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Updates on Softwood-to-Ethanol Process Development

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Abstract

Softwoods are generally considered to be one of the most difficult lignocellulosic feedstocks to hydrolyze to sugars for fermentation, primarily owing to the nature and amount of lignin. If the inhibitory effect of lignin can be significantly reduced, softwoods may become a more useful feedstock for the bioconversion processes. Moreover, strategies developed to reduce problems with softwood lignin may also provide a means to enhance the processing of other lignocellulosic substrates. The Forest Products Biotechnology Group at the University of British Columbia has been developing softwood-to-ethanol processes with SO_2-catalyzed steam explosion and ethanol organosolv pretreatments. Lignin from the steam explosion process has relatively low reactivity and, consequently, low product value, compared with the high-value coproduct that can be obtained through organosolv. The technical and economic challenges of both processes are presented, together with suggestions for future process development.

Index Entries: SO_2 steam explosion; softwoods; ethanol; lignin; organosolv.

Introduction

Lignocellulosic biomass comprises the bulk of agricultural and forest residues potentially available for bioconversion processes. In Canada, for example, it has been estimated that the amount of lignocellulosic biomass in these residue streams totals approx 9.4 × 10^6 mt/yr (*1–9*). Almost half of these residues (4.1 × 10^6 mt) are estimated to be generated from forest harvest and wood processing operations, of which nearly 40% (1.6 × 10^6 mt) are generated in British Columbia. The majority of Canadian forests is softwood (67%) or mixed wood (18%); therefore, softwood biomass from the

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forest products industry is the most likely feedstock in these locations *(6)*. The softwood feedstock chosen for this study was Douglas-Fir (*Pseudotsuga menziesii*).

All lignocellulosics, including herbaceous biomass from agricultural plants, and woody biomass from hardwood and softwood tree species, comprise a combination of cellulose, hemicellulose, and lignin. Softwoods, including species of pine, spruce, hemlock, and fir, have a unique chemical composition that differs from agricultural residues or hardwoods. These differences create particular challenges and potential opportunities for bioconversion. There is more hemicellulose in softwoods, with a lower xylose content, and higher mannose content, relative to hardwood species. Softwoods too are characterized by having only two principal phenylpropane units (coumaryl and guaiacyl) that form the basic building blocks of lignin, whereas hardwoods and herbaceous plants have additional syringyl units *(10)*. Interestingly, this simplification of lignin chemistry increases the difficulty of delignification, owing to the enhanced stability of the lignin in condensed form when exposed to acidic conditions *(11)*.

This unique chemistry makes softwood lignocellulosic material an extremely challenging material for bioconversion. This article is focused on pretreatment technologies to overcome problems associated with delignification of Douglas-Fir in an attempt to make the entire softwood-to-ethanol process more commercially viable and feedstock-robust. Ultimately, the results of these investigations may also be applicable to the processing of agricultural residues or hardwoods and the design of bioconversion process suited to a range of substrates. For this reason, corn fiber is included as a reference substrate in the analysis.

The bioconversion of softwood to ethanol can be divided into four individual process elements: pretreatment, hydrolysis to sugars, fermentation of sugars to ethanol, and coproduct recovery. The pretreatment stage promotes the physical disruption of the lignocellulosic matrix in order to facilitate acid- or enzyme-catalyzed hydrolysis. Pretreatments can have significant implications on the configuration and efficiency of the rest of the process and, ultimately, also the economics. This study reviews the effect of changing a feedstock (Douglas-Fir and corn fiber) on the process design of a steam-explosion process and using a different pretreatment (ethanol organosolv) with the same feedstock (Douglas-Fir).

Steam-Explosion Pretreatment

Steam-explosion technology has been investigated over the course of the past 100 yr as a possible alternative to existing mechanical or chemical pulping techniques *(12)*. In this process, high-pressure, high-temperature steam is introduced into a sealed chamber containing woody lignocellulosic material in the form of chips (Fig. 1) or agricultural residues (Fig. 2). After 1–5 min, the pressure is released, causing the steam to expand within

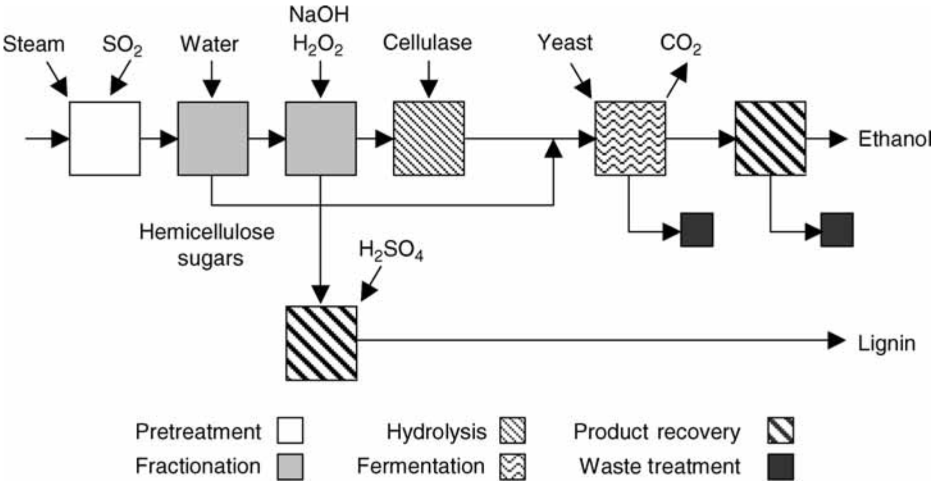

Fig. 1. Douglas-Fir steam explosion process flow diagram.

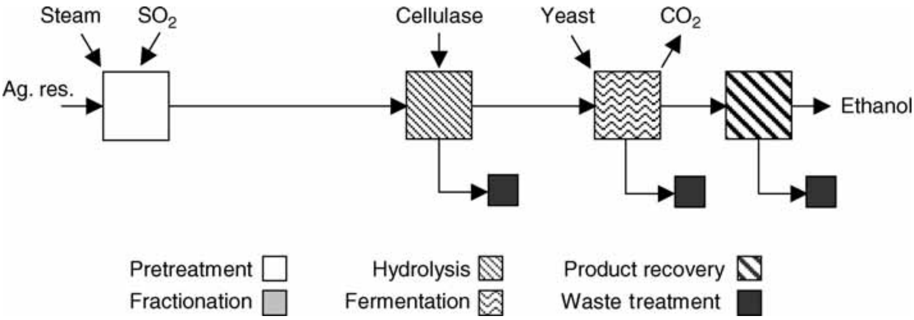

Fig. 2. Corn fiber steam explosion process flow diagram.

the lignocellulosic matrix, separating individual fibers with minimal loss of material. After cooling, the material may be further processed to ethanol as shown in the figures. This process has been shown to work fairly well with agricultural residues, and promising results have been shown with hardwood chips *(13–17)*. We have found steam explosion to be less effective for softwoods, perhaps owing to the impact of lignin condensation, in which dissolved lignin recombines into macromolecules and becomes attached to the surface of cellulose fibers. We have also found it necessary to add a catalyst to aid hemicellulose hydrolysis and removal *(18,19)*.

From our previous work we have determined the optimum conditions, material balances, and process design for SO_2-catalyzed steam explosion of Douglas-Fir *(13,20)* and corn fiber *(21)*. Owing primarily to lignin (amount and type), the processes are very different (Figs. 1 and 2). The Douglas-Fir process requires delignification before enzymatic hydrolysis whereas the corn fiber does not. This study will discuss primarily the economic implications of these differences.

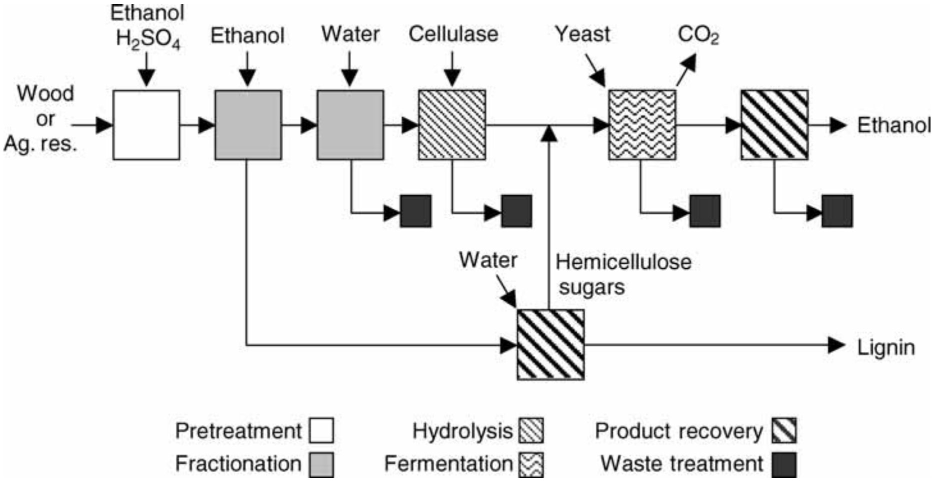

Fig. 3. Douglas-Fir organosolv process flow diagram.

Organosolv Pretreatment

The delignification of wood in a nonaqueous polar solvent is generally referred to as organosolv pulping and was originally developed for pulp and paper applications. Variations of this method have also been used for preparation of lignin in the laboratory *(10)*. The organosolv process has demonstrated certain advantages over traditional chemical pulping options, including the ability to operate at smaller scales than Kraft mills, owing to simplified requirements for recovery of pollutants. Pulp produced using this method tends to be of high quality, and has proven to be competitive with conventional pulps. Important advantages of organosolv processes are the ability to isolate and recover lignin in a relatively unadulterated form and good recovery of hemicellulosic sugars *(22)*.

The ethanol organosolv process (Fig. 3), and related processes using organic solvents, involves chemical breakdown of lignin and solubilization of lignin fragments. Ethanol is added to lignocellulosic material in the form of chips in a reactor vessel, which is then heated to process conditions and agitated to ensure good mixing. The reactor is then cooled and the fibrous lignocellulosic material is recovered for further processing to ethanol. Ultimately, because the product and solvent are the same (ethanol), only one chemical stream needs to be recovered, which simplifies the process design by reducing the number of steps required. Depolymerization of the lignin macromolecule occurs primarily through cleavage of α-aryl ether, β-aryl ether, and β-*O*-4 linkages, the latter of which influence up to 90% of delignification of softwoods *(23,24)*. It is not yet clear what the relation is between cleavage mechanism and the subsequent differences between pretreatments. Lignin condensation, a major problem in steam-explosion pulping, occurs relatively slowly owing in part to the countering effect of organic solvents that retain the lignin components in solution and slow recombination of macromolecules *(25)*.

Interest in the organosolv process from the pulp industry has been variable. In late 1980s, Repap Enterprises announced a CDN$ 45,000,000 investment in an Alcell demonstration pulp mill in New Brunswick, Canada, using hardwood chips and an aqueous ethanol liquor to produce 33 t of pulp per day *(26,27)*. It was anticipated that this plant would eventually expand into a full-scale operation *(28,29)*. Repap had initiated the construction of a 450-mtpd commercial mill in Atholville, New Brunswick. However, declining pulp prices and a glut in production capacity brought an end to this enterprise *(30)*. More recently, the Alcell pilot facility was bought by Lignol Innovations Corp., a company dedicated to producing high-value lignin products, xylose coproducts, and bioethanol. The pilot plant has been relocated to Vancouver, British Columbia, where it forms the basis of Lignol's research and development facility. Figure 3 shows the Lignol process diagram for Douglas-Fir. It is difficult to generate a full material balance from the pilot plant owing to a lack of sufficient sampling ports. For this study the material balance was derived from the work of Mirochnik *(31)* using lab-scale equipment described further in the following section.

Methods

Steam Explosion

In this study, SO_2 was chosen as the catalyst for steam explosion in part because it is less corrosive than other options, such as H_2SO_4 *(32)*. Samples of 100 g (dry) Douglas-Fir chips were impregnated overnight with anhydrous SO_2 (4.5% w/w). These samples were then steam-exploded at 195°C with a retention time of 4.5 min. These pretreatment conditions were based on past work that optimized the recovery of carbohydrate (hemicellulose and cellulose) in a hydrolyzable and fermentable form *(13,33)*. In our past work we have shown that without a further lignin removal posttreatment the cellulose hydrolysis yields are very low, i.e., 20–30% *(13,20)*. A variety of these posttreatments have been tried by a number of researchers, although for the purposes of this article a posttreatment of hot alkaline peroxide was used. The conditions for the posttreatment were 1% H_2O_2 on a w/v basis to the steam-exploded biomass, a reaction temperature of 80°C, a pH of 11.5 (adjusted through additions of NaOH), and a retention time of 45 min *(31)*.

The pretreatment for corn fiber was based on more recent work *(21)* with the same criteria and methods used for Douglas-Fir to produce the optimized conditions (190°C, 5 min, and 3% SO_2 w/w). Posttreatment was shown to be unnecessary with corn fiber. There was no attempt to assess the effect of the processing conditions for Douglas-Fir or corn fiber on the properties of lignin to produce high-value coproducts.

Organosolv Pretreatment

The pretreatment was done at 7 : 1 liquor-to-wood ratio by weight, based on oven-dry wood weight. The concentration was chosen to facilitate good coverage of Douglas-Fir wood chips by liquor. The pretreatment liquor was prepared to be 50% ethanol concentration and the H_2SO_4 was added to adjust pH to 2.4 at room temperature (20°C). The Douglas-Fir wood chips were placed in the reactor, covered with pretreatment liquor, and thoroughly mixed to ensure even liquor distribution. The reactor was sealed and placed in the heating element, and the contents of the reactor were allowed to reach the reaction temperature. The average time to temperature was approx 1 h. Temperature increases following a logarithmic curve with large increases in the early portion of heating, followed by lower increases as the desired temperature was approached. For organosolv pretreatment, experimental conditions were not predetermined and thus a partial factorial design was applied to determine a combination of temperatures (181–202°C) and reaction times (15–90 min). Based on the yield of sugars from the washed pretreated solids, optimum enzymatic hydrolysis conditions were determined to be 188°C for 15 min.

On completion of each reaction, the reactor was rapidly cooled in a bucket of ice and water. Once the temperature was below 80°C, the reactor's outlet valve was fully opened to accelerate depressurizing of the chamber. The lid of the reactor was removed when pressure in the reactor fell to zero and the strong black liquor was decanted from the pretreated substrate. The pretreated substrate was then thoroughly washed with 2 L of 70% ethanol, and weak black liquor was decanted from the substrate. Finally, the pretreated substrate was washed in water, in order to remove residual water-soluble compounds and ethanol. Warm distilled water was added at a volume of 20 times the dry weight of the substrate and the substrate was filtered through a Buchner funnel lined with FisherBrand coarse filter paper. The washed substrate was then stored in an airtight plastic bag in a 4°C refrigerator. The washed pretreated solids were sampled in order to determine moisture content, Klason lignin, acid-soluble lignin, and sugar (carbohydrate) contents.

Enzymatic Hydrolysis

Enzymatic hydrolysis on washed pretreated solids was carried out at 2% consistency in 50 m*M* acetate buffer solution (pH 4.8) in 100 mL septa vials. Two antibiotics were added to each sample in order prevent bacterial growth, 40 μg/mL of tetracycline and 30 μg/mL of cyclohexamide (Sigma Aldrich, USA). Enzymes were added based on the predetermined sugar content of the samples (IU per cellulose). Two enzyme complexes were added: celluclast (Novozymes, North America [NA]), a commercial cellulase mixture with activity of 43 filter paper units (FPU)/mL, and

Table 1
Feedstock Composition

	Douglas-Fir	Corn fiber
Moisture content	0.5	0.6
Cellulose	0.43	0.46
Hemicellulose	0.23	0.36
Galactose	0.02	0.02
Mannose	0.13	0.07
Xylose	0.03	0.17
Arabinose	0.01	0.10
Lignin	0.28	0.08
Total	0.94	0.9

Novozyme188 (Novozymes, NA), a β-glucosidase solution with activity of 346 CBU/mL. The enzymes were loaded at 7, 10, and 14 FPU/g of cellulose and at a FPU-CBU ratio of 2:1.

Enzymatic hydrolysis reactions were conducted at 45°C and mixing speed of 150 rpm for 48 h. Samples volumes of 0.5 mL were withdrawn at 1, 2, 24, and 48 h. The samples were boiled for 5 min and then centrifuged at 16,500*g* for 5 min using a microcentrifuge. The supernatant was then removed and stored in the freezer for further sugar analysis.

Measurement of Process Metrics

Samples of Douglas-Fir and corn fiber material were collected before and after pretreatment and characterized using standard methods (Table 1). Sugar concentrations were determined using a Dionex high-performance liquid chromatography system fitted with an anion exchange column (Dionex CarboPac™ PA1) and an ED40 electrochemical detector. Deionized water was used as an eluent at a flow rate of 1 mL/min; 1 *M* NaOH was used to equilibrate the column after elution of sugars. To optimize baseline stability and detector sensitivity, 0.2 *M* NaOH was added postcolumn. Klason lignin content was determined according to the TAPPI standard method T-222. The hydrolysate from Klason lignin determination was collected and analyzed for sugars and acid-soluble lignin. This sugar was determined as described earlier, except that sugar standards were autoclaved at 120°C for 1 h to compensate for changes during hydrolysis. Acid-soluble lignin was determined in the hydrolysate according to TAPPI method UM-250.

After pretreatment, cellulose factions were subjected to enzymatic hydrolysis using a mixture of cellulase (Celluclast) and β-glucosidase (Novozym 188) in a ratio of 1:2 (FPU:CBU). Batch hydrolysis experiments were conducted in duplicate at 2% consistency of glucose in 50 m*M* acetate buffer, pH 4.8, with 4-mg tetracycline per 100 mL buffer as antibiotic. Hydrolysis was performed at 45°C on a rotary shaker at 150 rpm with periodic sampling for sugar analysis. Fermentation was carried out using a spent sulfite liquor-adapted strain of *Saccharomyces cerevisiae.* The yeast was maintained at 4°C on YPD medium (2% glucose, 1% yeast extract, 2% peptone, and 1.8% agar). For each batch of fermentation, the yeast was pregrown in 50 mL of YP medium (1% glucose, 1% yeast extract, and 1% peptone) at 30°C, 150 rpm shaker for 24 h, transferred into 200 mL of fresh medium, and cultivated for a further 24 h. The culture was then centrifuged at 5000 rpm for 10 min. Cells were collected and washed twice with water, and adjusted to a density of 125 g/L for fermentation; fermentation took place in a 1-L vessel. Ethanol production following fermentation was determined by gas chromatography using a Hewlett Packard 5890 gas-chromatography system, as previously described *(33)*. Ethanol yield is expressed as percentage theoretical maximum based on initial sugar content in the washed pretreated solids, based on the assumption that 0.51 g ethanol may be produced per gram of glucose.

Technoeconomic Assessment and Monitoring Model

This study focused on evaluating the effectiveness of the two pretreatment methods described in Methods section in terms of economic performance, within the context of the entire wood-to-ethanol bioconversion process. In order to do so, a model of the bioconversion process was applied. Within the framework of existing lignocellulose-to-ethanol models, our group has developed the technoeconomic assessment and monitoring (TEAM) model, which has appeared in the past with the acronym "STEAM" *(34)*. The TEAM model is built on a Microsoft Excel platform and uses a flow sheet simulator structure to describe the subprocesses in the bioconversion of lignocellulosics to ethanol. By altering the model parameters associated with each subprocess, different scenarios can be assessed for their economic feasibility. The model is essentially a series of individual modules that represent each of the various subprocesses and the calculations associated with each of these elements. Each unit operation or piece of equipment within a subprocess has associated properties, including calculation routines. For example, details for the steam reactor contained within the steam-explosion subprocess can be accessed through the model, and the parameters of temperature, pressure, time, pH, and sample size can be controlled.

The TEAM model was used to simulate the bioconversion process for model facilities using different pretreatments and feedstocks. The model facility was assumed to be a first-generation plant able to process 35,500 metric t of dry raw material yearly, with on-line time being 355 d/yr, and producing ethanol at 94% purity. Material balances using equipment models and laboratory data were used to determine the flow rates and composition of all streams in the process. Energy balances derived from equipment models and laboratory data were used in the steam-explosion pretreatment, enzymatic hydrolysis, and fermentation sections to determine partial energy flows primarily for costing purposes. Sizing of this

Table 2
Costs Used in Evaluations

	Cost/unit (CDN$)
Chemicals	
SO_2	0.25/L
Ethanol	0/L
Defoamer	0.5/kg
NaOH (50%)	0.46/kg
H_2O_2	0.6/kg
Cellulase enzymes	3.3×10^6 FPU
H_2SO_4 (93%)	0.11/kg
Acetic acid	0.72/kg
$(NH_4)_2HPO_4$	1.5/kg
Sodium phosphate	1.6/kg
Sodium acetate	1.6/kg
Corn steep liquor	0.36/kg
Coproducts	
Solid fuel	0.03/kg
CO_2	0/kg
Utilities	
Electricity	36.6/MW h
Cooling water	0.02/L
Process water	0.24/L
Process steam	11.7/t
Other costs	
Property tax and insurance	1.5% of fixed capital
Working capital	8% of fixed capital
Contingency and fee	18% of fixed capital

equipment for the model was carried out through equipment vendor information and rules of thumb *(35,36)*.

All of the costs utilized in the TEAM model are summarized in Table 2, with the exception of labor and maintenance costs, which were both determined on an individual equipment or subprocess basis and adjusted for inflation through the chemical engineering index for that particular type of equipment. Costs for steam-explosion pretreatment, enzymatic hydrolysis, and fermentation were calculated based on laboratory observations as previously reported *(34)*. Capital and operating costs for organosolv pretreatment, lignin recovery, and ethanol recovery stage were quoted by Lignol Innovations. Equipment cost was estimated from various reports, vendor quotations, and adjusted to other capacities using vendor information or six-tenth rule. Fixed capital investment and working capital were estimated as suggested by Ulrich *(36)*. The annual cost of the fixed capital was obtained by multiplying the fixed capital investment by an annualization factor of 0.103, corresponding to an annual interest rate of 6% and a 15-yr project life. It should be noted that the interest rate used in the model is low, and that higher value on capital will skew these results. No salvage value was assumed for the equipment at the end of the pay-back period.

For the purposes of this study the raw material cost was assumed to be zero, in order to determine the influence of process design elements on production cost. Feedstock costs vary widely and are often heavily influenced by factors outside the control of a process engineer, such as transportation distance, weather, and markets. Chemical costs are based on estimates of delivery to Tembec's temiscaming pulping facility. Electricity, water, and steam costs as used in the model (Table 2) are based on British Columbia rates in late 1990s, which are lower than current costs across North America. However, all of the cost comparisons are provided on a basis relative to our current, best lab results for ethanol production from SO_2 steam explosion of Douglas-Fir, which has been assigned a normalized value of 100%. Thus, each of the costs provided in the following section should be interpreted as relative costs.

Results and Discussion

Technical Performance of Pretreatments

In Table 3, the technical metrics of steam-exploded Douglas-Fir, steam-exploded corn fiber, and ethanol organosolv-treated Douglas-Fir are compared. Several significant details should be highlighted. It is clear that the steam-explosion pretreatment is not ideal for Douglas-Fir. The recovery of glucose, hemicellulose sugars, and lignin after pretreatment is significantly lower than found with steam-exploded corn fiber, or with organosolv-treated Douglas-Fir. The slightly lower lignin recovery may serve as further evidence of the difficulty that softwood lignin poses, and the tendency found in the steam-explosion pretreatment process for lignin redeposition and condensation on the surface of fibers. Avoiding the problem of lignin condensation and redeposition is one of the primary drivers for choosing a different pretreatment method for softwoods.

One of our research goals has been to optimize the steam-explosion pretreatment in order to preserve lignin in the biomass, whereas reducing the formation of inhibitors to the hydrolysis process. In a work by Pan et al. *(37)*, it has been shown that 35.5–43.2% of lignin may be removed from steam-exploded Douglas-Fir through the application of 1% NaOH (w/w) at room temperature. This posttreatment was effective in enhancing enzymatic hydrolysis yield from 50% to 85%. Among the conclusions that may be drawn from this work is that an "active" portion of lignin impedes hydrolysis, and that lignin inhibition might be significantly reduced by selective removal or modification of this active fraction.

The inhibitory nature of lignin for enzymatic hydrolysis has being explored by Berlin et al. *(38)*, who have shown that lignin interferes with enzymatic hydrolysis by binding to the enzyme, forming a triple complex

Table 3
Technical Metrics

	Steam explosion		Organosolv
	Douglas-Fir	Corn fiber	Douglas-Fir
Glucose recovery (%)[a]	85	95	90
Hemicellulose recovery (%)[a]	74	95	90[a]
Lignin recovery (%)[a]	94	99	99
Hydrolysis yield (%)	>95	>95	>90
Substrate loading (%)[b]	2	2	2
Enzyme loading (FPU/g cellulose)	20	10	14
Hydrolysis time (h)	48	24	24
Fermentation yield (%)[c]	>90	>90	>90
Fermentation time (h)	48	6	8
Lignin opportunities	Energy only	Energy only	High value

[a] Percentage of original.
[b] Percentage on w/w basis.
[c] Percentage of theoretical.

of enzyme–substrate inhibitor. On a mass basis, lignin inhibition has been found comparable to inhibition by glucose, but not competitive in nature. Engineering of enzymes with lower lignin affinity could provide a useful strategy for improvement of cellulase activity on lignocellulosic substrates *(39)*.

The lower glucose and hemicellulose sugar recovery found with steam-explosion of Douglas-Fir is another problem that is particularly important to resolve. A significant amount of the sugars that could be utilized in ethanol production, as well as in other products, is lost during steam explosion. This may in part have to do with the physical architecture of the steam-explosion system, and the fact that soluble hemicelluloses escape in solution in the wash from this system. Recent work in our laboratory has shown that diverting this hemicellulose-soluble stream, which contains both hexoses and pentoses, to the fermentation stage and combining it with a high-consistency hydrolysate (10% w/v) has the result of doubling the initial sugar concentration to 54.3 g/L, increasing hexose sugar concentration by greater than 50%, and achieving a high-yield ethanol production of 0.46 g/g, or 90% of theoretical *(33)*. Unfortunately, this adds a level of process complexity to the system, which in turn increases costs.

Obviously, one of the goals of pretreatment should be to introduce the least amount of process complexity in order to add minimal cost to the total process. Although effective steam-explosion of Douglas-Fir may not be possible under this criterion, the method remains suitable for other substrates. Table 3 highlights the high recovery rates and relative ease of hydrolysis associated with steam-exploded agricultural residues. Corn fiber can be effectively hydrolyzed in half the time, with half the enzyme loading, when compared with Douglas-Fir. This indicates that steam-explosion pretreatment remains an effective tool for the processing of these types of agricultural wastes. Other softwoods, such as Norway spruce (*Picea abies*), may respond to steam explosion in a manner closer to corn fiber than Douglas-Fir thus eliminating the costly delignification stage *(40)*. Currently, joint efforts between UBC and the University of Lund are underway to confirm this difference in pretreatment response. The relation between pretreatment selection and feedstock characteristics is one of particular interest as the processing of lignocellulosic materials begins to enter the commercial sphere. This work indicates that other options may have to be explored for specific substrates.

Another way in which pretreatment costs may be reduced is by lowering chemical usage or the costs of delignification. Ethanol organosolv pretreatment was first undertaken for the processing of Douglas-Fir because of its ability to simultaneously achieve both of these goals. As shown in Table 3, the organosolv pretreatment with Douglas-Fir substrate compares closely with the steam-exploded corn fiber substrate. The use of ethanol as a pulping liquor means that liquor recovery and product recovery may be combined, reducing process costs and lowering chemical usage; however, it may also act as an inhibitor in the fermentation process. Finally, the lignin recovered through the organosolv process has been shown to have reactive properties that are significantly improved over steam-exploded lignin. This creates opportunities for value-added coproducts that may reduce the overall costs of delignification for this process.

Economic Performance of Pretreatments

In Fig. 4, the process economics for steam-exploded Douglas-Fir, steam-exploded corn fiber, and ethanol organosolv-treated Douglas-Fir are compared. As stated in the methodology, all of the cost comparisons are provided on a relative basis to the current best lab results for the SO_2 steam explosion of Douglas-Fir, which has been made equal to 100%. Thus, the data in Fig. 4 should be interpreted as relative costs to the steam-exploded Douglas-Fir case. In addition, no additional coproduct values, including that of lignin, are included in calculating the overall prices.

The economic performance of steam-exploded Douglas-Fir is significantly worse than corn fiber in large part owing to the fractionation (or delignification) cost associated with the process. As stated before, the unique nature of softwood lignin, and the fact that there is relatively more of this material when compared with hardwoods and agricultural residues, is in large part to blame for this issue. As stated in the preceding section, a major goal of ethanol organosolv pretreatment is to reduce process costs over steam-explosion by reducing some of the delignification costs. As shown in Fig. 4, the organosolv method is highly effective in doing so. Fractionation or delignification costs are almost completely removed in the organosolv process, which to a large degree accounts for

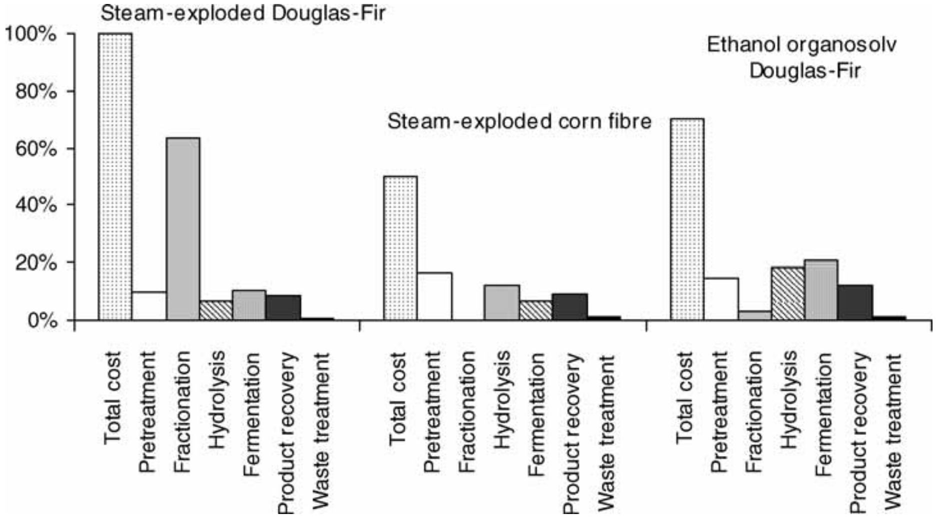

Fig. 4. Process economics for three bioconversion processes.

the reduction in relative price by almost 25% over steam-exploded Douglas-Fir.

The effectiveness of steam explosion for agricultural residues is also shown in Fig. 4. Overall process costs are relatively low for steam-exploded corn fiber, and whereas pretreatment is a significant portion of these costs, it is fairly balanced by the other subprocesses. One important message that can be taken from Fig. 4, and which holds true with each pretreatment and substrate, is the relatively low impact that the enzymatic hydrolysis subprocess has on overall costs. Previous work *(41)* identified the cost of enzymes as a critical cost issue, but lower enzyme costs have changed this scenario. Our analysis indicates that the overall cost of delignification associated with steam-explosion pretreatment remains a large hurdle to overcome for softwood lignocellulosic substrates. Alternative pretreatment technologies, such as organosolv, may prove to be a more beneficial method for handling softwood substrates.

It is worth restating that no additional coproduct values, including that of lignin, are included in calculating the overall costs shown in Fig. 4. The value of lignin coproducts has been shown to be a crucial factor in making the softwood-to-ethanol process economically viable *(13,42)*. Further economic analysis was carried out, using the TEAM model, to test the sensitivity of the bioconversion of Douglas-Fir using the organosolv pretreatment to variations in the lignin value. We found that ethanol production costs decrease significantly as the value of the lignin rises. Sufficiently high lignin values of approx 1.5 times the normalized ethanol production cost from steam-exploded Douglas-Fir render ethanol production from the bioconversion process cost neutral, as the coproduct value can cover the costs of ethanol generation. These costs include unit operations for pretreatment, fractionation and delignification, hydrolysis, fermentation, product recovery, and waste treatment. However, they do not include the cost of biomass, which could easily double the cost of the process, given current market conditions. The results indicate that high-value lignin coproducts can economically justify ethanol production, and suggest that further research should focus on developing these products.

Conclusions

In our laboratory, we have found that we can reduce lignin condensation, chemical usage, and cost for delignification, and partially reduce lignin inhibition by simply optimizing pretreatments, or through the addition of effective posttreatments. We have found that steam explosion technically works with agricultural residues, hardwoods, and softwoods, to produce ethanol and a burnable form of lignin. The choice of feedstock determines whether it can currently be done economically and the complexity of the process.

When considering softwood biomass as a substrate, lignin separation and utilization becomes a critical issue in addition to the enzymatic hydrolysis step. With steam-explosion pretreatment, a delignification stage is currently required, which is costly, producing a low-value lignin. Our laboratory is working on methods to reduce the cost of delignification with steam-explosion technology. Recent results indicate that ethanol organosolv pretreatment may be useful in entirely avoiding this stage.

Ethanol organosolv of softwoods produces a lignin with more reactive properties, as well as a cellulose fraction with good hydrolysis rates and yields. This is owing to the nature of the substrate after organosolv pretreatment, which is more amenable to hydrolysis, even with relatively high original lignin content. With ethanol organosolv pretreatment, enzyme loadings and recoveries of the solvent and hemicellulose sugars remain issues to be resolved. The ethanol organosolv process has a potential to produce both high-value lignin coproducts and low-cost ethanol, making this process a promising avenue for further investigation.

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References

1 Bowyer, J. L. and Stockmann, V. E. (2001), *Forest Prod. J.* **51(1),** 10–21.
2 CCFM (2003), *Table 5.3—Net Merchantable Volume of Roundwood Harvested by Ownership, Category, Species Group and Province/Territory, 1990–2002*, *Compendium of Canadian Forestry Statistics*, Canadian Council of Forest Ministers, Ottawa, Ontario, http://nfdp.ccfm.org/default.htm.
3 FAO (2002), *FAOStat Agriculture Data*, Food and Agriculture Organization of the United Nations, Rome, Italy, http://apps.fao.org/page/collections?subset=agriculture.
4 FAO (2002), *FAOStat Forestry Data*, Food and Agriculture Organization of the United Nations, Rome, Italy, http://apps.fao.org/page/collections?subset=forestry.
5 Mabee, W. E., Gregg, D. J., and Saddler, J. N. (2003), *Ethanol from Lignocellulosics: Views to Implementation*, Report to IEA Bioenergy Task 39, Vancouver, Canada.
6 NRCan (2003), *The State of Canada's Forests 2002–2003*, Natural Resources Canada, Ottawa, Ontario, p. 18.
7 Panshin, A. J. and de Zeeuw, C. (1980), *Textbook of Wood Technology*, 4th ed., McGraw-Hill, Toronto, Ontario, p. 213.
8 Statistics Canada (2003), *CANSIM II, Table 051-0001: Estimates of Population, by Age Group and Sex, Canada, Provinces and Territories, Annual*, Statistics Canada, Ottawa, Ontario, http://cansim2.statcan.ca.
9 Statistics Canada (2003), *Census of Agriculture*, Statistics Canada, Ottawa, Ontario, http://www.statcan.ca/english/Pgdb/census.htm.
10 Sjöström, E. (1993), *Wood Chemistry*, Academic Press, San Diego.
11 Shimada, K., Hosoya, S., and Ikeda, T. (1997), *J. Wood Chem. Technol.* **17,** 57–72.
12 Avellar, B. K. and Glasser, W. G. (1998), *Biomass Bioenerg.* **14,** 205–218.
13 Boussaid, A. L., Esteghlalian, A. R., Gregg, D. J., Lee, K. H., and Saddler, J. N. (2000), *Appl. Biochem. Biotechnol.* **84–86,** 693–705.
14 Brownell, H. H., Yu, E. K. C., and Saddler, J. N. (1986), *Biotechnol. Bioeng.* **28,** 792–801.
15 Carrasco, J. E., Saiz, M. C., Navarro, A., Soriano, P., Saez, F., and Martinez, J. M. (1994), *Appl. Biochem. Biotechnol.* **45–46,** 23–34.
16 Nguyen, Q. A., Tucker, M. P., Boynton, B. L., Keller, F. A., and Schell, D. J. (1998), *Appl. Biochem. Biotechnol.* **70–72,** 77–87.
17 Nguyen, Q. A., Tucker, M. P., Keller, F. A., Beaty, D. A., Connors, K. M., and Eddy, F. P. (1999), *Appl. Biochem. Biotechnol.* **77**, 133–142.
18 Boussaid, A., Jarvis, J., Gregg, D. J., and Saddler, J. N. (1997), In: *The Third Biomass Conference of the Americas*, Overend, R. P. and Chornet, E. (eds.), Montreal, Canada, pp. 873–880.
19 Donaldson, L. A., Wong, K. K. Y., and Mackie, K. L. (1988), *Wood Sci. Technol.* **22,** 103–114.
20 Yang, B., Boussaid, A., Mansfield, S. D., Gregg, D. J., and Saddler, J. N. (2002), *Biotechnol. Bioeng.* **77**, 678–684.
21 Bura, R. (2004), *PhD Thesis*, University of British Columbia, Vancouver, Canada.
22 Pye, E. K., Klein, W. R., Lora, J. H., and Cronlund, M. (1987), *The Alcell^{TM} Process. Solvent Pulping—Promises & Problems Conference*, Appleton, WI, pp. 55–67.
23 Bose, S. K. and Francis, R. C. (1999), *J. Pulp Paper Sci.* **25,** 425–430.
24 Meshgini, M. and Sarkanen, K. V. (1989), *Holzforschung* **43,** 239.
25 Evtiguin, D. V., Neto, C. P., and Silvestre, A. J. D. (1997), *J. Wood Chem. Technol.* **17,** 41–55.
26 Lora, J. H., Wu, C. F., Pye, E. K., and Balatinecz, J. J. (1989), In: *Lignin: Properties and Materials.* American Chemical Society Symposium Series, **397**, 312–323.
27 Mullinder, J. (1989), *Pulp Paper J.* **42(7),** 31.
28 Fales, G. (1988), *Paper Age* **104(10),** 40
29 Karl, W. (1988), *Pulp Paper J.* **41(7),** 17, 21.

30 Anonymous (1998), *PIMAs North American Papermaker* **6,** 18.

31 Mirochnik, O. (2004), *MASc Thesis*, University of British Columbia, Vancouver, Canada.

32 Galbe, M. and Zacchi, G. (2002), *Appl. Microbiol. Biotechnol.* **59,** 618–628.

33 Robinson, J., Keating, J. D., Mansfield, S. D., and Saddler, J. N. (2003), *Enzyme Microb. Technol.* **33**, 757–765.

34 Gregg, D. J. and Saddler, J. N. (1997), *Appl. Biochem. Biotechnol.* **63–65**, 609–623.

35 Perry, P. H. and Green, D. (1984), *Perry's Chemical Engineers' Handbook*, 6th ed., McGraw-Hill, New York.

36 Ulrich, G. D. (1984), *A Guide to Chemical Engineering Process Design and Economics*, Wiley and Sons, New York.

37 Pan, X., Arato, C., Gilkes, N., et al. (2005), *Biotechnol. Bioeng.* **90(4),** 473–481.

38 Kurabi, A., Berlin, A., Gilkes, N., et al. (2004), *Appl. Biochem. Biotechnol.* **121–124**, 219–230.

39 Berlin, A., Gilkes, N., Kurabi, A., et al. (2004), *Appl. Biochem. Biotechnol.* **121–124**, 163–170.

40 Wingren, A., Soderstrom, J., Galbe, M., and Zacchi, G. (2004), *Biotechnol. Prog.* **20**, 1421–1429.

41 Aden, A., Ruth, M., Ibsen, K., et al. (2002), *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover*, National Renewable Energy Lab, Golden, CO, NREL Report No. TP-510-32438.

42 Gregg, D. J., Boussaid, A., and Saddler, J. N. (1998), *Bioresour. Technol.* **63**, 7–12.