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ORIGINAL PAPER

Flexible biorefinery for producing fermentation sugars, lignin and pulp from corn stover

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Abstract A new biorefining process is presented that embodies green processing and sustainable development. In the spirit of a true biorefinery, the objective is to convert agricultural residues and other biomass feedstocks into value-added products such as fuel ethanol, dissolving pulp, and lignin for resin production. The continuous biomass fractionation process yields a liquid stream rich in hemicellulosic sugars, a lignin-rich liquid stream, and a solid cellulose stream. This paper generally discusses potential applications of the three streams and specifically provides results on the evaluation of the cellulose stream from corn stover as a source of fermentation sugars and specialty pulp. Enzymatic hydrolysis of this relatively pure cellulose stream requires significantly lower enzyme loadings because of minimal enzyme deactivation from nonspecific binding to lignin. A correlation was shown to exist between lignin removal efficiency and enzymatic digestibility. The cellulose produced was also demonstrated to be a suitable replacement for hardwood pulp, especially in the top ply of a linerboard. Also, the relatively pure nature of the cellulose renders it suitable as raw material for making dissolving pulp. This pulping approach has significantly smaller environmental footprint compared to the industry-standard kraft process because no sulfur- or chlorine-containing compounds are used. Although this option needs some minimal post-processing, it produces a higher value commodity than ethanol and, unlike ethanol, does not need extensive processing such as hydrolysis or fermentation. Potential use of low-molecular weight lignin as a raw material for wood adhesive production is discussed as well as its use as cement and feed binder. As a baseline application the hemicellulosic sugars captured in the hydrolyzate liquor can be used to produce ethanol, but potential utilization of xylose for xylitol fermentation is also feasible. Markets and values of these applications are juxtaposed with market penetration and saturation.

Keywords Biorefinery · Cellulosic ethanol · Low-molecular weight lignin · Pulping · Dissolving pulp

Introduction

Fuel ethanol is in ascendance recently. The U.S. is planning to replace its gasoline consumption by 20% over the next 10 years with alternative fuels [8]. The current fuel ethanol market in the U.S. is about 180 billion gal/year. This provides an opportunity for cellulosic ethanol since corn-based ethanol can supply only about 12.8–17.8 billion gal/year based on NCGA (National Corn Growers Association, Chesterfield, MO, USA) estimates [39].

In this context, a new biorefining process is presented that embodies green processing and sustainable development. In the spirit of a true biorefinery, the objective is to convert agricultural residues and other biomass feedstocks into value-added products such as fuel ethanol, dissolving pulp, and lignin for resin production. Successful commercialization of this technology would result in a sustainable green process with positive environmental impacts such as reduction in emissions of greenhouse gases and criteria pollutants. Although data specific for corn stover are discussed, the proposed biorefinery scenario is generically applicable to other biomass feedstocks.

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Alternative approaches to developing a biorefinery

There are several technologies for developing a biorefinery, and they fall into two major approaches: thermochemical and biochemical. This discussion is limited to the latter. In this arena, concentrated acid hydrolysis, two-stage dilute acid hydrolysis, and enzymatic hydrolysis are the major options for producing fermentation sugars for conversion into transportation fuels. Concentrated acid hydrolysis is well understood; however, the economic upside compared to its current performance is limited. Although the enzymatic approach has to bear the highest current costs due to undeveloped enzyme markets, it can leapfrog the more established acid-based routes due to its untapped long-term potential for improved economics [30]. This is attributable to advantages of the enzymatic route such as superior yields, minimal byproduct formation, low energy requirements, and milder operating conditions [15, 25, 26, 31, 54].

Enzymatic hydrolysis of cellulosics requires a pretreatment step, which in the case of PureVision is a fractionation step. Some of the chief alternatives include: dilute acid, SO_2 impregnation followed by steam explosion, and organosolv. Compared to dilute acid or SO_2 impregnation followed by steam explosion, the fractionation process discussed here differs in terms of producing a value-added lignin product rather than burning it as fuel. This approach is truer to the spirit of a biorefinery. Nonspecific binding of cellulases to lignin is a major factor during enzymatic hydrolysis and, unlike these approaches, biomass fractionation results in a low-lignin substrate. Also, instead of a batch or plug flow reactor used in these alternative pretreatments, the fractionation process uses countercurrent mode in pretreating the biomass. Although the organosolv process also produces a value-added lignin product, the fractionation process uses much shorter residence times for delignification and also produces a discrete hemicellulosic sugar stream. The following summarizes distinguishing features of the PureVision fractionation technology:

1. Ability to fractionate biomass into its three major components.
2. Continuous countercurrent pretreatment of biomass.
3. Production of low-lignin cellulose (2–4% Klason lignin on dry weight basis) that requires less enzyme, resulting in decreased cost of fermentation sugars and ethanol.
4. Production of a purified, sulfur-free, low-molecular weight (MW) lignin, which can be used as a biobased raw material for manufacturing a myriad of industrial and consumer products.
5. Process versatility to gear the cellulose stream toward glucose or pulp/cellulose derivatives.
6. Leads to flexible biorefineries that are capable of producing a wide range of petroleum-substitute products—not limited to biofuels—and shown to be economically feasible based on preliminary analysis.

Process description

The basic process schematic for biomass fractionation is shown in Fig. 1. A screw feeder meters feedstock into the extruder (a 27 mm twin-screw extruder from Entek Extruders, Lebanon, OR, USA). The feedstock is wetted with water to assist plug formation. Varying screw pitch along the length facilitates the creation of two dynamic plugs in the first stage, and high pressure pumps deliver liquids into the reactor against operating pressures. Pretreatment occurs in the first stage via autohydrolysis (although the system is designed to allow acid addition as well). The sugars formed travel countercurrently and are transported quickly—depending on the liquid flow rate—toward the exit, and degradation reactions are hindered as a result. Furthermore, solid/liquid (S/L) separation is accomplished in situ and at process temperature. A progressive cavity pump is used to discharge the first stage liquor while maintaining prevailing pressure in the reaction chamber; it is used in an unconventional way in that the pressure is progressively reduced rather than raised. No heat loss occurs because the hot dewatered pretreated solids (~50%) advance to the second stage without flashing as is the case when S/L separation is decoupled from the hydrolyzer as with a plug-flow reactor. Cocurrent delignification occurs in the second stage with sodium hydroxide as a catalyst. Two alternating valves discharge the reacted slurry while maintaining prevailing pressure. The exiting slurry is subjected to hot S/L separation, yielding a liquid stream rich in lignin and a solid cellulose product.

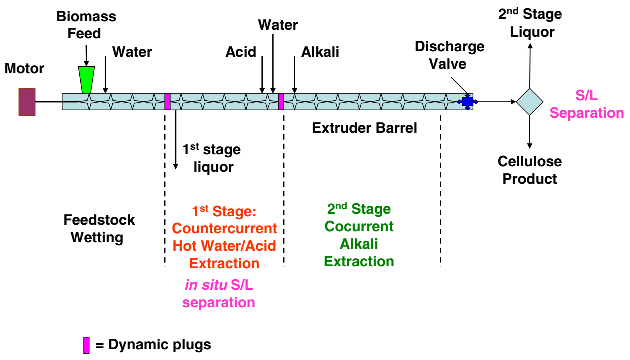

Fig. 1 Schematic of the PureVision process

Materials and methods

Feedstock

Colorado corn stover was used as feedstock, which has the following major components (dry wt basis): 35.2% glucan, 19.8% xylan and 16.9% lignin.

Enzymatic hydrolysis

NREL's (National Renewable Energy Laboratory, Golden, CO, USA) Laboratory Analytical Procedure #009 was used for enzymatic saccharification of corn stover solids [5]. Saccharification was carried out in 10 mL Oak Ridge centrifuge tubes (polycarbonate, Nalgene) and the insoluble solids concentration was 5 wt%. The tubes were placed in the shaker at about 30° angle to ensure bulk mixing. The solids were subjected to carbohydrate and Klason lignin analyses [50] prior to enzymatic hydrolysis. Sugar concentrations were determined by HPLC [51].

Pulp properties

Corn stover pulp was diluted and mixed to break any fiber bundles and dirt lumps. The mixer speed was then reduced and grit was removed from the pulp by overflow flotation of the clean pulp from the agitated bucket. The clean pulp was dewatered; this step also cleaned the pulp removing remaining dissolved materials. The resultant pulp was used in making handsheets to assess its potential.

Standard tests performed on the handsheets were grammage, caliper, tensile strength, stretch, tensile energy absorption (T.E.A.), burst (Mullen), tear, folds, stiffness and porosity (Gurley). Unbleached pine and Southern hardwood pulps from a pulp mill were washed and dewatered. The mill pulps were then refined in a laboratory valley beater. The standard composition is equal parts of pine and hardwood for the top ply of a linerboard. The blends substitute the Pure Vision pulp for various amounts of the hardwood pulp. The following TAPPI (Technical Association of the Pulp and Paper Industry, Norcross, GA, USA) standard protocols were used:

T200sp01 Laboratory beating of pulp (valley beater method)
T205sp02 Forming handsheets for physical test of pulp
T220sp01 Physical testing of pulp handsheets
T227om99 Freeness of pulp (Canadian standard freeness)
T402sp03 Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products
T403om02 Bursting strength of paper
T411om97 Thickness of paper, paperboard and combined board
T414om98 Internal tearing resistance of paper
T460om02 Air resistance of paper
T494om01 Tensile properties of paper and paperboard
T511om02 Folding endurance of paper
T566om02 Bending resistance of paper.

Results and discussion

Typical process performance and characteristics of fractions are given here for background. Operating conditions derived from preliminary optimization are summarized here. The first stage—operated at 210°C in autohydrolysis mode—yields 60–65% xylose recovery. The second stage—with operating conditions of $T = 220°\text{C}$, NaOH charge = 0.06 g/g biomass, and residence time = 11 min—achieves ≥90% overall delignification and yields about 85–90% of incoming glucan (solids fraction). Characteristics of the three fractions are given below.

First stage liquor: relatively low in furfural and HMF; furfural <2 g/L or 1.5% of xylan in the incoming corn stover feedstock (xylan equivalent basis); HMF <0.1 g/L or 0.05% of glucan in the incoming corn stover feedstock (glucan equivalent basis)
Solids stream:cellulose with a residual lignin content of 2–3 wt%; can be geared toward pulp/cellulose derivatives
Second stage liquor: low-MW lignin; average MW of 1,000 versus 50,000 for kraft lignin, which is highly condensed

A typical biorefinery would yield from 100 mt of dry corn stover: 28–30 mt dry cellulose (wet solid/slurry form), 12–15 mt dry lignin (dry solid form), and 12–13 mt dry xylose (solution form). Various applications of these fractions are discussed below.

Enzymatic hydrolysis

Economical bioconversion requires the following: a well-pretreated substrate, an efficient cellulase system, and an effective microorganism. Cellulose hydrolysis is effected via a synergistic action of endoglucanases, exoglucanases, and β-glucosidases. Table 1—adapted and extended from Esteghlalian et al. [14]—lists enzyme-, substrate- and process-related factors that affect the efficiency of enzymatic hydrolysis, which constitutes a major cost for the overall bioconversion process [17]. By minimizing residual lignin in the substrate, PureVision's process addresses the issue of irreversible binding of enzymes onto lignin.

The cellulose stream from the PureVision process is adaptable to either sugar or pulp applications; the high cellulose content of solids from the two-stage process renders

Table 1 Factors affecting enzymatic hydrolysis

Enzyme related factors	Substrate related factors	Process related factors
Reaction heterogeneity (soluble enzyme vs. insoluble substrate)	Cellulose crystallinity	Process configuration (reconciliation of optimal conditions for cellulases vs. ethanologen)
Irreversible binding of enzymes onto lignin	Cellulose degree of polymerization	Operating parameters: pH, temperature, duration
Gradual loss of synergism in cellulase mixture	Feedstock particle size	Enzyme loading
Substrate dependence of synergism and binding (specificity) of enzyme components	Lignin barrier (content and distribution)	Solids level
End-product inhibition	Substrate's available surface area (pore volume)	Bulk mixing, diffusion limitations
Thermal inactivation of enzyme	Cell wall thickness (coarseness)	Batch versus continuous mode
	Substrate composition	Reactor design

them a good candidate for making dissolving pulp, which can further be converted into cellulose derivatives. Sugar production will be discussed first. The corn stover solids from the two-stage process were subjected "as-is" to enzymatic hydrolysis using Genencor's Spezyme. The NREL base case assumes an enzyme loading of 12 FPU/g cellulose [1]; an enzyme loading of 5 FPU/g cellulose was used in this work. A typical hydrolysis profile is depicted in Fig. 2.

Figure 3 shows a direct effect of lignin removal on enzymatic digestibility. Conversely, an inverse relationship is found between lignin content of solids and enzymatic digestibility (data not shown). This is attributed to nonspecific binding of cellulases to lignin. It can also be interpreted to mean that for lower lignin content of solids we can use proportionately lower enzyme loading to achieve the same hydrolysis performance. If we assume that we can extrapolate based on the design point with lowest lignin removal efficiency, we get the plot of Fig. 4.

Other investigators have shown net enzyme consumption with lignin-free cellulose to be reduced by as much as a factor of five compared to that needed to hydrolyze biomass after conventional pretreatments that leave a significant fraction of residual lignin [35]. The predicted reductions in enzyme consumption are much smaller in our work. Cellulose digestibility in flow through reactors has also been shown to be related to xylan removal as well as lignin

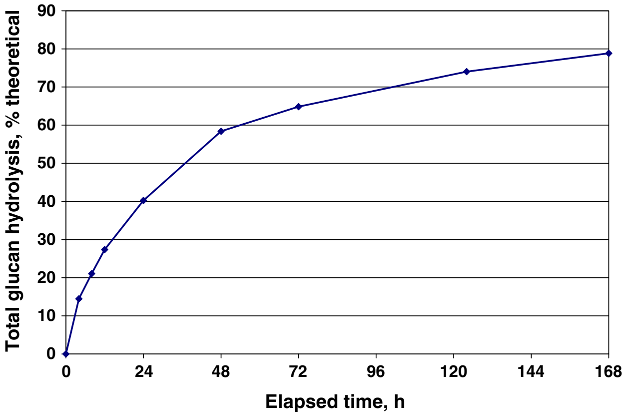

Fig. 2 Total glucan hydrolysis profile for "as is" solids containing 4% lignin at enzyme loading of 5 FPU/g cellulose

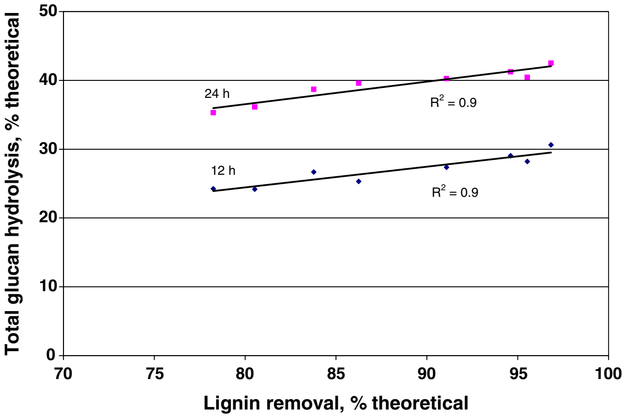

Fig. 3 Effect of lignin removal efficiency on enzymatic digestibility

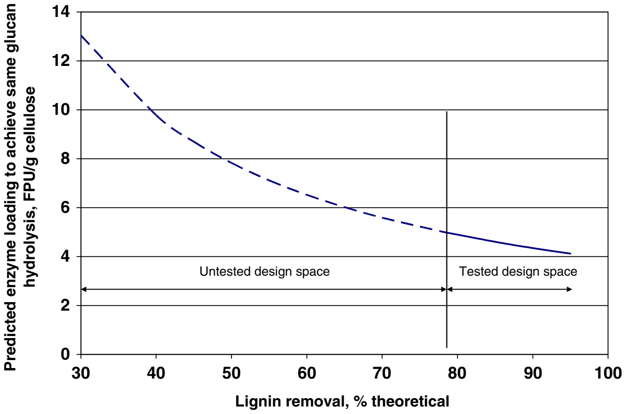

Fig. 4 Predicted enzyme loading to achieve same glucan hydrolysis

removal [58]; in our work xylan removal was constant. A caveat should be offered that extrapolation in the untested design space is probably not entirely reliable. However, some speculations can be put forward albeit with caution. Using pretreated corn stover containing 28% lignin (traditional dilute-acid pretreatment with lignin removal efficiency of 10–20% theoretical), about 80% hydrolysis was obtained by Kadam et al. [27] in 7 days with 12 FPU/g cellulose. In comparison, a similar hydrolysis performance is possible with the PureVision substrate containing 4% lignin (lignin removal efficiency of ca. 90% theoretical) at 5 FPU/g cellulose (Fig. 2). Although the predicted enzyme loading based on Fig. 4 is >12 FPU/g cellulose, these observations at least qualitatively agree with Fig. 4. Also, the former substrate was washed whereas the latter was used "as is." Hence, an unwashed substrate may need an enzyme loading closer to that predicted.

Advantages of PureVision substrate

As the solids substrate from PureVision's fractionation process is very high in cellulose (85–90%), 10% solids release enough sugars to yield about 5% ethanol during SSF/HHF (SSF: simultaneous saccharification and fermentation; HHF: hybrid hydrolysis and fermentation), which is considered as a minimum ethanol concentration in terms of reasonable distillation energy. Obviously, increasing solids loadings achieved through a fed-batch mode will yield higher sugar and hence, higher ethanol concentration thereby reducing distillation energy. It should be possible to achieve final effective solids concentration of 25% in a fed-batch mode. Figure 5 illustrates the benefit of high glucan content of pretreated solids on predicted theoretical ethanol concentration in wt% (taking into account CO_2 loss) assuming SSF/HHF with 25% solids (final effective concentration). It should be emphasized that these are merely *theoretical* (based on 0.51 g ethanol/g sugar) and not actual ethanol concentrations. The PureVision substrate, besides needing less enzyme, achieves 50% higher ethanol concentration compared to a typically pretreated substrate.

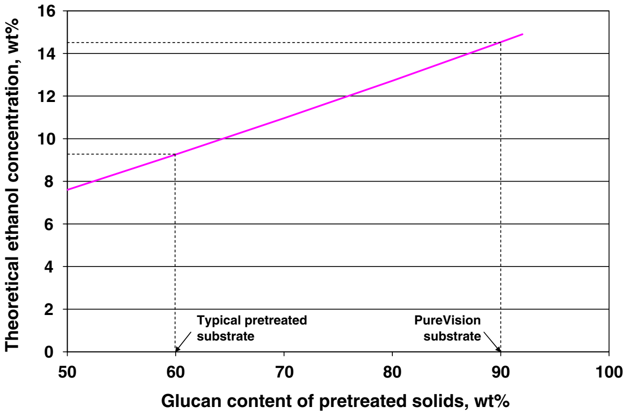

Fig. 5 Predicted effect of glucan content of pretreated solids on theoretical ethanol concentration (taking into account the loss of CO_2 mass)—25% solids during SSF/HHF

Pulp and paper production

Corn stover pulp, selected properties of which are listed in Table 2, was blended with other pulps to test it as a partial substitute for hardwood pulp. Unbleached pine and Southern hardwood pulps were utilized in conjunction with corn stover pulp. The corn stover pulp substitutes for various amounts of the hardwood pulp in the blends, with pine pulp remaining at 50%. The standard composition is equal parts of pine and hardwood, i.e., 50% each for the top ply of a linerboard, which is a target application.

Corn stover pulp substituted hardwood pulp at 10 and 30% levels, the hardwood pulp portion was reduced accordingly with softwood pulp staying constant at 50%. TAPPI standard handsheets of the pure corn stover pulp and pulp blends were made for physical testing. Figure 6 shows that corn stover pulp may be blended at 10–20% level without too much degradation of pulp properties. Corn stover pulp reduced the strength of the sheet as the proportion was increased. Bulk, porosity and Taber stiffness showed slight increase showing that the substitution of corn pulp produced open structure sheet than the standard softwood/hardwood blend. Caliper and porosity increased indicating that the corn pulp produced a more bulky, open sheet than the standard hardwood. A 10% substitution of hardwood pulp by the corn stover pulp does not show much change in most of the properties investigated.

Environmental burdens of pulping

Environmental burdens of kraft pulping process are significant (Table 3). Extremely malodorous emissions of reduced sulfur compounds—measured as total reduced sulfur (TRS)

Table 2 Selected properties of corn stover pulp

Parameters	Values
Fiber properties	
Length (mm)	0.77
Width (µm)	38.0
Coarseness (mg/m)	0.11
Curl index (%)	23.2
Weighted distribution of fibers (%)	
0–0.2 mm	15.4
0.2–0.5 mm	27.0
0.5–1.0 mm	34.2
1.0–3.0 mm	18.9
3.0–7.0 mm	4.5

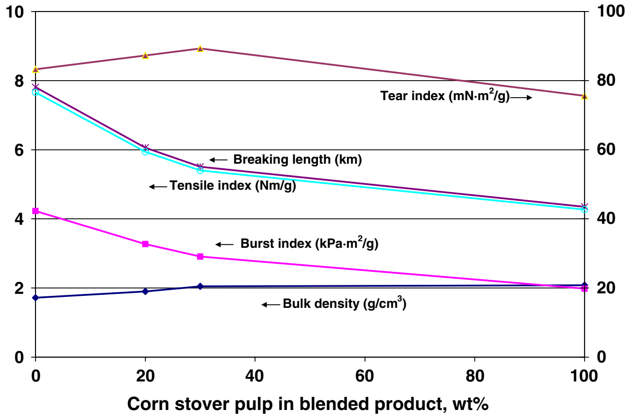

Fig. 6 Properties of blends made with pulps from the two-stage fractionation process

Table 3 Emissions from pulp and paper manufacturing

Parameter	Maximum recommended value
Air emissions	
Particulate matter	100 mg/Nm^3 (for recovery furnace)
Hydrogen sulfide	15 mg/Nm^3 (for lime kilns)
Total sulfur emitted	
Sulfite mills	1.5 kg/t ADP
Kraft and other mills	1.0 kg/t ADP
Nitrogen oxides	2.0 kg/t ADP
Liquid effluents	
COD	15 kg/t ADP
AOX	2 kg/t ADP
Total P	0.05 kg/t ADP
Total N	0.4 kg/t ADP

World-Bank [57]

ADP air dried pulp, *COD* chemical oxygen demand, *AOX* adsorbable organic halides

including hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide—occur during kraft pulping. Typical emission rates, in kg/mt of air dried pulp (ADP), are: TRS 0.3–3, particulate matter 75–150, sulfur oxides 0.5–30, nitrogen oxides 1–3, and volatile organic compounds (VOCs) 15 (from black liquor oxidation). Liquid effluents release chlorinated organic compounds (which may include dioxins, furans, and others, collectively referred to as adsorbable organic halides or AOX) at a rate of 0–4 kg/mt of ADP. Potential environmental pollution abatement for the kraft process is expected to be primarily capture and control because there are few if any methods available for eliminating pollution at the source. Sulfite mills emit 50% higher TRS than kraft mills. Green pulp production via the PureVision process will eliminate all of the TRS emissions, a major environmental benefit. Monetization of these advantages can offer a significant edge to the pulping process proposed here.

Furthermore, separation of hemicellulose before pulping is also beneficial to downstream operations. Removal of 4-*O*-methyl-α-D-glucuronic acid groups, which exist in the xylan structure as part of the arabinoglucuronoxylan in softwood and glucuronoxylan in hardwood, occurs during alkaline pulping of wood. This leads to the formation of 2-*O*-(4-deoxy-*β*-L-threo-hex-4-enopyranosyluronic acid)-D-xylitol (hexenuronic acid-D-xylitol); this structure is commonly referred to as hexenuronic acid and abbreviated as HexA [7, 32, 53]. HexA reacts with numerous bleaching agents, such as ozone, chlorine dioxide or peracids [3, 6, 55], and thus consumes these expensive and environmentally malevolent chemicals. HexA is responsible for as much as half of the bleach demand for hardwood kraft pulps. Ragauskas and Perine [43] recommend a prehydrolysis step of hot-water extraction prior to pulping since it improves delignification during pulp bleaching. They claim that this is one of the two fundamental approaches that would transform pulp mills into forest biorefineries, the other being the use of black liquor as a source of chemicals, followed by gasification of liquor residuals. Hence, prehydrolysis is expected to be equally beneficial as practiced in the PureVision process, and the pulp thus produced will require less bleaching chemicals. Also, this fractionation approach recovers lignin as an intermediate that can be used in making chemicals such as adhesives.

Short fiber pulps

Although it is considered necessary in North America to use long fibers, i.e., with a fiber length of 2–4 mm, short fiber pulps are routinely used elsewhere in the world. In the manufacture of printing and writing papers long fibers have a tendency to flocculate and hence, it is necessary to shorten the fibers by beating. With short fiber pulps only a low-intensity beating is needed to attain the necessary sheet strength. Concomitantly, short fibers contribute to smoother surface and higher opacity. Although some printing papers are manufactured from 100% hardwood pulp, about 20% of long fiber pulp is necessary to enhance the wet strength of the paper web when passing through the press section of the paper machine, especially the faster machines. For low-grade wrapping kraft papers, the furnish can be made up of mostly short fiber pulp, with a small amount of long fiber pulps. Corrugating board is made of one or several layers of corrugating medium covered on one or both sides by kraft liner or chip-board. However, the best corrugating medium product is manufactured from a neutral sulfite semichemical short fiber pulp. Thus, for the most important grades of papers, short fiber pulps can be used.

Average fiber lengths for various hardwoods range from 0.65 to 1.85 mm [21, 42]. Corn stover fibers from the PureVision process are then similar in length to eucalyptus fibers which have fiber length of 0.65 mm. Eucalyptus is widely used in Brazil and S. Africa. Eucalyptus fiber length is small; it is actually the shortest hardwood fiber available. Hence, the corn stover fibers may be used in selected paper applications.

Dissolving pulp

Cellulose is a polymer with a molecular formula $(C_6H_{10}O_5)_n$. Dissolving pulp is a high-purity cellulose pulp with low levels of hemicellulose and lignin; typical dissolving pulp specifications are tabulated in Table 4. These pulps are treated to form soluble reactive carbohydrate chains that are then extruded into fibers or films. This relatively pure cellulose is well suited as a raw material for various cellulose-based products such as staple fibers, films, cellulose ethers (carboxymethyl, ethyl, methyl), cellulose esters (acetates, propionates, butyrates) and regenerated celluloses such as viscose and microcrystalline cellulose.

Dissolving pulp production

Dissolving pulp was produced until World War II exclusively from purified cotton linters. For lower purity applications such as for viscose, it was produced via the acid sulfite process using somewhat higher temperature and acidity in concert with longer cooking times to remove more of the hemicellulose. The customary kraft process is not proficient in hemicelluloses removal, and residual pentosans interfere with the chemical conversion of cellulose to viscose, cellulose ethers or acetates. The hemicelluloses can only be effectively solubilized when exposing wood chips to acid hydrolysis prior to alkaline pulping. Currently, dissolving pulp is produced via the acid sulfite and prehydrolysis kraft processes. The acid sulfite process is the most common, but suffers from a disadvantage of pulps with a broad MW distribution of cellulose.

A method for making dissolving pulp from cellulosic fiber is disclosed in the patent literature [19, 24]. The fiber is treated in a three-stage sequence: (1) alkali extraction stage, (2) xylanase treatment stage, and (3) additional alkali extraction stage. Placing the xylanase treatment stage between two alkali extraction stages yields a dissolving pulp exhibiting both a very low xylan content of about ≤2.6 wt% and a very low mannan content of about ≤1.5 wt%. In their process, these low xylan and mannan levels could not be achieved with treatments of only an alkali extraction stage, only a xylanase treatment stage, or only two stages of a xylanase treatment stage and an alkali extraction stage. In an alternative process for producing dissolving pulps, most of the hemicellulose is removed in a prehydrolysis step followed by sulfate pulping to high cellulose pulps containing small amounts of hemicellulose. This pulp is then extracted with NaOH (50–150 g/L) at a temperature of 10–60°C and washed to remove any residual hemicellulose from the pulp. The pulp exhibits reduced swelling tendencies, improved mercerizing properties, and reduced energy needs in the process [29].

Table 4 Corn stover pulp versus typical dissolving pulp specifications (dry wt%)

Component	Specification	Corn stover pulp
α-Cellulose	≥94	89.0
Pentosans	≤3.0	3.9
Extractives	≤0.2	2.9
Ash	≤0.5	2.4

Cellulose pulp from the PureVision fractionation process is well suited for making dissolving pulp because it is already high enough in cellulose and low in xylan and lignin, as is shown in Table 4. A simple alkaline treatment would be sufficient to produce dissolving pulp.

Fiber separation

The low replacement levels of corn stover pulp for hardwood pulp stems from its short fiber length, i.e., 0.77 mm. However, based on fiber length distribution, about 15–20% of the fiber can be used directly for paper applications. Substitution of hardwood pulp with these longer fibers is expected at much higher levels, i.e., up to 50% or total replacement of hardwood pulp in the blends. Using the remainder of shorter stover fibers thus separated for cellulose derivatives is a prudent approach.

Fiber separation segregates pulp fibers into different fractions based on their specific physical properties such as fiber length or flexibility. The fibers with particular attributes can then be gainfully directed to the most appropriate process and product. For example, separated long fibers can be used in a high-value reinforcing pulp, the shorter fibers being sent to lower-end applications [16]. The board industry utilizes fiber separation to selectively improve the facets of various layers [13, 28]. Also, fiber fractionation and subsequent processing of recycled fibers production have been demonstrated to improve strength and brightness [37]. In industrial pressure screens such as the Messmer Fiber Classifier, the fiber is circulated at a high uniform velocity across the screen thereby compelling the fibers to orient themselves parallel to the wire mesh. Achieved fiber orientation is not disturbed because water flows through the screen at a low enough velocity, and the design also prevents fibers from jamming the screen.

Average fiber length is a fundamental pulp property that has been shown, other aspects remaining the same, to relate to the strength properties of paper. It may be beneficial to separate long fibers from the PureVision process and use them in a paper application. The remaining shorter fibers can be used for dissolving pulp.

For North America, it is probably necessary to separate out the long fibers for paper applications. Such fractionation also removes fines from the furnish and relinquishes it to the short fiber stream. As mentioned above, fractionation is an essential part of producing multilayer paperboard. The long fiber component is mostly responsible for strength, and the short fiber components contribute to the smoothness and opacity of the sheet. In corrugated containers, the short fraction is used as the corrugated medium, while the stronger long fraction is used for the liner [4]. Thus, fiber separation yields two fiber streams that are more valuable individually than the original feed stream by itself. This approach is applicable to fibers from the PureVision process.

Lignin

MW distribution of hydrolyzed lignin from second stage liquor is shown in Fig. 7. Using an average phenylpropane unit MW of 180–200, the peak at around 1,000 can be interpreted as a pentamer. A majority of the lignin has a MW of <10,000; this is in contrast with an average MW of 50,000 seen for kraft lignin. A lower MW signifies more reactivity thereby facilitating further conversion to value-added products.

Lignin-based adhesives

A variety of wood adhesive types are currently available for wood utilization, and there is a large market for wood adhesives. North American adhesive resin requirements for wood composites were 1.8 million t [45]. Resin adhesives are a vital part of glued wood composites and constitute 32% of the total manufacturing cost of the item being glued and marketed.

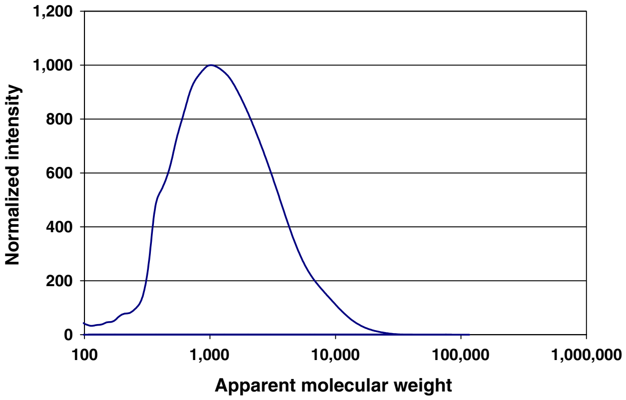

Fig. 7 Molecular weight distribution of hydrolyzed lignin

The high abundance of lignin as a waste product in pulp mills has attracted attention as a raw material alternative to nonrenewable petroleum-derived chemicals in the production of wood adhesives. Lignin substitution into phenol formaldehyde (PF) resins is generally limited to <20–30% because cure times increases with the amount of lignin. Bagasse-derived lignin has been used as an adhesive for particleboard manufacture [20]. Hume et al. [22, 23] describe a polyvinyl alcohol and lignin sulfonate containing adhesive possessing sufficient adhesion, wherein the lignin sulfonate to polyvinyl alcohol ratio can vary from 1 to 8.

PF resins are an important adhesive employed in the production of wood-based panels for exterior use, which requires superior water resistance. They are produced via the reaction between phenol and formaldehyde; this reaction is catalyzed by alkali and yields a thermosetting polymer called a resole. Other phenolic compounds such as resorcinol can also react with formaldehyde in a similar way to provide polymers with similar structure and properties. However, phenol is a toxic substance of petrochemical origin, and the recent jump in crude oil prices makes a case for developing alternative resin feedstock. Lignin, a benign renewable resource, can be used as a raw material to produce environmentally friendly industrial products such as wood adhesives and sealers and also reduce demand on fossil fuels, a nonrenewable resource. Also, phenol prices have doubled in recent years to about $0.8 per lb due to rising crude prices.

Lignin can be methylolated by reaction for 5 h at 55°C with formaldehyde (formaldehyde/lignin ratio of 0.38 by weight) in the presence of sodium hydroxide (NaOH/lignin ratio of 0.2 by weight); this construct can be used in place of phenol [12]. Use of a methylolated softwood ammonium lignosulfonate as partial substitute of phenol in resol resins manufacture has been reported [2]. Sellers and coworkers have done extensive work in successfully using lignins as an extender in PF resin adhesives [40, 41, 44, 46–48, 56]. Hence, lignin from the PureVision process can be similarly utilized to make PF resins.

Xylose utilization

In the baseline scenario, the xylose-rich first stage liquor is expected to be fermented to ethanol. This can be achieved in separate pentose fermentation or in SSCF (simultaneous saccharification and cofermentation) mode. However, it can also be used to make specialty products; it should be emphasized that these will be small markets and a single large refinery may saturate the market. One such possibility is xylitol. The first stage liquor from PureVision biorefinery is expected to contain about 50 g/L xylose and a concentration of 150 g/L is usually needed for industrial xylitol fermentation. China is a major producer of xylitol, and xylose is typically concentrated by triple effect evaporation prior to conversion to xylitol. Alternatively, reverse osmosis (RO) can be used to concentrate the feed 15% xylose. RO is considered preferable over evaporation for concentrating sugars as it prevents carmelization and saves energy. Data on concentrating sugars such as glucose, maltose, lactose, and xylose using RO are available in the literature [33, 59]. Nanofiltration has also been used for concentrating xylose liquor in the production of xylitol [36]. Studies are underway to ferment the first stage liquor using *Debaryomyces hansenii*, which has been shown to be an efficient xylitol fermenter [10, 11, 52].

The first stage liquor contains pentoses in oligomeric form. Xylo-oligosaccharides (XOs), also called xylo-oligomers, are low-digestible sugars and utilized by most *Bifidobacterium* species. They are sold as functional food additive, mostly in Asian markets, and selectively promote the proliferation of bifidobacteria in human intestine. Hence, XOs can be classified as prebiotics. Prebiotics are defined as "nondigestible food ingredients that are selectively metabolized by colonic bacteria that have the capacity to improve health." They are distinct from most dietary fibers like pectin, celluloses, xylan, which are not selectively metabolized in the gut. The desired degree of polymerization for XOs as prebiotics is 2–7, which can be achieved via controlled enzymatic hydrolysis by an endo-xylanase.

Markets and values

Although a detailed economic analysis is required to assess process feasibility, which is a focus of another publication in print, it is instructive to present the value-added nature of products that are possible. As mentioned above, the U.S. is planning to replace its gasoline consumption by 20% over the next 10 years with alternative fuels [8]. Given the current fuel ethanol market in the U.S. of ca. 180 billion gal/year and the limited capacity of corn-based ethanol, the market for cellulosic ethanol is predicted to be substantial. Fuel ethanol prices generally follow gasoline prices. Hence, at current relatively high crude oil prices, ethanol production via the biorefining process presented here should eventually be economically feasible.

World production of dissolving pulp in 2003 was 3.7 million t [49]. Although the market is much smaller than kraft pulp, dissolving pulp commands $4,000 per t versus about $500 per t for the latter. Wood adhesive resin consumption was 2 million t in 2001 with market prices of approximately $0.46 per kg. Phenolic resin market was about 500,000 t/year, which is a small market considering the scale of future biorefineries. However, other potential larger-volume lignin markets are as concrete binder ($275 per mt) and as feed binder ($385–465 per mt). The current estimated lignin market is 1.8 million mt/year, and a few PureVision biorefineries can be built without saturating these markets. Furthermore, other even larger volume applications are possible in the future such as an antioxidant additive for hot-mix asphalt (HMA) [18, 34, 60]. HMA is used to build new roads, but its most prevalent application is in patches and repairs. About 500 million t of HMA are produced every year [60], and future biorefineries can exploit these yet untapped markets.

The value of xylitol market is currently $340 million with applications in mouthwashes and toothpastes, chewing gums as well as in foods for special dietary uses. With xylitol prices currently ranging from $4–5 per kg, this represents <100,000 t/year. Global xylitol consumption was 43,000 t in 2005, the U.S. and Western Europe accounting for 30 and 37% of the total xylitol consumption, respectively [9]. Hence, xylitol is a niche market from a biorefinery standpoint. The market price of prebiotic XOs is about $15 per kg [38]; however, this is definitely a niche application.

Conclusion

A new biorefining process is presented that—in the spirit of a true biorefinery—converts corn stover and other biomass feedstocks into value-added products such as fuel ethanol, dissolving pulp, and lignin for resin production. The continuous biomass fractionation process yields a liquid stream rich in hemicellulosic sugars, a lignin-rich liquid stream and a solid cellulose stream. Enzymatic hydrolysis of this relatively pure cellulose stream requires significantly lower enzyme loadings because of minimal enzyme deactivation from nonspecific binding to lignin. A correlation was shown to exist between lignin removal efficiency and enzymatic digestibility. The cellulose produced was demonstrated to be a suitable replacement for hardwood pulp, especially in target application of the top ply of a linerboard. Also, the relatively pure nature of the cellulose renders it suitable as raw material for making dissolving pulp. This pulping approach has significantly smaller environmental footprint compared to the industry-standard kraft process because no sulfur- or chlorine-containing compounds are used. Along with use as cement and feed binders, low-MW lignin can potentially be used in wood adhesive production. As a baseline application, the hemicellulosic sugars captured in the hydrolyzate liquor can be used to produce ethanol, but potential utilization of xylose for xylitol fermentation is also feasible. Although data specific for corn stover are presented, the proposed biorefinery scenario is generically applicable to other biomass feedstocks. Successful commercialization of this technology would result in a sustainable green process with positive environmental impacts such as reduction in emissions of greenhouse gases and criteria pollutants.

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