Application of Sequential Aqueous Steam Treatments to the Fractionation of Softwood

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Abstract

The FIRST (Feedstock Impregnation and Rapid Steam Treatment) approach was used in this study to isolate extractives, hemicellulose, lignin, fibers, and cellulosic fines of softwood. With hydrolysis and fermentation of the hemicellulose and cellulosic fines fractions, this approach produces four co-products: extractives, cellulose, lignin, and ethanol. The first unit operation uses aqueous/alcohol to remove and recover the extractive rich fraction. The second unit operation uses steam treatment to destructure the matrix and solubilize a large fraction of the hemicelluloses. The third unit operation uses alkaline delignification to dissolve a lignin fraction. The fourth unit operation uses the refining process to separate fibers from cellulosic fines. The fibers are bleached. The yields of lignin and bleached cellulose were about 20.0 kg and 38.3 kg out of 100 kg initial dry pine, respectively. The recovered hemicelluloses were 23.3 kg (containing 16.1 kg hexoses and 5.0 kg pentoses) and the cellulose fines derived hexoses amounted to 3.4 kg out of 100 kg initial dry pine. When the two liquors containing the hemicellulose sugars and the cellulose fines-derived hexoses were fermented for ethanol production, an ethanol yield of 6.8 kg was obtained.

Index Entries: Pretreatment; softwood; hydrolysis; steam explosion; fractionation; ethanol.

Introduction

The fractionation of lignocellulosic biomass for co-production of chemicals and ethanol has been investigated in this article focusing on softwoods. The latter (pine and spruce) contain 43–45% cellulose, 20–23% hemicellulose, and 28% lignin. The hemicelluloses are composed mainly of glucomannan and some xylan.

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Different processes, such as physical, chemical, hydrothermal pretreatment, have been used for the pretreatment of lignocellulosic biomass *(1)*. Physical pretreatments typically employ mechanical means to reduce feedstock particle size, thus increasing surface area. A variety of chemicals—acids, alkaline, organic solvents, and oxidizing agents—have been considered as pretreatment agents. Effective approaches include dilute-sulfuric acid *(2–4)*, ammonia *(5,6)*, and lime *(7)*. Combined physical and chemical pretreatments have been shown to be more effective than physical or chemical treatments alone *(8)*.

Aqueous-Steam Treatment

A method that has emerged as being cost effective in destructuring the lignocellulosic matrix is hydrothermal pretreatment. It refers to the use of hot water as liquid or vapor or both to pretreat biomass with no addition of external catalyst *(9,10)*. It has been found, however, that the effectiveness of steam treatment is enhanced when combined with a chemical agent that serves as a catalyst to promote the breakdown of cellulosic structure for purposes of increasing chemical reactivity and enzyme accessibility. The use of H_2SO_4 as a catalyzing agent with steam pretreatment has been the most extensively studied combination because of its effectiveness and low cost. SO_2-catalyzed steam pretreatment has also been thoroughly studied *(11,12)*.

Fractionation of biomass has been studied as an option for the simultaneous production of hemicellulose, lignin, and cellulose fractions with reasonable yield and purity *(13,14)*. Steam treatment at temperatures of about 200°C and short residence times of < 5 min are of interest for biomass fractionation. Such temperature favors destructuring and hemicellulose solubilization, while a short residence time limits depolymerization and degradation of carbohydrates. Coupling steam treatments and alkali delignification leads to the separation of hemicelluloses, lignin, and cellulose in the biomass. Their upgrading can thus be done as separate process streams: (1) water-soluble hemicellulosic-derived sugars, (2) alkali-soluble lignin, and (3) water- and alkali-insoluble cellulose fractions *(15,16)*.

The process of hydrothermal pretreatment efficiently increases enzymatic hydrolysis of hardwood and agricultural residues. Softwoods are generally recognized as being much more refractory than hardwoods or agricultural residues, owing to the fact that softwoods have a more rigid structure and contain more lignin. Softwood species require more severe steam treatment conditions with longer residence times and an acid catalyst. Acid-catalyzed steam treatment is therefore more appropriate for softwoods *(11,17)*.

Fermentation and Ethanol Production

The most frequently used microorganism for fermenting ethanol in industrial processes is *Saccharomyces cerevisiae*. This yeast can ferment

glucose and mannose—the most and second most abundant sugars in softwood. After adaptation, *S. cerevisiae* can also ferment galactose *(11)*. The third most abundant sugar in softwood is xylose. *Pichia stipitis* has been used for xylose fermentation *(18)*. Slinger et al. *(19)*, for example, reported that *P. stipitis,* NRRL Y-7124, converted 150 g/L of xylose into 52 g/L of ethanol at a yield of 0.39g/g. The fractions (hemicellulose-rich liquor and cellulosic fines) derived from the aqueous/steam fractionation of perennial forages were used as carbon sources for ethanol production by Belkacemi et al. *(20)*. The glucose-rich hydrolyzate from cellulosic fines was easily fermented to 80–90% of theoretical ethanol yield with *S. cerevisiae* or *Pachysolen tannophilus*. The pentose-rich hydrolyzate from water-soluble hemicelluloses was fermented to only 20% of the theoretical ethanol yield with *P. tannophilus.*

The objectives of this study were (1) to adapt existing methodology to the fractionation of prototype softwoods in order to isolate extractives, hemicellulose, lignin, cellulose-rich fibers, and cellulosic fines; (2) to optimize the fractionation process for cellulose fiber recovery and for dissolution of hemicelluloses as molasses; and (3) to evaluate the ethanol productivity from two streams—namely, the liquor rich in hemicelluloses and the posthydrolyzed cellulosic fines.

Materials and Methods

Feedstock

Pine chip samples (approx 1 cm as typical dimension) were collected from Cansorb Industries Corporation (Cleveland, NC) and stored in plastic bags at 5°C. The average moisture content was 32.6%. The composition (dry and ash-free basis) of the feedstock (determined using standard techniques) were as follows: glucan 48.0%, mannan 12.1%, lignin 26.1%, xylan 8.2%, galactan 3.7%, and arabinan 1.9%.

Pretreatment Screening

A screening study was conducted to determine appropriate process conditions to destructure and disaggregate the wood matrix thus facilitating solubilization of the hemicelluloses. Pine chip samples previously extracted and nonextracted with aqueous ethanol were impregnated with hot water or dilute H_2SO_4 (1%, w/w) at various temperatures (60°C, 64°C, and 80°C) and contact times (15, 60, and 360 min). The liquid/wood weight ratio used was 7.5. After pressing at 200 psig, the wet solids were steam exploded at various temperatures (190°C, 200°C, 215°C, 220°C, and 225°C) and reaction times (2, 3, and 4 min). The contents of the vessel were then suddenly discharged into hot water with 2% acid to wash the treated material. Following the washing, the oligomers were converted into

monomers by raising the temperature to the boiling point. A liquid filtrate and a wet solid lignocellulose were obtained.

The steam pretreatment was evaluated based on a severity index, which describes the severity of the pretreatment as a function of treatment time (min) and temperature (°C), where $T_{ref} = 100°C$ *(21).*

$$\log(R_0) = \log\left[\exp\left(\frac{T - T_{ref}}{14.75}\right)\right]$$

t, time (min); *T*, temperature (°C).

Aqueous/Steam Fractionation

The fractionation process and conditions used for softwood fractionation are shown in Table 1.

Aqueous Ethanol Extraction

The raw (wet) pine chip sample (2500 g) was extracted using an aqueous ethanol solution (Ethanol: H_2O, 50:50). The material was extracted at 80°C with reflux for 60 min. The aqueous ethanol plus hot water washing (95°C) and pressing led to solubilization of the extractives. Some suspended fines were observed but were not enough to be quantified.

Fractionation of Hemicellulose-Derived Sugars

The hot water washed and pressed material from the previous operation that was steam treated at 220°C for 3 min. The operation, conducted in batch mode, used approx 225 g of water-saturated material per batch. Upon discharge from the reactor (i.e., the explosion), the hot treated material was dumped into a reservoir containing hot water. The amount of water was preestablished so that the accumulated liquor from successive "explosions" reached a dissolved solids concentration of about 10 wt%. The fibrous residue was separated from the liquor by pressing. The operation simulates a countercurrent washing operation plus a screw press disengagement of the wet solids.

Posthydrolysis

The resulting hemicellulose-rich liquor generated from the previous step was then heated (100–120°C for 60 min) after addition of H_2SO_4 (2%, w/w). The oligomers derived from the hemicelluloses were then converted to simple sugars (hexoses and pentoses). The concentration of sugars in the liquor was typically between 7 and 8 wt%. Higher concentrations, up to 15 wt%, were reached by reverse osmosis as practiced in the sugar syrup sector. The liquors, within the range of sugar concentrations just indicated, were used as substrates for ethanol production.

Table 1
Fractionation Process and Parameters of the optimized process

Aqueous ethanol extraction	
Ethanol concentration	50% (w/w)
Temperature	80°C
Time of reaction	60 min
Hot water impregnation	
Liquid solid ratio	7.5
Temperature	95°C
Time of reaction	60 min
Steam treatment #1	
Temperature	220°C
Time of reaction	3 min
Post-hydrolysis	
Load of H_2SO	2% (w/w)
Time of reaction	60 min
Temperature	100–120°C
NaOH impregnation	
Load of NaOH	10.0% (w/w)
Liquid solid ratio	7.5
Temperature	20°C
Time of reaction	10min
Steam treatment #2	
Temperature	190°C
Time of reaction	3 min
Fibers bleaching	
Load of NaOH	0.4%
Load of H_2O_2	5% (w/w)
Temperature	60°C
Time of reaction	60 min
Impregnation of fines	
Load of H_2SO	6.0% (w/w)
Liquid solid ratio	7.5
Temperature	20°C
Time of reaction	15 min
Steam treatment #3	
Temperature	200°C
Time of reaction	1.5 min

Separation and Rrecovery of Lignin

Lignin was extracted with alkali (NaOH) from the water insoluble fibers (wet solid residue of initial steam treatment). The extraction method used was NaOH impregnation and steam treatment. The NaOH impregnation was conducted using a liquid/solid ratio (L/S) (5.0 and 7.5), NaOH loading of 0.4%, 8%, and 10% and impregnation temperature and time combinations of 100°C, 60 min and 20°C, 10 min. The impregnated material obtained after pressing at a pressure of 200 psig was steam

exploded at 190°C for 3 min. The contents of the vessel were discharged into water, then allowed to cool. Filtration allowed recovery of the lignin as black liquor and the delignified fiber. The alkaline-soluble lignin was easily precipitated by acid although its further processing and upgrading is to be carried out in the same alkali solution.

Fractionation of Fibers

Screening the delignified fibers generated long and short (fines) cellulose rich fibers. The long cellulose fibers were bleached with 5% H_2O_2 (60°C, 60 min) and 0.4% NaOH to obtain bleached fibers, whereas the short cellulosic fibers were subjected to a higher severity steam treatment for subsequent fermentation to ethanol.

Impregnation and Steam Ttreatment of Cellulosic Fines

The cellulosic fibers from the previous step were impregnated with 6% H_2SO_4 (liquid/solid ratio of 7.5) at 20°C for 15 min. The solid fibers obtained after impregnation and pressing at 200 psig were then steam treated at 200°C for 1.5 min. The contents of the vessel were discharged in water, allowed to cool, and then processed to extract hexose-rich liquor to be used as a substrate for ethanol production.

Fermentation

S. cerevisiae (ATCC 36859) and *P. stipitis* (ATCC 58785) were obtained from the American Type Culture Collection (Rockville, MD). Working stock cultures were grown at 26°C for 24 h on YM agar and YM broth. The inocula were started in 250-mL shake flasks with 100 mL of medium, incubated in a rotary shaker at 25–27°C and 200 rpm. Cells were harvested with 0.1% peptone solution by centrifugation at 34,000 rpm for 10 min.

The liquors obtained from the fractionation process were concentrated to sugar concentration between 5 and 10%. The liquors were supplemented with 0.5 g/L $(NH_4)_2HPO_4$, 0.025 g/L $MgSO_4 \cdot 7H_2O$, 0.1 mol/L NaH_2PO_4, and 1 g/L yeast extract. The nutrient type and amount added were based on the research method of Soderstrom et al. (3). *S. cerevisiae* and *P. stipitis* were used at a concentration of 10 g DM/L. Fermentation was performed in 250 mL flasks with a working volume of 100 mL, incubated in a rotary shaker at 30°C and 200 rpm. Samples were withdrawn every 24 h and analyzed for ethanol and sugar concentration.

Analysis

The sugar analysis was done via HPLC according to the methods established at the National Renewable Energy Laboratory. Duplicate analyses were made on a variety of samples. Deviations amounted to ± 6% over the values indicated. The ethanol and sugar analysis for the fermentation was conducted at North Carolina A &T State University using HPLC with a KC-811 ion exclusion column.

Table 2
Sugar Recovery (%) in Pretreated Residue After Different Impregnation
and Steam Treatments

Condition									
Impregnation		Steam treatment							
T (°C)	t (min)	T (°C)	t (min)	Severity	Glucose	Mannose	Xylose	Galactose	Arabinose
1%H_2SO_4, no previous treatment									
60	60	190	2	2.95	68.0	17.1	22.9	47.9	54.6
64	15	200	4	3.55	67.7	11.8	16.7	33.6	29.7
1%H_2SO_4, previous extracted with aqueous ethanol									
60	60	190	2	2.95	85.7	20.6	28.9	51.4	36.8
60	15	190	3	3.13	86.5	18.4	22.4	34.4	49.0
60	15	215	3	3.86	31.1	11.4	16.2	34.0	24.7
Hot water, no previous treatment									
60	15	220	2	3.83	92.8	34.5	36.9	38.8	19.3
60	15	215	4	3.98	92.2	32.1	41.6	50.1	38.6
60	60	215	4	3.98	95.8	27.9	40.0	47.2	36.8
80	360	225	3	4.16	90.1	22.2	33.4	44.2	36.6
Hot water, previous extracted with aqueous ethanol									
95	60	220	3	4.01	96.8	30.0	43.0	47.5	56.2

The component recovery in solid residue and dissolution in liquors was calculated based on the following equations:

$$\% \text{ recovery} = 100 \times \frac{C_{\text{in solid residues}}}{C_{\text{before treatment}}}$$

$$\% \text{ dissolution} = 100 \times \frac{C_{\text{infiltrate}}}{C_{\text{before treatment}}}$$

Results and Discussion

Screening of Pretreatment

During the screening pretreatment, the samples previously extracted with aqueous ethanol as well as the non-extracted samples were impregnated with 0.1% H_2SO_4 or just hot water and steam exploded at different severities. Tables 2 through 4 present the (a) sugar recovered in solid residue, (b) sugar dissolution in the filtrate and (c) sugar degraded after steam explosion, respectively. The sugar degraded was calculated as the difference between mass of component recovered and 100%. It can be seen from Fig. 2 that after aqueous ethanol extraction, while the extractives were solubilized carrying minor (essentially insignificant) amounts of suspended solids, most of the cellulose and hemicellulose sugars remained unhydrolyzed in the recovered fibers.

Table 3
Sugar Dissolution (%) in Liquors After Different Impregnation and
SteamTreatments

Condition									
Impregnation		Steam treatment							
T (°C)	t (min)	T (°C)	t (min)	Severity	Glucose	Mannose	Xylose	Galactose	Arabinose
1%H_2SO_4, no previous treatment									
60	60	190	2	2.95	8.2	63.0	51.9	65.9	46.0
64	15	200	4	3.55	5.6	57.0	42.0	67.2	49.4
1%H_2SO_4, previous extracted with aqueous ethanol									
60	60	190	2	2.95	12.3	72.3	68.0	74.5	47.9
60	15	190	3	3.13	12.9	67.6	60.9	66.5	53.7
60	15	215	3	3.86	41.7	90.9	24.4	93.7	60.2
Hot water, no previous treatment									
60	15	220	2	3.83	4.2	54.9	36.1	52.7	25.5
60	15	215	4	3.98	5.4	56.1	32.7	58.6	29.9
60	60	215	4	3.98	6.0	62.6	37.3	63.4	36.4
80	360	225	3	4.16	5.4	56.8	27.2	45.7	21.9
Hot water, previous extracted with aqueous ethanol									
95	60	220	3	4.01	6.7	59.7	38.0	39.4	20.7

Table 4
Degraded Sugar (%) After Different Impregnation and Steam Treatments

Condition									
Impregnation		Steam treatment							
T (°C)	t (min)	T (°C)	t (min)	Severity	Glucose	Mannose	Xylose	Galactose	Arabinose
1%H_2SO_4, no previous treatment									
60	60	190	2	2.95	23.9	20.0	25.2	—	—
64	15	200	4	3.55	26.7	31.3	41.3	—	21.0
1%H_2SO_4, previous extracted with aqueous ethanol									
60	60	190	2	2.95	2.0	7.1	3.1	—	15.3
60	15	190	3	3.13	0.6	14.0	16.7	—	—
60	15	215	3	3.86	27.2	—	59.4	—	15.1
Hot water, no previous treatment									
60	15	220	2	3.83	2.9	10.6	24.3	8.5	55.3
60	15	215	4	3.98	2.4	11.9	25.6	—	31.5
60	60	215	4	3.98	—	9.6	22.8	—	26.8
80	360	225	3	4.16	4.6	21.0	39.5	10.1	41.5
Hot water, previous extracted with aqueous ethanol									
95	60	220	3	4.01	—	10.0	19.0	13.1	23.1

For both the samples previously extracted with aqueous ethanol and the non-extracted samples, the 1% H_2SO_4 impregnation caused more solubilization of the hemicelluloses than autohydrolysis upon steam treatment. It can be seen from Table 2 that, for the samples impregnated with 1% H_2SO_4, less hemicellulosic sugars remained in the residual fiber. As

expected, more severe treatment conditions resulted in increased cellulose (potential glucose) degradation. For the previously aqueous/ethanol extracted with 1% H_2SO_4, impregnated samples, steam explosion at 215°C for 3 min. (severity 3.86) led to 41.7% solubilization and 27.2% degradation. There was only about 12% of glucan solubilization and less than 2% of degradation when the samples were steam treated at 190°C for 2 or 3 min (severity 2.95 and 3.13). The maximum glucose recovery (96.81%) in the residual fiber was obtained for samples previously extracted with aqueous ethanol, and autohydrolysis steam exploded at 220°C for 3 min (severity 4.01).

Comparing the samples previously extracted with aqueous ethanol and non-extracted samples, it can be seen that at the same treatment severity, extracted samples showed more hemicellulose solubilization and less hemicellulose degradation. For the previously aqueous-ethanol extracted samples, 12.3%, 72.3%, and 68.0% of glucan, mannan, and xylan were solubilized and 2.0%, 7.1%, and 3.1% of glucan, mannan, and xylan were degraded after 0.1% H_2SO_4 impregnated steam treatment at 190°C for 2 min (severity 2.95); however, for the previously non-extracted samples, 8.2%, 63.0%, and 51.9% glucan, mannan, and xylan was solubilized, and 23.9%, 20.0%, and 25.2% of glucan, mannan, and xylan was degraded (see Tables 2 and 3). For the hot-water-impregnated steam treatment, maximum glucan recovery (96.8%), dissolution (6.6%), and minimum glucan degradation were obtained for samples previously extracted with aqueous ethanol and exploded at 220°C for 3 min (severity 4.01). The effects of previously aqueous ethanol extraction on dissolution and degradation of other hemicellulose-derived sugars are not significant for the no-acid hot-water-impregnated steam treatment.

From the previous analysis, more glucan recovery and hemicellulose dissolution were obtained with the previously aqueous ethanol extracted samples. It was, therefore, concluded that after the aqueous ethanol extraction, the hot water washing/impregnating was sufficient, without any addition of acid, to solubilize a significant fraction of the hemicelluloses.

Process Considerations

The process experimented in this study is shown in Fig. 1. Numbers in brackets refer to mass of initial biomass feedstock present in each stream. Extractives, hemicellulose, lignin, fibers, and cellulosic fines of softwood samples were obtained by successive sequential treatments. The sugar concentrations of the process stream after each treatment are shown in Fig. 2. After aqueous ethanol extraction, hot water washing and pressing and steam treatment were followed by liquor and fiber separation; the hemicellulose-derived mono- and oligosaccharides are obtained in the filtrate. The hemicellulose-derived sugars are primarily mannose, glucose, and xylose with minor mounts galactose and arabinose. The yield of
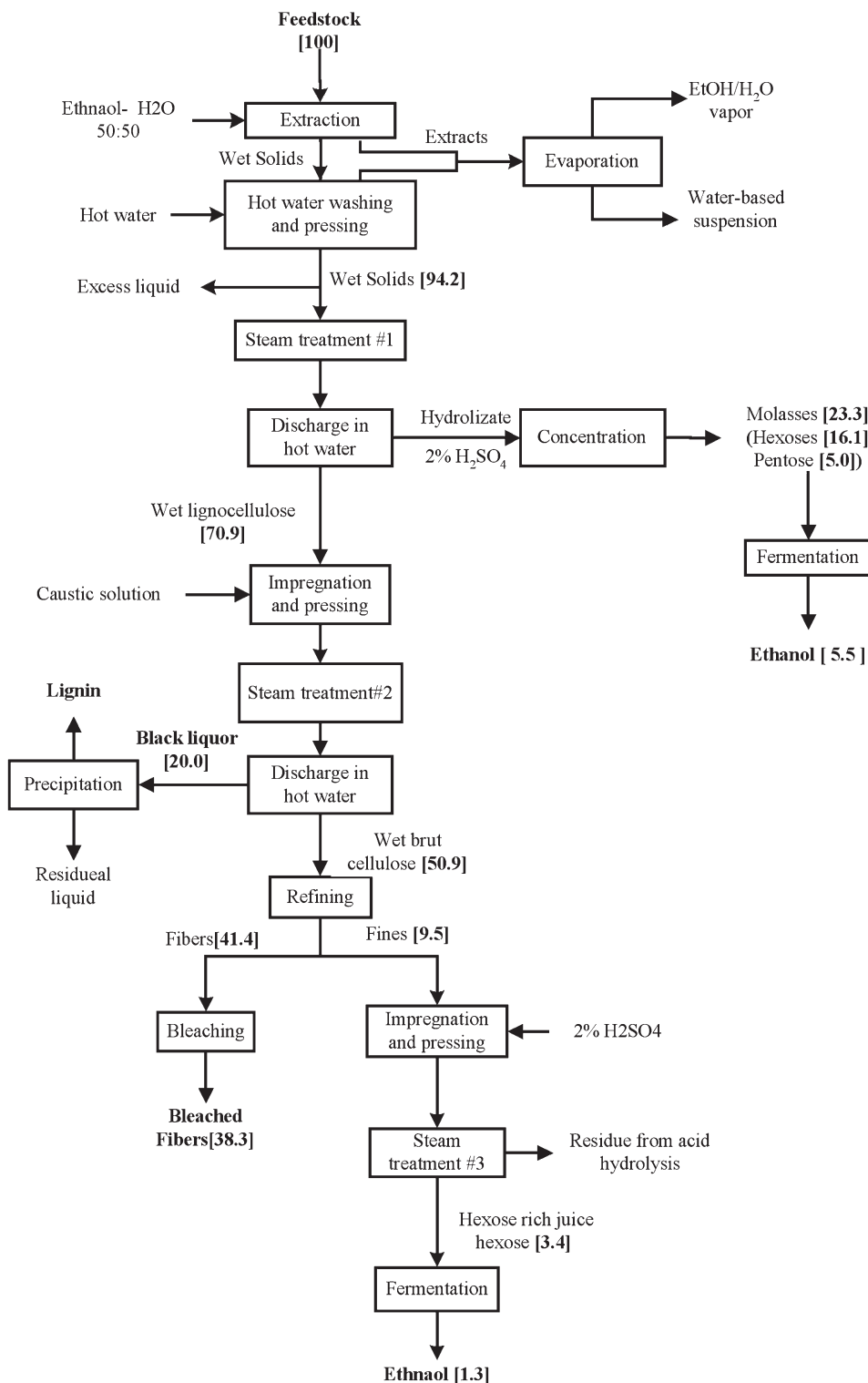
Feedstock [100]

Ethnaol- H2O 50:50 → Extraction

Wet Solids

Extracts → Evaporation → EtOH/H₂O vapor

Water-based suspension

Hot water → Hot water washing and pressing

Excess liquid ← Wet Solids **[94.2]**

Steam treatment #1

Discharge in hot water → Hydrolizate 2% H₂SO₄ → Concentration → Molasses **[23.3]** (Hexoses **[16.1]** Pentose **[5.0]**)

Fermentation

Ethanol [5.5]

Wet lignocellulose **[70.9]**

Caustic solution → Impregnation and pressing

Steam treatment#2

Lignin

Black liquor [20.0]

Precipitation ← Discharge in hot water

Residueal liquid

Wet brut cellulose **[50.9]**

Refining

Fibers**[41.4]**   Fines **[9.5]**

Bleaching   Impregnation and pressing ← 2% H2SO4

Bleached Fibers[38.3]

Steam treatment #3 → Residue from acid hydrolysis

Hexose rich juice hexose **[3.4]**

Fermentation

Ethnaol [1.3]

Fig. 1. Schematic diagram of the aqueous/steam fractionation process.

Feedstock [100g]
  1.9% arabinose, 3.7% galactose
  48.2% glucose, 8.2% xylose
  12.2% manose

Extraction EtOH-
H$_2$O(50:50)

Extracted Material [94.2]
  3.8% arabinose, 5.6% galactose
  46.1% glucose, 8.3% xylose
  13.1% manose

Filtrate [23.3]
4.6% arabinose, 13.0% galactose
18.0% glucose, 18.0 % xylose
46.0 % manose

Steam treatment
(220°C, 3min, no acid)

Post hydrolysis 2% H$_2$SO$_4$

Steam Treated Soild Residue [70.9]
  2.8% arabinose, 3.6% galactose
  59.6% glucose, 4.7% xylose
  5.3% manose

Precipitation of
black liquor

Lignin [20.0]

10% NaOH Impregnation +
steam treatment(220°C, 3min)

Refinning

Fibers[41.41]
traces % arabinose, traces% galactose
95.5% glucose, 5.0% xylose
4.1% manose

Fines[9.52]
traces% arabinose, traces% galactose
85.0% glucose, 4.8% xylose
3.8% manose

5% H$_2$O$_2$ Bleaching

6% H$_2$SO$_4$ impregantion +
steam treatment

Bleached Fibers[38.26]
traces % arabinose, traces% galactose
103.5% glucose, 5.0% xylose
4.0% manose

Filtrate [3.4]
traces% arabinose, traces% galactose
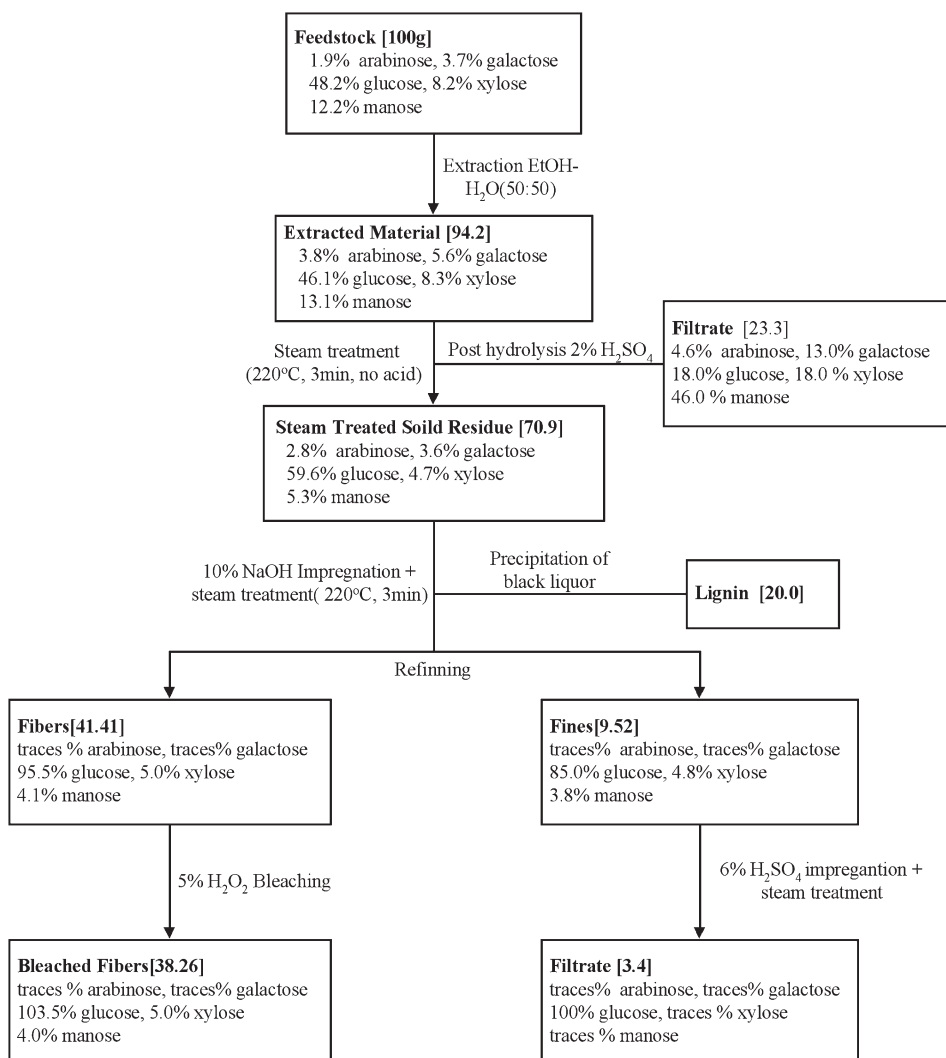100% glucose, traces % xylose
traces % manose

Fig. 2. Sugar concentration in the processing stream.

hemicellulose-rich liquor after explosion and acid hydrolysis was 23.3 kg (16.1 kg of hexoses and 5.0 kg of pentoses) out of 100 kg initial dry material.

   After the water-insoluble fiber was alkali delignified, the lignin was recovered from the alkali extraction solution by acid precipitation and filtration. Such precipitation is not needed when the lignin is to be further depolymerized to marketable oxyaromatics. The dissolution of lignin and total sugars caused by the alkaline delignification is shown in Table 5. Dissolution of 21.3% of lignin was obtained when the water-insoluble fiber was delignified in a 0.4% NaOH solution at 100°C for 60 min. Impregnation with 8% and 10% NaOH solution followed by pressing at 200 psig and steam treatment at 190°C for 3 min (severity 3.13) led to 55.8% and 81.9% dissolution

Table 5
Lignin and Sugar Dissolution After NaOH Impregnation and Steam Treatment

Condition							Lignin dissolution (%)	Total sugar dissolution (%)
NaOH Impregnation				Steam treatment				
Loading (%)	L/S	T (°C)	t (min)	T(°C)	t (min)	Severity		
0.4	5	100	60	—	—	—	21.3	15.5
8.0	7.5	20	10	190	3	3.13	55.8	13.6
10.0	7.5	20	10	190	3	3.13	81.9	21.0

Table 6
Composition Fibers and Cellulosic Fines After Alkaline
Delignification and Screening

Fraction	Composition (%)				
	Glucan	Mannan	Xylan	Lignin	Ash
Fibers	95.5	4.1	5.0	11.0	0.4
Fines	85.0	3.8	4.8	20.5	1.4

of lignin. The alkali impregnation and steam treatment also induced a 13.7% and 21.0% dissolution of total sugars (mainly hemicellulose-derived sugars) for the NaOH loading of 8% and 10%, respectively. The lignin yield after alkali delignification and steam treatment was 20.0 kg out of 100 kg initial dry material (Fig. 1).

After alkali delignification and steam treatment, the cellulose-rich solid residue was screened to remove the fines fraction from the fibers. It can be seen from Table 6 that the fiber samples have much less lignin than the fines. After bleaching with 5% hydrogen peroxide at 60°C for 60 min and 0.1 N NaOH, the lignin and ash content of the fibers was substantially reduced. The yield of cellulose after screening and bleaching was 38.3 kg out of 100 kg initial dry material (Fig. 1). Such cellulose, i.e., high quality chemical pulp, is a key objective of this work since it is produced without any use of sulfur.

Although the cellulosic fines fraction is not a suitable material for chemical pulp production, it can be used to produce ethanol via enzymatic or acid hydrolysis. In this study, the cellulosic fines were impregnated with 6.0% H_2SO_4 with liquid/solid ratio of 7.5 for 15 min at 20°C. The impregnated material was then pressed and steam treated to hydrolyze the fines for producing a hexose-rich juice. The yield of hexoses in the acid hydrolyzed juice was 3.4 kg out of 100 kg initial dry material (Fig. 1). The utilization of such cellulosic fines for ethanol production may be not economically feasible, but it was done to complete the study and provide

Table 7
Ethanol Production from Liquors Resulting from the Acid Posthydrolyzed
Dissolved Hemicelluloses and from the Steam Treated Cellulosic Fines

Fraction	Composition (%)					Ethanol	
Fraction	Glucan	Mannan	Xylan	Galactan	Arabinan	Yield (L/kg)	Efficiency (%)
Liquor rich in hemicellulose sugars	18.0	46.0	18.4	13.0	4.6	0.31	51%
Juice rich in hexose derive from fine fiber	100	—	—	—	—	0.48	75%

reference data. Use of the fines for energy production may be a simpler operation.

Ethanol Production

The fractions of liquor rich in hemicellulose and hexose derived from cellulosic fines were further studied for the ethanol production potential from these two fractions. The composition and ethanol conversion efficiency of the liquors resulting from the acid posthydrolyzed dissolved hemicelluloses and from the steam-treated cellulosic fines are shown in Table 7. These results show that *S. cerevisiae* and *P. stipitis* can be used to ferment the liquor rich in hemicellulose sugars and hexose rich juice from fine fiber to ethanol. The ethanol conversion efficiency for the two streams of hemicellulosic sugar-rich liquor and juice derived from cellulosic fines were 51% and 75%, respectively. The ethanol yields for the two streams were 0.31 L/ kg liquor rich in hemicellulosic sugar and 0.48 L/kg juice rich in cellulosic fines derived sugar, respectively. As shown in Fig. 1, a total of 7.1 kg ethanol can be produced from the two streams out of 100 kg of initial dry pine. The ethanol yield and conversion efficiency were only used to show the possibility of ethanol fermentation from the sugar-rich liquors. Fermentation conditions need to be further optimized to obtain higher yields of ethanol.

Conclusions

The FISRT approach has proved to be effective as a method for the fractionation of softwood (pine) into its constitutive polymers. Hemicellulose-rich liquor was recovered after a three-step treatment including (1) aqueous ethanol extraction, (2) hot water washing and pressing, and (3) steam treatment. The hemicellulose rich liquor was further acid hydrolyzed and fermented to produce ethanol using mixed species of *S. cerevisiae* and *P. stipitis*.

The alkali delignification allowed the separation of a lignin-rich liquor and a cellulose-rich solid residue. When combined with steam treatment, an alkali loading of about 10% is required to produce high yield of dissolved lignin.

The cellulosic fines were hydrolyzed to a hexose-rich juice using acid impregnation and steam treatment as well. The hexose-rich juice could be fermented to ethanol using yeast *S. cerevisiae.*

This study has demonstrated a successful approach to fractionate lignocellulosic biomass into four different product streams (cellulose fibers, lignin, extractives, and ethanol), which could contribute to the economic feasibility of biomass utilization.

Further optimization of the impregnation, alkali delignification, and steam treatment sequences may result in additional improvement of the lignin and fiber yields. In addition, the extractives need to be considered as a clean feedstock for the isolation of specific molecules as fine and specialty chemicals. Work in this area is being pursued. Optimization of the fermentation process and using high-performance yeast could result in increased ethanol yield from the molasses rich in hemicellulose-sugars and from the hexose-rich juice.

Integration of residual streams as feedstocks for energy production is an inherent component of the FIRST approach not discussed in this paper but essential to the overall strategy.

Acknowledgments

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