



Woody biomass pretreatment for cellulosic ethanol production: Technology and energy consumption evaluation [☆]

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ABSTRACT

This review presents a comprehensive discussion of the key technical issues in woody biomass pretreatment: barriers to efficient cellulose saccharification, pretreatment energy consumption, in particular energy consumed for wood-size reduction, and criteria to evaluate the performance of a pretreatment. A post-chemical pretreatment size-reduction approach is proposed to significantly reduce mechanical energy consumption. Because the ultimate goal of biofuel production is net energy output, a concept of pretreatment energy efficiency (kg/MJ) based on the total sugar recovery (kg/kg wood) divided by the energy consumption in pretreatment (MJ/kg wood) is defined. It is then used to evaluate the performances of three of the most promising pretreatment technologies: steam explosion, organosolv, and sulfite pretreatment to overcome lignocelluloses recalcitrance (SPORL) for softwood pretreatment. The present study found that SPORL is the most efficient process and produced highest sugar yield. Other important issues, such as the effects of lignin on substrate saccharification and the effects of pretreatment on high-value lignin utilization in woody biomass pretreatment, are also discussed.

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1. Introduction

Although current research and development attention has been focused mainly on agricultural residues and dedicated energy crops such as corn stover and switchgrass, woody biomass (hardwoods and softwoods) remains a very important feedstock for cellulosic ethanol production. About 370 million oven dry (od) tons of woody biomass, accounting for 30% of the total biomass projected to be available for biofuel, can be sustainably produced annually in the United States (Perlack et al., 2005). Woody biomass is also sustainably available in large quantities in various other regions of the world, such as Scandinavia, New Zealand, Canada, and South America. Furthermore, short-rotation intensive culture or tree farming offers an almost unlimited opportunity for woody biomass production (Foody and Foody, 1991). To promote biodiversity and sustainable and healthy forest and ecosystem management and to meet local and regional bioenergy needs, woody biomass will be a critical part of biomass supply mix in the future bioeconomy.

The major differences between woody and nonwoody (agricultural) biomass are their physical properties and chemical compositions. Woody biomass is physically larger and structurally stronger

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and denser than agricultural biomass (Table 1). Chemically, woody biomass has higher lignin content than agricultural biomass (Table 1). As a result, woody biomass is more recalcitrant to microbial and enzymatic actions than nonwoody biomass. This is particularly true for softwood species. For example, typical enzymatic saccharification efficiency of softwood cellulose after dilute acid pretreatment is only about 40% (Zhu et al., 2009a). In addition, more energy is required to overcome the recalcitrance of woody biomass through pretreatment for enzymatic saccharification. Compared with agricultural biomass, woody biomass has many unique features. For example, woody biomass can be harvested year round, which eliminates long-term storage. Its higher density significantly reduces transportation cost. Furthermore, its higher lignin content increases energy density. Its near-zero ash content (Table 1) eliminates dead load in transportation and processing. Moreover, woody biomass, in particular softwood species, generally has a lower content of pentoses than agricultural biomass (Table 1), which is favorable for bioconversion to ethanol. This is because (1) pentose recovery yield is often low due to its decomposition to furfurals – fermentation inhibitors – in thermal–chemical pretreatments, and (2) fermentation of pentoses to ethanol is relatively difficult. Therefore, woody biomass has significant advantages over agricultural biomass for cellulosic ethanol production if its strong recalcitrance to cellulases can be overcome.

Substantial research efforts have been made in biochemical conversion of agricultural biomass for cellulosic ethanol production. Progress from these efforts can also be applied to woody

Table 1

Density and composition of representative lignocellulosic biomass (softwoods, hardwoods and herbages).

	Density (kg/m ³) ^a	Composition (%)									
		Ash	Extractives	Lignin	Arabinan	Galactan	Glucan	Xylan	Mannan	Carbohydrates	G/C ratio
Spruce ^b	370	0.3		28.3	1.4	2.7	43.2	5.7	11.5	64.5	0.670
Lodgepole pine ^b	380		4.9	27.9	1.6	2.1	42.5	5.5	11.6	63.3	0.671
Ponderosa pine ^b	390			26.9	1.8	3.9	41.7	6.3	10.8	64.5	0.647
Douglas-fir ^c	425	0.4		32.0	2.7	4.7	44.0	2.8	11.0	65.2	0.675
Loblolly pine ^c	470	0.4		28.0	1.7	2.3	45.0	6.8	11.0	66.8	0.674
Red pine ^c	390	0.4		29.0	2.4	1.8	42.0	9.3	7.4	62.9	0.668
Red maple ^c	490	0.2		24.0	0.5	0.6	46.0	19.0	2.4	68.5	0.672
Aspen ^b	350			23.0	0.0	0.0	45.9	16.7	1.2	63.8	0.719
Salix ^d		0.9		26.4	1.2	2.3	41.4	15.0	3.2	63.1	0.656
Yellow poplar ^e		1.9	2.8	23.3	0.5	1.0	42.1	15.1	2.4	61.1	0.689
Hybrid poplar DN34 ^e		0.8	2.1	23.9	0.6	0.6	43.7	17.4	2.9	65.2	0.670
Eucllyptus saligna ^e		1.2	4.2	26.9	0.3	0.7	48.1	10.4	1.3	60.8	0.791
Corn stover ^e	~130	11.0	11.9	18.2	1.9	0.7	30.6	16.0	0.5	49.7	0.616
Corn stover ^e	~130	11.5	4.8	20.2	2.0	0.7	38.1	20.3	0.4	61.5	0.620
Switch grass ^e	~108	6.8	5.5	23.1	1.5	0.5	35.9	19.6	0.4	57.9	0.620
Switch grass ^e	~108	9.4	12.6	27.6	1.1	0.3	31.9	10.6	0.3	44.2	0.722
Switch grass ^e	~108	4.0	2.0	24.1	1.5	0.5	42.6	23.1	0.3	68	0.626
Wheat straw ^e		10.2	13.0	16.9	2.4	0.8	32.6	19.2	0.3	55.3	0.590

^a Wood density data are for green wood from Isenberg (1980). Corn stover density from Shinnars et al. (2007); switch grass density from McLaughlin et al. (1999).

^b All carbohydrate data from our own work: spruce from Zhu et al. (2009a); lodgepole and ponderosa pine from Youngblood et al. (2009); aspen from Wang et al. (2009).

^c All carbohydrate, ash, and extractive data from Pettersen (1984).

^d All data from Sassner et al. (2008a).

^e All carbohydrate and ash data from US DOE Biomass program database, http://www1.eere.energy.gov/biomass/feedstock_databases.html.

biomass, especially those associated with downstream processing, such as consolidated bioprocessing (Lynd et al., 2005), xylose fermentation (Jeffries and Jin, 2004; Sedlak and Ho, 2004), and membrane technologies for distillation (Vane and Alvarez, 2008). However, upstream processes such as pretreatment and saccharification for woody biomass are uniquely different from those for nonwoody materials because of differences in their physical and chemical properties. Because upstream processing is the key for successful commercial production of cellulosic ethanol (Lynd et al., 2008) and woody biomass is especially recalcitrant to enzymatic destructions, particular attention needs to be paid to (1) the effectiveness of pretreatment for complete wood cellulose saccharification and (2) the energy consumption for woody biomass pretreatment, in particular for wood-size reduction to the level for effective enzymatic saccharification. Unfortunately, limited research efforts and resources have been devoted to these critical areas. This is also true in the United States despite its making cellulosic ethanol as a major alternative fuel for the next 15 years; i.e., 16 billion gallons (60 billion liters) cellulosic ethanol by 2022 (US Energy Security and Independence Act of 2007). Therefore, the main objective of the present review is to discuss these two specific technical issues in the upstream processing of woody biomass for cellulosic ethanol production. A concept of process energy efficiency for evaluating pretreatment performance will then be defined. The integrated forest biorefinery concept through value prior to pulping (VPP) recently proposed by the pulp and paper industry will be briefly discussed as well.

2. Pretreatment of woody biomass

Feedstock pretreatment has been recognized as a necessary upstream process (Lynd, 1996; Yang and Wyman, 2008) to remove biomass recalcitrance for downstream microbial and enzymatic processing during cellulosic ethanol production. A representative pretreatment includes both physical and chemical steps. Physical pretreatment refers to the reduction of physical size of biomass feedstock to increase enzyme-accessible surface areas (Zhu et al., 2009b). Chemical pretreatment refers to the process of using

chemicals to remove or modify key chemical components that interfere with biomass cellulose saccharification, mainly hemicelluloses and lignin.

Feedstock pretreatments reported in the literature have almost exclusively focused on chemical pretreatments. Physical pretreatment, i.e., biomass size reduction, has been overlooked. For example, significantly size-reduced materials were used in chemical pretreatments (Wyman et al., 2005), but no information about the size-reduction process was provided. In fact, physical pretreatment/size reduction was even not included in process cost analyses in some key literature (Galbe and Zacchi, 2007; Lynd et al., 2008). This is most likely because most research studied agricultural biomass, and energy consumption in the size reduction of agricultural biomass was insignificant. Unfortunately, size reduction has also been ignored in woody biomass studies. A recent comprehensive study on poplar wood bioconversion to ethanol (Wyman et al. 2009), conducted by the Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) sponsored by the US Departments of Energy and Agriculture, used size-reduced wood particles passing through a ¼-in. (6-mm) screen to compare sugar and ethanol yields from different pretreatment processes. The study did not provide information about the amount of energy consumed for wood-size reduction through chipping and milling before chemical pretreatments. As will be reviewed later in this section, size reduction of woody biomass is energy-intensive.

The most investigated pretreatment processes for woody biomass include dilute acid, steam explosion, organosolv, and sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL) (Zhu et al., 2009a). A separate mechanical size-reduction step is required for the dilute acid and SPORL processes, whereas in situ thermo-chemical size reduction/fiberization takes place in steam explosion and organosolv processes during chemical pretreatment. In this section, we will evaluate chemical pretreatment technologies based on the overall performance when integrated with their respective size-reduction process. Specifically, we will examine both the total monomeric sugar yield and the total energy consumption for producing the substrate through both the physical and chemical pretreatments.

2.1. Pretreatment technologies for woody biomass

2.1.1. Dilute acid pretreatment

Dilute acid pretreatment is the most studied process for agriculture biomass (Wyman et al., 2005). The application of dilute acid pretreatment to woody biomass can achieve some level of success in that it can provide satisfactory cellulose conversion with certain hardwood species. However, data on dilute acid pretreatment of woody biomass are scarce. As a part of the CAFI study conducted at the US National Renewable Energy Laboratory, dilute acid pretreatment of a poplar wood yielded a total sugar recovery of 82.8% with a cellulase loading of 15 FPU/g cellulose (Wyman et al., 2009). The pretreatment was carried out at 190 °C and 2% acid charge on wood using a size-reduced wood feedstock passing through a ¼-in. (<6 mm) screen. Further size reduction after dilute acid pretreatment was achieved through a flashing (mild steam explosion) process. Recently Wang et al. (2009) reported a cellulose conversion of over 80% from a eucalyptus substrate. The substrate was derived from direct dilute acid pretreatment of wood chips (6–38 mm) at 180 °C with a sulfuric acid charge of 1.84% on od wood followed by a disk-milling process for size reduction. The cellulase loading was 15 FPU/g substrate.

Dilute acid pretreatment failed to provide satisfactory enzymatic cellulose conversion for softwood. Cellulose conversion was only about 40% when spruce wood chips were pretreated at 180 °C with an acid charge of 1.84% on od wood followed by disk milling (Zhu et al., 2009a). The cellulose saccharification could be enhanced by a two-stage acid hydrolysis (pretreatment) using steam; glucose recovery of about 80% theoretical was achieved at the expense of increased thermal energy cost (Monavari et al., 2009a).

2.1.2. Acid-catalyzed steam pretreatment

Acid-catalyzed steam explosion is the most common steam pretreatment for woody biomass (De Bari et al., 2007; Galbe and Zacchi, 2002; Monavari et al., 2009b; Sassner et al., 2008a,b; Soderstrom et al., 2004; Wingren et al., 2003; Cullis et al., 2004; Ewanick et al., 2007). Wood chips or chip-sized wood materials are first impregnated with acid catalyst either in the gas phase with SO₂ or in aqueous phase with sulfuric acid before steam pretreatment. Pretreated wood chips were disintegrated into fibers or fiber bundles through steam explosion during discharge. Acid-catalyzed steam pretreatment is actually another form of dilute acid pretreatment in which the pretreatment is carried out in vapor phase rather in aqueous phase. The explosion feature has now been used in dilute-acid operations for further size reduction. Typical acid or SO₂ charge on od wood varied from 0% to 5%, and temperature ranged from 190 to 210 °C for hardwoods and 200–220 °C for softwoods. Pretreatment time varied from 1 to 10 min.

The data presented in Table 2 represent the most complete information, in terms of sugar recovery, from recent steam-explosion studies. Good success in sugar recovery from hardwoods has been achieved with total monomer sugar recovery from 65% to 80% from poplar species (Table 2). The results from steam-explosion pretreatment of softwood species are not encouraging. The best results for total monomer sugar recovery is only about 65% theoretical (Table 2) for a single-stage pretreatment. Two-stage steam explosion can improve the sugar yield, but thermal energy consumption will be significantly higher than single-stage steam explosion. However, the increase in total sugar yield is marginal based on the data (Table 2) reported by Soderstrom et al. (2004).

Note that the wood chips used in the studies listed in Table 2, except for those in the work by Ewanick et al. (2007), are much

Table 2
Sugar recovery yields in steam-explosion pretreatment of woody biomass (only monomeric sugars, no oligomers, are included in the data.).

Source ^a	Feedstock	Pretreatment conditions	Cellulase loadings ^b	Sugar yield in pretreatment hydrolysate ^c		EHGY ^d	Total sugar yield ^e
				Xylose	Glucose		
<i>Hardwood</i>							
De Bari et al. (2007)	Aspen, sawmill wood chips	10.0 min at 205 °C; SO ₂ 0.9%	21.9/12.6	40/6.3		78/37	65/43.3
		3.0 min at 205 °C; SO ₂ 0.7%	19.6/12.6	57/9.0		75/36	68/45.0
Sassner et al. (2008a)	Salix, 4-year old, 2–10 mm wood chips	8.0 min at 200 °C; H ₂ SO ₄ 0.25%	21.1/15.0	36/5.4	4/1.7	81/33.5	64/40.6
		8.0 min at 200 °C; H ₂ SO ₄ 0.5%	23.4/15.0	60/9.0	10/4.1	80/33.1	73/46.2
Wyman et al. (2009)	Poplar, 15-year old, knife milled <6 mm	5.0 min at 190 °C; SO ₂ 3.0%	~16/	54/8.2	3/1.3	96/42.2	83/53.2
<i>Softwood</i>							
Ewanick et al. (2007)	Lodgepole pine (LP) Beetle killed LP 20 × 20 × 5 mm wood chips	5.0 min at 200 °C; SO ₂ 4.0%	20/			60/25.1	
		7.5 min at 195 °C; SO ₂ 4.0%	20/			68/28.5	
		5.0 min at 200 °C; SO ₂ 4.0%	20/			75/31.4s	
Ballesteros et al. (2000)	Pinus Pinaster, 8–12 mm wood chips	5.0 min at 215 °C; SO ₂ 4.5%	20/			73/30.6	
		4.0 min at 190 °C; SO ₂ 0%	19.0/12.6	~3.2		11/3.5	21/10
		8.0 min at 190 °C; SO ₂ 0%	18.8/12.6	~3.4		11/3.5	23/11
		4.0 min at 210 °C; SO ₂ 0%	22.7/12.6	~3.4		32/10.3	41/20
Soderstrom et al. (2004)	Spruce, 2–10 mm wood chips	8.0 min at 210 °C; SO ₂ 0%	22.1/12.6	~3.2		30/9.6	39/19
		5.0 min at 215 °C; SO ₂ 3.0%	25.9/15	60/7.1	17/9.1	59/31.5	67/47.6
		Two steps: Step I: 2.0 min at 190 °C; SO ₂ 3.0% Step II: 5.0 min at 210 °C; SO ₂ 0%	23.8/15	63/7.5	17/9.0	62/33.0	69/49.5
Monavari et al. (2009b)	Spruce, 5–6 mm wood chips	5.0 min at 200 °C; SO ₂ 2.5%	/15	66/7.7	13/5.6	50/21.7	59/40.0

^a De Bari et al. (2007) used an acid hydrolysis step after steam explosion to convert oligomeric sugars to monomeric sugars. SO₂ and H₂SO₄ charge on od wood base.

^b FPU (filter paper unit) per g cellulose (the first number) and FPU/g substrate (the second number).

^c Sugars dissolved in liquor during pretreatment (monomers only), reported in weight percent (wt.%) of original xylose (hardwood) or mannose (softwood) and glucose in wood (first number) and wt.% of od wood (the second number).

^d EHGY stands for enzymatic hydrolysis glucose yield; reported in weight percent (wt.%) of original glucose in wood (or wt.% theoretical, first number) and wt.% od wood (the second number). Wyman et al. (2009) reported a total glucose yield more than 100% theoretical, so EHGY of 96% must contained a positive error.

^e Total sugar includes monomeric sugars (xylose or mannose and glucose) in pretreatment liquor and glucose from enzymatic hydrolysis, reported in percent of all of the original monomeric sugars in wood (first number) and wt.% of od wood (the second number). Data for Ballesteros et al. (2000) include all hemicellulose sugars. The data for the rest of the studies only include glucose and xylose (hardwood) or mannose (softwood).

smaller than commercial wood chips. Literature review revealed inconclusive results on the effect of chip size on the performance of steam explosion when wood chip size was varied within 12 mm (2–12 mm in Ballesteros et al., 2000; 1–6 mm in Monavari et al., 2009b). However, significant effects of chip size on hemicellulose sugar recovery and enzymatic cellulose saccharification efficiency were observed when wood chip size varied from 0.6 to 50 mm (Cullis et al., 2004). Enzymatic cellulose saccharification efficiency of Douglas-fir at 30% moisture was increased by 30% when the size of wood chips was reduced from 50 to 0.6 mm even after applying disk milling to both the small- and large-sized wood materials after steam explosion. This suggests that more mechanical energy is required for further size reduction of commercial wood chips to achieve the results reported in Table 2.

Steam explosion can produce a relatively concentrated hemicellulosic sugar stream when the washing water is limited to minimum to extract sugars, e.g., <2× the biomass solids. It achieves both physical (thermal–chemical size reduction) and chemical pretreatments in one step. Compared with the processes using mechanical size reduction prior to chemical pretreatment with large liquid to wood solid ratio (*L/W*) ratio, steam explosion is relatively energy efficient. Two scenarios of aqueous chemical pretreatments in combination with two scenarios of mechanical size reduction are listed in Table 3 and compared with steam explosion. The first scenario of mechanical size reduction is disk milling prior to chemical pretreatment, and the second scenario is disk milling after chemical pretreatment (to be discussed in the next section). The disk-milling energy data are estimated based on mechanical pulp mill knowledge, our laboratory study (Zhu et al., *in press*), and literature (Schell and Harwood, 1994). Only the pretreatment with *L/W* of 3 or lower together with post-chemical-pretreatment mechanical size reduction is more energy efficient than the steam-explosion pretreatment. This is probably one of the reasons that steam explosion has attracted great interest for biomass, especially woody biomass, pretreatment. The main technical barriers for the steam explosion process include its scalability for commercialization and ineffectiveness with softwood species.

2.1.3. Organosolv pretreatment

Ethanol organosolv pretreatment can effectively remove the recalcitrance of woody biomass for enzymatic cellulose saccharification (Pan et al., 2005a, 2006a, 2008). The pretreatment has several advantages: (1) a separate size-reduction step is not necessary even when pretreatment is directly applied to commercial wood chips; (2) it produces a readily digestible cellulose substrate from almost all kinds of feedstock including softwood and hardwood species; and (3) it also produces very high purity and quality lignin with the potential of high-value utilizations (Kadla et al., 2002a,b; Pan et al., 2006b). Typical organosolv pretreatment conditions for woody biomass are temperatures about 160–190 °C, pretreatment time of 30–60 min, and ethanol concentration of 40–60%. When organosolv pretreatment was applied to poplar (Pan et al., 2006a) under the conditions of 180 °C, 60 min, 1.25%

H₂SO₄, and 50% ethanol, about 75% of the lignin was removed from the substrate and recovered as high-purity lignin. Approximately 80% of the xylan was separated from the substrate with 50% recovered as monomeric xylose in the soluble stream. About 88% of the glucan was retained in the substrate and was completely enzymatically hydrolyzed within 24 h. Despite the excellent cellulose conversion, hemicellulose recovery was low because of sugar decomposition at high temperatures in the presence of acid. The hemicellulose sugars dissolved in the water-soluble stream are not fermentable without extensive detoxification due to the high concentration of inhibitors (furfural, hydroxymethylfurfural, and soluble polyphenols from lignin). Furthermore, complete solvent (ethanol) recovery is a critical issue to the process economy. In summary, the organosolv process is a unique and promising biomass fractionation and pretreatment process, in particular for woody biomass. Its successful commercialization will depend on the development of high-value co-products from lignin and hemicelluloses.

2.1.4. Sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL)

The SPORL process was recently developed by the present authors at the U.S. Forest Service, Forest Products Laboratory and the University of Wisconsin-Madison (Zhu et al., 2009a; Wang et al., 2009). Unlike steam explosion and organosolv, SPORL is new to the biomass research community. In the process, wood chips first react with a solution of sodium bisulfite (or calcium or magnesium or other bisulfite) at 160–190 °C and pH 2–5 (for about 10–30 min in batch operations). The pretreatment liquor to wood ratio can be as low as 2–3, which ensures relatively concentrated hemicellulosic sugar stream and low chemical pretreatment energy consumption. The pretreated wood chips are then fiberized through mechanical milling (using a disk refiner) to generate fibrous substrate for subsequent saccharification and fermentation. The dissolved hemicellulose stream (a mixture of hexoses and pentoses) is fermentable. The fermentation of spent sulfite pulping liquor has been in industrial practice for commercial cellulose ethanol production for decades (Helle et al., 2004, 2008). Our initial study found that SPORL pretreatment hydrolysate is easier to ferment than spent sulfite liquor because of high sugar and low lignosulfonate concentrations. The dissolved lignin (lignosulfonate) can then be recovered and directly marketed as a co-product, such as dispersants in the existing market. Pretreatment acid can be easily and efficiently recovered as SO₂ using mature scrubbing technologies. The metal base of sulfite is mainly associated chemically with lignosulfonate that can be easily recovered as a co-product. If lignosulfonate is not recovered, magnesium sulfite may be a preferred choice to sodium or calcium sulfite as magnesium can be easily and completely recovered using a low-cost fluidized bed reactor, which is in industry practice. Hydrolysis lignin can be co-fired in the fluidized bed reactor to eliminate the need for a separate reactor to incinerate hydrolysis lignin. The SPORL technique can be integrated with steam-explosion pretreatment by using

Table 3

Energy consumptions in chemical and physical pretreatments under different conditions. All data are in MJ/kg od wood base.

Scenario	<i>L/W</i>	<i>T</i> (°C)	Thermal energy input	Net thermal energy ^a	Energy for wood chipping	Energy for chip milling	Total size reduction energy ^a	Total energy ^a
Aqueous	3	180	2.46	1.2/17	0.18	1.98	2.16/30	3.36/47
						0.18	0.36/5	1.56/22
Aqueous	5	180	4.18	2.1/29	0.18	1.98	2.16/30	4.26/59
						0.18	0.36/5	2.46/34
Steam explosion	1	215	3.51	1.8/25	0.18	0	0/0	1.98/28

^a Reported in MJ/kg wood (the first number) and in percent of the thermal energy of ethanol from wood (the second number, 7.2 MJ/kg wood based on 0.3 L ethanol/kg wood).

sulfite and acid as catalysts as disclosed in our patent application (Wang et al., 2008). The separate mechanical size-reduction step is not needed with steam explosion.

The removal of the strong recalcitrance of woody biomass by SPORL is achieved by the combined effects of dissolution of hemicelluloses, depolymerization of cellulose, partial delignification, partial sulfonation of lignin, and increasing surface area by fiberization through disk milling (Shuai et al., accepted for publication; Zhu et al., 2009a). Lignin sulfonation increased the hydrophilicity of SPORL pretreated substrates and reduced non-productive adsorption of enzymes on lignin. Typical bisulfite charge on od wood is about 1–3 and 6–9% for hardwood and softwood species, respectively. Acid application ranges from 0% to 2.0% on od wood for pH adjustment. Cellulose-to-glucose conversion over 90% can be easily achieved with enzyme loadings of 15 and 7.5 FPU/g substrate for softwoods and hardwoods, respectively, within 24 to 48 h. Mechanical energy consumption during post-SPORL pretreatment wood-size reduction can be as low as 20 W h/kg (<0.1 MJ/kg) (Zhu et al., 2009a; Zhu et al., in press). SPORL produced lower amounts of fermentation inhibitors, such as acetic acid, hydroxymethylfurfural (HMF), and furfural than dilute acid because of higher pretreatment pH (Shuai et al., accepted for publication; Zhu et al., 2009a; Wang et al., 2009). Excellent monomeric sugar recovery was achieved from spruce (Zhu et al., 2009a) with recovery of glucose, arabinose, galactose, xylose, and mannose about 93%, 54%, 86%, 76%, and 88%, respectively.

Because ethanol organosolv pretreatment is the most robust process in terms of removing softwood recalcitrance, we compare the results of enzymatic cellulose hydrolysis from SPORL pretreated softwood with those from organosolv under similar enzymatic hydrolysis conditions, i.e., 2% solid consistency, enzyme loadings of about 20 FPU cellulase and 30 CBU β -glucosidase per gram of cellulose. The results indicate that SPORL removed lignocellulose recalcitrance and achieved cellulose saccharification rate that matches those of organosolv pretreatments with equivalent enzymatic glucose yield (Fig. 1).

2.1.5. Other chemical pretreatments

Several other chemical pretreatments have been applied to woody biomass for ethanol production. A cold sodium hydroxide pretreatment (Zhao et al., 2008) can achieve about 70% enzymatic hydrolysis glucose yield from spruce when pretreatment was conducted at $-15\text{ }^{\circ}\text{C}$ in a 7% (w/v) NaOH solution with 12% (w/v) urea. The problem of the process is the difficulty in recovery of hemicelluloses sugars and that NaOH recovery is very expensive. Wyman et al. (2009) reported in the recent CAFI study that most pretreatments failed to produce satisfactory enzymatic sugar yields from poplar. For example, the ammonia-based processes, ammonia-fiber expansion (AFEX) (Balan et al., 2009) and ammonia-recycle percolation (ARP) (Gupta and Lee, 2009), only produced an overall sugar recovery of about 50%. Lime pretreatment produced a good sugar recovery from poplar at about 15 bar and $160\text{ }^{\circ}\text{C}$ (Sierra et al., 2009). However, in addition to difficulties in operating chemical reactions at very high pressure and temperature at a capacity of 1000 tons wood/day, equipment-scaling problem caused by lime will be a serious issue in commercial production.

2.2. Energy consumption for woody biomass pretreatment

2.2.1. Energy consumption for physical pretreatment (size reduction)

Size reduction of woody biomass is very similar to wood-fiber production, which involves two steps (Zhu et al., 2009b). The first step is a coarse mechanical size reduction, such as wood chipping that produces wood chips of around 10–50 mm in two dimensions and about 5–15 mm in the third dimension from wood logs. The second step is to further reduce the size of wood from chips to par-

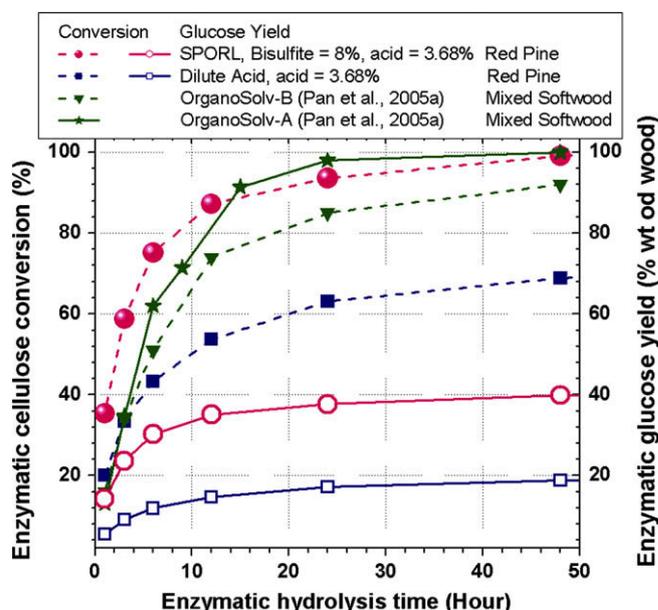


Fig. 1. Comparisons of enzymatic hydrolysis efficiency and glucose yield from softwood between sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL) and organosolv process.

ticles, fibers, and/or fiber bundles. It can be achieved thermochemically during chemical pretreatments, such as in steam explosion, organosolv process, and chemical pulping processes. It can also be achieved mechanically through grinding or milling, which consumes much more energy than the first step of coarse mechanical size reduction. Hammer-milling and other milling technologies can be used to break wood chips into particles/fibers such as in wood flour production. However, disk-milling technology represents one of the best fiberization processes for woody feedstock in commercial production at the scale of 1000 tons/day, equivalent to ethanol production capacity of 100 million liters/year. Disk milling has been practiced for several decades in the pulp and paper industry. Furthermore, the fiberization process of disk milling is favorable for efficient enzymatic saccharification (Zhu et al., 2009b). Therefore, we will focus on disk milling in the following discussion.

A simple energy balance calculation can demonstrate energy consumption for wood-size reduction. Assuming that ethanol yield from wood is about 300 L/ton of od wood with current technology and higher heating value of ethanol is about 24 MJ/L, total ethanol thermal energy from wood is 7.2 MJ/kg wood. Typical energy consumption to produce wood chips is about 50 W h/kg (0.18 MJ/kg wood). Depending on the fiberization process and the degree of milling, mechanical energy consumption for disk-milling wood chips to fibers and/or fiber bundles is between 150 and 800 W h/kg wood (Zhu et al., in press; Schell and Harwood, 1994), equivalent to 0.54–2.88 MJ/kg wood. Therefore, size-reduction energy consumption is about 10–40% of the ethanol thermal energy from wood. Considering the conversion efficiency of 30% from thermal energy (stored in ethanol) to electric-mechanical energy consumed in wood-size reduction, the thermal energy in ethanol produced from wood is just sufficient for wood-size reduction. It is obvious that significant reduction in wood-size-reduction energy consumption, preferably by a factor of 5–10 to about 0.1–0.4 MJ/kg, is required to achieve sensible net energy output from wood ethanol production. This requirement poses a significant challenge to cellulosic ethanol production from woody biomass.

Four factors affect energy consumption for wood-size reduction through disk milling: the degree of size reduction, the fiberization mechanism, and chemical or biological pretreatment of the wood

prior to size reduction, and milling process conditions. All these factors also affect the subsequent enzymatic cellulose saccharification. To address the degree of size reduction, proper characterization of biomass substrate is necessary. The geometric mean diameter of the substrate particles measured by traditional sieving and screening methods has been almost exclusively used for biomass substrate size characterization (Mani et al., 2004). This size measure is significantly affected by biomass substrate morphology such as particle aspect ratio (Zhu et al., 2009b). Most size-reduction processes produce fibrous substrate with wide ranges of particle (fiber) aspect ratio from 5 to 100. As a result, existing data on substrate size characterization has limited value. Enzyme-accessible surface area is of most interest for saccharification. Recently, we used a wet-imaging technique to determine the substrate-specific surface and found that specific surface can effectively correlate substrate enzymatic cellulose saccharification efficiency (Zhu et al., 2009b).

It is well understood that energy consumption in mechanical wood pulping depends significantly on how the wood chips were fiberized. Refiner mechanical pulps (RMP) are produced under atmospheric refining conditions with wood chips fractured through the lumen of wood tracheids. Thermomechanical pulps (TMP) are produced using low-pressure steam of about 2.4 bar ($\sim 134^\circ\text{C}$) to soften wood chips before disk refining. The wood chips are fractured in the S1 and S2 layer of cell wall. Medium-density fiberboard pulps (MDF) are produced under increased steam pressure of above 5 bar. Wood chips are fractured in the lignin-rich middle lamella (ML) when the steam temperature reaches the glass transition temperature of lignin (Irvine, 1985). The mechanical energy consumption of different fiberization mechanisms varies significantly. Typical energy consumptions in the first pass refining of wood chips for producing RMP, TMP, and MDF are about 800, 500, and 150 W h/kg od wood based on numerous experiments in laboratory and pulp mill commercial practice. The energy consumption in first pass refining of chemically pretreated wood chips (CTMP) is often lower than that for TMP. The surface chemical compositions of these pulps are very different. RMP exposes mostly cellulose on fiber surfaces, whereas MDF fibers are coated with lignin on their surface. This can be clearly seen from the color of these pulps with RMP being the lightest and MDF being brown. The difference in surface chemical composition certainly affects cellulose enzymatic saccharification, as revealed in our previous study (Zhu et al., 2009b). The significant variations in mechanical energy consumption of these different pulping processes may provide avenues for potential energy savings in biomass size reduction. However, attempts have not yet been taken to explore this potential.

The discussion above suggests that thermal or chemical pretreatment of wood chips can alter wood chip fiberization mechanism in disk milling and thereby reduce wood chip size-reduction energy consumption (comparing RMP, TMP, and CTMP). This is because the pretreatment alters the chemical composition and physical structure of wood by partially removing and modifying some cell-wall components such as hemicellulose and lignin. However, the approach of size reduction prior to chemical pretreatment has been proposed as the standard process flow for cellulosic ethanol production by several key pieces of the literature (Lynd, 1996; Yang and Wyman, 2008) and by the recent US Department of Energy biofuel research roadmap (DOE, 2005). This approach has a significant negative effect on the overall energy balance and net energy output in biofuel production from woody biomass as discussed at the beginning of this section. We propose to conduct size reduction after chemical pretreatment, post-chemical pretreatment size-reduction approach, to significantly reduce the energy consumption for wood-size reduction. This approach is used in steam-explosion pretreatment through the post-steam-

pretreatment discharge (flashing or explosion) process. Energy savings of about 30% were obtained in mechanical pulping when wood chips are pretreated by oxalic acid to partially remove wood hemicelluloses (Kenealy et al., 2007). In our recent study (Zhu et al., *in press*), we found that a factor of 2 reduction in size-reduction energy consumption can be easily achieved when dilute acid pretreatment was first applied to wood chips before disk milling. Reduction in size-reduction energy consumption by a factor of 4 was achieved when a novel SPORL pretreatment was applied to wood chips. Furthermore, near complete enzymatic saccharification was achieved for the substrates from disk-milling lodgepole (softwood) wood chips pretreated by the SPORL process.

The post-chemical pretreatment size-reduction approach has several benefits: (1) it takes advantage of chemical pretreatments to soften wood structure to reduce energy consumption in the subsequent size reduction; (2) it avoids the difficult and energy-intensive operation of mixing high-consistency pulp with chemicals during pretreatment when size-reduced biomass is used; (3) it also avoids the difficult process of separating fibers from pretreatment hydrolysate after pretreatment; and (4) it affords a low liquid to woody biomass ratio in chemical pretreatments that reduces thermal energy consumption and potentially produces a concentrated hemicellulose sugar stream favorable for fermentation. This is because liquid uptake of wood chips is much lower than fibers and/or fiber bundles because of the porous and hydrophilic nature of wood fibers.

Finally, Tienvieri et al. (1999) demonstrated that process conditions significantly affect disk refining (milling) energy consumption in mechanical pulping. (The energy savings that can be realized without sacrificing pulp quality is limited (Mihelich et al., 1972)). For example, only 7% energy savings was realized by decreasing primary-stage disk refining discharge consistency (the same as solids-loading) from 50% to 38% in commercial scale trial runs (Alami et al., 1995). However, the fiber qualities required for papermaking are not relevant to and therefore are no longer required for woody biomass saccharification. This provides the feasibility to optimize milling process conditions to decrease energy consumption for wood-size reduction to 20 W h/kg od wood (<0.1 MJ/kg) (Zhu et al., 2009a, b, *in press*), equivalent to that for agricultural biomass size reduction, while maximizing the enzymatic cellulose saccharification efficiency under nominal chemical pretreatment conditions. In a recent study using lodgepole pine, Zhu et al. (*in press*) found that reducing solids-loading in disk milling from 30% (the solids of the wood chips right after pretreatment) to about 20% can reduce disk-milling energy by 20%. We also found that opening the disk-plate gap from 0.38 to 1.52 mm can reduce disk-milling energy by 75% (or a factor of 4) when wood chips were pretreated by dilute acid or the SPORL (Zhu et al., *in press*) process. We did not observe any negative effects on the enzymatic saccharification of the resultant substrates in the ranges of disk-milling solids loading and disk-plate gap studied. Near complete saccharification was achieved for lodgepole pine pretreated by SPORL followed by disk milling with energy consumption of 20–50 W h/kg (0.07–0.18 MJ/kg).

2.2.2. Energy consumption for chemical pretreatment

Energy consumption in chemical pretreatment is mainly dictated by pretreatment temperature, liquid to wood solid ratio (L/W), and the heat of latent when steam is used. When wood-size reduction is achieved thermochemically, such as in steam explosion and the organosolv process, no additional energy for the size reduction is needed. Because the pretreatment temperature is dictated by the chemistry to achieve satisfactory enzymatic cellulose saccharification, the only parameter that can be adjusted to save energy in chemical pretreatment is L/W . When pretreatment is directly applied to wood chips, a L/W of 3 or lower is possible to

achieve satisfactory enzymatic cellulose saccharification (Zhu et al., *in press*). Thermal energy consumptions in chemical pretreatment under three scenarios are listed in Table 3. The energy was calculated based on enthalpy of the process stock at the given pretreatment temperature. For steam-explosion pretreatment, moisture is in vapor form. Net energy data for the two aqueous cases accounted for thermal energy recovery of 50% based on practical experiences in the pulp and paper industry. Net energy data for the steam explosion case accounted for recovery of low quality steam at 144 °C (Wingren et al., 2003). The energy consumption for steam explosion of 1.8 MJ/od kg wood is expensive, as it is equivalent to 25% of ethanol thermal energy from wood.

2.3. Effect of lignin on enzymatic hydrolysis of cellulosic substrate

Lignin accounts for 20–30% of woody biomass, and is a major barrier to enzymatic saccharification of wood cellulose. Mansfield et al. (1999) proposed that lignin retards cellulose hydrolysis by physical barrier and non-productive adsorption of enzymes. The former blocks or protects cellulose from being accessible to cellulases, and the latter prevents the cellulases from accessing the cellulose. Therefore, chemical delignification, lignin modification, and lignin preserving by chemical pretreatment can be effective means to overcome lignin recalcitrance to enzymes (Pan et al., 2004; Yang et al., 2002). Unfortunately, all the chemical delignification operations are expensive. This is one reason why full chemical delignification has not been adopted for woody biomass pretreatment.

Recent research has shown that delignification is not the only way to remove the recalcitrance of lignin. Physically blocking lignin, chemical modification of lignin, and lignin-preserving pretreatments are less expensive but promising. Non-productive (or non-specific) adsorption of cellulases on lignin significantly affects cellulose enzymatic hydrolysis. Covering the lignin using exogenous protein (bovine serum albumin – BSA) prior to enzymatic hydrolysis can reduce the adsorption of cellulases onto lignin and consequently enhance saccharification (Pan et al., 2005b; Yang and Wyman, 2006). Surfactants have also been used as lignin-blocking agents to enhance enzymatic saccharification of cellulose (Tu et al., 2009). Pan (2008) found that phenolic hydroxyl groups in lignin play an important role in affecting enzymatic hydrolysis of cellulose. Therefore, selectively blocking these functional groups is another way to overcome lignin recalcitrance. Evidence shows that the non-specific adsorption of enzymes depends on lignin source and structure. Certain types of lignin have particularly strong affinity to enzymes. Pan et al. (2005b) found that when lignin content of a steam-exploded Douglas-fir was reduced by 7%, from 43% to 36% using alkaline extraction, the enzymatic digestibility of the substrate was improved by 30%. The alkali-extracted lignin fraction contained more phenolic hydroxyl groups and showed strong affinity for protein, whereas the residual lignin had small effect on cellulose hydrolysis.

One example of lignin-preserving pretreatments is the SPORL method (Wang et al., 2009; Zhu et al., 2009a). The delignification extent during SPORL pretreatment was only about 20–30%. The lignin content of the pretreated substrates was increased to about 35% due to the dissolution of hemicellulose (Zhu et al., 2009a, *in press*, Wang et al., 2009). However, the SPORL substrates were readily digestible, and over 90% cellulose saccharification was achieved within 24 h with cellulase loading of about 20 FPU/g cellulose. Partial lignin sulfonation by the SPORL pretreatment increased lignin hydrophilicity and reduced lignin affinity to protein and the non-productive enzyme adsorption onto lignin, which contributed to the observed efficient cellulose saccharification of the SPORL substrates.

2.4. Effect of pretreatment on value-added lignin utilization

Value-added utilization of lignin can help offset the cost of cellulosic ethanol production and improve the economics of biorefining, in particular when high-lignin-containing woody biomass is used as feedstock. Pretreatment significantly affects the physical and chemical properties of the resultant lignin, and thereby affects its utilization for value-added products. Tremendous efforts have been made during the last 50 years to develop high-value lignin products as outlined in several excellent reviews (Lora and Glasser, 2002; Popa et al., 2008; Kumar et al., 2009). However, few breakthroughs have been achieved in developing commercially marketable lignin products. A well-known joke, “One can make anything from lignin but money,” vividly reflects the status and difficulties of lignin utilization. Today, lignosulfonate remains the most successful commercial lignin product. It is produced as a by-product from wood sulfite pulping for pulp and paper production. Because of its unique properties, lignosulfonate has been widely used as adhesives and dispersants (Fengel and Wegener, 1984). On the other hand, lignin from wood kraft pulping is mainly used as boiler fuel to produce steam and electricity by combustion. Combustion including gasification remains the only viable pathway for the utilization of high-volume hydrolysis lignin from future biorefineries.

When developing lignin co-products, one must consider the significant volume of lignin produced. The potential lignin production is about 50 million tons per year based on the US goal of 16 billion gallons (60 billion liters) cellulosic ethanol by 2022. In addition, one must take into account that the quality and potential market of the lignin products are greatly dependent on the pretreatment technology. Shevchenko et al. (2001) showed that the lignin from steam explosion and dilute acid pretreatment is less valuable because it is extensively condensed. Organosolv lignin is an excellent feedstock for high-value lignin because of its unique physical and chemical properties, such as high purity, reactivity, and thermal fusibility, and its low and uniform molecular weight (Pan et al., 2005a). Promising applications of the organosolv lignin include polymer composites (Lora and Glasser, 2002; Kubo and Kadla, 2004) and low-cost carbon fibers (Kadla et al., 2002b). Lignosulfonate from the SPORL pretreatment has existing market as adhesives, dispersants, and emulsifiers (Fengel and Wegener, 1984). However, new markets and products need to be developed because of the significant lignin volume from future biorefineries.

3. Evaluation of pretreatment process performance

Evaluation of pretreatment technologies in the literature has been primarily focused on sugar yield. The most comprehensive work on evaluating the performance of different pretreatment processes was carried out by the Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI). CAFI-I was focused on corn stover (Wyman et al., 2005) and CAFI-II was focused on poplar (Wyman et al., 2009). These two studies provided good understanding of the capabilities and limits for total sugar recovery of selected processes, such as dilute acid, ammonia-recycle percolation (ARP), ammonia-fiber expansion (AFEX), controlled pH, lime, and SO₂-catalyzed steam explosion. The studies did not provide the information on energy consumption for achieving the sugar yields by the selected processes. The ultimate goal of all biofuel technologies is net energy production simply because the whole idea of biofuel is about net energy output. Therefore, we believe that the technical performance of any pretreatment technologies needs to be evaluated based not only on total fermentable sugar production, but also on energy consumed for unit sugar production and its scalability for commercial production. We define pretreatment-process

energy efficiency as the total sugar yield divided by energy consumption in pretreatment as below:

$$\eta_{\text{Pretreatment}} (\text{kg sugar/MJ}) = \frac{\text{Total monomeric sugar yield (kg)}}{\text{Total energy consumption (MJ)}} \quad (1)$$

From the discussions above, steam explosion, organosolv, and SPORL represent the most promising technologies for woody biomass bioconversion. To provide comparative information about the performance of these technologies, we compare total sugar recovery as well as pretreatment energy consumption of these three processes based on studies using softwoods in the literature (Soderstrom et al., 2004; Pan et al., 2008; Zhu et al., 2009a). Because most published studies on these pretreatment processes were conducted in different laboratories around the world without coordination, it is very difficult to carry out an in-depth comparison. To ensure that the comparison is as objective as possible, the following criteria were used in choosing the studies listed in Table 4: (1) the completeness of the data reported to calculate mass and energy balances, (2) the recency of the study to represent the most updated technology, (3) the results of the study to represent or be close to the best performance of each process, and (4) studies from well recognized research groups around the world to ensure that the data used for comparison are accurate and represent the best results available. For example, Soderstrom et al. (2004) did not report xylose recovery in their study. The 70% xylose recovery (very high for steam explosion) used in Table 4 was from the work of Wingren et al. (2003). Both studies were published by Professor Zacchi's research group at Lund University, Sweden. Pan et al. (2008) did not conduct organosolv experiments at 180 °C, which is considered as about the optimal temperature for total sugar yield based on an optimization study using hardwood (Pan et al., 2006a). The data used for comparison in Table 4 were from pretreatment conducted at 170 °C with an enzymatic cellulose saccharification of 88% (not best for organosolv but very good). The enzymatic cellulose conversion was 100% at 187 °C but both xylose

and mannose recovery approached zero, which resulted in a lower total sugar yield than at 170 °C. Based on results from several studies including the work of Pan et al. (2006a, 2008) published by Professor Saddler's group at the University of British Columbia, Canada, the total sugar recovery at 170 °C (Pan et al., 2008) is very close to the best results for organosolv. Furthermore, the thermal energy consumption for aqueous organosolv pretreatment at 170 °C is about 6% lower than that at 180 °C, so the pretreatment energy efficiency at 170 °C should be very close to optimal at about 180 °C.

In calculating the pretreatment energy efficiencies listed in Table 4, thermal energy recovery was taken into account in determining net thermal energy consumption, as listed in Table 3 using the same assumptions discussed previously. The wood-chipping energy was assumed to be 50 W h/kg wood (0.18 MJ/kg). Thermal energy consumption in steam explosion is largely contributed by latent heat with a small effect from steam temperature. Therefore, only one temperature of 215 °C used in the study of Soderstrom et al. (2004) was used in the calculation. On the other hand, *L/W* has a significant effect on thermal energy consumption for aqueous organosolv pretreatment. Two *L/W*s of 4 and 3, significantly lower than 7 used in the study of Pan et al. (2008), were used to provide the most favorable estimations of organosolv process energy efficiency. Most of the work conducted by Pan (co-author of the present review and a former member of Professor Saddler's group at the University of British Columbia, Canada) used *L/W* of 7. A low *L/W* of 3 may affect uniformity of the pretreatment and dissolution of lignin in laboratory scale experiment. *L/W* of 4 is commonly practiced in commercial wood pulping. However, SPORL produced near complete cellulose conversion to glucose for softwood at *L/W* = 3 (Zhu et al., in press). To provide the most conservative estimations of SPORL process energy efficiency, two energy consumption levels of post-SPORL mechanical size reduction, 50 and 150 W h/kg wood, were used. Both of these levels are significantly higher than the lowest achieved level of 20 W h/kg wood reported in our previous studies (Zhu et al., 2009a, in press).

Table 4

Process performance comparisons among steam explosion, organosolv, and SPORL pretreatments. Pretreatment thermal energy data accounted energy recovery based on the same assumptions made in Table 3. Final pretreatment energy efficiencies are based on sugars yields at 65% carbohydrate equivalent due to the differences in carbohydrate content of the wood used in the three studies.

Measure	Unit	Steam explosion ^a	Organosolv ^b	SPORL ^c
Species		Spruce	Lodgepole pine	Spruce
Glucan		53.2%	43.2%	43.2%
Mannan		11.9%	11.6%	11.5%
Xylan		4.3%	7.1%	5.7%
Sum		69.4%	61.9%	60.4%
Wood-chipping energy	MJ(kW h)/ton od wood	180(50)	180(50)	180(50)
<i>Chemical pretreatment conditions:</i>				
Temperature		215 °C	170 °C	180 °C
<i>L/W</i>		1.0	4.0/3.0	3.0
Chemical pretreatment energy	MJ/ton od wood chips	1797	1433/1074	1143
Wood chip size-reduction energy	MJ(kW h)/ton od wood	0	0	540(150)/180(50)
Total energy consumption	MJ/ton	1977	1613/1254	1863/1503
Pretreatment soluble sugar yield	kg/ton od wood	211	134	228
Mannose		78	62	112
Glucose		100	35	68
Xylose		33	37	48
Cellulase loading	FPU/cellulose; FPU/substrate	25.9; 15	20;	24.4; 15
Enzymatic hydrolysis glucose yield	kg/ton wood	346	347	372
Total monomeric sugar yield at 65% carbohydrate equivalent	kg/ton wood	557	481	600
		522	505	646
Pretreatment energy efficiency, η at 65% carbohydrate equivalent	kg/MJ	0.26	0.31/0.40	0.35/0.43

^a Soderstrom et al. (2004). Xylose yield is estimated based on 70% recovery reported from the same lab (Wingren et al., 2003).

^b Pan et al. (2008). *L/W* of 7 was used in all the studies by this lab (not reported in this study). Two *L/W*s of 4 and 3 instead of 7 were used for optimistic estimations of pretreatment thermal energy consumption by organosolv.

^c Zhu et al. (2009a). *L/W* of 5 was used in the study. *L/W* of 3 was used to calculate pretreatment thermal energy consumption because near complete enzymatic hydrolysis conversion of cellulose was obtained at *L/W* = 3 (Zhu et al., in press). Two mechanical size-reduction energy consumptions of 50 and 150 kW h/ton od wood were used for conservative estimations of pretreatment energy efficiency of SPORL.

Published data (Table 4) show that SPORL produced the highest sugar yield among all three processes. Steam explosion consumed the highest amount of energy. As a result, steam explosion has the lowest pretreatment energy efficiency of 0.26 kg sugar/MJ among the three processes. Under favorable conditions, i.e., low L/W of 4 and 3, the pretreatment energy efficiencies of organosolv, 0.31 and 0.40 kg sugar/MJ, respectively, are still lower than the conservative estimations of 0.35 and 0.43 kg sugar/MJ for SPORL under mechanical size-reduction energy consumption of 150 and 50 kW h/ton, respectively. Additional thermal energy (not included in Table 4) is required to remove (recover) the solvent (ethanol) from the organosolv pretreatment hydrolysate before the sugars can be fermented using existing yeasts or other microbes. The main drawback of steam explosion is its poor enzymatic digestibility (about 60%). Therefore, it is expected that the performance of steam-explosion pretreatment, in terms of total sugar yield and pretreatment energy efficiency, can be improved and may match the performance of organosolv and SPORL when applied to hardwood species. The cause of low pretreatment energy efficiency of organosolv process is its low hemicellulose sugar recovery of <50% from the pretreatment hydrolysate. The post-SPORL pretreatment size-reduction approach significantly reduced total pretreatment energy consumption (Zhu et al., 2009a, in press). With excellent sugar recovery, SPORL could be the best process to deal with both hardwood and softwood biomass. On the other hand, SPORL is a new process and has not been well studied.

From a process scalability point of view, steam explosion has many hurdles to overcome. For example, steam explosion reactors that can handle over 1000 ton wood/day do not exist. On the other hand, SPORL pretreatment can be carried out using commercially available wood-pulping digesters. Mechanical size reduction of pretreated wood chips in the SPORL process can be easily implemented using modern commercial disk-milling technology for mechanical wood pulping. It is conceivable to carry out SPORL pretreatment along with mechanical size reduction in one integrated system using similar technologies as commercial chemical-mechanical pulping. Modern wood pulping has been in commercial scale production at similar scales of future biofuel production capacity for several decades. Therefore, SPORL appears to have significant advantages in building new commercial scale woody biomass biorefineries.

4. Integrated forest biorefinery – value prior to pulping (VPP)

Wood has long been used as the major feedstock for pulp and paper production. With the recent renewed interest in cellulosic ethanol production, the pulp and paper industry proposed the concept of VPP (van Heiningen, 2006; Thorp and Raymond, 2004). In VPP, the hemicelluloses are either partially or completely extracted out for biofuel production through a prehydrolysis step similar to pretreatment. The remaining solid (mainly cellulose and lignin) is further delignified for wood pulp or fiber production rather than saccharified. This is a very interesting idea because wood pulp or fibers are worth more than ethanol. Furthermore, the VPP concept can be easily retrofitted into existing pulp and paper mills without significant capital cost. It can be a potentially viable stepping stone for the world's oldest and largest biorefineries, pulp and paper mills, to become a major player of the future biobased economy.

The rationale of the VPP concept includes: (1) a significant amount of hemicelluloses are dissolved and lost in the spent liquor during Kraft pulping, the most efficient wood pulping process with the largest market share, and used as fuel during combustion of concentrated spent liquor in a recovery boiler. This is not an efficient way to use hemicelluloses because of their low heating value (half that of lignin, van Heiningen, 2006). In addition, the dissolu-

tion of the hemicelluloses consumes most of the pulping reagent, alkali. Therefore, the pre-extraction of hemicelluloses will reduce the alkali charge needed for pulping. (2) If the dissolved hemicelluloses can be recovered and converted to ethanol or other high-value products, it can improve the net energy efficiency and economics of pulping. (3) Ethanol has a much larger market than wood fiber. Many pulp and paper research organizations throughout the world are conducting various forms of VPP research work.

The key to the success of the VPP concept is fiber quality and pulp yield. This is because fiber quality has paramount importance for wood fiber producers, and fibers are worth much more than ethanol. However, few success stories have been reported. Fiber yield loss of 3–6% and reduced pulp tensile strength were found when hot-water prehydrolysis was applied to loblolly pine before Kraft pulping (Yoon and van Heiningen, 2008). Another option for VPP is to produce mechanical pulps after hemicellulose extraction (developed at the US Forest Service, Forest Products Laboratory). The key advantage of this concept is to reduce mechanical pulping energy. Because mechanical pulping is very energy-intensive (over 2000 kW h/ton od wood), savings in energy has significant importance. When oxalate acid in the form of diethyl oxalate (DEO) was used to partially extract hemicelluloses, mechanical pulping energy was reduced by about 30% while all pulp properties (tensile, tear, and burst strength) were slightly increased (Kenealy et al., 2007). Another option for VPP is to pre-extract hemicelluloses using near-neutral green liquor (a solution of sodium sulfide and carbonate from chemical recovery system of kraft pulping) to produce ethanol and acetic acid, and then cook the wood chips by Kraft pulping for fiber production (Mao et al., 2008). The process improved kraft pulp yield by 1% and increased tear strength.

5. Challenges in commercial production of cellulosic ethanol

Despite substantial progress in cellulosic ethanol research and development, many challenges remain to be overcome for commercial production. High energy consumption for biomass pretreatment remains a challenge, though the cost of energy consumption for woody biomass pretreatment can be reduced to the level used for agricultural biomass. Excellent wood cellulose saccharification efficiency can be achieved using organosolv, SPORL, and steam explosion (hardwood only) as discussed in this review. However, improvement in the yield of hemicellulose sugars is still needed. Process scalability is one of the key challenges for commercial production. Capital equipment required for commercial demonstrations of some technologies, such as steam explosion, does not exist. On the other hand, the pulp and paper industry has the capability and infrastructure of handling biomass on the scale of 1000 ton/day, equivalent to the scale of future cellulosic ethanol plant of 100 million liters/year. Therefore, processes that can use process technologies, capital equipment, and human capital in the pulp and paper industry will have a better chance to succeed. However, there is a lack of economic incentive for the pulp and paper industry to shift to a stand-alone biorefinery for ethanol production because fibers are still worth more than ethanol.

The recovery of pretreatment chemicals and wastewater treatment are also important issues in selecting pretreatment technologies in commercial production. The dilute acid and acid-catalyzed steam pretreatment can be performed without the recovery of the acid because of the low cost of sulfuric acid. However, substantial amounts of alkaline chemicals are required to neutralize the pretreatment hydrolysate. In addition, the salt produced from the neutralization needs to be properly disposed of. Furthermore, the dissolved organics in the stream of post-fermentation pretreatment

hydrolysate represent a significant amount of chemical oxygen demands and needs to be dealt with. On the other hand, the solvent ethanol used in the organosolv process can be easily recovered through distillation, but a significant amount of energy is required using current technology. As briefly outlined above, the recovery of the chemicals used in the SPORL process can be and have been commercially implemented using technologies, such as high efficiency wet scrubbers and fluidized bed reactors.

Finally, feedstock versatility is another factor to consider when choosing a pretreatment process. Cellulosic ethanol is a commodity product; therefore, one cannot afford high-grade feedstock in production. The pulp and paper industry has very limited choices in selecting wood sources for fiber production. Many pulp mills use sawdust and other residues available from lumber mills because lumber is more valuable than fiber (paper and paperboard). Pulp mills do not have the luxury to choose specific tree species or a particular section of trees for fiber production. Pulp mills tailor their production process to fit various grades of wood. Fiber (paper) is a more valuable commodity product than cellulosic ethanol. It is expected that future cellulosic ethanol refineries will have even less flexibility and choices in selecting feedstocks than pulp mills have today. Therefore, the pretreatment process must be versatile, i.e., effective on different feedstocks. Pretreatment processes that are only effective on certain feedstocks will have difficulties in commercial adoption. Challenges in developing integrated forest biorefineries include how to maintain pulp yield and strength and how to concentrate and ferment the hemicellulosic sugar stream that mainly contains pentose when hardwoods are used.

6. Conclusions

Pretreatment energy efficiency (η) can be defined as sugar production on unit energy consumption in pretreatment. Only when both the energy efficiency and total sugar production are measured can provide an objective evaluation of the performances of various pretreatment technologies. The post-chemical-pretreatment size-reduction approach can significantly reduce energy consumption to as low as 20–50 kW h/ton of wood. The SPORL process appears to have inherent advantages for woody biomass conversion especially for softwood species, in terms of total sugar production, process energy efficiency, lignin co-product potentials, and commercial scalability. Woody biomass is a very important feedstock for the future biobased economy. It has many advantages. However, issues specifically associated with woody biomass conversion in the upstream processing need to be addressed.

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