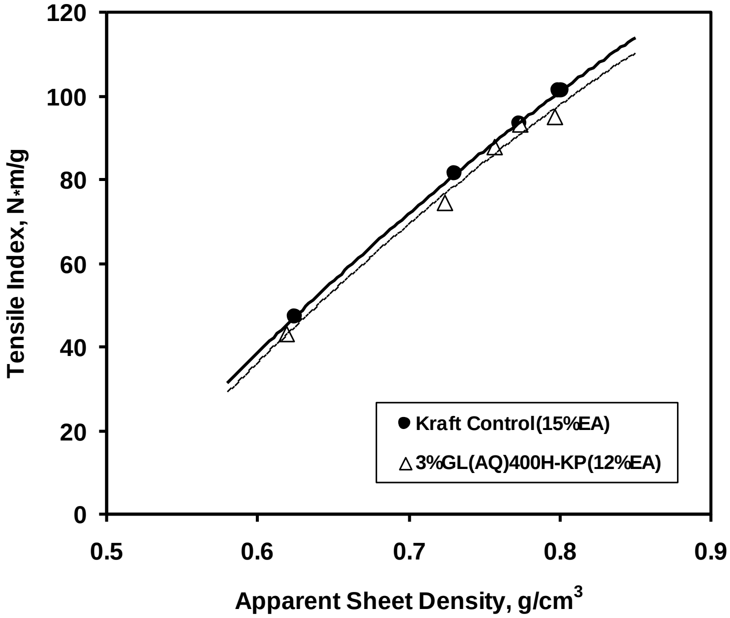


Figure 34 Plot of tensile index versus apparent sheet density for 3% GL (+AQ) 400H pre-extraction kraft pulps and control kraft pulps.

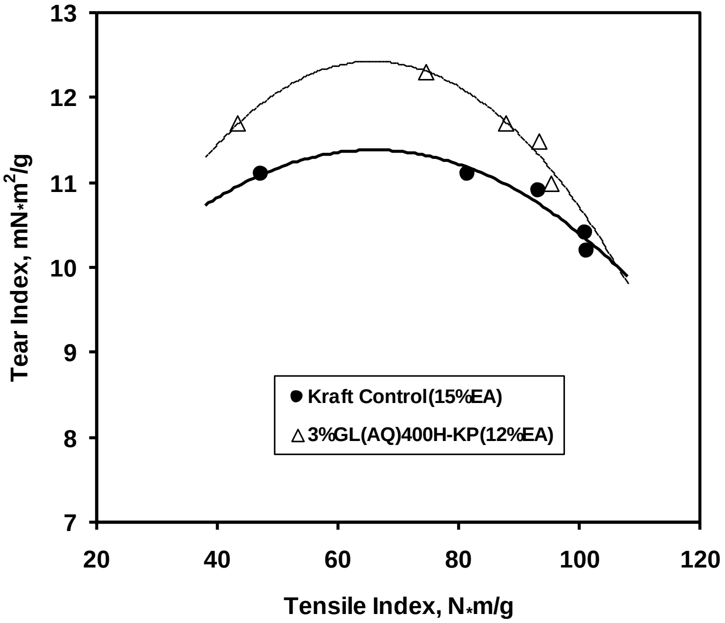


Figure 35. Plot of tear index versus tensile index for 3% GL (+AQ) 400H pre-extraction kraft pulps and control kraft pulps.

4.1.4.3 Conclusion

Near-neutral extraction with 3% NaOH or 3% green liquor(+0.05%AQ) at 140 and 160^{o}C for 60 to 110 minutes led to the removal of about 5 - 10% of wood substance from southern mixed hardwood chips. When the wood chips extracted at near-neutral condition with 3% GL (+0.05%AQ) were pulped at reduced effective alkali charges (12% EA), the delignification rate increased significantly while the overall pulp yield was similar as that of the kraft control (15% EA). The chips pre-extracted with a charge of 3% GL (+0.05%AQ) consumed about 2.5 - 3% less effective alkali during the subsequent kraft cooks compared to that of the control kraft cooks. Slightly lower refining response, comparable tensile strength and significantly increased tear resistance were observed in kraft pulps pre-extracted with 3% GL (+0.05%AQ) compared to corresponding conventional kraft pulps.

Therefore for hardwood these "near- neutral green liquor pre-extraction conditions do meet the requirements of the IFPR concept. At an H-factor of about 800 hours approximately 10% of the wood is dissolved, of which in the extract is identified: 22% as sugars (mostly oligomeric), 21% as acetate and 16% as lignin. Thus a disadvantage of this process is the relatively small amount sugars obtained in the extract, as well as a significant amount of degraded sugars and lignin. On the other hand, an advantage is the relatively high content of acetate which could be used for the production of acetic acid, a new high value chemical product in the IFBR.

4.1.5 GREEN LIQUOR PRE-EXTRACTION – KRAFT COOKING OF SOFTWOODS

4.1.5.1 Experimental

In the previous chapter it was shown that “near-neutral’ green liquor pre-extraction of hardwood chips led to dissolution of about 10% of wood substance in the extract, while the overall kraft pulp yield and strength properties were similar to those of the kraft control. Therefore in the present chapter Loblolly Pine chips were extracted with fresh green liquor solutions containing sufficient alkalinity to approximately neutralize the acids released upon treatment of the chip-liquor mass at elevated temperatures of 170, 180 and 190°C for various times. The same experimental procedures as those described in Chapter 4.1.3, where pre-extraction of Loblolly Pine chips was performed with pure water, were used in the present “near-neutral’ green liquor (GL) pre-extraction - kraft study. Again a liquor-to-wood ratio of 4.5 L/kg was used, and the GL (30% sulfidity) charges on oven-dry wood were varied as 2, 4 and 6%, all expressed as Na_2O. More experimental details may be found in references [76, 77].

Results and Discussion

Wood Weight Loss

The yield of the wood chips decrease due to dissolution of wood components into the extraction solution. Thus the wood weight loss (WWL) of wood chips measured after pre-extraction represents an overall effectiveness of the pre-extraction process used. WWL and freeze dry solid (FDS) content data obtained from the green liquor pre-extraction of the Loblolly Pine chips are summarized in Table 11.

As can be seen from the Table 11, WWL largely depends on the extraction temperature and time. The WWL increases from almost 4.2% at the mildest extraction condition (15 minutes at 170°C) to 15.8% at the most severe condition (90 minutes at 190°C). The WWL in the 2% green liquor (GL) pre-extraction was plotted against total extraction time (includes heating-up period) as shown in Figure 36. It can be seen that the WWL increases both with increasing extraction time and final temperature. Similar results were obtained with 4% and 6% GL pre-extraction.

In Figure 37, the WWL data are plotted against H-factor. H-factor is a means of expressing reaction time and temperature as a single variable [57]:

$$H-Factor \quad = \quad \int_0^t \exp\left(43.2-\frac{16{,}113}{T}\right)dt \qquad (8)$$

where T indicates the cooking temperature (K) and t is the cooking time (hours). It can be seen in Figure 37 that regardless of pre-extraction temperature, a single relationship between the WWL and H-factor is obtained at a given green liquor charge. This indicates that the activation energy of the kinetics of wood dissolution during GL pre-extraction is close to that of kraft cooking, i.e. 134 kJ/mol. The results in Figure 37 also show that higher WWL can be obtained with higher GL charge at a given pre-extraction H-factor. The WWL increases rapidly to 7, 8 and 10% at an H-factor of about 1,000 hrs for 2, 4 and 6% GL charge, respectively, and then levels off at higher H-factors. At an H-factor of 7,200 hours, the WWL reaches about 15% which compares to about 25% obtained by water pre-extraction described in our publication [78].

Table 11. Wood Weight Loss (WWL) and Freeze Dry Solids (FDS) of Extracts Data after Green Liquor Pre-Extraction of Loblolly Pine

Run	Green Liquor Charge (% as Na_2O)	T_{max} (^oC)	Time at T_{max} (min)	H-Factor (hrs.)	Wood Weight Loss, WWL (%)	Freeze Dry Solids, FDS (%)
1	2	170	15	184	4.24	9.00
2			45	794	6.13	9.63
3			90	1487	7.15	10.22
4		180	15	973	6.52	10.01
5			45	2153	9.25	11.93
6			90	3441	11.43	12.51
7		190	15	1777	8.24	10.53
8			45	4048	12.65	13.59
9			90	7250	14.58	12.33
10	4	170	15	184	6.05	14.13
11			45	794	7.98	15.48
12			90	1487	8.59	15.71
13		180	15	973	8.22	15.14
14			45	2153	10.43	16.18
15			90	3441	12.29	17.19
16		190	15	1777	10.55	17.01
17			45	4048	12.47	17.96
18			90	7250	15.19	17.82
19	6	170	15	184	7.45	20.21
20			45	794	10.27	21.51
21			90	1487	10.14	21.74
22		180	15	973	10.16	21.48
23			45	2153	12.31	22.10
24			90	3441	13.10	22.77
25		190	15	1777	-	-
26			45	4048	-	-
27			90	7250	15.8	24.08

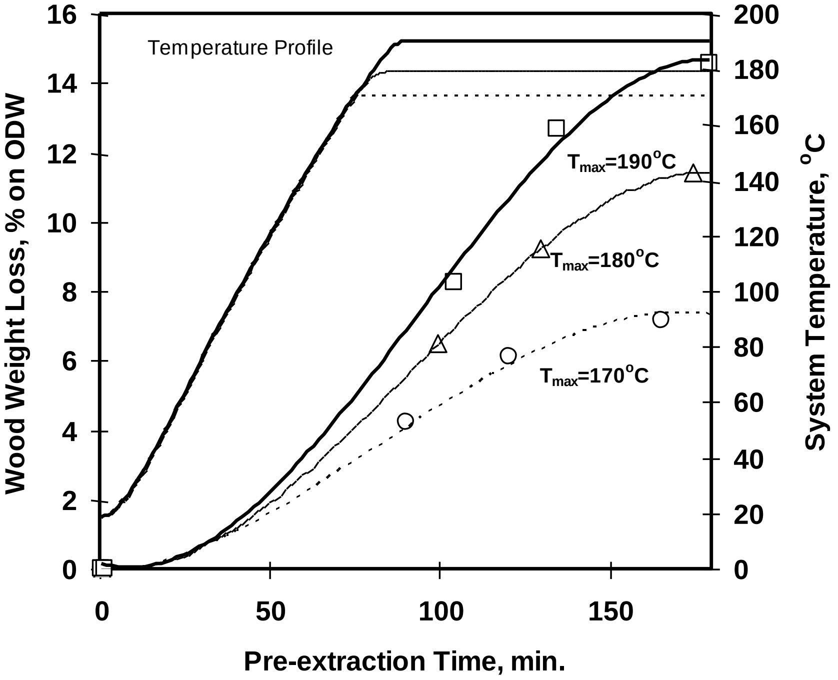


Figure 36. Wood Weight Loss versus Extraction Time for 2% Green Liquor Pre-Extraction of Loblolly Pine at Different Maximum Temperatures of 170, 180 and 190°C.

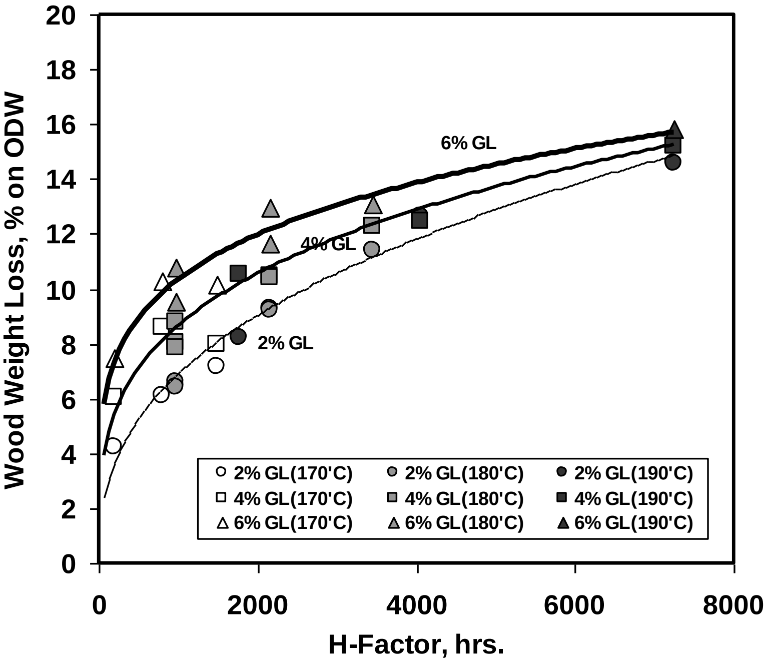


Figure 37. Wood Weight Loss versus H–Factor for Green Liquor Pre-extraction of Loblolly Pine Chips.

The solid contents of green liquor extracts determined by freeze drying (FDS) show almost twice higher values than the WWL as can be seen in Table 11. The excess values of FDS are clearly due to the fact that they include the weight of the inorganics which make up green liquor, i.e. sodium salts. Therefore, the weights of dissolved inorganic materials that were already known should be subtracted from the values of FDS to determine the amounts of dissolved organic materials (DOM) comparable to WWL. As indicated in Figure 38 for 6% green liquor pre-extraction, WWL and the DOM determined with subtracting the chemical charge from the FDS appear to be in a reasonable agreement supporting the internal consistency of the mass balance data. Similar results may have also been obtained in 2 and 4% GL pre-extractions (figures not shown).

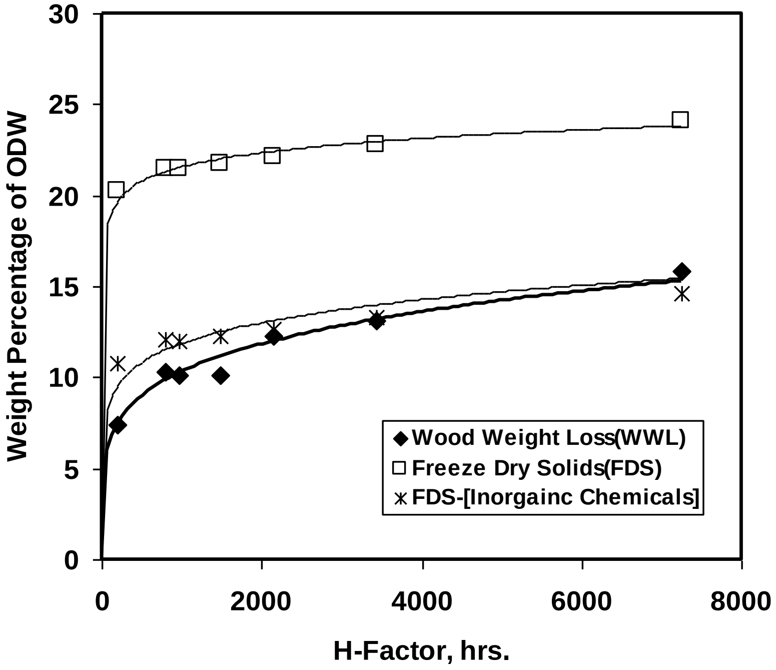


Figure 38. Plots of WWL, FDS and DOM as a function of Pre-extraction H-Factor.

Sugar Extracts

Wood hemicelluloses are relatively easily hydrolyzed by acid to their monomeric components mainly consisting of D-glucose, D-mannose, D-galactose, D-xylose and L-arabinose as compared to cellulose. The wood sugar contents in the green liquor extracts were determined using HPAEC (High Pressure anion Exchange Chromatography). The HPAEC analysis was conducted both before and after hydrolysis of the extracts with 4% H_2SO_4 at 121 °C for one hour in an autoclave. The yield of sugars in polymeric form in the extract can be calculated from the increase in monomeric sugar content caused by the acid hydrolysis. The concentrations of arabinose, galactose, glucose, xylose and mannose after acid hydrolysis expressed in percentage based on oven dry wood are shown in Table 12.

Table 12. HPAEC Sugar Analysis of Green Liquor Extract of Loblolly Pine Chips

Green Liquor Charge (% as Na_2O)	T_{max} (^oC)	Time at T_{max} (min)	Monosaccharides (%, based on oven dry wood)				
			Arabinose	Galactose	Glucose	Xylose	Mannose
2	170	15	0.17	0.15	0.12	0.29	0.17
		45	0.18	0.24	0.09	0.55	0.16
		90	0.27	0.24	0.13	1.06	0.18
	180	15	0.22	0.29	0.12	0.82	0.16
		45	0.30	0.30	0.16	1.49	0.26
		90	0.19	0.44	0.23	1.25	0.60
	190	15	0.22	0.20	0.13	1.04	0.27
		45	0.17	0.33	0.28	1.43	0.59
		90	-	0.41	0.32	-	0.66
4	170	15	0.11	0.17	0.08	0.25	0.07
		45	0.13	0.21	0.07	0.33	0.07
		90	0.20	0.32	0.08	0.49	0.07
	180	15	0.15	0.21	0.07	0.47	0.07
		45	0.22	0.28	0.08	0.75	0.07
		90	0.27	0.25	0.11	0.91	0.10
	190	15	0.21	0.30	0.10	0.77	0.10
		45	0.27	0.23	0.08	1.08	0.11
		90	0.27	0.29	0.11	1.30	0.13
6	170	15	0.10	0.18	0.08	0.21	0.07
		45	0.17	0.23	0.10	0.28	0.06
		90	0.18	0.32	0.08	0.41	0.06
	180	15	0.14	0.22	0.07	0.39	0.05
		45	0.20	0.24	0.09	0.58	0.06
		90	0.24	0.22	0.08	0.70	0.06
	190	15	-	-	-	-	-
		45	-	-	-	-	-
		90	0.29	0.33	0.09	1.12	0.08

As reported in our previous publication [78], approximately 4 to 5% monomeric sugars based on the oven dry weight of wood chips were found in the pure water extraction around the final pH of 4. In the GL extraction, however, no trace of monomeric sugars in the fresh extract (i.e. before acid hydrolysis) was detected. This indicates that all the measured sugars extracted with GL solution are in their polymeric forms. The amount of sugar extracted decreases as GL charge increases from 2% to 6%. When the sugars extracted with 2% GL are plotted against H-Factor in Figure 39, it can be seen that a higher sugar extraction yield is obtained for xylose than mannose. Xylose extraction reaches a maximum of about 1.5% whereas the other wood sugars remain below about 0.5%. Compared to the maximum sugar yields of the pure water extracts (2.7% and 6.9% in xylose and mannose, respectively), much lower sugar yields were observed in GL extraction, particularly for mannose.

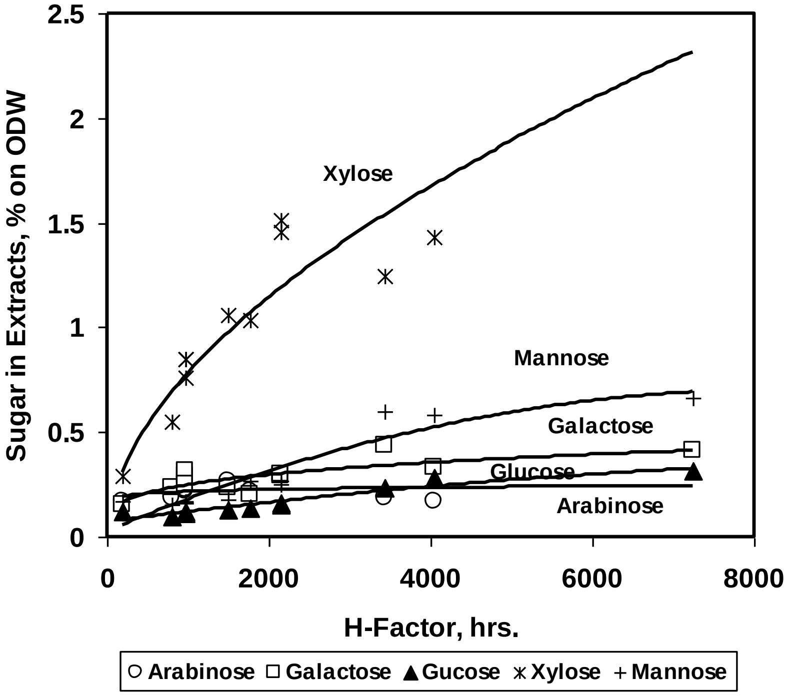


Figure 39. Sugar Extracted versus H-Factor for 2% Green Liquor Pre-extraction of Loblolly Pine Chips.

Hemicellulose Components in the Extracts

Mannose found in the extracts must originate from O-acetyl-galactoglucomannan (AcGGM) which is the principal hemicellulose in softwoods at about 20 w/w%. The backbone of AcGGM is a linear chain built up by (1→4)-linked β-D-glucopyranose and β-D-mannopyranose units. The α-D-galactopyranose residue is linked as a single-unit side chain to the linear chain by (1→6)-bonds. In the galactose-rich fraction of AcGGM, it is known that the ratio galactose:glucose:mannose is 1:1:3 [79]. The C-2 and C-3 positions in glucomannan chain are also partially substituted by acetyl groups (O-acetyl), on the average of one group per 3-4 hexose units, which indicates the average ratio of O-acetyl:mannose is 1:3. Xylose in the extracts must originate from the major sugar component arabino-4-O-methylglucuronoxylan (MeAGX) which is the second abundant hemicelluloses in softwoods at 5-10w/w %. The MeAGX is composed of a frame work containing (1→4)-linked β-D-xylopyranose units that are partially substituted by 4-O-methyl-α-D-glucuronic acid groups, on the average two units per ten xylose units. In addition, the backbone contains α-L-arabinofuranose units, on the average 1.3 units per ten xylose units. These generally known monomeric ratios in AcGGM and MeAGX were used to calculate their content in the GL extracts using the experimentally determined concentrations of mannose and xylose respectively, i. e.,

$$AcGGM(\%) = Man(\%) \times \frac{1[M_{AcO}] + 1[M_{Gal}] + 1[M_{Glu}] + 3[M_{Man}]}{3[M_{Man}]} \qquad (9)$$

and

$$MeAGX(\%) = Xyl(\%) \times \frac{2[M_{MeGUA}] + 1.3[M_{Ara}] + 10[M_{Xyl}]}{10[M_{Xyl}]} \qquad (10)$$

where, $Man(\%)$ and $Xyl(\%)$ are contents (based on od wood) of mannose and xylose monosugars in the extracts, respectively, and M_{AcO}, M_{Gal}, M_{Glu}, M_{Ara}, M_{Man} and M_{Xyl} and M_{MeGUA} are molecular weights of O-acetyl group, galactose, glucose, arabinose, manose and xylose units and 4-O-methyl-α-D-glucuronic acid group, respectively. The calculated dissolved amounts of AcGGM and MeAGX are plotted against H-factor as shown in Figure 40. It can be seen that the AcGGM and MeAGX contents increased with increasing H-factor. In addition, as green liquor charge increases from 2% to 6% both the AcGGM and MeAGX extracted amounts decrease significantly. This indicates that the extraction of both AcGGM and MeAGX are largely caused by acid-catalyzed hydrolysis rather than alkaline cleavage of glycosidic bonds or by an endwise degradation mechanism. Furthermore compared to the extraction yields obtained when using pure water, the yields of AcGGM and MeAGX are relatively low in the green liquor extraction, reaching a highest value of only about 2% MeAGX and about 1% of AcGGM. The latter is particularly low because it is the most abundant hemicelluloses in softwoods.

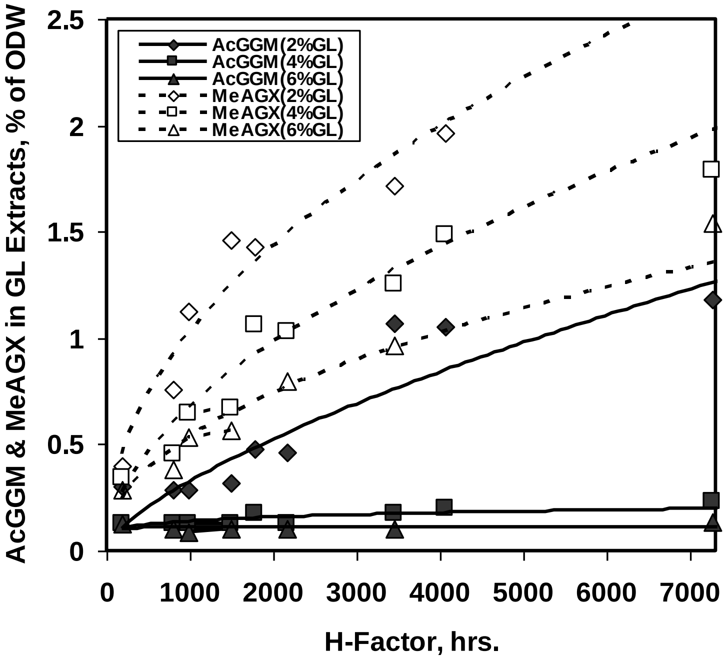


Figure 40. Plots of AcGGM and MeAGX in Green Liquor Extracts versus H-Factor (The solid line indicates the MeAGX and the dotted line AcGGM contents).

Total Organics

The major organic components in the extracts are cellulose, hemicelluloses and lignin. The lignin content was determined by UV absorbance at 280 nm wave length. The total amount of cellulose, C, and hemicelluloses, H, in the extracts were calculated from the content of monosugars (glucose (Glu), mannose (Man), arabinose (Ara), xylose (Xyl) and galactose (Gal)) determined by HPAEC analysis, using the following equations:

$$C = Glu * (\frac{162}{180}) - \frac{Man}{b} * (\frac{162}{180}) \tag{11}$$

with b = 4.15 (average value for number of mannose units per glucose unit in glucomnnan of Pine/Spruce wood, based on Janson [67]).

$$\begin{aligned} H &= (Ara + Xyl) * (\frac{132}{150}) + (Gal + Glu + Man) * (\frac{162}{180}) - C \\ &\cong AcGGM + MeAGX \end{aligned} \tag{12}$$

The major organic compounds in GL pre-extracts including hemicelluloses, celluloses, total sugar, lignin and total organics and final liquor pH are summarized in Table 13. The hemicellulose contents can also be calculated by the summation of AcGGM and MeAGX expressed in equations 9 and 10. As can be seen from Table 13, there is very good agreement between the hemicellulose contents calculated from equations 9 and 10 and those from equations 11 and 12. This indicates that the approximation made to determine both AcGGM and MeAGX is valid. The wood compounds including hemicelluloses, cellulose and lignin in green liquor extracts are plotted against H-factor in Figure 41. It can be seen that the three major wood components present in the extracts obtained at different temperatures and times are each well described by single curves. The amount of extracted lignin, hemicelluloses and cellulose increase approximately linearly with H-factor in the GL pre-extraction process. Lignin shows a higher yield than that of the two polysaccharides. As expected, cellulose showed the highest resistance against dissolution in the GL pre-extraction, maintaining a minor level of 0.05 to 0.15% in the extracts over the entire H-factor range and green liquor charges. Whereas the amount of hemicelluloses decreased significantly with increasing green liquor treatments, the amount of extracted lignin increased significantly. Since dissolved lignin may negatively affect the ethanol fermentation or bioconversion processes in a bio-refinery, green liquor pre-extraction conducted at lower charges is recommended.

Table 13. Components in Green Liquor Extract of Loblolly Pine Chips in % on OD wood

Green Liquor Charge (% as Na_2O)	T_{max} (^oC)	Time at T_{max} (min)	Hemicelluloses (%)		Cellulose, C (%)	Total Sugar (H+C) (%)	Lignin, L (%)	Total Organics (H+C+L) (%)	Final Liquor pH
			H	AcGGM+ MeAGX					
2	170	15	0.74	0.70	0.07	0.81	1.12	1.93	7.50
		45	1.03	1.04	0.05	1.08	1.28	2.36	6.38
		90	1.58	1.78	0.08	1.66	2.15	3.81	5.93
	180	15	1.36	1.41	0.07	1.43	1.85	3.28	6.64
		45	2.13	2.51	0.09	2.22	1.78	4.00	5.53
		90	2.32	2.79	0.08	2.40	1.67	4.27	4.66
	190	15	1.58	1.91	0.06	1.64	1.50	3.14	6.12
		45	2.36	3.02	0.13	2.49	2.14	4.63	4.65
		90	1.11	1.18	0.14	1.25	2.42	3.67	4.35
4	170	15	0.54	0.47	0.05	0.59	1.72	2.31	7.95
		45	0.67	0.58	0.05	0.72	2.01	2.73	7.11
		90	0.97	0.80	0.06	1.03	2.26	3.29	7.65
	180	15	0.81	0.77	0.05	0.86	2.46	3.32	7.45
		45	1.19	1.16	0.06	1.25	2.77	4.02	6.81
		90	1.37	1.43	0.08	1.45	2.48	3.93	6.46
	190	15	1.23	1.24	0.07	1.30	2.78	4.08	7.35
		45	1.51	1.68	0.05	1.56	2.87	4.43	6.61
		90	1.78	2.02	0.07	1.85	2.36	4.21	5.82
6	170	15	0.51	0.41	0.05	0.56	2.38	2.94	9.07
		45	0.67	0.49	0.07	0.74	2.88	3.62	7.87
		90	0.88	0.67	0.06	0.94	2.95	3.89	8.07
	180	15	0.72	0.63	0.05	0.77	3.57	4.34	7.73
		45	0.98	0.91	0.07	1.05	3.78	4.83	7.33
		90	1.09	1.07	0.06	1.15	3.97	5.12	7.07
	190	15	-	-	-	-	-	-	-
		45	-	-	-	-	-	-	-
		90	1.63	1.68	0.07	1.70	3.01	4.71	6.91

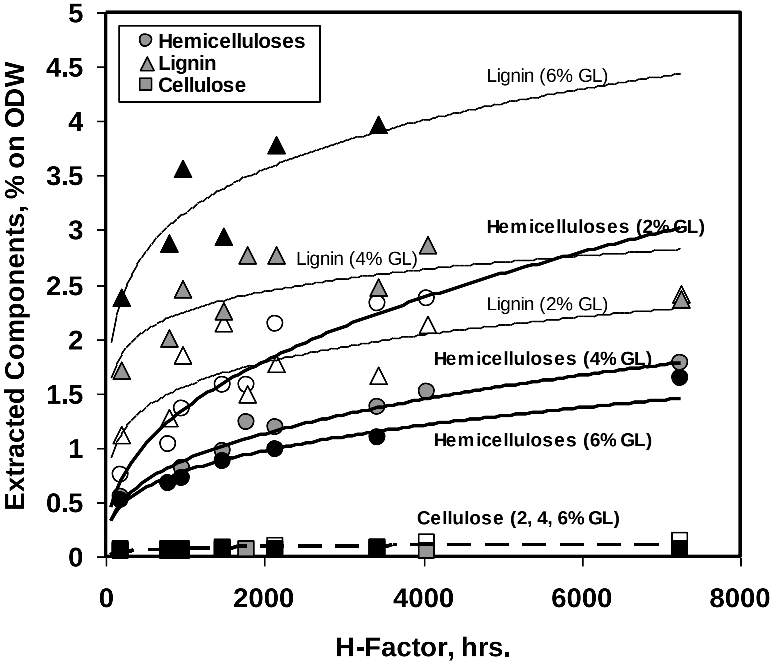


Figure 41. Extracted Wood Components versus H-Factor

pH of GL Extracts

Extraction of Loblolly pine chips with neutral water causes acidic conditions due to release of acetic acid by hydrolysis of the acetyl groups in glucomannan. The acidity may cause the degradation of cellulose through the acidic auto-hydrolysis at high temperatures leading to a serious loss of pulp yields and strength in paper products. At alkaline conditions glucomannan is rapidly degraded by the peeling reaction, while xylan is dissolved in oligomeric form [4]. Therefore hot alkaline extraction of softwoods to recover hemicelluloses is not effective for softwoods contrary to what was found for hardwoods in chapter 4.1.4. At mild alkaline conditions such as GL pre-extraction (initial pH≈13), however, the alkaline conditions would only exist at the start of extraction due to the initial neutralization by acetic acid released from the wood. Therefore at low charges of GL the extraction process pH can be maintained at neutral or slight acidic conditions during most of the duration of the extraction. The final liquor pH was plotted against extraction H-factor as shown in Figure 42. The liquor pH rapidly dropped from alkaline to neutral in the early stages of extraction up to an H-factor of about 500. In case of 2% green liquor extraction, the liquor pH reached the lowest pH level up to around 4.5 at an H-factor of around 4,000, whereas in 4% and 6% green liquor extractions, the liquor pH never came below 6. Therefore the low sugar content in the extracts at 4% GL, and even more so at 6 % GL, may be explained by extensive degradation of AcGGM in particular.

The total sugar yields were plotted against final liquor pH in Figure 43. It can be seen that the total sugar yield increases significantly from about 0.5% to 2.5% as the pH drops from the mild alkaline (pH of 8) to acidic pH of 4.5) respectively. The highest sugar yield of 2.5% was obtained with 2% green liquor pre-extraction. These results again confirm that a low GL charge is preferable for higher sugar extraction yield since it would avoid prolonged time at alkaline conditions during the GL pre-extraction.

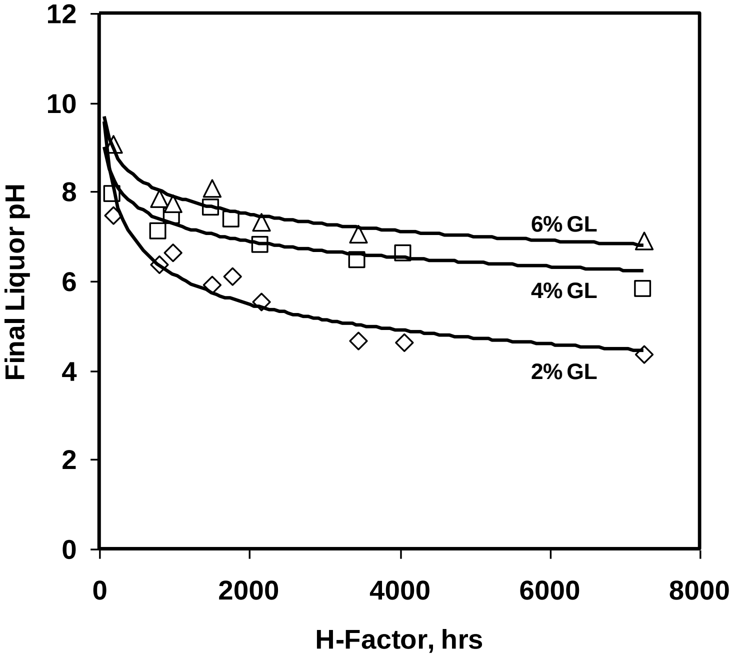


Figure 42. Final pH versus Pre-extraction H-Factor.

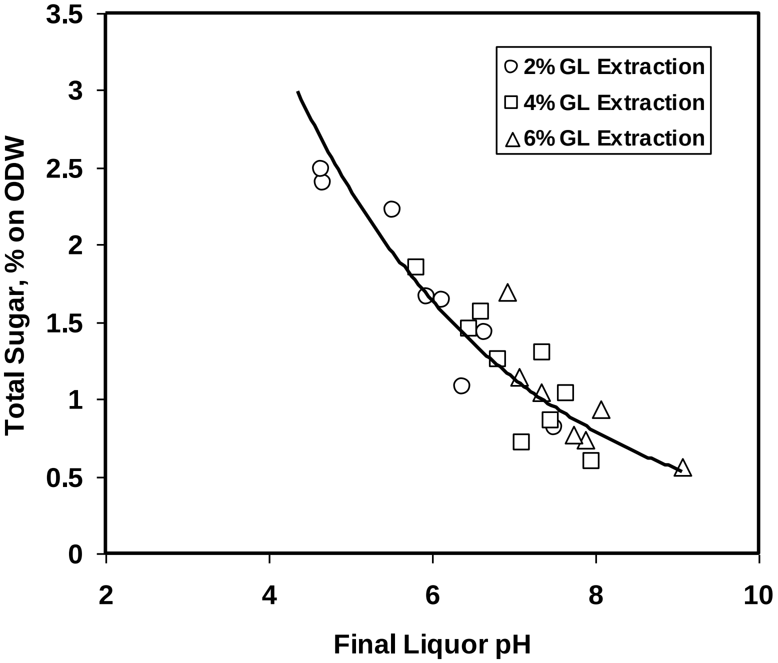


Figure 43. Total Sugar Yield versus Final Liquor pH.

Extraction Material Balance

A mass balance analysis based on total amount of measured organics was performed to test the internal consistency of the data. The total amount of organics was calculated as the sum of the major wood components in the green liquor extracts, i.e. cellulose, hemicelluloses and lignin as presented in Table 13. This value of the total organics was plotted against WWL at 170, 180 and 190^{o}C as shown in Figure 44. It can be seen that the total amount of measured organics is always significantly smaller than the WWL. The dotted arrow indicates the mass balance loss. For example at a WWL of 10% on wood, less than 4% total organics were measured in the GL extracts. If it is considered that at 2% GL extraction about half of the measured organics is lignin, then it is clear that the large mass balance loss is mostly cause by degradation of the AcGGM. Other contributions to the mass balance loss are low molecular organic substances such as acetic acid, formic acid, methanol, furfural, etc. as well as 4-O-methyl glucuronic acid.

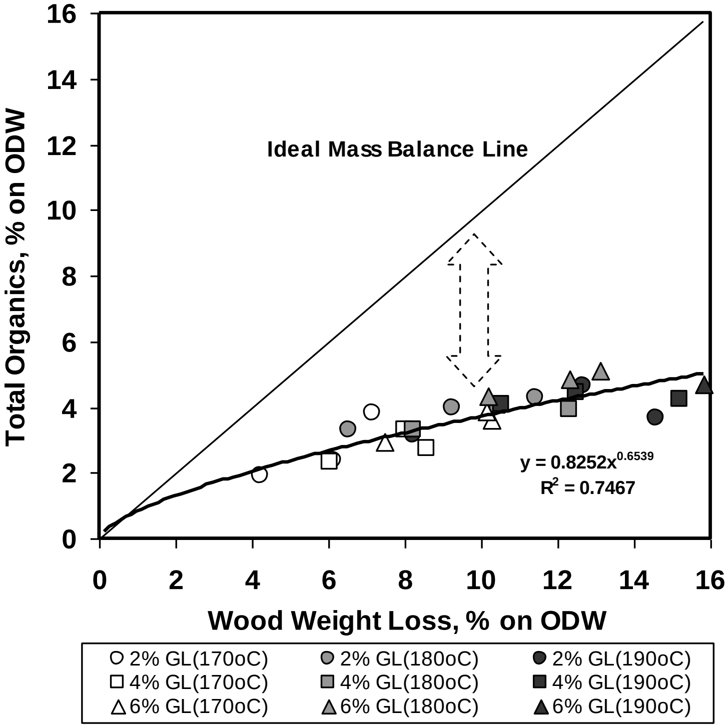


Figure 44. Mass Balance Analysis on Green Liquor Extraction Loblolly Pine Chips.

4.1.5.3 Conclusions

As with GL extraction of hardwoods, the effect of time and temperature on total weight loss and wood component removal during GL extraction of Loblolly Pine, a softwood, could be well described by a single control parameter, the H-factor. The total weight loss increases from about 4% at the mildest extraction condition of 2% GL at 170 ^{o}C for 15 minutes to about 15% at the severest conditions of 2 -6 % GL at 190 ^{o}C for 90 minutes. Sugar components were only present in their polymeric forms in the green liquor extract. The maximum yields of arabinoglucuroxylan and galactoglucomannan were about 2 and 1%, respectively. The dissolved hemicellulose and lignin content is at a similar level at 2% green liquor charge. With increasing green liquor charge, however, the dissolved lignin content significantly increased while that of the hemicelluloses significantly decreased. A very small amount of cellulose was extracted (0.05 to 0.15% based on oven dry wood over the entire H-factor range and green liquor charges). The total sugar yield in the extracts increases significantly from about 0.5% to 2.5% as the pH drops from the mild alkaline (pH of 8) to acidic pH of 4.5) at 6% GL charge to 2% GL charge respectively. These results again confirm that a low GL charge is preferable for higher sugar extraction yield since it would avoid prolonged time at high temperature alkaline conditions which favor extensive degradation of AcGGM in particular. This leads to a large mass balance discrepancy between the total amount of organics identified analytically and the total weight loss of the wood chips. This mass balance loss is mostly cause by degradation of the AcGGM. Other contributions to the mass balance loss are low molecular organic substances such as acetic acid, formic acid, methanol, furfural, etc. as well as 4-O-methyl glucuronic acid. Since it is known (chapter 4.1.3) that an acidic pH will lead to significantly lower kraft pulp yield and strength properties relative to the corresponding kraft control pulp, **the near-neutral green liquor extraction process applied to softwood does not meet the requirements of the IFPR concept**.

4.2 ADSORPTION STUDIES OF HARDWOOD EXTRACTS

4.2.1 Preliminary adsorption studies

Experiments with fresh and recirculated green liquor-AQ extracts (GL pre-extraction at 140^{o}C for 90 minutes and L/W=4.5 on mixed southern hardwood producing extracts called XGQ-A, XGQ-B and XGQ-C) were conducted to study the hemicellulose adsorption on pulp. The experimental scheme and nomenclature of the extracts are shown in Figure 45.

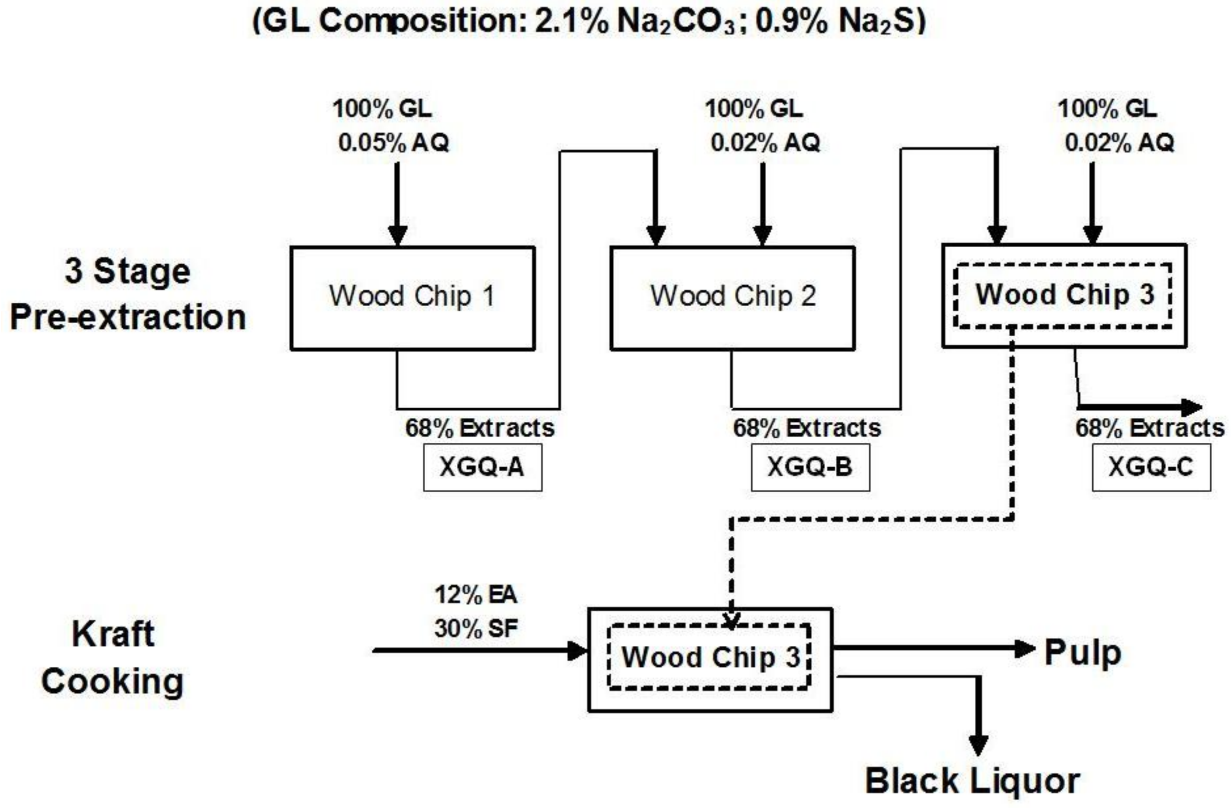


Figure 45. Experimental Scheme for Green Liquor Extraction and Recirculation

The different XGQ liquors were mixed in a plastic bag with the unbleached kraft pulp obtained after extraction and kraft cooking, i.e. on the pulp shown in Figure 45. Thus liquor XGQ-A is obtained after extraction of fresh southern mixed hardwoods using fresh green liquor. XGQ-B extract is obtained by reinforcing the XGQ-A extract with fresh GL at 3% charge but only 0.02% AQ for extraction of a new batch of fresh chips. The new XGQ-B liquor is then again reused in the same manner to produce XGQ-C extract. Thus in these experiments the effect of recirculating the GL extract is studied with the objective to increase the concentration of the dissolved wood in the extract, and thereby the amount adsorbed on the pulp. The adsorption experiments were performed in a constant temperature bath of 90°C at two different consistencies; 5.2 and 10%. After vacuum filtration, washing and drying, the adsorption yield and kappa numbers were measured. The results are summarized in Tables 14 and 15.

Table 14. Adsorption of XGQ liquor for 60 minutes at 90°C and 10% consistency

No	Treatment	Adsorption Yield(%)	Kappa	Residual Lignin(%)	Lignin-free Yield(%)
1	Water	99.69			
2	Water	100.26	14.54	2.16	98.11
3	Water	100.51			
4	XGQ-A	101.17	17.93	2.68	98.49
5	XGQ-A	101.54			
6	XGQ-A	101.43	17.31	2.60	98.83
7	XGQ-B	101.35	17.34	2.60	98.75
8	XGQ-B	101.31			
9	XGQ-B	102.04			
10	XGQ-C	101.84	18.07	2.73	99.22
11	XGQ-C	102.26			
12	XGQ-C	101.95			

Table 15. Adsorption of XGQ liquor for 60 minutes at 90°C and 5.2% consistency

No	Treatment	Adsorption Yield(%)	Kappa	Residual Lignin(%)	Lignin-free Yield(%)
1	Water	99.35	14.93	2.20	97.15
2	Water	99.57			
3	XGQ-A	100.40	17.19	2.55	98.04
4	XGQ-A	100.42	17.01	2.53	97.89
5	XGQ-A	100.58			
6	XGQ-B	100.71	16.63	2.48	98.23
7	XGQ-B	100.88	16.97	2.53	98.35
8	XGQ-C	100.62	17.32	2.58	98.04
9	XGQ-C	100.76	17.77	2.65	98.11
10	XGQ-C	100.91	17.48	2.61	98.30

Before the adsorption experiments the XGQ-A, B and C liquors were pre-filtered on a 325 mesh screen to remove fiber particles which otherwise would interfere with the pulp fiber yield measurements. The filtrates both before and after adsorption were analyzed by GPC to determine the concentration of dissolved hemicellulose and lignin (see Table 16). This analysis technique was used during the initial phase of the project because at this time the HPAEC analysis method (see 4.1.4) was not operational. Also included in Table 16 are the concentration of very fine suspended solids determined by microfiltration on glass fibers, and the dry solids content after microfiltration determined by freeze-drying.

Table 16. XGQ Composition before and after Adsorption on Pulp

XGQ	Adsorption	Suspended Solids from Micro-filtering (mg/ml XGQ)	Dissolved Solids from Freeze Drying (mg/ml XGQ)	Dissolved Hemicellulose Concentration (mg/ml XGQ)	Dissolved Lignin concentration (mg/ml XGQ)
A	Before	1.295	17.1	4.078	4.760
	After	0.261	16.8	0.054	4.577
B	Before	1.544	25.3	6.647	6.887
	After	0.397	15.1	0.181	5.929
C	Before	2.071	30.0	8.320	8.030
	After	0.459	28.6	0.289	5.982

Using the data in Tables 14 – 16, it can be seen in Figure 46 that the adsorption yield increases by increasing the number of recirculations of the XGQ liquor. These results indicate that a yield increase of almost 2% can be achieved at 10% consistency with the XGQ-C liquor. The increasing yield obtained with increasing number of XGQ circulation is caused by the increased dissolved hemicellulose concentration in the XGQ extract which has gone through more recirculation stages. This hypothesis is further strengthened by the linear relationship between adsorption yield and hemicellulose concentration shown in Figure 47.

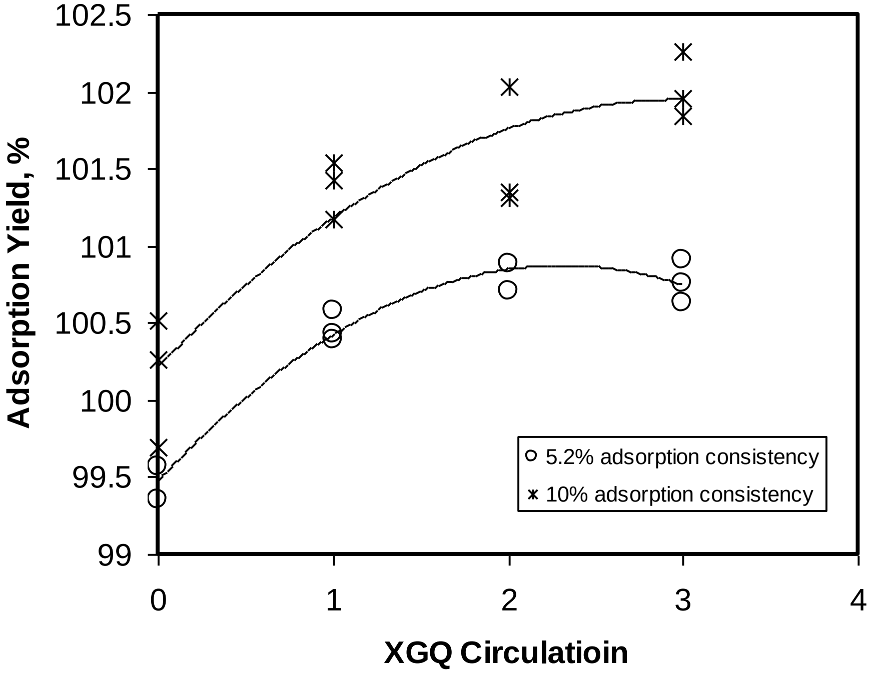


Figure 46. Adsorption Yield versus XGA recirculation.

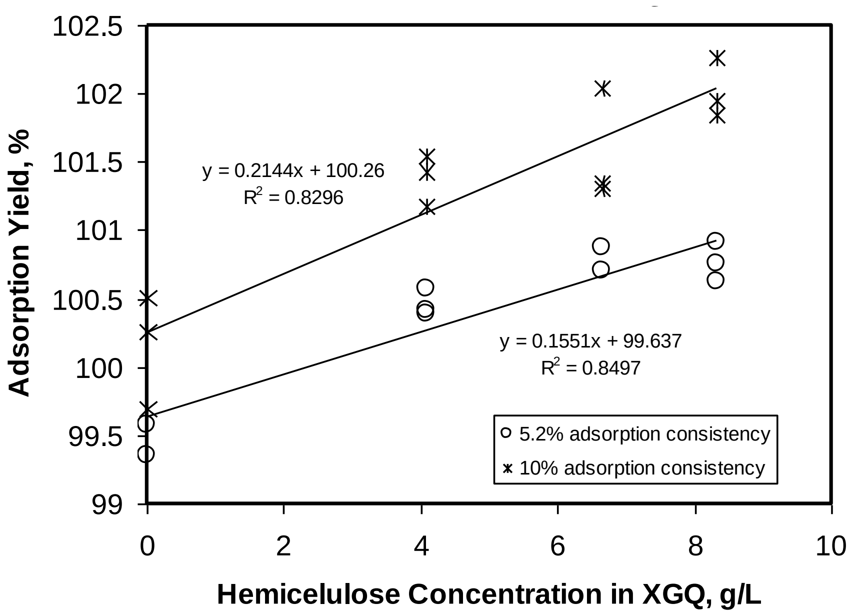


Figure 47. Adsorption Yield versus Hemicellulose Concentration in XGQ Extract

The Kappa number of pulps after adsorption is plotted in Figure 48. The data shows that the kappa number is not increasing significantly by increasing the XGQ circulation. Thus it appears that only a finite amount of lignin is adsorbed from the XGQ liquor despite the increase in lignin content in the extracts which are more recirculated.

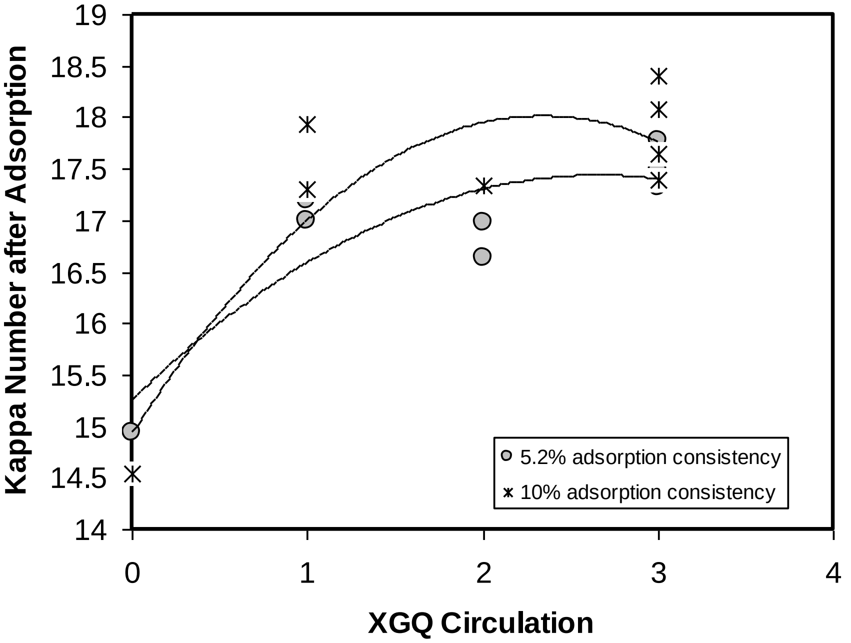


Figure 48. Kappa number versus XGQ recirculation

The dissolved hemicellulose and lignin expressed in percent based on the concentration of dissolved solids obtained by freeze drying are listed in Table 17. Also included in Table 7 is the inorganic (determined and reported as ash) content of the dissolved solids, and a column called undissolved material. The latter represents the material which does not dissolve in the solvent used for GPC analysis. Finally the Sum column represents the sum of the percentages for the hemicellulose, lignin, ash and undissolved material. It can be seen that the Sum is close to 100% for the extracts after adsorption when the extract contains very little hemicellulose. This independent mass balance check gives support to the accuracy of the GPC analysis for lignin. However for the extracts before adsorption the SUM exceeds 100% by about 14%. Thus it appears that there may be an error in the hemicellulose concentration determined by GPC. In later studies it was determined by HPAEC that the amount of sugar oligomers in the extract after GL pre-extraction at 140^{o}C for 90 minutes and L/W=4.5 are only about 1.2 g/L (see Table 10). Therefore it appears that indeed most of the dissolved hemicellulose is absorbed, but that the concentration determined by GPC as shown in Figure 47 is a factor 4 too high.

Table 17. Composition Mass Balance of Extract before and after Adsorption on Pulp

XGQ	Adsorption	Hemi-cellulose (%)	Lignin (%)	Ash (%)	Un-dissolved material (%)	SUM
A	Before	23.8	27.8	51.2	10.9	113.7
	After	0.32	27.2	49.8	18.9	96.2
B	Before	26.3	27.1	50.2	10.2	113.8
	After	0.72	23.6	53.5	19.3	97.1
C	Before	27.8	27.1	49.5	10.3	114.7
	After	1.01	20.9	54.4	22.3	98.6

4.2.2 Adsorption of Pre-Extracted Hemicelluloses on Brown Stock Pulp

Experimental conditions and procedures

Materials

Wood chips: The same mixed hardwood chips (35% Gum (both sweet and black), 35% Southern Red Oak, 15% Red Maple, 12% Poplar and Sycamore and 3% Southern Magnolia) obtained from International Paper Inc as described in 4.1.1 were used in these adsorption studies. In addition, Loblolly Pine chips were used as representative of softwoods. All barks and knots were removed. The chips were screened using a Weyerhaeuser classifier. The wood fractions passing a 1-inch size screen, but remaining on the 7/8-inch and 5/8 inches round screens were collected. The chips were then classified for chip thickness to obtain chips that were less than 10 millimeters thick. The wood chips were air dried to a constant moisture level (~ 9%) and stored in plastic bags for later extraction and pulping experiments.

Green liquor: Green liquor used in this investigation was prepared in our laboratory and is representative of industrial green liquor composition. Table 18 shows green liquor composition.

Table 18. Green liquor composition

NaOH, g Na_2O/L	10.15
Na_2S, g/ Na_2O/L	29.30
Na_2CO_3, g Na_2O/L	69.36
AQ, % on wood	0.05
AA, g/l	39.45
EA, g/l	24.80
TTA, g/l	108.81
Sulfidity, %	74.26
Liquor density, g/ml	1.1484
Liquor solids, g/l	108.81

Pulp: The hardwood pulp for the current experiments was a Pre-extracted Kraft southern mixed hardwood pulp with the following screened properties: yield 43.17%, Kappa No. 16.01.

Hemicelluloses extraction and pulping procedures

The extraction and pulping operations were performed in an M&K digester. The digester is computer controlled by externally heating the recirculating liquor using electricity. 600 g screened wood chips (O.D.) were loaded in the digester for each experiment. A laboratory-made green liquor (GL) was used for hemicelluloses extraction from the wood chips (see Table 18). The extraction conditions are shown in Table 19. When the extraction was completed, the liquor was cooled down, drained, its volume measured and then filtered and stored in a cold room for further use. The extracted wood chips were used for continued pulping in the same digester.

Table 19. Wood chips extraction conditions

Wood chips load, g	600
Green liquor charge on wood, %	3.0
Liquor to wood ratio, L/kg od wood	4.0
Ramp time, min.	50
Extraction temperature, °C	160
Extraction time, min.	110

Both the hardwood and softwood chips were cooked in the M&K digester. 800 gram of wood chips (o.d.) was placed in the 10L digester and GL plus water was added at L/W of 4 L/kg. It took 70 minutes to reach the maximum pulping temperature. In total four pulps were prepared for the current adsorption study; two conventional Kraft pulps and two pre-extracted modified Kraft pulps for both the hardwood and softwood chips. The pulping conditions and results are shown in Table 20.

The cooked wood chips were defiberized in a slusher and the pulp was screened to remove rejects. The pulp was then rinsed in the screening setup and subsequently spin-dried using a laboratory centrifuge. After homogenizing for 30 minutes in a laboratory homogenization mixer at low speed, the pulps were stored in a refrigerator and the moisture content was determined for each sample. The Kappa number of the pulps was determined by TAPPI Standard method T-236.

Table 20. Pulping conditions

Pulp ID	Cook EA charge %	H-Factor
Regular Kraft pulp (HW)	15.0	1400
Pre-extracted Kraft pulp (HW)	12.0	1400
Pre-extracted Kraft pulp (SW)	13.5	1400
Regular Kraft pulp (SW)	15.5	1400

Hemicelluloses adsorption

Small scale adsorption procedure

About 2 g (O.D.) pulp (accurate to 0.0001 g), and a predetermined amount of extraction liquor and water were thoroughly mixed in a thermal seal plastic bag and sealed. The bag was put in a water bath and kept at a set temperature for the required time. Afterwards, the sample was transferred onto a pre-weighed filter paper in a filtration funnel. The extraction liquor was drained and stored for further measurements. The pulp sample was thoroughly washed by using 1000 ml deionized water and then air-dried in a constant temperature and humidity room at TAPPI standard conditions. The dried pulp sample was weighed and its moisture content measured. The adsorption yield was determined as the weight difference between the adsorbed pulp and original pulp divided by the weight of the original pulp (all od weights).

Large scale pulp adsorption procedure

Pulp adsorption was performed on a larger scale for pre-extracted Kraft pulp in order to subject the pulp to beating and then to physical strength testing. Pulp adsorption was carried out using an electrically heated rocking batch digester, which rotated at a frequency between 2 and 6 revolutions per minute through an arc of approximately135 degrees.

The adsorption process was performed by using pre-extracted modified Kraft pulp derived from both hardwood and softwood chips. The applied extraction liquor was obtained by extracting hardwood chips. The same adsorption conditions were applied for both hardwood and softwood pulp. The adsorption conditions and adsorbed pulp properties are summarized in Table 21. After adsorption, the pulps were well-washed, de-watered using a laboratory centrifuge, homogenized using a laboratory mixer and stored in a refrigerator. The adsorption yield was then calculated from the weight difference between the adsorbed pulp and the original pulp. It should be noted that the extracts to pulp ratio (g/g) refers to the weight of dissolved organics per weight of pulp. In practice this will be about 0.2 kg/kg. However in the tests shown in Table 21 this ratio is 20 times higher.

Table 21. Adsorption conditions and results for large scale pulp samples

Adsorption conditions		Adsorbed pulp Kappa	
Pulp consistency %	2.5	Hardwood	Softwood
Extracts ratio to pulp	4.0	22.24	39.83
Temperature °C	95	Adsorption yield %	
Time min	60	Hardwood	Softwood
pH	5.5	6.23	6.01

Pulp refining and physical strength testing

Pulp beating was performed in a PFI mill according to TAPPI Procedure T-248. The softwood pulps were refined to 2500, 5000, 7500, and 10,000 revolutions. The hardwood pulps were refined to 2000, 4000, 6000, and 8000 revolutions.

Hand sheets were made from the refined pulp samples, using Standard TAPPI Procedure T-220. At least 8 hand sheets were prepared for each pulp sample at each beating condition.

Pulp freeness of the refined pulp was tested using standard TAPPI Method T-227.

The following physical properties were tested using the standard TAPPI Testing Procedure as noted: Sheet Thickness T-220 (T-411), Burst Strength T-220 (T-403), Tear Strength T-220 (T-414), and Tensile Strength T-220 (T-494).

Sugar and lignin analysis

Pulp samples after adsorption were first hydrolyzed for one hour at 4% H_2SO_4 and 121 °C in an autoclave. The mono sugar content was determined by High Performance Anion Exchange

Chromatography with Pulse Amperometric Detection (HPAEC-PAD). The lignin content was determined by UV analysis at 280 nm absorbance.

Results and Discussion

Extract properties

During the extraction process, the charged green liquor inorganic chemicals are consumed by the wood. ABC titration was performed on the extract liquor to determine the chemical composition. All caustic alkali and sulfide were found to be consumed by the wood as can be seen in Table 22. It also shows that the extract liquor is slightly weak acidic, that the solids content is about 3% of which about 85% is organics and 15% inorganics. A small amount of sodium carbonate is still detected according to the ABC titration.

Table 22. Extract liquor properties

GL addition % on wood	3	4
pH	5.25	5.65
Extracts concentration g/l	36.01	38.60
Dissolved solids %	98.03	99.05
Undissolved solids %	1.97	0.95
NaOH g/l	0	0
Na_2S g/l	0	0
Na_2CO_3 g/l	3.49	4.81

The detailed composition analysis of the organics in the extract liquor is presented in Table 23. Based on 10% of extract yield (on od wood), we acquire 44% of anhydro-sugars; 20% of acetic acid; and 13% of lignin. Based on extracted sugars, 80% is xylan of which the most part is oligomeric (85%). The amount of extract which can be drained from 1 kg of wood chips is 2.7 Liter.

Table 23. Chemical composition of extract liquor

Content	% on Wood	% on Extracts
Arabinan	0.1	0.99
Galactan	0.3	2.97
Mannan	0.2	1.98
Glucan	0.4	3.96
Xylan	3.4	33.66
Lignin	1.3	12.87
Glucuronic Acid	2.4	23.76
Acetyl groups	2	19.80
Total yield	10.1	100.00
Hemicelluloses %	6.8	67.33

Since only polymeric hemicelluloses and lignin may be adsorbed on pulp (produced at a yield of about 50% from the original wood), the maximum theoretical yield increase due to adsorption may be estimated as 5% on wood or about 10% on pulp.

Pulping of pre-extracted wood chips

Pre-extracted Kraft pulping for both hardwood and softwood are compared with conventional kraft pulping in Table 24. It shows that in order to reach the same Kappa, the pre-extracted-kraft pulp requires a lower effective alkali charge; HW 2.3%, SW 1.3%. Furthermore, at the same final kappa, the hardwood pre-extracted kraft pulp has 1.5% lower yield than the conventional kraft pulp, while there is no significant effect on the yield for SW pulp.

Table 24. Comparison of pre-extracted kraft pulp and conventional kraft pulp.

Pulp ID	Cook EA charge %	Total EA charge %	H-Factor	Screened yield %	Kappa
Regular Kraft pulp (HW)	15.0	15	1400	47.53	17.70
Pre-extracted Kraft pulp (HW)	12.0	12.67	1400	46.04	17.11
Pre-extracted Kraft pulp (SW)	13.5	14.17	1400	43.69	27.80
Regular Kraft pulp (SW)	15.5	15.5	1400	43.78	30.52

Optimization of hemicelluloses adsorption

Experimental design

A central composite experimental design was used for optimization of the hemicelluloses adsorption. Four factors were selected as adsorption variables: fiber consistency (%), the ratio of extracts to fiber (g extracts/g fiber), adsorption temperature and time. The experimental variables and level range are shown in Table 25, and the coding level of each variable is shown in Table 26. All experimental data are summarized in Table 27.

Table 25. Variables and ranges

Factor	Unit	Variable range
Fiber consistency (X_1)	g/100g liquor	0.1 ~ 8.0
Extract to fiber ratio (X_2)		0.1 ~ 5.0
Temperature (X_3)	C	40 ~ 95
Treatment time (X_4)	min	20.0 ~ 120.0

Table 26. Coding of factor levels

Code	X_1	X_2	X_3	X_4
-2	0.1	0.1	40	20
-1	2.1	1.3	53.8	45
0	4.1	2.6	67.5	70
1	6.0	3.8	81.3	95
2	8.0	5.0	95.0	120

2.1.2. Optimization investigation

The adsorption yield, Y, in Table 27 may be described by the regression equation 13 as:

$$Y=11.29+0.84X_1+2.16X_2+1.63X_3+0.52X_4+0.22X_1X_3+0.47X_2X_3+0.28X_2X_4-0.12X_3X_4-0.93X_1^2-0.70X_2^2 \quad \text{(Equation 13)}$$

Table 27. Experimental design data

Std Order	Sample ID	Fiber consistence %	Extracts ratio to fiber	Temperature C	Time min	Yield %
1	1	2.1	1.3	53.8	45.0	6.24
10	7	6.0	1.3	53.8	95.0	7.26
7	13	2.1	3.8	81.3	45.0	12.08
6	14	6.0	1.3	81.3	45.0	9.41
15	15	2.1	3.8	81.3	95.0	13.82
3	8	2.1	3.8	53.8	45.0	8.75
16	16	6.0	3.8	81.3	95.0	14.24
17	5	0.1	2.6	67.5	70.0	3.34
12	9	6.0	3.8	53.8	95.0	9.55
18	19	8.0	2.6	67.5	70.0	11.56
27	20	4.1	2.6	67.5	70.0	10.73
20	21	4.1	5.0	67.5	70.0	14.17
30	22	4.1	2.6	67.5	70.0	11.31
19	6	4.1	0.1	67.5	70.0	2.56
31	25	4.1	2.6	67.5	70.0	11.85
13	3	2.1	1.3	81.3	95.0	8.39
29	26	4.1	2.6	67.5	70.0	11.45
8	17	6.0	3.8	81.3	45.0	13.77
21	23	4.1	2.6	40.0	70.0	7.75
23	30	4.1	2.6	67.5	20.0	9.09
11	10	2.1	3.8	53.8	95.0	10.41
9	2	2.1	1.3	53.8	95.0	6.63
2	11	6.0	1.3	53.8	45.0	6.70
5	4	2.1	1.3	81.3	45.0	8.81
26	27	4.1	2.6	67.5	70.0	11.39
22	24	4.1	2.6	95.0	70.0	14.48
28	28	4.1	2.6	67.5	70.0	11.12
24	29	4.1	2.6	67.5	120.0	12.68
25	31	4.1	2.6	67.5	70.0	11.20
14	18	6.0	1.3	81.3	95.0	9.24
4	12	6.0	3.8	53.8	45.0	8.61

Effects of the process factors on adsorption yield

Based on regression equation 13, the main effects of all process factors on the adsorption yield are shown in Figure 49. When each factor was changed in the region of the experimental design as shown on the X-axis, the other three factors were kept constant at the mid-level. Both temperature and time showed a (nearly) linear effect on the adsorption yield, while the fiber consistency and the extract to fiber ratio showed a nonlinear influence. Furthermore, in comparison of all factors, the adsorption time is relatively insignificant although a longer time would increase the adsorption yield. More specifically, of the other three important variables; fiber consistency, extracts ratio and temperature, their ranking in terms of impact on the adsorption yield changed at different application levels as can be seen in Figure 49.

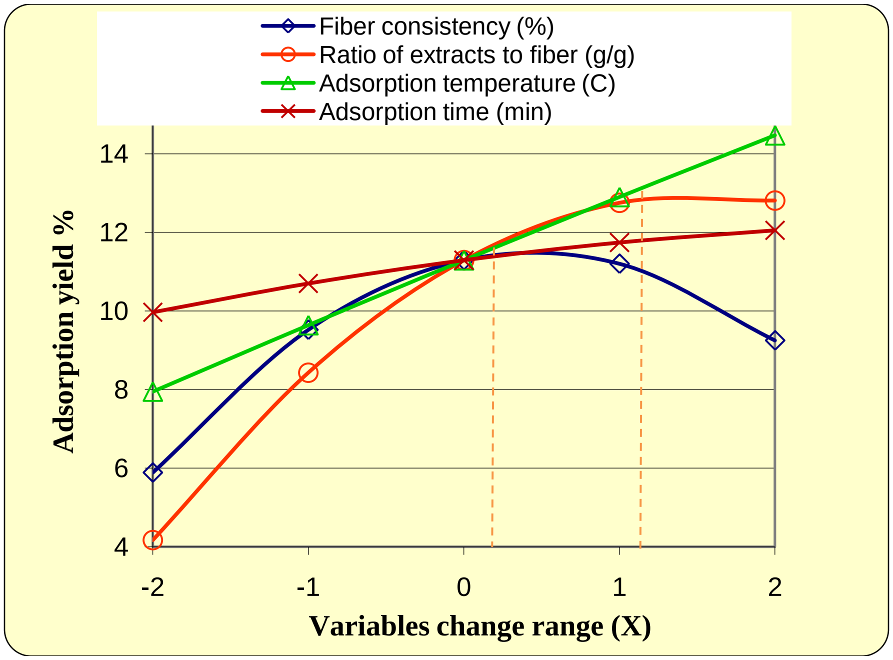


Figure 49. General profile of all process factors on adsorption yield, Y
(X_1: Fiber consistency, X_2: The ratio of extracts to fiber, X_3: Temperature, X_4: Time)

Below the mid-point application level, the contribution of the 4 parameters on the adsorption yield is ranked in the order of increasing impact: fiber consistency, extract ratio and temperature. However, at high application levels the ranking of the variables in terms of increasing contribution to the adsorption yield is: temperature, fiber consistency and extract ratio. Finally, a higher temperature and longer time always lead to higher adsorption, while both fiber consistency and extracts ratio changed from having a positive effect to a negative effect on the adsorption yield when the application level increases from the lowest to the highest levels.

As Figure 49 shows, the fiber consistency mainly exhibits a quadratic effect on hemicelluloses adsorption. The experimental data demonstrate that a fiber consistency of about 5.0% would lead to the highest hemicelluloses adsorption. Higher fiber consistency decreases the transport distance for the organics to the fibers, while an overly thick pulp slurry reduces the viscosity of the pulp suspension, therefore reducing the adsorption amount. The extract to fiber ratio is another important factor in the process of hemicelluloses adsorption. The increase of the extracts ratio always led to increased hemicelluloses adsorption as shown in Figure 49. Both variables of adsorption temperature and time resulted in enhanced hemicelluloses adsorption, but with different efficiencies. When temperature was raised from the low to the high level, the adsorption yield nearly doubled. However, extending the adsorption process from 20 minutes to 120 minutes only increased adsorption by a few percent. The results indicate that extending adsorption time would not be an efficient way for improving hemicelluloses adsorption. It should be noted that the increased adsorption with increasing temperature is not consistent with the nature of physical adsorption, whereby adsorption decreases with increasing temperature. This indicates that a more complex mechanism is involved in hemicelluloses adsorption.

To summarize, the investigation of the main operating variables suggest that the adsorption process should be carried out at medium fiber consistency (~ 5%), an extract to fiber ratio of about 4 at the highest temperature to obtain optimal adsorption of the hemicelluloses.

Effect of extract and pulp types on adsorption yield

Earlier we showed that hardwood pulp could adsorb a substantial amount from xylan-rich extracts generated from hardwood. In this section we also determine the adsorption ability when using softwood (Loblolly Pine) pulp and softwood (Loblolly Pine) extracts. The hardwood and softwood extractions were carried out in the digester using the same standard GL extraction conditions. Both extraction liquors were separately applied on hardwood Kraft pulp at the same adsorption conditions. The comparison of the adsorption yields using extract liquors from hardwood and softwood are shown in Figure 50. Clearly the adsorption yield using softwood extract is much lower than using hardwood extract; 3% versus 10%. The reason is likely due to the fact that the dissolved hardwood glucoronoxylan is predominantly oligomeric while the dissolved softwood galactoglucomannan is mostly degraded to hydroxyl acids due to the peeling reaction.

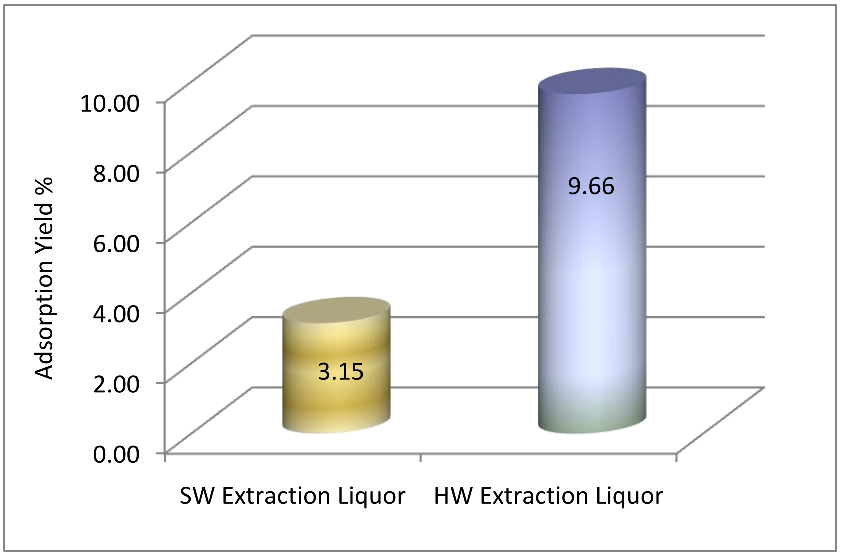


Figure 50. HW and SW extract adsorption on hardwood pulp

(Conditions: Original liquor, Pulp consistency 1.5%, Extract to pulp ratio 2.0, temperature 90 C, 60 minutes)

The adsorption ability of kraft Loblolly Pine pulp is compared with that of Southern mixed hardwood pulp using the standard hardwood extraction liquor at the same adsorption condition. The result is presented in Figure 51. Interestingly, softwood pulp exhibited even stronger adsorption of the xylan extract than the hardwood pulp. The result suggests that it may be advantageous to use a hardwood extract to increase the yield and modify the properties of a parallel softwood kraft pulp line.

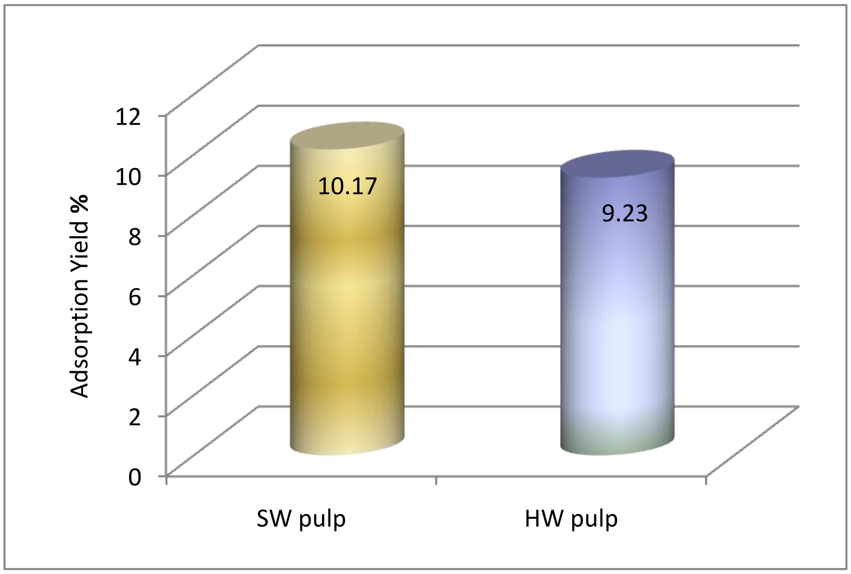


Figure 51. Comparison of adsorption yield using hardwood extracts for hardwood and softwood pulp (Conditions: Original liquor, Pulp consistency 1.5%, Extract to pulp ratio 2.0, temperature 90 C for 60 minutes)

Besides hemicelluloses, lignin also adsorbs onto the cellulosic kraft pulp fibers. As shown in Figure 52, the amount of lignin adsorption is linearly correlated with the total adsorption yield. From the slope it can be calculated (0.5 x 0.15 g lignin/g pulp/kappa) that the adsorbed material contains about 7.5% lignin, i.e. the adsorbed hemicelluloses contain about 8% of lignin. Hence, hemicelluloses adsorption results also in a kappa number increase of the pulp. Generally, one percentage yield increase results in 0.4~0.5 kappa increase.

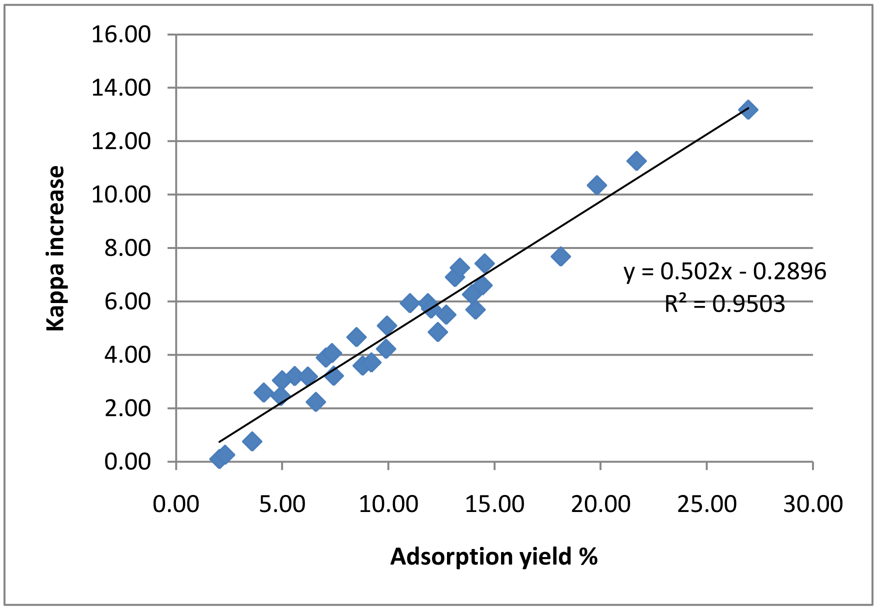


Figure 52. Lignin co-adsorption

Kinetics of hemicelluloses adsorption

A series of adsorption experiments were conducted at different temperatures to study the kinetics of hemicelluloses adsorption. The results in Figure 53 demonstrate that the major amount of hemicelluloses is adsorbed in 60 minutes. Furthermore, it clearly shows that higher temperatures lead to significant higher adsorption yields. It suggests that diffusion of the hemicellulose oligomers into the porous structure of the fiber cell wall plays a critical role for both the rate and final quantity of hemicellulose adsorption.

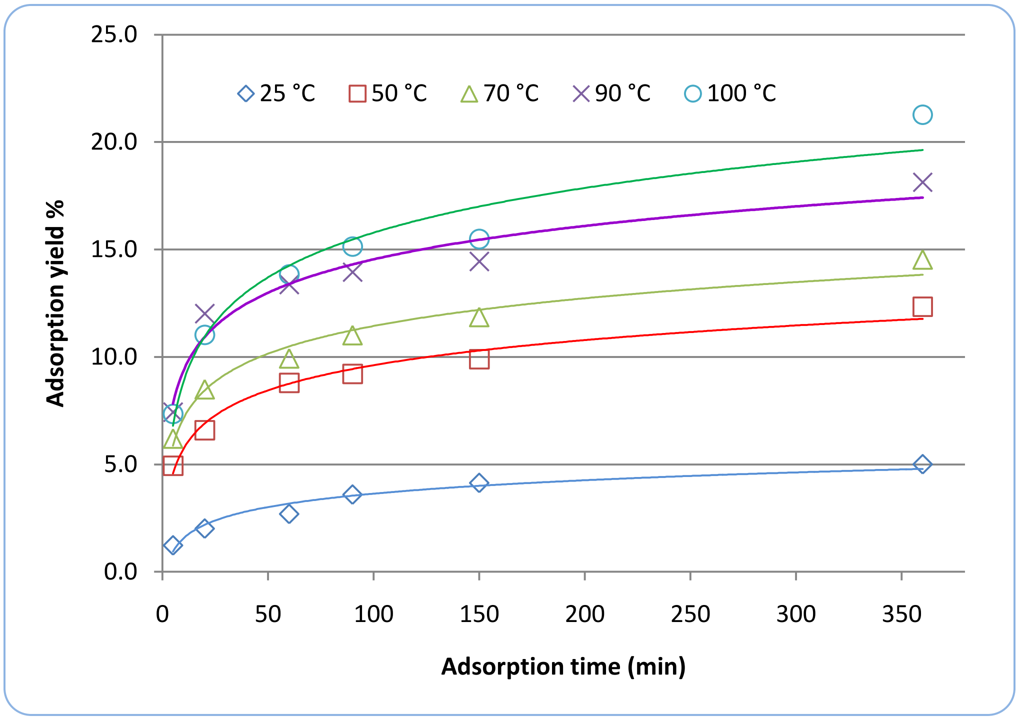


Figure 53. Kinetic process of hemicelluloses adsorption

Adsorption of hemicellulose extract at practical conditions

When adsorption is performed by using the drained GL hardwood extract on the total amount of final hardwood kraft pulp (i.e. 6 liter of extract per 1 kg hardwood kraft pulp), a relatively low adsorption yield of 1.3% on dry pulp is obtained (see Figure 54). The reason for the low value compared to the earlier reported values is that in the earlier sections we have used undiluted extract, while in the practical case the extract is diluted several times to reach the optimum consistency of 5%.

In order to increase the adsorption yield, different retention aids were applied. The results in Figure 54 show that the application of these retention aids at a charge of 0.5% on pulp increases the yield several fold. Guar gum in particular is very effective and raises the yield increase to 4.2%.

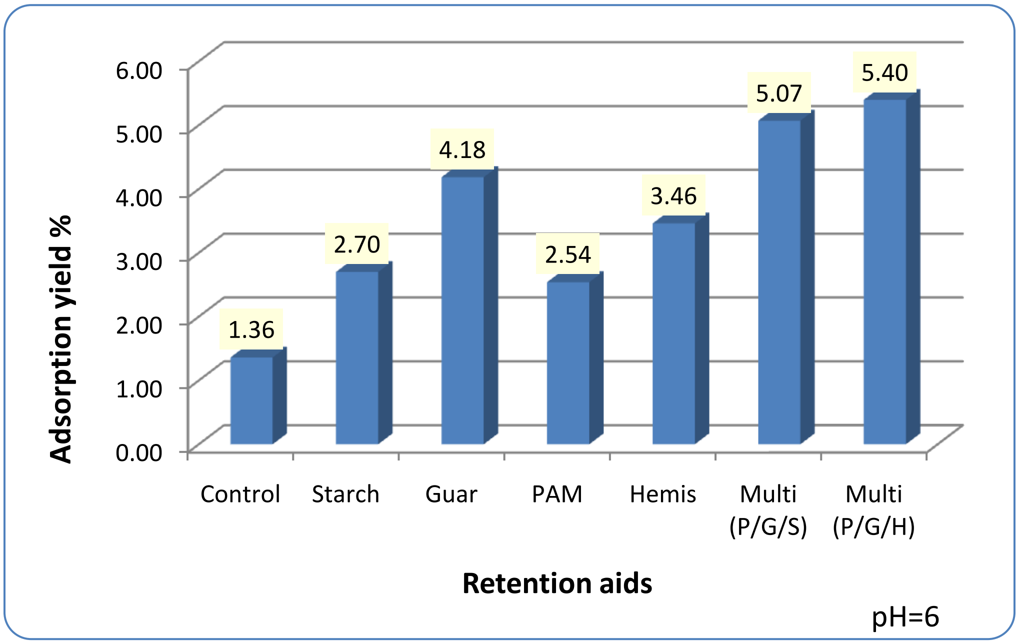


Figure 54. Comparison of retention aids (adsorbed at original pH of 6)

(Adsorption conditions: 90 C, 60 min, retention aids charge 0.5% on pulp, pulp consistency 5%, Extracts liquor ratio to pulp 6 L/kg)

In order to produce bleached pulp, the kraft pulp with adsorbed hemicelluloses will be subjected to additional process steps such as oxygen delignification and several bleaching treatments. Of these processes, the alkaline treatments are critical because they may lead to desorption of the adsorbed hemicelluloses. Figure 55 shows the comparison of hemicelluloses retention after alkaline treatment (charge of 2% caustic on pulp for 60 minutes at 70 °C and 10% consistency) for adsorbed pulp produced under near neutral (pH of 6) and alkaline conditions. It can be seen that only 10% of the yield is retained after alkaline treatment of the pulp produced under near neutral adsorption conditions, while more than 80% of the yield is retained when the adsorption is performed under alkaline (pH of 11.5) conditions. The result suggests that adsorption in alkaline environment would be advantageous to reduce loss of adsorbed hemicelluloses in the following alkaline processes despite the lower yield gain during the initial adsorption (1.13 versus 1.36%). Therefore the effectiveness of the various retention aids for hemicelluloses adsorption at alkaline conditions (in this case the pH was maintained at 10) was investigated. The results are plotted in Figure 56. By comparing the these results with those in Figure 52, it is found that adsorption at this alkaline condition results in a relative loss of 10-50% adsorption yield compared to that obtained at the original near-neutral condition (pH 6). A maximum adsorption yield of approximately 3% was obtained with guar gum as retention aid. If the charge of guar gum is reduced to 0.1% on pulp at adsorption conditions of pH 11.5, 90 C for 60 minutes at 5% consistency, then the adsorption yield is 1.69%. This yield decreases to 1.56% after further alkaline treatment (charge of 2% caustic on pulp for 60 minutes at 70 °C and 10% consistency).

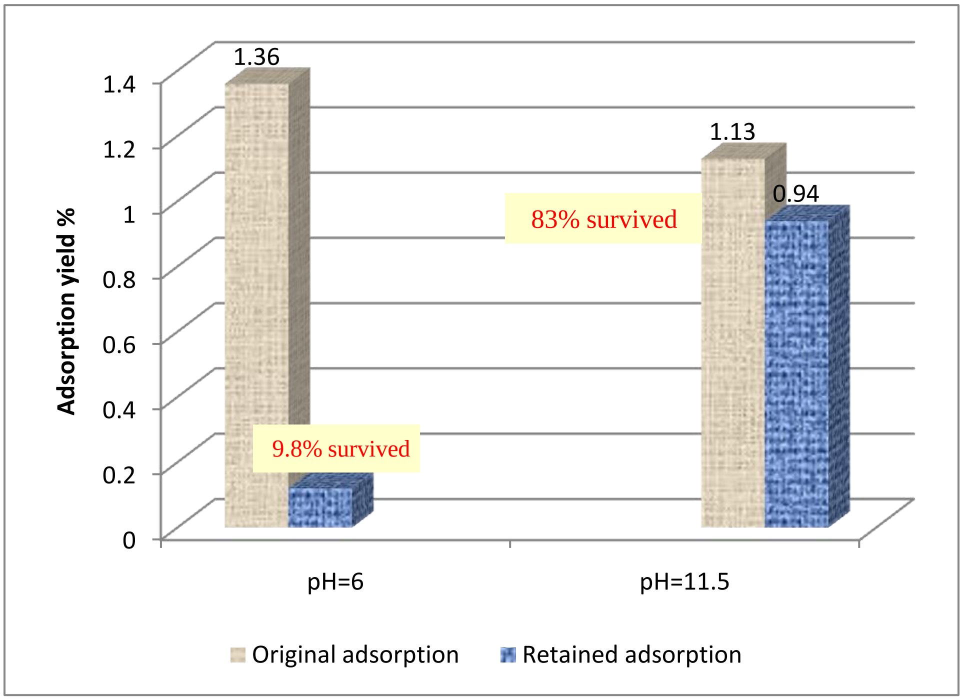


Figure 55. Retention of hemicelluloses after alkaline treatment

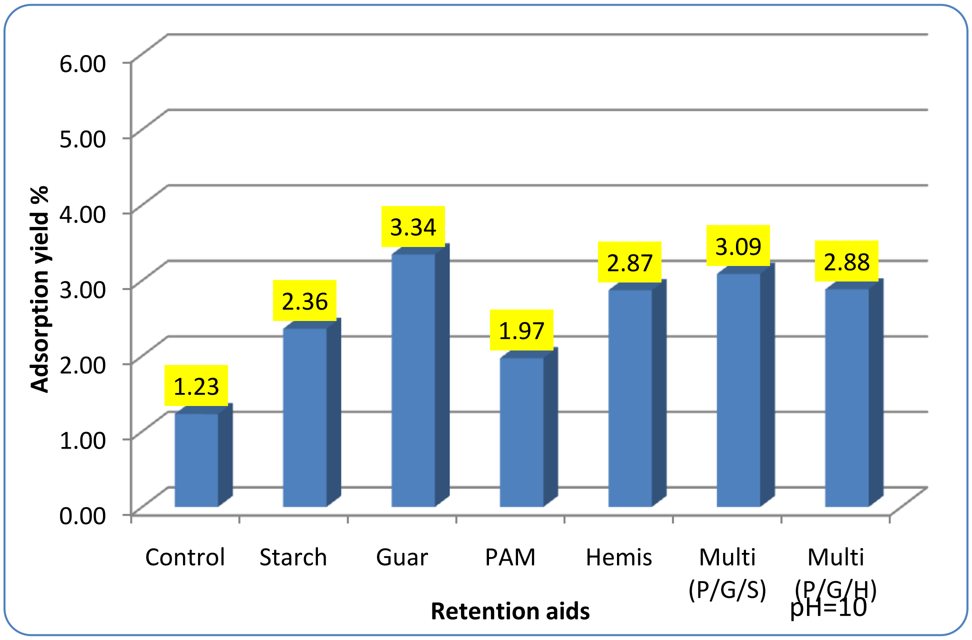


Figure 56. Comparison of various retention aids (adsorbed at pH=10)

(Adsorption conditions: 90 C, 60 min, retention aids charge 0.5% on pulp, pulp consistency 5%, Extracts liquor ratio to pulp 6:1)

Summary of hemicellulose adsorption at practical conditions

Direct application of raw GL hardwood extract liquor for hemicelluloses adsorption onto hardwood kraft pulp leads to a yield increase of about 1%. With typical wet-end retention aids this may be increased to about 5% of adsorption yield. However, most of this yield increase is lost during subsequent alkaline treatments in the bleach plant. By performing the adsorption at alkaline conditions the major part of the adsorption loss during alkaline treatment in the bleach plant may be avoided. The optimum permanent yield increase of about 1.5% (on pulp) was obtained with the addition of a retention aid (charge of 0.1% guar gum) during adsorption of the GL hardwood extract liquor at pH 11.5, 90 C for 60 minutes at 5% consistency.

Influence of Adsorption on Paper Physical Strength

The developments of the Canadian Freeness (CSF) during the beating process for both the softwood and hardwood pulps are shown in Figure 57 and Figure 58 respectively. It shows that the adsorbed pulps are easier to beat than the corresponding conventional Kraft and pre-extracted modified Kraft pulps. The results demonstrate a significant positive effect of adsorption on pulp beatability. For an equivalent freeness, the adsorbed softwood pulp requires fewer beating revolutions than the standard Kraft pulp, 2000-3000 beating revolution reduction for hardwood pulp and about 1000 revolution reduction for softwood pulp.

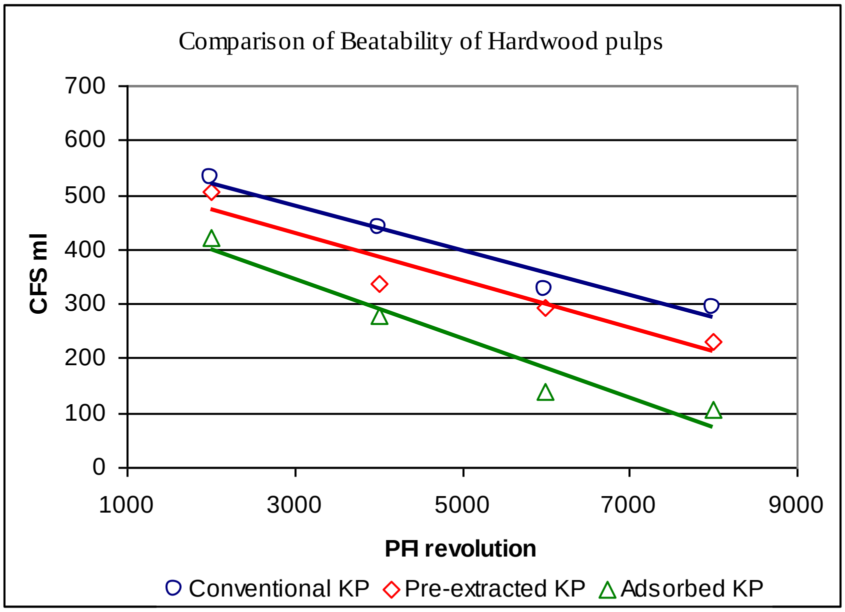


Figure 57. Comparison of beatability of hardwood pulps

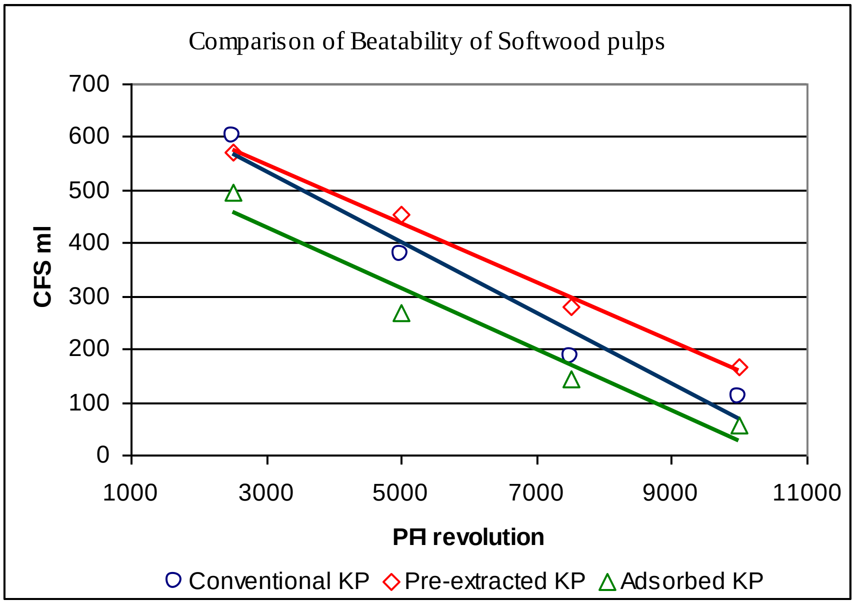


Figure 58. Comparison of beatability of softwood pulps

The development of tensile and burst strengths in the beating for the three hardwood kraft pulp samples; conventional Kraft, pre-extracted Kraft and hemicelluloses adsorbed Kraft pulp, are shown in Figure 59. It can be seen that compared to conventional Kraft pulp the hemicelluloses adsorbed kraft pulp exhibits up to 20% of increase in tensile strength and a 10-25% increase in burst strength. This indicates that the adsorbed hemicelluloses strengthen fiber bonding, presumably by the increase of free hydroxyl groups on the fiber surface from the adsorbed hemicelluloses. Figure 59 also displays that the pre-extracted kraft pulp have a slower development rate for both tensile and burst strengths than other two pulps. As a result, the pre-extracted pulp shows a higher strength than the conventional Kraft pulp at a low beating level, while it has even lower strength than Kraft pulp at a high refining level.

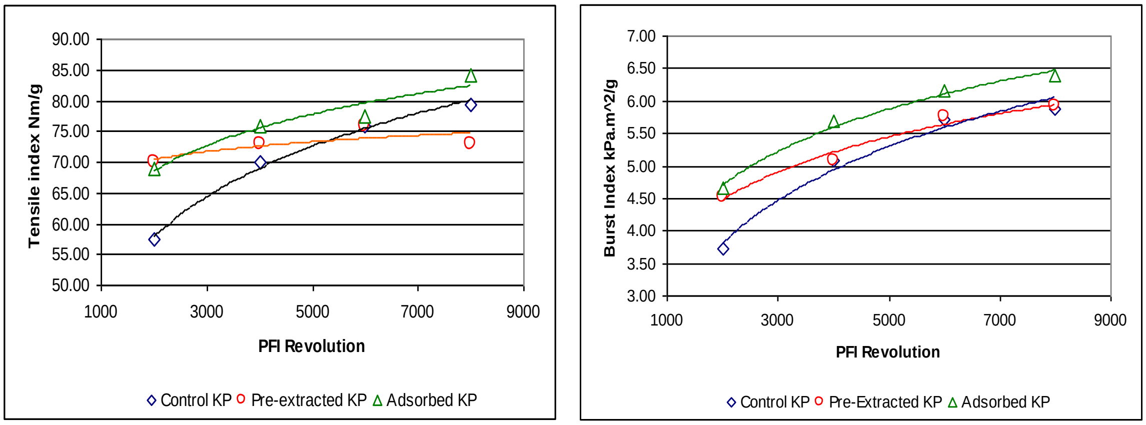


Figure 59. Tensile and burst strength development during PFI beating (Hardwood pulp)

When comparing paper strength it is most meaningful to compare tear strength at a certain tensile level. Figure 60 shows this comparison of the three hardwood pulps; tear strength at tensile index 70 (N.m/g). It is clear that an increase of about 8% in tear strength at tensile 70 N.m/g can be obtained by hemicelluloses adsorption compared with conventional KP. For pre-extracted Kraft pulp, although higher tear strength was observed in the initial stage of refining than the conventional Kraft pulp, no difference was observed with the conventional Kraft pulp.

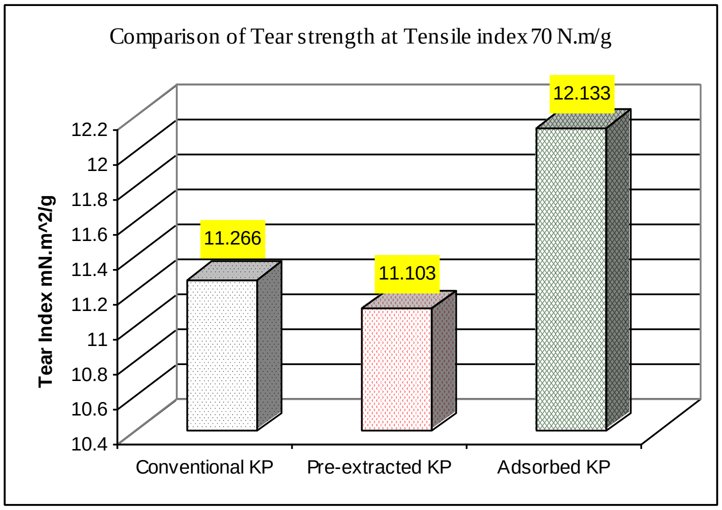


Figure 60. Comparison of hardwood pulp tear strength at tensile index 70 N.m/g

Because of the poor adsorption properties of softwood extracts, hardwood extracts were applied for softwood pulp adsorption in the current work. Similar to hardwood pulp, the adsorption of hardwood hemicelluloses also improved the softwood pulp strength properties. Both tensile and burst strength increased as shown in Figure 61. Compare to the conventional Kraft pulp, 10% - 20% increase in tensile strength was achieved, which is similar to that found for hardwood adsorbed pulp. However, an increase of only about 5% in burst strength was observed, which is much less than that obtained for hardwood adsorbed pulp.

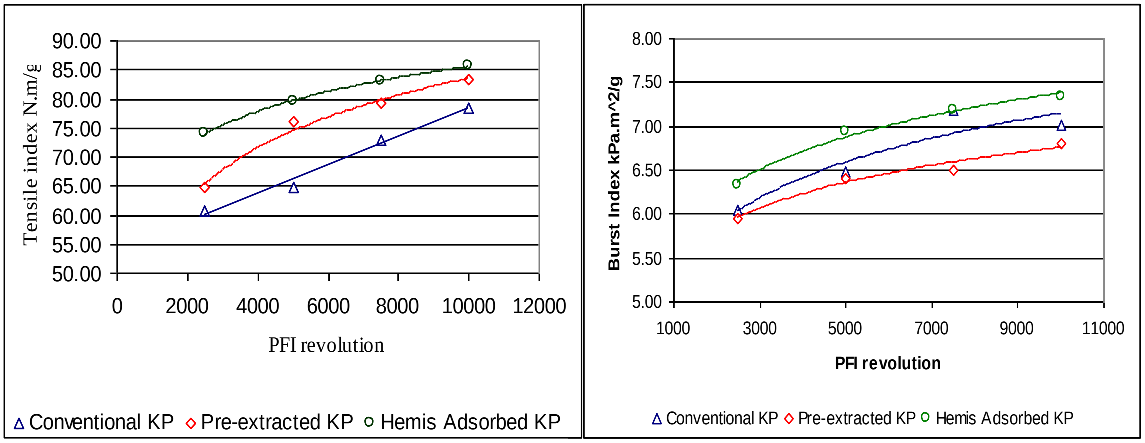


Figure 61. Comparison of softwood pulps in tensile and burst strength

Contrary to what was found for hardwood pulp, the tensile and burst strength of the adsorbed softwood kraft pulp did not show higher tear strength as can be seen in Figure 62. However, when comparing paper tear strength at tensile 70- Nm/g the adsorbed pulp still had a 10% higher tear strength than conventional Kraft pulp as shown in Figure 63. Thus, although adsorbed softwood pulp showed lower tear strength at a certain beating level, its greater tensile development during refining resulted that the adsorbed pulp reached a higher tensile strength at less refining, thereby reducing fibers cutting and improving the tear strength.

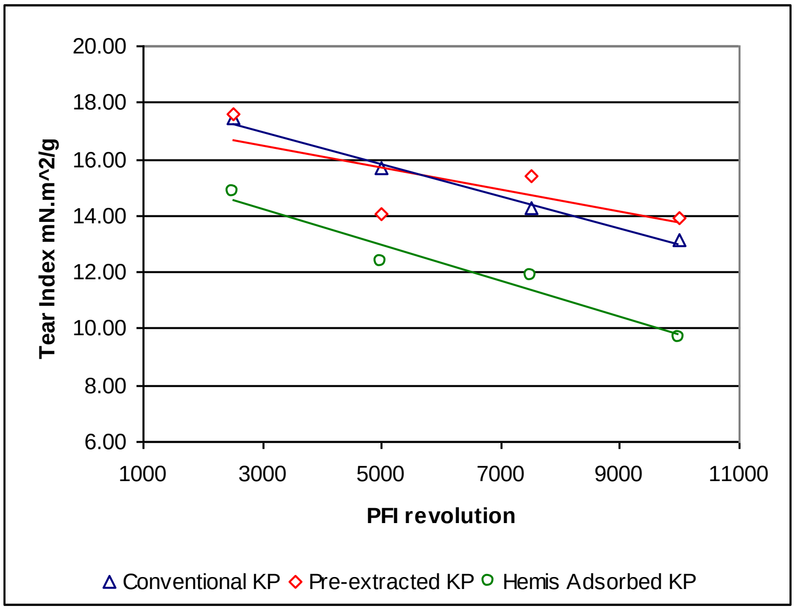


Figure 62. Comparison of tear strength development of softwood pulps during refining

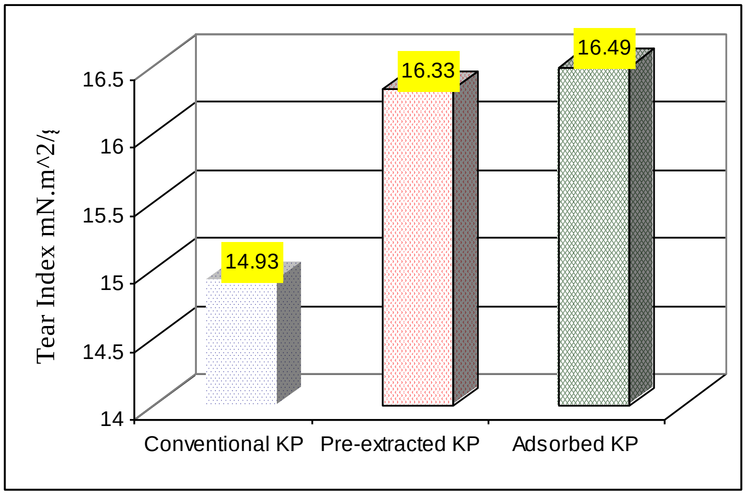


Figure 63. Comparison of softwood pulp tear strength at tensile index 70 N.m/g

Summary of the effect of extract adsorption on paper physical strength

Xylan-rich extracts were produced from hardwood using “green liquor” and applied for adsorption to both hardwood and softwood kraft pulps derived from the extracted wood. The resulting pulps were refined in a PFI mill and the physical strength properties of paper sheets made from these pulps were tested. The main findings are:

Adsorbed xylan-rich hemicelluloses significantly improve pulp beatability for both hardwood and softwood pulp. Compared to the conventional Kraft and pre-extracted Kraft pulps, the adsorbed pulps showed a quicker freeness development during pulp refining. Also, significant physical strength improvements were achieved for adsorbed hardwood pulp. Compare to the conventional Kraft pulp, a 20% increase in tensile strength and 10-25% increase in burst strength were obtained. At a constant tensile strength of 70 N.m/g the tear strength increased by up to 8% for the adsorbed pulp. Adsorbed softwood pulp showed a smaller relative improvement in physical strength properties compared to conventional softwood kraft pulp than that found for adsorbed hardwood pulp.

4.3 PRODUCTION AND TESTING OF SHEET MOLDING COMPOUNDS (SMCS)

The objective of this study was to fabricate partially renewable SMC's and compare their water absorption and micro-mechanical performance to that of totally synthetic SMC's. Kenaf fibers and wood solids obtained by hot-water extraction of Maple wood were used for the partially renewable SMC's. In order to evaluate and predict how the various components may interact in a cross-linked composite SMC, the surface energy and acid-base characteristics of natural fibers, glass fibers, wood extract solids, and a SMC prepreg mixture were determined by Inverse Gas Chromatography (IGC). Dynamic Mechanical Thermal Analysis, DMTA, was used to determine how the components in the SMC changed as a function of hydrothermal aging by analyzing the glass transitions of the individual components in the SMC.

Manufacture and preparation of synthetic SMC samples

A compression mold made of carbon steel was designed and fabricated to produce a Sheet Molding Compound (SMC) of approximately 18 cm by 18 cm. To make the molded SMC, an industrial B-stage SMC was acquired from AOC Resins (Valparasio, Indiana, USA). The B-stage SMC was successfully compression molded into C-stage SMC at the Advanced Engineered Wood Composites Center (AEWC) at the University of Maine. Samples of 7 x 3 x 45 mm were cut from the SMC. These samples were dried to constant weight, and then sanded to 1.8 mm thickness for DMTA analysis from -60ºC to 260°C at 1 Hz frequency and 1°C per minute ramp rate to obtain physical property and environment aging data. The Tan Delta for the hydro thermally soaked samples was determined with the DMTA. The latter data was used to make a hypothesis about possible chemical reactions taking place in the SMC matrix during soaking. The hydrothermal tests simulate an accelerated exposure of the SMC to the environment.

Hydrothermal aging and DMTA testing of the synthetic SMC samples.

The DTMA testing results of the hydrothermally aged SMCs indicated that a thickening reaction for the polyester and metal oxide intensified with hydrothermal aging. The peak intensity for the glass transition of poly(vinyl acetate) decreased with aging as has been previously reported. However, HPLC results indicate that no acetic acid was formed during the hydrothermal aging. This disagrees with literature reports of the hydrothermal decomposition of poly(vinyl acetate) degrading to poly(vinyl alcohol) and acetate. HPLC analysis of aqueous aging solution indicated the presence of large molecules but no acetic acid. Considering the decrease in intensity for the poly(vinyl acetate), the large molecules may be some of the low profile additive. Since no glass transition peak was found for poly(vinyl alcohol) in previous work, and in the current investigation, the hypothesis that the large molecules in the aging solution may be poly(vinyl acetate) seems plausible. Styrene was shown to be present in the aging solution by HPLC. Details may be found in our paper (80).

Inverse gas chromatography, (IGC), analysis

Inverse gas chromatography, (IGC), with kenaf fibers was completed. Initial experimental work focused on getting meaningful results by proper packing of IGC columns and designing experiments. Experiments were conducted at three temperatures, 27°C, 35°C, 45°C. Inverse gas chromatography is done to characterize fiber and matrix surface energies to determine appropriate fiber sizing agents. Acid base interactions for the bast Kenaf fibers were determined. The acid base constants for the fibers should be compared to the acid base character of the matrix to determine appropriate sizing agents to maximize the interaction of the matrix with the fiber. The polyester prepreg material and chopped glass strands were characterized by IGC. Details may be found in our paper (81). Due to the heterogeneous nature of the material new flow rates as well as operating parameters for the IGC experiments had to be determined. Complete characterization of the polyester prepreg material from 30°C to 120°C, 15 fiber types, and chopped glass reinforcement was completed. Details are given in our paper (82).

Fabrication of the partially renewable SMC's

Partially renewable SMC's containing glass and Kenaf fibers as reinforcement were fabricated. The used prepreg SMC was donated by AOC resins, kenaf by Kenaf industries, glass fibers from Owens Corning, and the peroxide initiator from Akzo Nobel. This material was used to compound SMC with glass and natural fibers. In some of the SMC's the fibers were surfaced sized with styrene maleic anhydride (SMA). SMA was selected as a sizing agent due to the IGC results which indicated that it would produce the most favorable interaction between the fibers and the polyester matrix. Specifically, the IGC results indicated that the polyester prepreg material had an experimental dispersive surface energy value of 47 mJ/m^2 that compared well with a rule of mixture analysis of the components in the SMC giving a value of 50 mJ/m^2 both at 30°C. IGC results also indicated that the kenaf-prepreg material has a higher acid base interaction then the glass-prepreg material and that surface sizing of the kenaf fibers with styrene-maleic anhydride may improve the cohesiveness of the final kenaf based SMC. IGC results also indicated that wood solids obtained by hot water extraction of *acer rubrum* had a dispersive energy close to that of polystyrene and should be miscible in the prepreg material.

In the actual sizing operation SMA was suspended in pure styrene and used to fully impregnate an appropriate weight of fibers. The charge of SMA was 2 % on oven dry weight of the fibers. During compression molding the SMA and styrene should react to form bonds between the fibers and the polyester matrix material. In addition, the SMA decreases the hydrophilicity of the Kenaf resulting in a more cohesive material after molding. Then the samples were hydrothermally aged and tested according to the experimental protocol developed (80).

Results and Discussion

Hygrothermal aging was done by soaking SMC samples at 70°C for 3, 168, and 1032 hour time intervals. Water uptake by the SMC material was determined gravimetrically. It can be seen in Figure 64 that standard SMC fabricated with glass reinforcement had a water uptake less than 5 weight percent after 1032 hours. SMC fabricated with kenaf had water uptakes at 1032 hours approaching 20 weight percent. After sizing the Kenaf-based SMC with SMA, the total water absorbed decreased to approximately 12% representing a 40% decrease in water absorbed by the SMC without SMA sizing. However even with SMA sizing the water absorption is still much higher than the glass fiber based SMCs indicating that kenaf based SMCs are not suitable for exterior applications or applications were water contact occurs.

It was then explored whether a biobased polymer could be used to substitute for polystyrene as a low profile additive in the SMC. A hemicellulose extract was produced by hot water extraction of *Acer rubrum* wood strands. Water at 160◦C applied for 90 minutes removed approximately 16% of the wood weight. The extract was composed primarily of acetylated glucuronoxylans (63.9%) and lignin (17.6%). Details about the hot water extraction can be found in reference (83). It can be seen in Figure 62 that SMCs with hemicellulose extract solids added at 1.5 or 8% to a 30% glass reinforced SMC produced a partially renewable material which had water uptake similar to that of the standard SMC. It was also noted that during DMTA testing over the temperature range of –50˚C to 260˚C the glass based synthetic SMC was the most resilient to the heat ramps followed by the extract based SMC. This level of testing, however, effectively destroyed the kenaf based SMC.

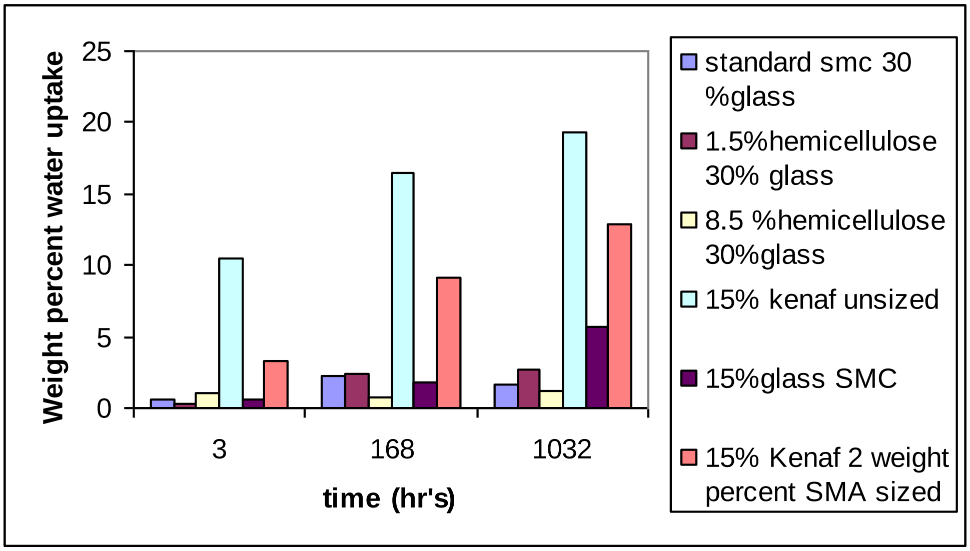


Figure 64. Water uptake of various SMC as a function of aging time.

More testing of SMCs containing the hemicellulose extract solids must be performed to determine the practical use of the hemicellulose extract in this application. Specifically the shrinkage of the SMCs during compression molding, tensile and impact properties and surface qualities need to be determined.

Conclusion

The replacement of glass reinforcement in SMC with Kenaf fiber leads to dramatic increases in water absorption of the final material. This makes kenaf unsuitable as a components in partially renewable SMCs. However, the integration of hemicellulose extract solids into the SMC matrix material has a negligible impact on the water adsorption of final product. Further work on the shrinkage, tensile, impact and surface properties of the hemicellulose containing SMCs needs to be performed in order to determine whether this is a practical use of hemicellulose extracts.

5. OVERALL CONCLUSIONS

The exploratory pre-extraction–kraft studies of hardwoods (Chapter 4.1.1) showed that when an acidic (pH of about 4) extract is produced by pre-extraction with pure water at high temperature (160^{o}C for 60 minutes) a final kraft pulp yield is obtained which is almost 7% lower than that of the control kraft cook. When the extract remains alkaline (pH about 13) by aqueous pre-extraction with 10% (on chips) NaOH then the final kraft pulp has a hemicellulose and cellulose loss both of about 2.0% (on chips) relative to that of the kraft control pulp. However by keeping the final extract pH close to neutral by adding only 3 or 3.5% NaOH (on chips) the total pulp yield was only about 1% lower than that of the control, while still about 8% wood substance was extracted. **Thus it was found that the pH of the extract must be kept near neutral at high temperature pre-extraction to avoid a significant loss in total pulp yield. This treatment was called "near-neutral" pre-extraction**.

Simple pre-extraction of wood chips before pulping is presently already applied in practice in the form of the pre-hydrolysis kraft process to produce dissolving grade pulp and specialty cellulose. However, in this process the extracted hemicellulose are not recovered but are carried along with pre-extracted chips, and then become part of the kraft black liquor during the cooking stage. In an IFBR on the other hand, the hemicellulose extract will be removed from the wood and used for production of higher value-added products. In order to better understand the effect of operating conditions during water pre-hydrolysis on the composition of the extract and that of the extracted wood, a series of hydrothermal pretreatments of a mixture of southern hardwoods were carried out at different temperatures of 130 ºC to 170 ºC for 100 minutes, and different times at 170°C. It was shown in Chapter 4.1.2 that xylo-oligosaccharides can be removed from hardwood in high yield without extensive delignification and degradation of cellulose. The effect of time and temperature on the dissolution of different wood components of a southern hardwood chips mixture can be expressed by a single parameter called P-factor. Xylan is the most abundant species in the reaction medium at P-factors higher than 200 hrs. Xylan mainly dissolves in oligomeric form however significant hydrolysis of xylo-oligomers to xylose takes place at the highest studied P-factor of about 1000 hrs. The extraction rate of xylan is initially slow and then it reaches a maximum at approximately a P-factor of 800 hrs. The rate of glucomannan removal shows the same behavior as that of xylan; however it is almost five times lower than that of xylan. Approximately 70% of hemicelluloses in original wood are extracted during autohydrolysis at P-factor of about 1000 hrs. The acidity of the hemicellulose extract increases with increasing P-factor and reaches a plateau around P-factor of 800 hrs in the present range of study. No significant amount of furfural and HMF was generated under the present extraction conditions. The results show that xylan may be efficiently extracted from hardwood without significant removal of cellulose and only a small dissolution of lignin.

Water pre-extraction – kraft pulping of Loblolly Pine is explored in Chapter 4.1.3 with the objective to obtain the same yield and physical pulp properties as that of the corresponding conventional kraft pulp of the same kappa number. Again it was found that the effect of time and temperature during pure water extraction on wood weight loss and wood component removal may be described by a single parameter, the H-factor. For all practical purposes the H-factor (which is routinely used in kraft pulp production) is essentially the same as the P-factor. This implies that the activation energy of the kinetics of wood dissolution during pure water extraction (also called autohydrolysis) is the same as that of kraft cooking. The total polymeric sugar content in the extract reaches a maximum of about 8% at an H- factor of about 500 hrs with a minor removal of 0.3% cellulose and 0.5% lignin. The sum of all monomeric and polymeric sugars reaches a maximum of about 12% at an H-factor of about 1500 hours. The maxima in polymeric and total sugar content in the extract are caused by acid hydrolysis due to acetic acid released from the hemicelluloses. Therefore the extraction of softwood with water should be terminated before the pH drops below about 3.5. The delignification rate constants for kraft cooking of water pre-extracted chips are 40 to 60% higher than corresponding kraft control cooks performed at 15% effective alkaline charge and 30% sulfidity. Unfortunately the total pulp yield based on the original wood at kappa 30 is 3 and 6% lower than the control at pre-extracting H-factors of 200 and 500 hours respectively, while the alkali consumption is the same as the control. Also the water pre-extraction kraft pulps are more difficult to refine and have a lower tensile strength due to their lower hemicellulose content compared to the control. **Therefore autohydrolysis of softwood does not satisfy the requirement of the IFPR concept** pursued in the present study, since the final pre-extracted kraft pulp has significant lower yield and physical properties than that of the corresponding conventional kraft pulp.

Practical implementation of the “near-neutral” pre-extraction treatment (Chapter 4.1.1) would favor the use of mill-available alkali sources such as green liquor or Na_2CO_3. Therefore a new set of pre-extraction experiments were performed on Southern mixed hardwoods with green liquor (GL)+AQ as described in Chapter 4.1.4. AQ or anthraquinone is a yield preserving additive used in alkaline pulping. The alkali charge during pre-extraction was 3% on wood as Na_2O, while the AQ charge was 0.05% on OD wood. No AQ was added during cooking, including the control kraft cooks. The sulfidity of the green liquor was 30% on a TTA basis. Near-neutral extraction with 3% NaOH or 3% green liquor(+0.05%AQ) at 140 and 160^{o}C for 60 to 110 minutes led to the removal of about 5 - 10% of wood substance from southern mixed hardwood chips. When the wood chips extracted at near-neutral condition with 3% GL (+0.05%AQ) were pulped at reduced effective alkali charges (12% EA), the delignification rate increased significantly while the overall pulp yield was similar to that of the kraft control (at 15% EA). The chips pre-extracted with a charge of 3% GL (+0.05%AQ) consumed about 2.5 - 3% less effective alkali during the subsequent kraft cooks compared to that of the control kraft cooks. Slightly lower refining response, comparable tensile strength and significantly increased tear resistance were observed in kraft pulps pre-extracted with 3% GL (+0.05%AQ) compared to corresponding conventional kraft pulps. **Therefore for hardwoods these “near- neutral green liquor pre-extraction conditions do meet the requirements of the IFPR concept.** At an H-factor of about 800 hours approximately 10% of the wood is dissolved, of which in the extract is identified: 22% as sugars (mostly oligomeric), 21% as acetate and 16% as lignin. Thus a disadvantage of this process is the relatively small amount sugars obtained in the extract, as well as a significant amount of degraded sugars and lignin. An advantage is the relatively high content of acetate which could be used for the production of acetic acid, a new high value chemical product in the IFBR.

The near-neutral green liquor extraction process was also applied to Loblolly Pine chips (Chapter 4.1.5). The total weight loss increases from about 4% at the mildest extraction condition of 2%

GL at 170 ^{o}C for 15 minutes to about 15% at the severest conditions of 2-6 % GL at 190 ^{o}C for 90 minutes. Sugar components in the extract were only present in their polymeric forms. The maximum yields of arabinoglucuroxylan and galactoglucomannan (GGM) were about 2 and 1%, respectively. With increasing green liquor charge, the dissolved lignin content significantly increased while that of the hemicelluloses significantly decreased. The total sugar yield in the extracts increases significantly from about 0.5% to 2.5% as the pH drops from mild alkaline (pH of 8) to acidic pH of 4.5 at 6% GL charge to 2% GL charge respectively. These results confirm that a low GL charge is preferable for higher sugar extraction yield since it would avoid prolonged time at high temperature alkaline conditions which favor extensive degradation of GGM in particular. Since it is known (chapter 4.1.3) that an acidic pH will lead to significantly lower kraft pulp yield and strength properties relative to the corresponding kraft control pulp, **the near-neutral green liquor extraction process applied to softwood does not meet the requirements of the IFPR concept**.

The adsorption of GL hardwood extract liquor onto hardwood and softwood kraft pulp to increase the total yield is reported in Chapter 4.2. Using simulated industrial GL at an extraction H-factor of about 800 hrs and 3% GL charge in a recirculating digester produced an extract containing 4.4% (on wood) of total anhydro-sugars, 2% of acetic acid and 1.3% of lignin. 80% of the sugars is xylan of which 85% is oligomeric. Since only polymeric hemicelluloses and lignin may be adsorbed on pulp (produced at a yield of about 50% from the original wood), the maximum theoretical yield increase due to adsorption may be estimated as 10% on pulp. However, direct application of raw GL hardwood extract liquor for hemicelluloses adsorption onto hardwood kraft pulp leads to a yield increase of about 1% (on pulp). With typical wet-end retention aids at a charge of 0.5% on pulp this may be increased to about 5% adsorption yield. However, most of this yield increase is lost during subsequent alkaline treatments in the bleach plant. Fortunately it was found that by performing the adsorption at alkaline conditions the major part of the adsorption loss during alkaline treatment in the bleach plant may be avoided. Thus the optimum permanent yield increase of about 3 and 1.5% (on pulp) was obtained with addition of a retention aid (charge of 0.5 and 0.1% guar gum respectively) during adsorption of GL hardwood extract liquor at optimal conditions of pH 11.5, 90 C for 60 minutes at 5% consistency. Paper sheets made from refined adsorbed pre-extraction kraft pulps. It was found that pulp beatability was improved for both hardwood and softwood pulp. Also, significant physical strength improvements were achieved for the beaten adsorbed kraft pulps. **Further study is needed to determine whether the improvements in pulp yield and properties constitute an economic scenario of this IFPR concept.**

In chapter 4.3 it was explored whether the wood solids in a hot water extract of *Acer rubrum* wood strands could be used to substitute for polystyrene as a low profile additive for the production of SMC. It was found that the use of hemicellulose extract solids did not change the water adsorption properties of the final product. Further work on the physical properties of the hemicellulose containing SMCs still need to be completed. The use of Kenaf fibers to replace glass fibers in SMC was unsuccessful due to a dramatic increase in water absorption properties.

6. ACCOMPLISHMENTS

The discovery of the "near-neutral" green liquor extraction process for hardwood was filed as a US patent application called: "Treating a lignocellulosic material", U.S. 2008142176 (2008). The inventors are: Adriaan Reinhard Pieter van Heiningen, Sung-Hoon Yoon, Haixuan Zou, Jianer Jiang and Gopal C. Goyal, i.e. the PI and two co-workers, and collaborators of International Paper (J. Jiang and G. Goyal). The discovery formed the basis for a commercial Integrated Biorefinery that will extract hemicelluloses from wood chips to make biofuel and other specialty chemicals. The pulp production process will be maintained as is proposed in the present researched IFBR concept. This Integrated Biorefinery will be constructed by Red Shield Acquisition LLC (RSA) at the Old Town kraft pulp mill in Maine. RSA in collaboration with the University of Maine will develop and commercialize the hemicellulose extraction process, the conversion of the hemicellulose sugars into butanol by fermentation, and the separation of specialty chemicals such as acetic acid from the extract. When operating the facility will produce 1.5 million gallons per year of butanol and create 16 new "green collar" jobs. The successful project will demonstrate the technical and economical feasibility to convert lignocellulosic extract to biofuel that will form the basis for a series of commercial scale biorefineries. RSA received a 30 million dollar award from DOE in January 2010 to assist RSA with the demonstration of the Integrated Biorefinery at the Old Town mill. Previously, a spare pulp digester was converted to a new extractor, and in 2009 it was demonstrated that a good hemicellulose extract could be produced, while simultaneously producing market pulp. Since then more than 250 hours of operational experience has been acquired by the mill generating a hemicellulose extract while simultaneously producing market pulp at a scale of 1000 tonnes (OD)/day of mixed northern hardwood chips.

Publications in refereed journals resulting from the IFPR research (18)

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