Techno-Economic Analysis of the Optimum Softwood Lignin Content for the Production of Bioethanol in a Repurposed Kraft Mill

Shufang Wu,[a,b,*] Hasan Jameel,[b] Hou-min Chang,[b] and Richard Phillips [b]

Kraft pulping is one possible pretreatment for softwood to economically produce bioethanol. This work evaluates the techno-economic potential of using the kraft process for producing bioethanol from softwoods in a repurposed or co-located kraft mill. Pretreated loblolly pine was enzymatically hydrolyzed at low enzyme dosages of 5 and 10 FPU/g of substrate. Pretreated residue with 13% lignin content had the highest sugar recovery, 32.7% and 47.7% at 5 and 10 FPU/g, respectively. The pretreated residues were oxygen delignified and refined. In all cases, oxygen delignification improved sugar recovery, while refining was mostly effective for pulps with high lignin content. At 5 FPU/g, the sugar recovery for all kraft pulps was 51 to 53% with oxygen delignification and refining. Increasing the enzyme dosage to 10 FPU/g increased the sugar recovery for these pulps to greater than 60%. Economic analysis for the pulps with different initial lignin content showed that kraft pulps with an initial lignin content of 6.7% with oxygen delignification had an ethanol yield of 285 L/ODt wood and the lowest total production cost of $0.55/L. Pulps with initial lignin content of 18.6% had a total production cost of $0.64/L with an ethanol yield of 264 L/ODt wood.

Keywords: Bioethanol; Softwood; Kraft Pulp; Biomass; Enzymatic hydrolysis

*Contact information: a: Jiangsu Provincial Key Lab of Pulp and Paper Science and Technology, Nanjing Forestry University, Nanjing 210037, China; b: Department of Forest Biomaterials, NC State University, Box 8005, Raleigh, NC 27695-8005 USA; *Corresponding author: shufang-w@hotmail.com*

INTRODUCTION

Lignocellulosic biomass is the most abundant renewable resource on earth. In the past decade, there has been a growing interest in using this biomass as feed stock for the production of bioethanol (Faaij 2006; Ragauskas *et al.* 2006; Jørgensen *et al*. 2007; Bozell 2008; Regalbuto 2009; Tilman *et al.* 2009). It is not practical to convert lignocellulosic biomass directly to ethanol; several unit operations must be employed. The modern biotechnical process of converting lignocellulosic biomass to ethanol includes pretreatment, enzymatic hydrolysis, and fermentation. In the past few decades, many pretreatment strategies have been developed to make the lignocellulosic substrate more susceptible to enzymatic hydrolysis. Following pretreatment, enzymatic hydrolysis is a key operation for the bioconversion of carbohydrates in lignocellulosic biomass into fermentable sugars by enzymatic hydrolysis. It is an important factor because the cost of the enzymes has a great impact on the economic feasibility of bioethanol production on a commercial scale. The price and dosages of cellulolytic enzymes have been progressively reduced due to intensive research by enzyme producers such as Novozymes and Genencor (Zhang *et al.* 2006). Although substantial progress has been achieved to improve the

enzymatic hydrolysis of lignocellulosic biomass, the rate of saccharification is slow and often incomplete, especially at low enzyme loadings.

Lignocellulosic biomass, especially softwood, has natural resistance to biological degradation because of its morphological structure and chemical composition. Many softwood pretreatment methods have been studied, including acid hydrolysis (Kumaar *et al*. 2012; Normark *et al*. 2014), wet oxidation (Rana *et al.* 2012; Njoku *et al.* 2012*;*), steam explosion (Brownell *et al*. 1986; Ewanick *et al.* 2007), SO_2 pretreatment (Sassner *et al*. 2005), oxygen delignification (Yang and Wyman 2008; Wu *et al*. 2012), catalytic pretreatment (Hakola *et al.* 2010), Organosolv (Pan *et al*. 2007), aqueous ammonia soaking (Kim and Lee 2007; Ko *et al*. 2009), sulfite pretreatment (Zhu *et al*. 2009), green liquor pretreatment (Wu *et al*. 2010), and alkali pretreatment (Salehian *et al*. 2013). These pretreatment methods affect enzymatic hydrolysis of biomass differently and also introduce different degrees of complexity in process technology and chemical cost/recovery. Most pretreatments for softwood are not capable of producing bioethanol from softwood economically due to the high amount of enzymes necessary for the conversion of the carbohydrates to monomeric sugars or due to the complexity of the pretreatment process. Kraft pulping is one possible pretreatment that may be used for softwood since it is capable of decreasing the lignin content to levels that are amenable to efficient enzymatic hydrolysis using low dosages of enzymes. The kraft white liquor pretreatment process can be used in a repurposed kraft pulp mill for ethanol production, taking advantage of recent pulp mill closures as a result of declining demand in pulp and paper (Gonzalez *et al*. 2011). This process can also be used in a kraft mill that repurposes only a fraction of its production for the production of bioethanol.

There are two compelling reasons to use the kraft process for lignocellulosic biomass pretreatment. First of all, the inorganic chemicals used for pretreatment are recovered and the dissolved organics and residual lignin are burned to produce energy, thereby minimizing the operating costs. The process and the equipment are proven technologies used in many pulp mills, and thus involve low risk for investment. Secondly, all fermentable sugars are recovered in a single step during the enzymatic hydrolysis stage, and this approach provides sugar at a concentration suitable for fermentation to ethanol. However, this does require that the pretreatment retains polysaccharides in the pulp while facilitating subsequent enzymatic hydrolysis for high conversion of sugar.

Softwood is a major wood resource in many parts of the world. Any repurposing of old kraft mills will probably include softwoods for economic reasons and because softwood can be grown quite readily on plantations, especially in the United States. Therefore, the current work evaluates the techno-economic potential of using the kraft process for producing bioethanol from softwoods in a repurposed or co-located kraft mill.

EXPERIMENTAL

Materials

Loblolly pine from a paper mill in the southeastern United States was used in this study. The chips were screened and accepted in the size range from 3/8 in (9.5 mm) to 5/8 in (15.9 mm) for pretreatment.

Methods

Pretreatment

Pretreatment was carried out in a 7-L M/K Digester (M/K Systems Inc., Danvers, MA) with 700 g of oven-dry (OD) chips. The chips were cooked with white liquor containing sodium hydroxide and sodium sulfide at different alkali charges (14, 16, 18, and 19% active alkali as Na_2O on wood, 25% sulfidity) and the contents pulped to the target H Factor of 600, 800, 1500, and 1800 at a maximum temperature of 170 °C with a liquor to wood ratio of 4. After pulping, the samples were washed with tap water. The chips were then disintegrated using a refiner at a 0.005-in (0.13-mm) gap and then screened using a 0.008-in (0.2-mm) screen plate. The rejects were refined with a disk gap of 0.001-in (0.03-mm) and then added back to the accepted fraction. The pulp was then centrifuged and fluffed (the fluffer is self-made one, pulp were passed through the fluffer for simple dispersion) for further processing. The yield was measured by centrifuging and fluffing samples and measuring the consistency and total weight.

Oxygen delignification and refining

Oxygen delignification was carried out in a 2.8-L reactor in an oven heated by blowing hot air. Kraft pulp (KP) (100g OD) was treated with NaOH on pulp at 10% consistency under 100 psig oxygen pressure and at 110 °C for 60 min (excluding time to temperature of 45 min). After delignification, the pulp was washed with cold tap water, centrifuged, and fluffed. Pulp yield was measured by consistency and total weight.

Refining

Pulp (30 g OD) was refined in a PFI mill (Norwegian pulp and Paper Institute, Oslo, Norway) at 10% consistency for 9,000 revolutions. After refining, pulp was collected and hydrolyzed with an enzyme mixture which was described as a section of enzymatic hydrolysis.

Enzymatic hydrolysis

An enzyme mixture was prepared by Novozymes Cellic® CTec2 cellulase enzyme and Cellic® HTec2 hemicellulase enzyme in the ratio of 1 FPU: 1.2 FXU, respectively. (FPU: Filter Paper Unit; FXU: Fungal-Xylanses Unit). The activity of the CTec2 cellulase was determined according to a standard method (Ghose 1987), and one FPU is the amount of enzyme that releases 1 μmol of glucose equivalents from Whatman No.1 filter paper *per* minute. The activity of the HTec2 hemicellulase was determined according to a standard method (Ghose 1987), and one FXU is defined as the amount of enzyme that releases 1 μmol of xylose equivalents from xylan *per* min. The enzyme dosage is expressed in FPU per gram of substrate.

Enzymatic hydrolysis was carried out with 1 g of pulp at 5% consistency with 5 and 10 FPU at pH 4.8 (acetate buffer) and 50 °C for 48 and 96 h. After enzymatic hydrolysis, the mixture was centrifuged and the supernatant was collected, boiled for 5 min, and centrifuged again. An aliquot of the supernatant was used for determination of sugar content. The residue from the enzymatic hydrolysis was washed and centrifuged (3x), freeze-dried in a water suspension, and weighed to determine the weight loss. The efficiency of enzymatic hydrolysis was estimated by sugar yield (SY) and sugar recovery (SR). The sugar yield was based on the weight of each enzymatic substrate, and sugar recovery was calculated by using the sugar yield divided by its sugar in the raw material (based on the weight of original wood).

Analytical methods

Lignin and carbohydrate contents of raw and pretreated materials were analyzed using the National Renewable Energy Laboratory (NREL) procedure (Sluiter *et al*. 2008). The acid soluble lignin (ASL) was determined by absorbance at 205 nm in an HP 8453E UV-VIS spectrometer (Agilent, Santa Clara, CA). Sugar analysis was carried out with ion chromatography (ICS-3000, Dionex, Sunnyvale, CA) using a CarboPacTMPA1 (2 × 250 mm) as the analytical column and a CarboPacTMPA1 (4 × 50 mm) as the guard column. Sodium hydroxide solution (0.1 M) was used as the eluent. The sugar contents in enzymatic hydrolyzates were measured using high-performance liquid chromatography (HPLC, Agilent Technology 1200 series; Palo Alto, CA). The concentrations of glucose, xylose, galactose, mannose, and arabinose were determined. The separation was performed by a Shodex SP0810 column with deionized water as the eluent at a flow rate of 0.6 mL/min at 80 °C.

RESULTS AND DISCUSSION

Cost of Biomass

Biomass delivered costs in the Southeast United States for seven feedstocks (Loblolly pine, Eucalyptus, Natural hardwood (mixed Southern hardwoods), Switchgrass, Miscanthus, Sweet sorghum, and Corn stover) were modeled in supply chain and economic models to deliver 453,597 dry ton *per* year to a biorefinery (Gonzalez *et al.* 2011d), considering the most recent published costs and biomass productivity (Kumar and Sokhansanj 2007; Bransby *et al*. 2005; Timber-Mart-South 2007). Biomass delivered costs for forestry feedstock were found to range from $69 to $71 *per* dry ton, and agriculture biomass delivered costs ranged from $77.6 to $102.5 *per* dry ton, as shown in Fig. 1. Lower delivered costs *per* ton of biomass and carbohydrate were found for Loblolly pine as compared to Eucalyptus and natural hardwoods. Agricultural biomass showed the highest cost *per* ton. As a result, Loblolly pine will always be an attractive source of biomass in the southern United States.

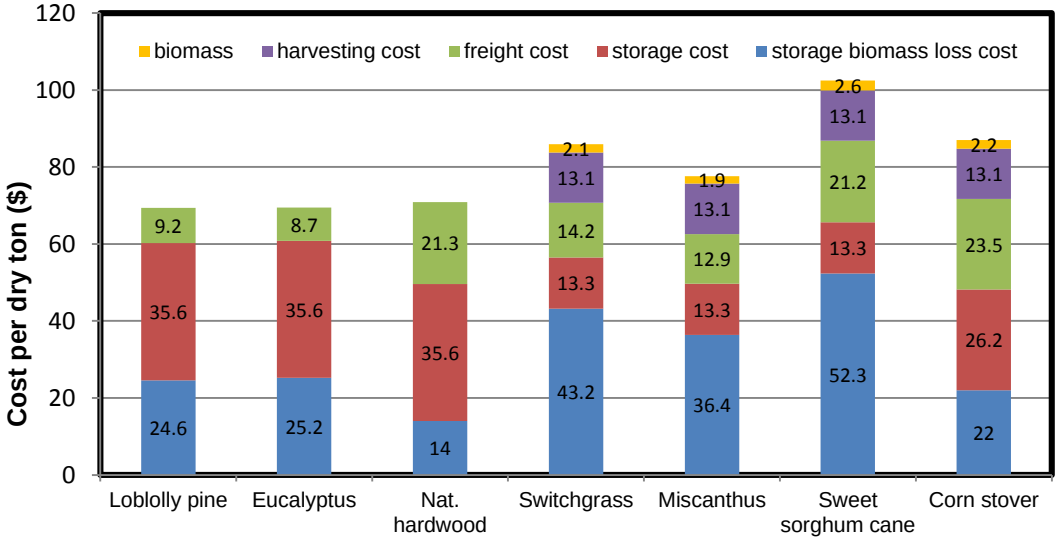

Fig. 1. Biomass delivered cost for each feedstock, considering 5% covered area and annual supply of 453,597 dry ton *per* year (Gonzalez *et al*. 2011d)

Kraft and Oxygen Pretreatments

Kraft pulping is one possible pretreatment that may be used for softwood because it is capable of decreasing the lignin content to levels that are amenable to efficient enzymatic hydrolysis using low dosages of enzymes. Southern pine chips were pulped to various lignin contents using the conditions shown in Table 1. The lignin content varied from about 18.6 to 4.8%. All the pulps were also oxygen delignified using the conditions shown in Table 2. The actual lignin content and the chemical compositions for the kraft pulps and the oxygen delignified pulps are shown in Table 3. Both the original kraft pulps and the pulps after oxygen delignification were used for enzymatic hydrolysis.

Table 1. Pulping Conditions, Lignin content, and Yield for the Various Pulps

	KP-L18	KP-L13	KP-L6	KP-L4
H-factor	600	800	1500	1800
Cooking temperature (°C)	170	170	170	170
Active alkali (%, as Na_2O)	14	16	18	19
Sulfidity (%)	25	25	25	25
Solid to Liquor ratio	4	4	4	4
Yield (%)	59.9	52.6	46.9	45.1
Lignin content, %	18.6	13.0	6.7	4.8

Table 2. Results from Oxygen Delignification and Conditions

	KP-L18-O	KP-L13-O	KP-L6-O	KP-L4-O
Oxygen press (MPa)	0.7	0.7	0.7	0.7
Temperature (°C)	110	110	110	110
NaOH charge (%)	9	8	6	5
$MgSO_4$ (%)	0.1	0.1	0.1	0.1
Time (min)	60	60	60	60
Yield (%)	80.9	87.4	96.4	96.6
Lignin content (%)	13.0	9.7	1.4	1.2
pH	8.7	9.7	9.9	10.7
Yield (% of wood)	48.5	46.0	45.2	43.6

Table 3. Chemical Composition of Pulps

	Hexosan		Pentosan			Sum	Lignin	Total Balance
	Glu	Gla	Man	Ara	Xyl			
Wood	42.8	2.4	11.0	1.3	7.3	63.8	28.0	91.8
KP-L18	37.1	0.5	3.4	0.5	5.2	46.7	11.1	57.8
KP-L13	35.2	0.4	3.2	0.4	4.7	43.9	6.8	50.7
KP-L6	35.1	0.2	3.0	0.2	3.9	42.4	3.1	45.5
KP-L4	35.3	0.0	2.9	0.2	3.7	42.1	2.2	44.3
KP-L18-O	34.7	0.4	2.5	0.5	3.7	41.8	6.3	48.1
KP-L13-O	34.6	0.3	2.4	0.4	3.2	40.9	4.5	45.4
KP-L6-O	35.8	0.0	2.4	0.1	3.1	41.4	0.9	42.3
KP-L4-O	35.6	0.0	2.3	0.1	3.0	41.0	0.7	41.7

All values as % of original wood

As can be seen in Table 1, the yield of pine pretreated by kraft ranged from 59.9 to 45.1% based on the original weight of wood, which corresponds to lignin content that varied from 18.6 to 4.3%. The carbohydrate content decreased from 63.8% to 40.9 to 46.7% (based on original wood) due to the peeling reaction and alkaline hydrolysis during pretreatment. Oxygen delignification followed by kraft pretreatment reduced the lignin

content by 0.7 to 6.3% (based on original wood) under the conditions employed; the carbohydrates content decreased to around 41%. In the kraft pretreatment, almost 80% of the mannan was lost, while only around 14 to 18% of the glucan was lost. However, during oxygen delignification, the loss of carbohydrates is quite low.

Enzymatic Hydrolysis

The weight loss of the kraft pulp was used to evaluate the effects of enzyme loading on enzymatic hydrolysis efficiency at 96 h, and the results are shown in Fig. 2. Increased enzymatic hydrolysis of wood biomass was observed with decreasing lignin content. The weight loss of all four pulps increased rapidly when enzyme dosage increased from 5 to 10 FPU/g of substrate, with the increase in enzymatic hydrolysis slower beyond 10 FPU/g, especially for the low lignin content pulps. As a result, enzyme loading 5 and 10 FPU/g of substrate was used in this study, and it is expected that economical dosage of enzymes will lie between these two enzyme dosages.

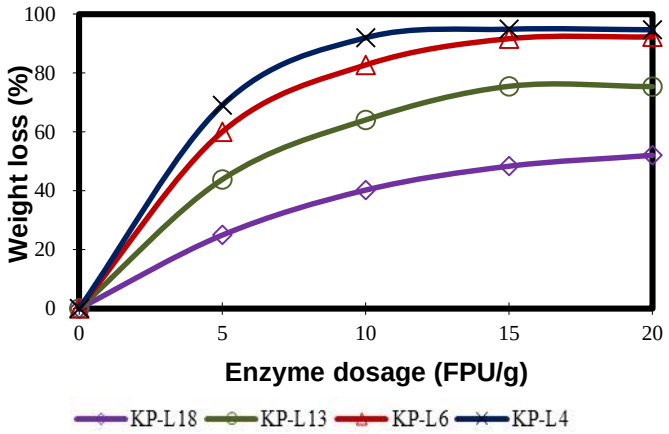

Fig. 2. Effect of enzyme dosage on EH of kraft pulp

Enzymatic hydrolysis of kraft pulps and the pulps after oxygen delignification were carried out for 48 h, and the weight loss of the pulps and the sugar yield of hydrolyzate were used to evaluate the efficiency of enzymatic hydrolysis. It should be noted that at high sugar yields, especially for the oxygen delignified pulps, the weight loss was always higher than the sugar yield, as shown in Figs. 3, 4, 5, and 6. Preliminary studies have shown that some of the sugars in the enzymatic hydrolyzate existed as a polymer instead of as a monomer, especially for softwoods (The detail is being studied and will be reported in a separate paper). This may be due to the absence of mannanase in the enzyme mixture, or perhaps due to the presence of alduronic acid instead of monomeric sugars.

Lignin is one of the major barriers to enzymatic hydrolysis, and removal of lignin usually improves enzymatic hydrolysis (Mooney *et al.* 1998; Chang and Holtzapple 2000). The enzymatic hydrolyses were evaluated based on sugar yield, which is the amount of sugars that form enzymatic hydrolysis/sugar in the pretreated residue. The results show that the lignin content is very important for sugar yield, as can be seen from Fig. 3, where at an enzyme loading of 10 FPU/g of substrate for 48 h, both the sugar yield and weight loss increased with decreasing lignin content. The sugar yield increased from 31.6% to 67.5% (based on pulp) as the lignin content decreased from 18.6% to 4.8%. Refining these pulps increased the sugar yield.

The overall process was also evaluated in terms of sugar recovery. Sugar recovery is defined as the quantity of sugar recovered from enzymatic hydrolysis divided by the amount of carbohydrates in the wood. The sugar yield from enzymatic hydrolysis and the pulp yields were used to calculate the sugar recovery. Sugar recovery takes into account the impact of both the pretreatment and the enzymatic hydrolysis process. The highest sugar recovery was achieved with KP-L6 (lignin content of 6.7%). The sugar recoveries were 43.5% and 54.8% at enzyme dosages of 5 and 10 FPU/g of substrate, respectively. However, these sugar recoveries are too low to be economically viable.

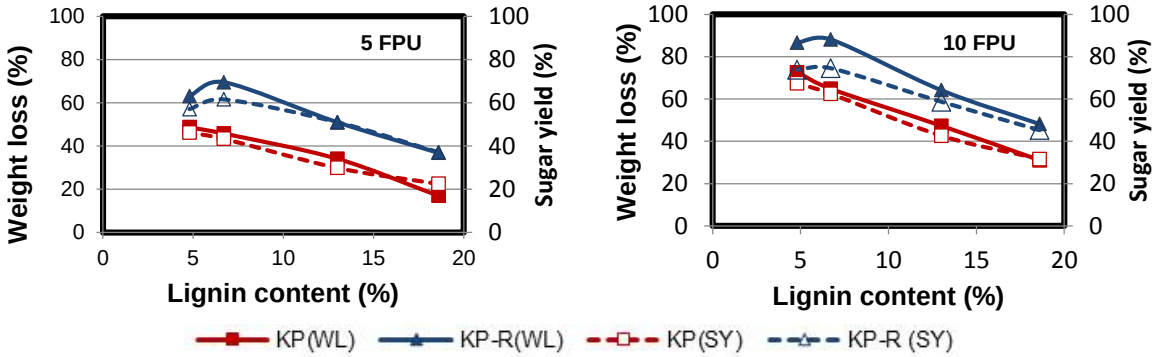

Fig. 3. Weight loss and sugar yield of kraft pretreated pine in enzymatic hydrolysis at enzyme loadings of 5 and 10 FPU/g of substrate (KP: kraft pulp, KP-R: kraft pulp with refining, WL: weight loss, SY: sugar recovery)

To further improve the sugar recovery from the enzymatic hydrolysis, oxygen delignification of the kraft pretreated pulp was carried out. As can be seen in Fig. 4, the lignin content range decreased to 2.0 to 13.0% from 4.8 to 18.6% and the sugar yield increased to 72.2 to 87.6% (based on pulp). With refining, the sugar yield improved 16%, 11%, 1%, and less than 1% for the KP-L18-O, KP-L13-O, KP-L6-O and KP-L4-O pulps, respectively. Refining improved sugar yield only for the cases with high lignin content or lower enzyme charge. When the lignin content was lower than 2% and the enzyme charge was over 10 FPU/g of substrate, the impact of refining on sugar yield was small.

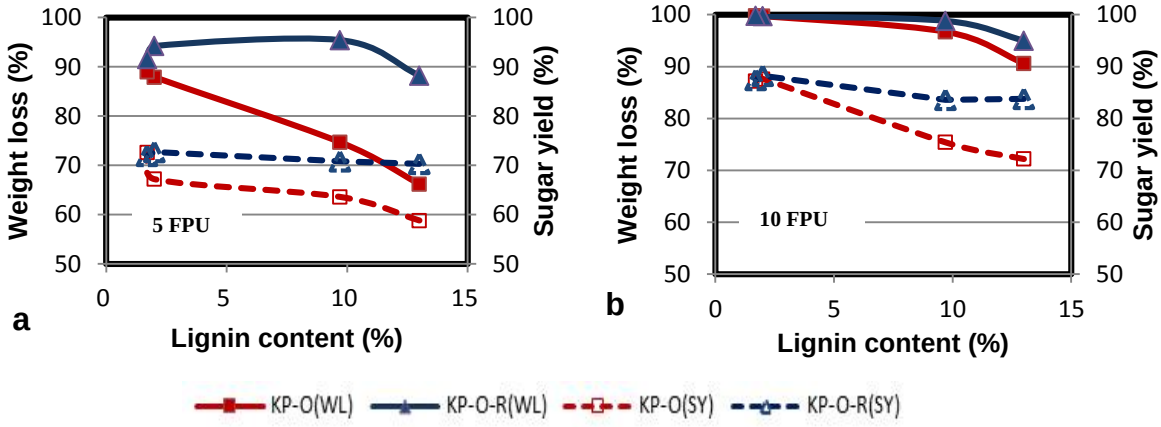

Fig. 4. Weight loss and sugar yield of kraft pretreated followed by oxygen delignified pine in enzymatic hydrolysis at enzyme loadings of (a) 5 and (b) 10 FPU/g of substrate (KP-O: kraft pulp with oxygen delignification; KP-O-R: kraft pulp with oxygen delignification and refining.)

When comparing the enzymatic hydrolysis sugar yields at the same lignin content, kraft pretreatment followed by oxygen delignification was more effective than kraft pretreatment. As shown in Fig. 5, the lignin content was 13% for both KP-L18-O and KP-L13. At an enzyme dosage of 5 FPU/g of substrate and 48 h, the sugar recoveries of KP-L18-O and refined KP-L18-O were 44.7% and 53.4%, respectively. However, the sugar recoveries of KP-L13 and refined KP-L13 were only 24.6% and 42.1%, respectively. This effect was also observed at higher enzyme dosages. With an enzyme charge of 10 FPU/g, the sugar recoveries for KP-L18-O and KP-L13 were 54.9% and 35.1%, respectively; after refining, the sugar recoveries were 63.7% and 48.5%, respectively. The reasons for the difference in enzymatic hydrolysis efficiency between kraft pretreatment and oxygen delignification may be due to the different delignification mechanism and the presence of oxidized lignin. This observation needs further evaluation and will be reported in a subsequent study.

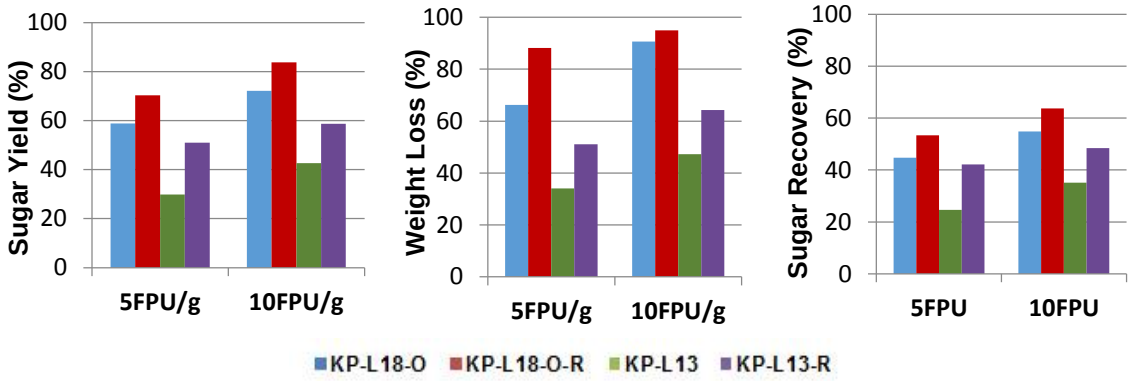

Fig. 5. Comparison of EH efficiency at the same lignin content (Any of the pulps having –R attached to the end mean the pulp was refined in PFI prior to enzymatic hydrolysis)

For some cases, enzymatic hydrolysis was carried out for both 48 and 96 h, as can be seen in Fig. 6, which shows that both weight loss and sugar yield were improved with increasing enzymatic hydrolysis time. The increase in enzymatic hydrolysis between 48 and 96 h was between 25 and 42% for unrefined kraft pulps and between 7 and 22% for refined kraft pulps. The impact of increased time was more significant for unrefined pulps. Refining increased microfibrillation, and thus made cellulose more accessible to hydrolysis enzymes. The improved the accessibility of the enzyme on the fiber probably helps with the overall kinetics of the enzymatic hydrolysis. For the kraft pulps followed by oxygen delignification, 48 h is sufficient and increasing the enzymatic hydrolysis time was not very beneficial. In a commercial operation, 48- or 96-h enzymatic hydrolysis can be used. The lower time will result in significant savings in capital for enzymatic hydrolysis.

Figure 7 shows the sugar recovery for the various options studied. At 5 FPU/g, all the sugar recoveries were below 60%. At 10 FPU/g, the highest sugar recovery achieved was about 64% for K120 oxygen delignification and refining. The sugar recovery for the K40 and K30 oxygen delignified pulp was 60% without refining because refining these two pulps did not markedly increase the sugar recovery. However, the sugar recovery for the K120 and K80 oxygen delignified pulps improved with refining and was greater than 60%. About 60% sugar recovery can be achieved by many of the options studied, and the decision of the chosen pretreatment process will depend on the overall economics and the capabilities of the mill.

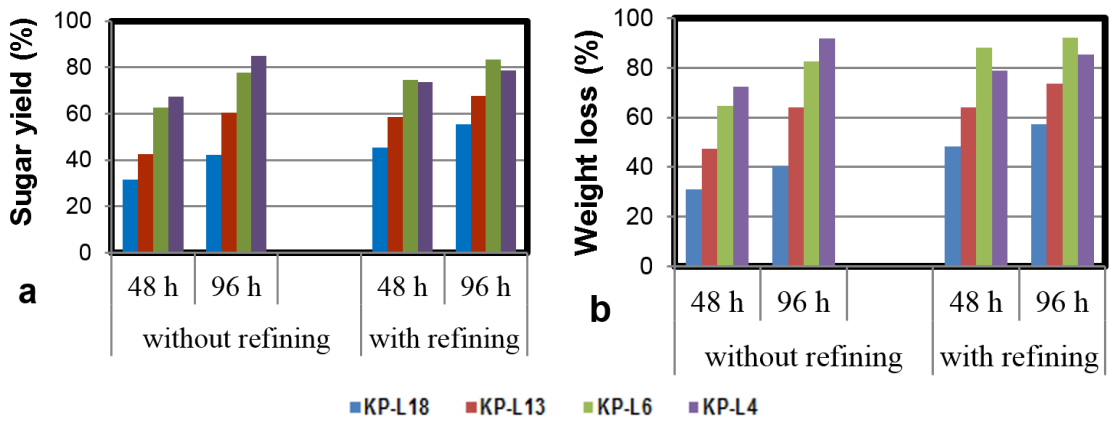

Fig. 6. (a) Sugar yield and (b) weight loss of kraft pretreated and kraft followed by oxygen delignified pine in enzymatic hydrolysis at 48 h and 96 h

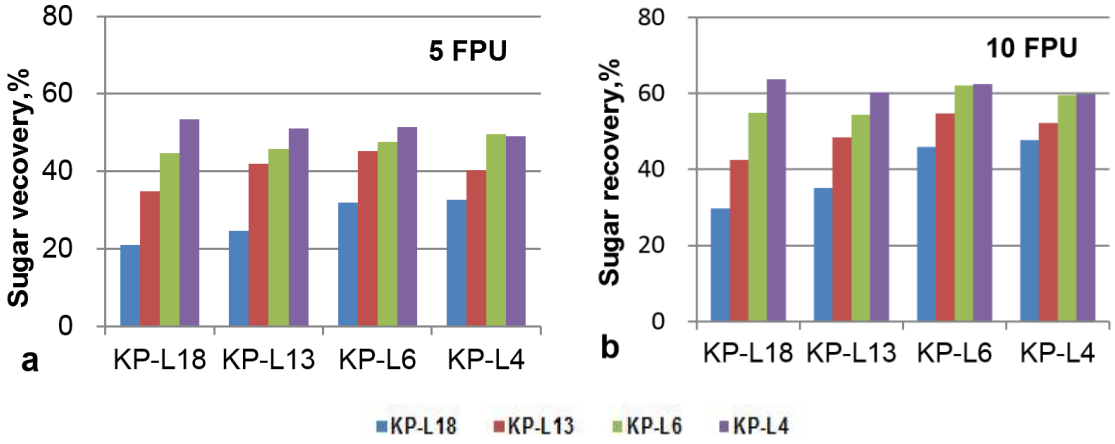

Fig. 7. Comparing the sugar recovery of kraft pretreated and kraft pretreated followed by oxygen delignified pine in enzymatic hydrolysis at enzyme loadings of (a) 5 and (b) 10 FPU/g of substrate

Economic Analysis

Economic analysis was done using standard investment finance techniques, and some key simulation results are displayed in Table 4. In brief, the financial project life was set at 15 years with a steady feedstock input of 454,545 dry metric tons per year. Total operating hours were assumed to be 96% availability (8400 hours per year). A depreciation schedule of 10 years straight line was used in the analysis. The tax rate was set at 35% with tax loss carry forward where the negative profits in previous years can be carried forward to offset part of taxes in profitable years. A terminal value in year 15 of five times of year-15 EBITDA was assumed. A discount rate of 12% was set which is consistent with other studies (Frederick *et al*. 2008; Gonzalez *et al*. 2011a). The capital cost was determined based on all the investment required for the process modifications. The equipment costs were based on old pulp and paper mill studies. All equipment costs were escalated to the present. In all cases direct cost factors were used to estimate installation. The maintenance and capital reinvestment was estimated as a function of the Replacement Asset Value (RAV), where the investment cost to replace the original asset escalates annually in cost at 2%. Other mill fixed costs were estimated at 3% of replacement asset value and overhead was assumed to be 2% of annual sales.

Figure 8 shows the process of repurposing a kraft mill for ethanol production. According to the methods, which were described by Gonzalez *et al*. (Gonzalez *et al*. 2011b), the economics for some of the different options are shown in Table 4 for 10 FPU/g enzyme dosage.

Economic analysis of pulps with different initial lignin contents (expressed as a kappa number) and 10 FPU/g enzyme dosages shows that kraft pulps with an initial lignin content of 6.7% had an ethanol yield of 285 L/ODt wood and the lowest total production cost of $0.55/L. Pulps with an initial lignin content of 18.6% had a higher total production cost of $0.64/L, and the ethanol yield was 264 L/ODt wood.

Table 4. Economic Evaluation of the Various Options

	KP-L18		KP-L13		KP-L6	
	Quantity	Enzyme 10 FPU/g Cost/unit	Quantity	Enzyme 10 FPU/g Cost/unit	Quantity	Enzyme 10 FPU/g Cost/unit
Loblolly Pine, BDt	454,545	$70.87	454,545	$70.87	454,545	$70.87
Annual Ethanol Production, million liters	120		138		130	
Ethanol Yield per BDt	264		303		285	
CAPEX, Total and per Annual Liter	$67,165,410	$0.56	$67,962,834	$0.49	$63,978,144	$0.49
Biomass Cost/liter		$0.29		$0.25		$0.27
Enzyme Cost/liter		$0.20		$0.15		$0.14
Energy Credit/liter		($0.08)		($0.04)		($0.07)
Direct Cost/liter		$0.43		$0.39		$0.36
Indirect cost/liter		$0.21		$0.19		$0.19
Cash Cost/liter		$0.55		$0.49		$0.47
Total Cost/liter		$0.64		$0.57		$0.55
Minimum Ethanol Revenue		$0.59		$0.53		$0.51
IRR (%)		12		12		12

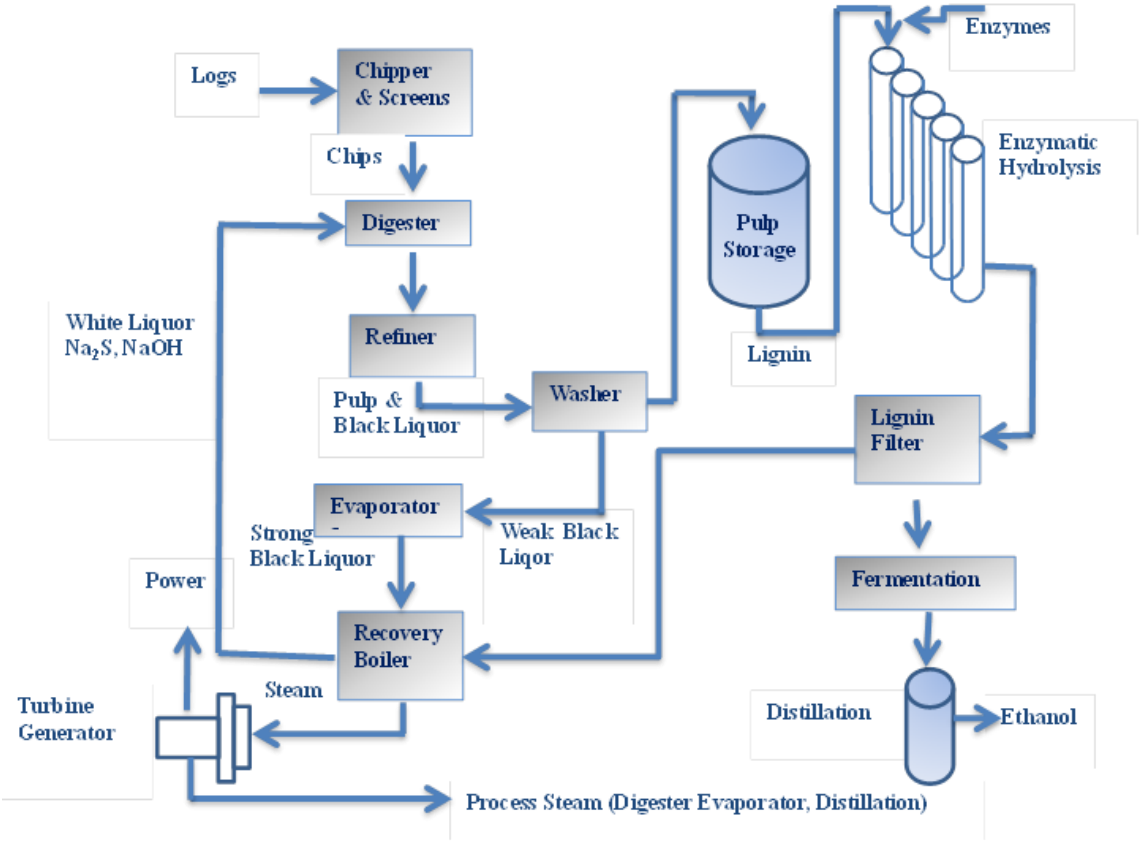

Fig. 8. Conceptual diagram of repurposing a kraft mill for ethanol production

CONCLUSIONS

1. Pretreated residue of K40 with refining had the highest sugar recoveries, 45.3% and 54.8% at 5 and 10 FPU/g, respectively. This level of sugar recovery is not economically feasible. The pretreated residues were oxygen delignified and refined to improve the overall sugar yield at low enzyme doses. In all cases, oxygen delignification improved sugar recovery, while refining was only effective for pulps with high lignin content. At 5 FPU/g, the sugar recovery for the KP-L18 and KP-L6 kraft pulps was about 53% with oxygen delignification and refining. Increasing the enzyme dosage to 10 FPU/g increased the sugar recovery for both of these pulps to greater than 60%. These levels of sugar recovery enable a competitive process for the production of ethanol from softwoods.
2. Economic analysis shows that a lignin content of 6.7% followed by oxygen and without refining had the lowest production cost, $0.55/L. This cost is lower than the current selling price for ethanol in the US.

ACKNOWLEDGMENTS

The authors are grateful for the support of a consortium of industrial members (Wood to Ethanol Consortium I) through a grant to North Carolina State University. The experiments were carried out in the Department of Forest Biomaterials, North Carolina State University.

REFERENCES CITED

Bozell, J. J. (2008). "Feedstocks for the future - Biorefinery production of chemicals from renewable carbon," *Clean* 36(8), 641-647. DOI: 10.1002/clen.200800100

Bransby, D., Smith, H., Taylor, C., and Duffy, P. (2005). "Switchgrass budget model: An interactive budget model for producing & delivering switchgrass to a bioprocessing plant," *Industrial Biotechnology* 1(2), 122-125.

Brownell, H., Yu E. K. C., and Saddler, J. N. (1986). "Steam-explosion pretreatment of wood: Effect of chip size, acid, moisture content and pressure drop," *Biotechnology and Bioengineering* 28(6), 792-801. DOI: 10.1002/bit.260280604

Chang, V. S., and Holtzapple, M.T. (2000). "Fundamental factors affecting biomass enzymatic reactivity," *Appl Biochem Biotechnol* 84-86(1-9), 5-37. DOI: 10.1385/ABAB:84-86:1-9:5

Ewanick, S. M., Bura, R., and Saddler, J. N. (2007). "Acid-catalyzed steam pretreatment of lodgepole pine and subsequent enzymatic hydrolysis and fermentation to ethanol," *Biotechnology and Bioengineering* 98(4), 737-746. DOI: 10.1002/bit.21436

Ewanick, S., Bura, R., and Saddler, J. N. (2007). "Acid-catalyzed steam pretreatment of Lodgepole pine and subsequent enzymatic hydrolysis and fermentation to ethanol," *Biotechnology and Bioengineering* 98(4), 737-746. DOI: 10.1002/bit.21436

Faaij, A. (2006). "Modern biomass conversion technologies," *Mitigation and Adaptation Strategies for Global Change* 11(2), 343-375. DOI: 10.1007/s11027-005-9004-7

Frederick Jr, W., Lien, S., Courchene, C., DeMartini, N., Ragauskas, A., and Iisa, K. (2008). "Co-production of ethanol and cellulose fiber from Southern Pine: A technical and economic assessment," *Biomass and Bioenergy* 32(12), 1293-1302. DOI: 10.1016/j.biombioe.2008.03.010

Gonzalez, R., Treasure, T., Phillips, R., Jameel, H., Saloni, D., Abt, R., and Wright, J. (2011a). "Converting *Eucalyptus* biomass into ethanol: Financial and sensitivity analysis in a co-current dilute acid process. Part II," *Biomass and Bioenergy* 35(2), 767-772. DOI: 10.1016/j.biombioe.2010.10.025

Gonzalez, R., Treasure, T., Phillips, R., Jameel, H., and Saloni, D. (2011b). "Economics of cellulosic ethanol production: Green liquor pretreatment for softwood and hardwood, greenfield and repurpose scenarios," *BioResources* 6(3), 2551-2567.

Gonzalez, R., Phillips R., Jameel H., Abt R., Pirraglia A., Saloni D., and Wright J. (2011d). "Biomass to energy in the southern united states: Supply chain and delivered cost," *BioResources* 6(3), 2954-2976.

Gonzalez, R., Treasure, T., Wright J., Saloni, D., Phillips, R., Abtb, R., and Jameel H. (2011c). "Exploring the potential of *Eucalyptus* for energy production in the Southern United States: Financial analysis of delivered biomass. Part I," *Biomass and Bioenergy* 35(2), 755-766. DOI: 10.1016/j.biombioe.2010.10.011

Hakola, M., Kallioinen, A., Kemell, M., Lahtinen, P., Lankinen, E., Leskel, M., Repo, T., Riekkola, T., Siika-aho, M., Uusitalo, J., Vuorela, S. and Weymarn, N. (2010). "Liberation of cellulose from the lignin cage: A catalytic pretreatment method for the production of cellulosic ethanol," *ChemSusChem* 3(10), 1142-1145. DOI: 10.1002/cssc.201000217

Jørgensen, H., Kristensen, J. B., and Felby, C. (2007). "Enzymatic conversion of lignocellulose into fermentable sugars: Challenges and opportunities," *Biofuels Bioproducts & Biorefining* 1(2), 119-134. DOI: 10.1002/bbb.4

Kim, T. H., and Lee, Y. Y. (2007). "Pretreatment of corn stover by soaking in aqueous ammonia at moderate temperatures," *Applied Biochemistry and Biotechnology* 137-140(1-12), 81- 92. DOI: 10.1007/s12010-007-9041-7

Ko, J. K., Bak, J. S, Jung, M. W., Lee, H. J., Choi, I. G., Kim, T. H., and Kim, K. H. (2009). "Ethanol production from rice straw using optimized aqueous ammonia soaking pretreatment and simultaneous saccharification and fermentation," *Bioresource Technology* 100(19), 4374-4380. DOI: 10.1016/j.biortech.2009.04.026

Kumar, A. and Sokhansanj, S. (2007). "Switchgrass (*Panicum vigratum* L.) delivery to a biorefinery using integrated biomass supply analysis and logistics (IBSAL) model," *Bioresource Technology* 98(5), 1033-1044. DOI: 10.1016/j.biortech.2006.04.027

Mooney, C. A., Mansfield, S. D., Touhy, M. G., and Saddler, J. N. (1998). "The effect of initial pore volume and lignin content on the enzymatic hydrolysis of softwoods," softwoods to sugars?," *Bioresource Technology* 121(10), 90-198. DOI:

Bioresource Technology 64(2), 113-119. DOI: 10.1016/S0960-8524(97)00181-8

Njoku, S. I., Ahring, B. K., and Uellendahl, H. (2012). "Pretreatment as the crucial step for a cellulosic ethanol biorefinery: Testing the efficiency of wet explosion on different types of biomass," *Bioresource Technology* 124(11), 105-110. DOI: 10.1016/j.biortech.2012.08.030

Normark, M., Winestrand, S., Lestander, T. A., and Jönsson, L. J. (2014). "Analysis, pretreatment and enzymatic saccharification of different fractions of Scots pine," *BMC Biotechnology* 14. DOI:10.1186/1472-6750-14-20

Pan, X., Xie, D., Yu, R.W., Lam, D., and Saddler, J. N. (2007). "Pretreatment of lodgepole pine killed by mountain pine beetle using the ethanol organosolv process: Fractionation and process optimization," *Ind. Eng. Chem. Res.* 46(8): 2609-2617. DOI: 10.1021/ie061576l

Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick Jr., W. J., Hallett, J. P., Leak, D. J., Liotta, C. L., *et al.* (2006). "The path forward for biofuels and biomaterials," *Science* 311(5760), 484-489. DOI: 10.1126/science.1114736

Rana, D., Rana, V., and Ahring, K. B. (2012). "Producing high sugar concentrations from loblolly pine using wet explosion pretreatment," *Bioresource Technology* 121(10), 61-67. DOI: 10.1016/j.biortech.2012.06.062

Regalbuto, J. R. (2009). "Cellulosic biofuels - Got gasoline?," *Science* 325(5942), 822-824. DOI: 10.1126/science.1174581

Salehian, P., Karimi, K., Zilouei, H., and Jeihanipour A. (2013). "Improvement of biogas production from pine wood by alkali pretreatment," *Fuel* 106(4), 484-489. DOI: 10.1016/j.fuel.2012.12.092

Sassner, P., Galbe, M., and Zacchi, G. (2005). "Steam pretreatment of *Salix* with and without SO_2 impregnation for production of bioethanol," *Appl. Biochem. Biotechnol.* 124(1-3), 1101-1117. DOI: 10.1385/ABAB:124:1-3:1101

Tilman, D., Socolow, R., Foley, J. A., Hill, J., Larson, E., Lynd, L., Pacala, S., Reilly, J., Searchinger, T., Somerville, C., and Williams, R. (2009). "Beneficial biofuels - The food, energy, and environment trilemma," *Science* 325(5938), 270-271. DOI: 10.1126/science.1177970

Timber-Mart-South. Logging rates no. 4th Quarter. Warnell School of Forestry and Natural Resources. Univeristy of Georgia, Athens, GA; 2007.

Wu, S., Chang, H., Jameel, H., and Phillips, R. (2010). "Novel green liquor pretreatment of loblolly pine chips to facilitate enzymatic hydrolysis into fermentable sugars for

ethanol production," *Journal of Wood Chemistry and Technology* 30(3), 205-218. DOI: 10.1080/02773811003746717

Wu, S., Chang, H., Jameel, H. and Phillips, R. (2012). "Effect of additives on polysaccharide retention in green liquor pretreatment of loblolly pine for enzymatic hydrolysis," *Journal of Wood Chemistry and Technology* 32(4), 317-327 DOI: 10.1080/02773813.2012.678959

Yang, B., and Wyman, C. E. (2008). "Pretreatment: The key to unlocking low-cost cellulosic ethanol," *Biofuels Bioproducts & Biorefining* 2(2), 26-4026. DOI: 10.1002/bbb.49

Zhang, P. Y. -H., Himmel, M., and Mielenz, J. (2006). "Outlook for cellulase improvement: Screening and selection strategies," *Biotechnol Advances* 24(5), 452-481. DOI: 10 1016/j.biotechadv.2006.03.003

Zhu, J. Y., Pan, X. J., Wang, G. S., and Gleisner, R. (2009). "Sulfite pretreatment (SPORL) for robust enzymatic saccharification of spruce and red pine," *Bioresource Technology* 100(8), 2411-2418. DOI: 10.1016/j.biortech.2008.10.057

Article submitted: June 18, 2014; Peer review completed: August 9, 2014; Revised version received: August 27, 2014; Second revision received and accepted: September 23, 2014; Published: September 26, 2014.