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THE STATUS OF AND KEY BARRIERS IN LIGNOCELLULOSIC ETHANOL PRODUCTION: A TECHNOLOGICAL PERSPECTIVE

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ABSTRACT

The development of biorefineries to produce fuel ethanol and commodity chemicals from lignocellulosic biomass is a potential alternative to current reliance on non-renewable resources. However, many technological barriers remain despite research progress in the past several decades. This article examines the major process barriers in biochemical conversion of biomass to cellulosic ethanol. We review the key pretreatment processes, including a process recently developed by the authors for biomass conversion, and the technical potentials for commercialization. The importance of feedstock physical size reduction and issues related to size-reduction energy consumption and substrate size characterization are also discussed. The article also analyzes and compares enzymatic conversion of cellulose from different feedstocks and the recovery of hemicellulose sugars from different pretreatments. Finally, we discuss the commercial viability of the existing processes in terms of the availability of commercially proven capital equipment.

Keywords: Pretreatment, lignocellulose, bioenergy, saccharification, cellulosic ethanol, hydrolysis, size reduction, SPORL

1. INTRODUCTION

Many factors have contributed to the recently renewed interest in and serious consideration of cellulosic ethanol as an alternative to petroleum-based transportation fuel. In the United States, the Energy Independence and Security Act of 2007 mandates that our Nation produce 30 billion gallons of biofuel by 2020. About 16 billion gallons need to be from cellulosic biomass. Science has recognized that greenhouse gas emissions from burning fossil fuel such as petroleum contributes to global climate change. The increased demand of energy in developing nations such as China and India and gradual depletion of petroleum worldwide reserves have driven oil prices to record highs. Geopolitical and national security reasons have also contributed to the inevitability of seeking alternative energy, especially from renewable and sustainable sources.

Bioenergy can be sustainable using modern technology coupled with sound policies [1]. The United States alone can sustainably produce 1.3 billion tons of biomass annually, 30% of which would come from woody biomass [2]. The theoretical ethanol production from 1.3 billion tons of biomass is about 130 billion gallons [3], or more than 60% of the total U.S. annual gasoline consumption. This rosy picture of the availability of massive biomass may not be the case for other countries, such as China. However, simply using modern converting technology to replace traditional biomass burning practices can free up a significant amount of biomass for transportation fuel production in many countries.

With the potential availability of over one billion tons of biomass annually, aggressive research strategies have been developed through various workshops in the United States in recent years. Particularly notable are three workshops that this article will discuss. The first workshop focused on biochemical conversion of biomass to liquid fuel, was sponsored by the U.S. Department of Energy (DOE) in December 2005, and produced a joint Research Agenda [4]. The. The second workshop was sponsored jointly by the U.S. National Science Foundation, the American Chemical Society, and the DOE in June 2007

[5]. This workshop focused on thermochemical conversion of biomass to liquid fuel. The third workshop was sponsored by the U.S. Forest Service in December 2007 [6], focusing on partnership and collaboration for sustainable production of forest biomass and woody biomass conversion technologies.

In addition to workshops, major research and development investments have also been put into place around the world. The DOE established three bioenergy research centers to focus on fundamental understanding of lignocellulose bioconversion [7]. The centers are located in three major geographical regions in the United States: The Joint BioEnergy Institute hosted by the University of California-Berkeley in the Pacific West, the Great Lakes Bioenergy Research Center hosted by the University of Wisconsin-Madison in the Midwest, and the Bioenergy Science Center hosted by the DOE Oak Ridge National Laboratory in the Southeast. The direct investment in five years will be at US$ 375 million for the three centers.

In China, the Chinese Academy of Science (CAS) established the Qingdao Institute of Bioenergy and Bioprocess Technology (QIBEBT) with funding from CAS and the Shandong provincial and Qingdao municipal governments. The mission of QIBEBT is to investigate and develop sustainable energy resources to sustain national economic growth, to reduce the dependence on fossil fuel, to protect the environment, and to stimulate local economic and social development. The initial investment of QIBEBT is 350 million yuan equivalent to US $50 million in addition to 6.5 hectares of land donated by the City of Qingdao.

The private sector has also invested in woody biomass technologies. For instance, British Petroleum will invest US $500 million over 10 years for the Bioenergy Science Institute hosted by the University of California-Berkeley. These investments are expected to bear fruit for sustainable and economical production of biofuels from biomass.

The objective of the present article is to examine the status of and key barriers to biochemical conversion of lignocellulose to ethanol.

2. STATUS AND CHALLENGES IN CELLULOSIC ETHANOL PRODUCTION

Biochemical conversion of lignocellulose through saccharification and fermentation is a major pathway for liquid fuel production from biomass [4, 5]. In this approach, biomass cellulose is converted to glucose using microbial or enzymatic actions. The glucose is then converted to alcohols through fermentation. Unlike starch as an energy storage material, nature produces plants such as wood with cellulose as the backbone for cell-wall structural materials. Cellulose is strong and protected by other chemical components, such as hemicellulose and lignin, in the cell walls of biomass. As a result, biomass has natural resistance—often called “recalcitrance”—to microbial and enzymatic deconstruction [8].

The recalcitrance of lignocellulose is one of the major barriers to the economical production of biobased fuels and chemicals. The technical approach to overcome recalcitrance has been pretreatment of biomass feedstock to remove the barriers and make cellulose more accessible to hydrolytic enzymes for conversion to glucose. Typically, both physical and chemical pretreatments have been used. Physical pretreatment refers to the reduction of physical size of biomass feedstock to increase enzyme-accessible surface areas [9, 10] and decrease the crystallinity of cellulose. Chemical pretreatment refers to the process of using chemicals to remove or modify key chemical components that protect cellulose in biomass, mainly hemicellulose and lignin. Lack of low-cost and high-activity cellulose hydrolytic enzymes is another barrier to cellulosic ethanol production.

Other key technical barriers include the difficulty in fermenting the five carbon sugars produced from biomass hemicelluloses and the cost of distillation of alcohol from the weak fermentation broth. Table 1 shows the current and future processing costs of ethanol from corn stover based on DOE analysis [11]. Rapid development in enzyme and yeast biotechnology in recent years has significantly reduced the cost of enzyme and fermentation cost for biofuel production [11]. Further reduction of enzyme and yeast costs is expected in the near future. Commercialization of advanced membrane technology [12, 13] is also expected in the next decade to significantly reduce the cost of separating weak ethanol from fermentation broth. On the other hand, the cost associated with feedstock pretreatment to overcome lignocellulose recalcitrance accounts for about 30% of ethanol production cost, which is not expected to decline in the foreseeable future (Table 1 [11]). Limited progress has been made in feedstock pretreatment, despite much research effort in the last several decades. Dilute acid pretreatment developed over a century ago is still the dominant process for biomass pretreatment today [10, 14, 15]. Therefore, the discussion part of this article will focus on feedstock pretreatment. Other than the production costs listed in Table 1, feedstock cost is also a major cost for cellulosic ethanol production.

TABLE 1: BREAKDOWN OF PROCESSING COSTS FOR ETHANOL PRODUCTION FROM CORN STOVER IN 2005 US DOLLARS

PROCESS	2005	2009	2012
Pretreatment	0.44 (27%)	0.31 (22%)	0.25 (30%)
Enzymes	0.32 (20%)	0.33 (24%)	0.10 (12%)
Saccharification Fermentation	0.31 (19%)	0.27 (20%)	0.10 (12%)
Distillation	0.18 (11%)	0.17 (13%)	0.15 (18%)
Balance of Plant	0.34 (21%)	0.27 (20%)	0.22 (27%)
All Processing	**1.59**	**1.35**	**0.82**

Data from the U.S. Department of Energy [11]. Numbers in parentheses indicate percentage of the total cost.

2.1 Physical Size Reduction of Biomass

As mentioned above, plants produce lignocellulosic biomass as a cell-wall structural material. Lignocellulose is often large, strong, and tough. To achieve effective microbial destruction of biomass for conversion to fermentable sugars, physical size reduction of biomass to the level of fibers or fiber bundles is necessary to increase microbial reaction surfaces [4, 9, 10]. However, the issue of physical size reduction has been completely overlooked in the cellulosic ethanol research community. The reason is likely in part because most cellulosic ethanol research has been focused on using agricultural residue that does not need a significant amount of mechanical energy to achieve satisfactory size reduction. However, size reduction is very energy intensive for certain feedstocks, such as wood, bamboo, giant reed, and bush crops. In wood-fiber production, there are two steps for size reduction. The first step is coarse size reduction, reducing the logs to chips of around 10 to 50 mm in two dimensions and about 5 to 15 mm in the third dimension. The second step is to further reduce the chips or chops to fibers about 2 mm long. The energy consumption in the first step is much lower than that in the second step.

Let us conduct a simple energy balance calculation using woody biomass to demonstrate the importance of size reduction for biomass refining. We assume that ethanol yield from wood is about 300 liters/ton of oven-dried wood with current technology. Higher heating value of ethanol is about 24 MJ/liter, which gives total wood ethanol energy of 7.2 MJ/kg wood. Typical energy consumption to produce wood chips is about 50 Wh/kg. The energy consumption in the second step through disk milling can be anywhere from 150 to 700 Wh/kg [16], depending on the fiberization process and the degree of milling. Assuming total size-reduction cost is 200 to 600 Wh/kg, which is equivalent to 0.72 to 2.16 MJ/kg, or 10 to 30% of the wood ethanol energy available.

Three factors affect energy consumption during size reduction: the degree of size reduction, the fiberization mechanism, and chemical or biological pretreatment prior to size reduction. All these factors also affect enzymatic cellulose saccharification. Most of the existing literature on size reduction was carried out for pellet, fiber, and wood flour production. Few studies on biomass size reduction have taken an integrated approach to examining energy consumption, enzyme-accessible substrate surface, and chemical pretreatment efficiency in terms of enzymatic cellulose conversion. Most reported work on size reduction has not conducted cellulose conversion [16-18] and only discussed energy consumption and substrate size. On the other hand, research work on enzymatic hydrolysis using size-reduced substrates did not provide information about the energy consumed to produce the substrate and/or a careful and complete characterization of the size of the substrate [19-21]. At most, substrates were characterized by sieving or screen methods [22-25]. Consequently, there is a knowledge gap linking energy consumption, substrate surface, and pretreatment efficiency.

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 screen methods has been almost exclusively used for biomass substrate size characterization [18]. This size measure is significantly affected by biomass substrate morphology such as particle aspect ratio [9]. Most size-reduction processes produce fibrous substrate with wide ranges of particle (fiber) aspect ratio of 5:100. As a result, existing data on substrate size characterization has limited value. Enzyme-accessible surface area is of most interest for saccharification. Holtzapple et al. [26] calculated specific surface area based on a spherical particle assumption to correlate energy consumption for comparing the efficiencies of several size-reduction processes. The spherical model for specific surface calculation is justifiable for particles with close to unity-aspect ratio, such as sawdust, but is questionable for most biomass substrates consisting of fibers. Recently, we developed a wet-imaging technique for the

characterization of biomass substrate [9]. In this technique, the two dimensions of each substrate fiber are measured in a flowing water channel by an optical microscopy using a charge-coupled device (CCD) camera (Fig. 1).

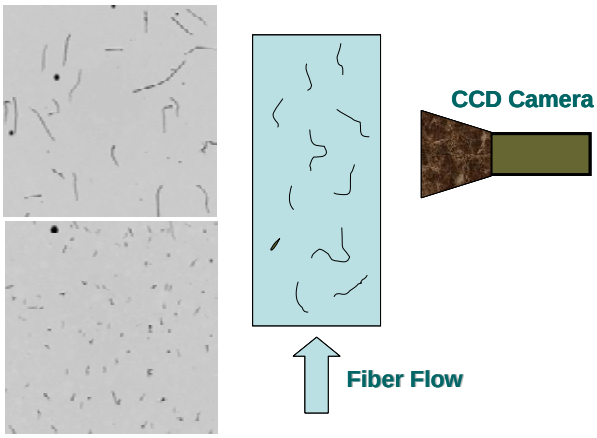

Fig. 1. A schematic diagram shows the wet-imaging technique and typical images acquired.

The total surface and volume of the substrate can be calculated using a cylinder model for each fiber. The volumetric specific surface can be determined by dividing the total surface of a sample by its volume (Eq. (1)) [9]. For most mechanically derived substrates, the cylinder assumption is reasonable as confirmed by scanning electron microscope pictures of the substrates [9]. If the substrate particles are spherical like sawdust, then a spherical model can be used to determine specific surface (Eq. (2)).

$$S_f^{\ V} = \frac{A_f}{V_f} = \frac{2\sum_i n_i (d_i^{\ 2} + 2 \cdot d_i \cdot L_i)}{\sum_i n_i d_i^{\ 2} \cdot L_i} = \frac{4\sum_i n_i d_i (L_i + d_i / 2)}{\sum_i n_i L_i \cdot d_i^{\ 2}} \approx 4 \cdot \frac{\sum_i n_i L_i \cdot d_i}{\sum_i n_i L_i \cdot d_i^{\ 2}} = \frac{4}{D_{L21}} \tag{1}$$

$$S_p^V = \frac{A_p}{V_p} = 6 \cdot \frac{\sum_i n_i d_i^{\ 2}}{\sum_i n_i d_i^{\ 3}} = \frac{6}{D_{32}} \tag{2}$$

Where S and A are the specific surface and total surface area of the substrate, respectively. Subscript f and p are fiber (cylinder model) and particle (sphere model), respectively. D_{L21} is fiber-length weighted-surface-length mean fiber diameter or "width". D_{32} is often called Sauter mean diameter (SMD). With this wet-imaging technique, we were able to objectively compare the efficiencies of different size-reduction and chemical pretreatment processes in terms of size-reduction energy consumption and cellulose to glucose conversion.

Energy consumption in mechanical pulping of wood 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 tracheid. Thermomechanical pulps (TMP) are produced using low-pressure steam about 2.4 bar (~134^{o}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. In the MDF production process, wood chips are fractured in the lignin-rich middle lamella (ML). This is because the steam temperature reaches the glass transition temperature of lignin [27]. Figure 2 shows the schematic of various fracture mechanisms of wood chips during fiberization. The energy consumption of different pulping processes varies significantly. Typical energy consumptions for producing RMP, TMP, and MDF are about 600, 450, 150 Wh/kg oven- dried wood, respectively. The energy consumption for chemical-thermomechanical pulp (CTMP) is just lower than that for TMP. The surface chemical compositions of these pulps are very different. RMP exposes mostly cellulose on fiber surface. MDF fibers are lignin-coated

on their surface. This can be clearly seen from the color of these pulps with RMP being the most light and MDF being brown. The difference in surface chemical composition certainly affects cellulose enzymatic conversion to glucose, as revealed in our previous study [9]. 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.

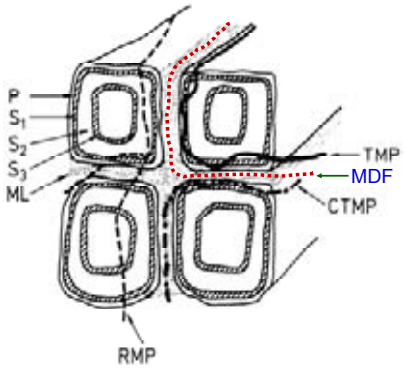

Fig. 2 A schematic diagram showing the various fiberization mechanisms of softwood (adapted from Franzen, *Nordic Pulp Paper Res. J.*, **1**:4, 1986 and Salmen, *Fundamentals of Mechanical Pulping*, in Book 5: Mechanical Pulping, Papermaking Science and Technology, Gullichsen and Paulapuro Eds., Fapet Oy, Finland, 1999). With permission to use from Nordic Pulp and Paper Research Journal and Finland Paper Engineers' Association.

The third factor affecting size-reduction energy consumption and enzymatic cellulose saccharification is chemical pretreatment. Most of the enzymatic cellulose saccharification research has used size-reduced substrate for the purpose of reducing substrate recalcitrance to achieve high cellulose conversion [19-21]. In fact, size reduction prior to chemical pretreatment is necessary for the dilute acid process [4, 10], one of the most investigated chemical pretreatment processes for cellulosic ethanol production. Chemical pretreatment alters the chemical composition and physical structure of biomass by partly removing some cell-wall components such as hemicellulose and lignin. As a result, size reduction after chemical pretreatment can reduce energy consumption. This energy savings may be insignificant for some agricultural biomass, such as corn stover or switch grass, but could be significant for biomass with strong physical integrity, such as wood, bamboo, and giant reed. This suggests that post-chemical pretreatment size reduction is preferred (Fig. 3) in cellulosic ethanol production to take advantage of chemical pretreatments for economical size reduction. Furthermore, different chemical pretreatments alter biomass structure to varying degrees and therefore affect post-pretreatment size-reduction energy savings.

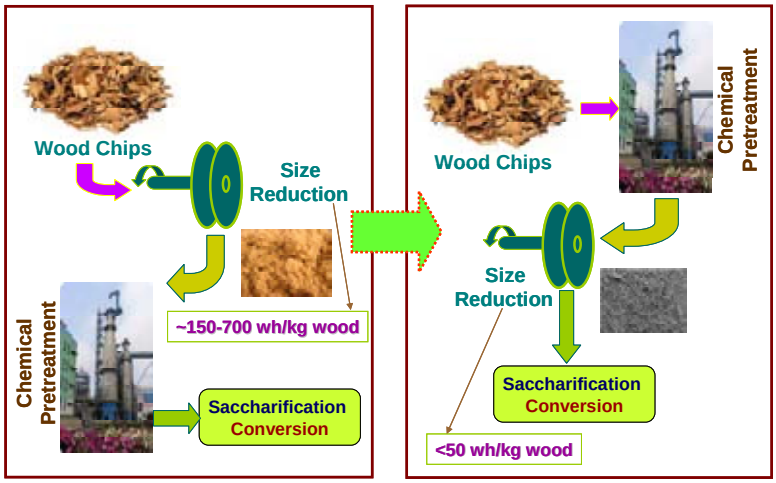

Fig. 3. Required order for size reduction operation from pre- to post-chemical pretreatment to reduce energy consumption.

This post-chemical pretreatment size-reduction process flow design has several benefits: (1) it takes advantage of chemical pretreatment to alter wood structure to reduce energy consumption in the subsequent size-reduction process; (2) it avoids the difficulties and high-energy consumption for mixing high-consistency pulp with chemicals in pretreatment when size-reduced biomass is used; (3) it can reduce thermal energy consumption in chemical pretreatment; and (4) it can potentially produce a concentrated hemicellulose sugar stream to reduce concentration cost. The rationale for (3) and (4) is that a low liquid to biomass ratio can be used in the chemical pretreatment of biomass with minimal size reduction (not fiberized, such as chips or chops). Liquid uptake of size-reduced (fiberized) feedstock is much higher than that of unreduced biomass (chips or chops) because of the porous and hydrophilic nature of biomass.

2.2 Chemical Pretreatment of Biomass

Existing enzymes cannot effectively convert lignocellulose to fermentable sugars without chemical pretreatment. The most promising pretreatment processes include a dilute acid process developed a century ago, steam explosion, organosolv, and sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL). Alkaline processes suffer from silica scaling in chemical recovery because many agricultural feedstocks, such as rice and wheat straw in China, have very high silica content. The scaling problem prohibits the recovery of alkaline chemicals from pretreatment liquor. Many small pulp mills were closed in China in the 1980s and 1990s because of environmental problems caused by direct discharge of spent liquor from alkaline pulping of wheat and rice straw.

2.2.1 Dilute Acid Pretreatment

Acid pretreatment for ethanol production was developed in Germany in the 19th century. In the United States, the U.S. Forest Service, Forest Products Laboratory (FPL) conducted extensive research using acid pretreatment for ethanol production from wood. The FPL work ended in the later 1970s [28]. The DOE National Renewable Energy Laboratory continued the work where FPL left off, and in the last 30 years has focused mainly on using corn stover as a feedstock.

Dilute acid pretreatment is the most studied process [15, 21, 28, 29]. Sulfuric acid is most frequently used because of its low cost; oxalic acid and acetic acid are also used [30]. With recent developments in enzyme technology, most processes use one-stage dilute acid pretreatment followed by enzymatic hydrolysis for cellulose conversion to glucose. The dilute acid pretreatment works fairly well on agricultural feedstocks, such as corn stover and rice/wheat straw. It removes hemicellulose and therefore the recalcitrance to enzymatic hydrolysis of cellulose. The success has been achieved on pilot scales [29]. Several demonstration projects (Verenium, Mascoma, Abengoa, and China-Petro) are based on dilute acid pretreatment. Based on pilot-scale operations [29], typical pretreatment conditions on pre-chopped corn stover are a ratio of five parts liquid sulfuric acid solution (1%, or pH ~1.5) to one part biomass solid and temperature of 180 to 190°C. The high ratio of liquid to solid of five is required because of the bulky nature of the feedstock after pre-chopping. The pretreatment time varies with pH and temperature. A typical combined severity factor (a function of temperature, time, and pH) for the pretreatment [31] is around 1.5. Enzymatic cellulose hydrolysis of about 80% was achieved at 6% cellulose consistency with enzyme loading of 15 FPU/g (filter paper unit) cellulose. Monomeric xylose recovery was only about 65% at maximum. About 15% of the xylan was converted to furfural and another 15% was uncovered during pretreatment. At low pH and/or temperature of 180°C or higher, a significant amount of furfural was produced, a common problem of pretreatment with acid [32], which results in low xylose recovery and is a major inhibitor to fermentation yeast. Furthermore, the acid also causes corrosion problems for the pretreatment digester. The ratio of liquid to solid of five or higher increases pretreatment thermal energy consumption, produces pretreatment hydrolysate with low sugar concentration, and limits the production capacity in commercial production.

The performance of dilute acid pretreatment is not entirely satisfactory for woody biomass, in particular softwoods. The requirement of size reduction prior to the pretreatment [4, 9, 10] makes the dilute acid process less suitable for pretreating feedstocks with strong physical integrity, such as woody biomass, bamboo, and giant reed, because of the high-energy consumption in size reduction, as discussed previously.

2.2.2 Acid-Catalyzed Steam Pretreatment

Just like dilute acid pretreatment that was initially developed for chemical pulping, steam pretreatment was derived from a failed steam explosion pulping process [33]. Acid-catalyzed steam explosion is the most common steam pretreatment [34-36]. SO_2 [37] or sulfuric acid [38, 39] has been used as a catalyst. Chip or chip-sized feedstocks are often first impregnated with acid catalyst either in gas phase with SO_2 or in the aqueous phase with sulfuric acid before steam pretreatment. The

further size reduction to fiber or fiber bundle level is accomplished through steam explosion. Acid-catalyzed steam pretreatment is actually another form of dilute acid pretreatment in which the pretreatment is carried out in the vapor phase rather in the aqueous phase. The explosion feature has now been used by many dilute acid operations for further size reduction. Therefore, the difference between dilute acid and Acid-catalyzed steam pretreatment is becoming less clear. However, steam pretreatment works well with hardwood when pretreatment is conducted at an elevated temperature of around 210°C [37, 39]. The effectiveness on hardwood is achieved at the expense of the large amount of energy consumption in steam explosion. Typical energy consumption for the pretreatment at 210°C is about 1.8 MJ/kg oven-dried wood even after accounting for low-quality steam recovery. The conversion of softwood cellulose is less satisfactory than that of hardwood [34]. Furthermore, total hemicellulose and glucose yield from pretreatment and enzymatic hydrolysis is about 70% [36]. Typical pretreatment conditions for wood are temperatures around 210°C, and SO_2 or sulfuric acid charge of 1-2% on oven-dried wood. Pretreatment time varies from 3 to 10 minutes. Steam explosion can produce a relatively concentrated hemicellulose sugar stream from the pretreatment hydrolysate when the washing water is limited to the minimum, e.g., less than two times the biomass solids. Just like dilute acid pretreatment, steam explosion has relatively low hemicellulose recovery of about 65% [10]. The scalability of the process is an issue for commercialization, as will be discussed later.

2.2.3 Organosolv Pretreatment

The development of organosolv pretreatment technology is directly related to organosolv pulping [40-42] just as steam pretreatment is to steam explosion pulping. The chemistry of organosolv pulping is fairly well understood [43]. Early work using organosolv pretreatment for fermentable sugar production was mostly conducted in the 1980s with some success [44, 45]. The ethanol organosolv process was originally designed to produce clean biofuel for gas turbine combustors and was further developed into the Alcell^{R} process for pulp production from hardwood [46-48]. The ethanol organosolv process is now the preferred process for biomass fractionation and pretreatment for biofuel production [49]. A demonstration project by Lignol (Vancouver, British Columbia, Canada) using the ethanol organosolv process is currently being funded by the DOE. The main advantages of the ethanol organosolv process are: (1) it produces a readily digestible cellulose substrate from almost all kinds of feedstock including softwood and hardwood [49, 50] and (2) it also produces very high purity and quality lignin with the potential of high-value applications [51]. Typical pretreatment conditions for woody biomass are temperatures around 175-195°C, pretreatment time around 60 minutes, ethanol concentration in pretreatment liquor of 50%, pretreatment liquor pH of about 2-3, typical liquid to biomass solid ratio of 4-7. In pretreating poplar wood [50], about 70% 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 almost all of it was converted to glucose. Despite the excellent cellulose conversion, xylose recovery rate was low. Furthermore, the relatively high liquor to solid ratio used in pretreatment produces lower hemicellulose sugar concentration in the pretreatment hydrolysate. It also increases thermal energy consumption in pretreatment. Therefore, the organosolv process is an expensive process.

2.2.4. Sulfite Pretreatment - SPORL

A (SPORL) was recently developed by the present authors at the U.S. Forest Service, Forest Products Laboratory and the University of Wisconsin-Madison [52, 53]. The SPORL was developed based on the fundamental understanding of sulfite wood pulping. The degrees of hemicellulose dissolution, cellulose depolymerization, and lignin sulfonation and condensation are controllable by varying pulping conditions, such as temperature and pH [54-56]. By properly controlling reaction temperature, pH, and time, it is possible to remove the lignocellulose recalcitrance through a mild sulfite pretreatment process.

Wood chips first react with a solution of sodium bisulfite (or calcium or magnesium or other bisulfite) at 160-180°C and pH 2-5 for about 30 minutes, and then are fiberized using a disk refiner to generate fibrous substrate for subsequent saccharification and fermentation. The removal of the recalcitrance of lignocellulose by SPORL is achieved by the combined effect of dissolution of hemicelluloses, depolymerization of cellulose, partial delignification (less than 30%), sulfonation of lignin, and increasing surface area by defiberization through disk refining. Lignin sulfonation increased the hydrophilicity of SPORL pretreated substrates and may have promoted the enzyme processes. The pretreatment liquor to biomass ratio is typically in a range of 2-3, significantly lower than that used in dilute acid and organosolv processes. Therefore, SPORL can produce a relatively concentrated hemicellulose sugar stream. The dissolved hemicellulose stream (a mixture of hexoses and pentoses) and lignin (lignosulfonate) can be separated using ultrafiltration. The former can be further fermented to ethanol, and the later is a high-value co-product that can be directly marketed. The fermentation of spent sulfite pulping liquor (SSL) has been in industrial practice for commercial cellulosic ethanol production for decades [57]

Typical pretreatment conditions of SPORL are temperatures at 170-190°C, and pH 2-5. For batch operation, a retention time is about 30 minutes. The bisulfite charge on biomass depends on the feedstock species. For example, bisulfite of about 8% is required for softwood, whereas only 4-6% and 2-3% are required for hardwood and for agricultural residual, respectively. Cellulose-to-glucose conversion over 90% can be easily achieved even for softwood with low-enzyme loading. The pretreatment is directly applied to wood chips without further size reduction. Furthermore, size-reduction energy consumption after pretreatment was only 20 Wh/kg oven-dried wood [52]. With excellent cellulose conversion and very low size-reduction energy consumption, SPORL fits the requirement for woody biomass conversion paradigm. SPORL also has low formation of hydroxymethylfurfural (HMF) and furfural, two of the main inhibitors to fermentation. The combined severity factor under optimal SPORL pretreatment conditions ranges from 1.3 to 1.7. When SPORL was applied to spruce, a softwood, under the conditions for optimal cellulose conversion [52], the HMF and furfural productions were about 7 and 3 mg/g oven-dried wood, respectively. This is an order of magnitude lower than the 50 and 25 mg/g produced using steam catalyzed pretreatment when glucose yield was maximized at a combined severity factor between 3.0 and 3.4 [32]. SPORL has an overall glucose recovery of 93% from spruce. SPORL also has excellent hemicellulose recovery. Major saccharides (arabinose, galactose, xylose, and mannose) yields are about 54%, 86%, 76%, and 88%, respectively, for spruce [52].

Because ethanol organosolv pretreatment is the most robust process in terms of removing lignocellulose recalcitrance, Figures 4a and 4b show the comparison of cellulose conversion between SPORL and organosolv pretreated softwood [52] and hardwood [53]. Very similar enzymatic hydrolysis conditions were used, i.e., 2% solid consistency, enzyme loadings of about 20 FPU cellulase and 30 CBU β–glucosidase /g cellulose. The results indicate that SPORL effectively removed lignocellulose recalcitrance and achieved cellulose conversion rates that match those of organosolv pretreatment with equivalent glucose yield. When SPORL is applied to corn stover, 90% enzymatic cellulose conversion can be achieved at the same time used for dilute acid pretreated substrate, but with only 50% of the enzyme loading used for the dilute acid substrate. Both the SPORL and dilute acid pretreatments were carried out with the same acid charge of 3.68% on oven-dried corn stover at the same temperature of 180°C for 30 minutes. Fermentation of SSL is a mature technology and has been practiced in the pulp and paper industry for many decades. With the good performance of newly developed yeast strain on SSL [57, 58], the prospect of achieving good ethanol yield through fermenting SPORL pretreatment hydrolysate is excellent.

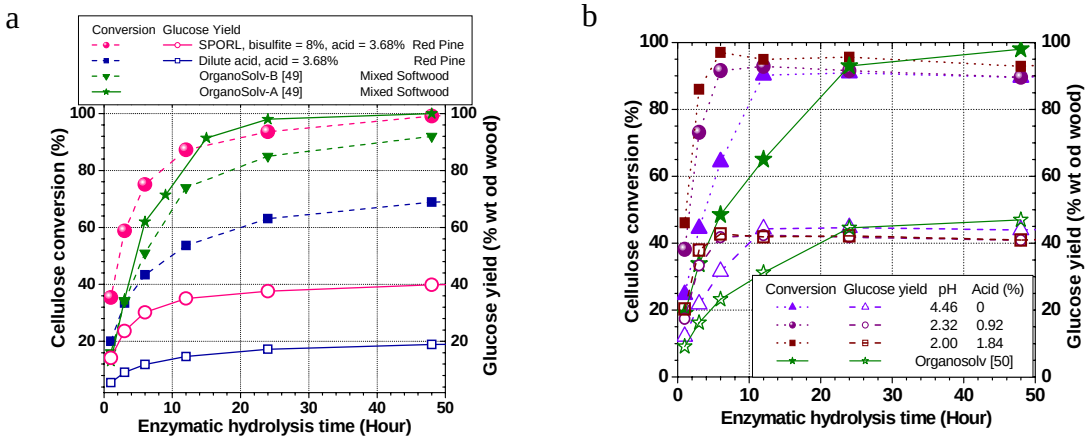

Fig. 4. Comparison enzymatic hydrolysis cellulose conversion and glucose yield between sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL) and the organosolv processes. (a) Softwood; (b) Aspen.

2.2.5. Other Pretreatments

Other pretreatments include alkaline and ionic liquid pretreatment. As discussed previously, alkaline pretreatments are not suitable for applications to agricultural residuals with high silica content, such as wheat and rice straw from many Asian countries, due to equipment corrosion caused by silica. Ionic liquid pretreated substrates have excellent enzymatic digestibility, but the process is too expensive to be commercialized in the near future. The Ammonia Fiber Explosion (AFEX) process has shown good overall sugar recovery for corn stover [59] and does not produce fermentation inhibitors. However, the process is not effective when applied to feedstocks with high lignin content [60], such as woody biomass.

Monomeric sugar recovery from poplar wood was only about 50% [61]. Furthermore, the recovery of ammonia is very difficult. The air emission of ammonia will likely be a problem in commercial production.

2.3 Challenges in Commercial Production of Cellulosic Ethanol

Despite much progress that has been made in cellulosic ethanol research and development, many challenges remain to be overcome for commercial production. Process scalability is one of the key challenges. Most processes have not been demonstrated in commercial scales. Capital equipment required for commercial demonstrations may not exist. For example, there is no commercially available equipment for conducting high-consistency saccharification of fibrous materials. Examining several promising pretreatment processes, a commercial-scale steam explosion device is still under development. On the other hand, the pulp and paper industry has the capability of handling biomass on the scale of 1,000 ton/day, equivalent to the scale of future cellulosic ethanol production of 100 million liters/year. The SPORL process can make full use the of capital equipment, process technologies, and human capital in the pulp and paper industry, which can significantly reduce technological and environmental barriers for commercialization. Specifically, a pulping digester can be used for the sulfite pretreatment, and a disk refiner can be used for size reduction after the pretreatment. In this regard, the dilute acid and SPORL pretreatments have excellent scalability, whereas the scalabilities of steam explosion, organosolv, and AFEX remain to be proven.

The recovery of pretreatment chemicals is also an important issue for commercialization of the process. 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 produced salt from the neutralization needs to be properly disposed of. On the other hand, the chemicals used in the SPORL process can be recovered using the technology that exists in the pulp and paper industry. Typically, fluidized bed reactors can be used to burn the spent liquor after the removal of hemicellulose sugars. Electric precipitators can be used to recover MgO particle and a wet scrubber can be used to recover SO_2. These two chemicals can be used to regenerate magnesium bisulfite. This recovery technology is mature. Recovery of ethanol from the ethanol organosolv process can be done through distillation, but is very costly.

Hemicellulose is a major component of biomass. Good recovery of hemicellulose sugars for fermentation is very important to the economics of cellulosic ethanol production. Most processes can recover the majority of hemicellulose sugars. However, the concentration is not satisfactory. From a fermentation stand point, hemicellulose sugar concentration of 150 g/L or higher is highly desirable to achieve an ethanol concentration in the fermentation broth of greater than 5% to significantly reduce distillation cost. Concentration of the pretreatment hemicellulose stream is required for all pretreatment processes. Modern ultrafiltration and reverse osmosis technologies are required to efficiently and reliably separate sugars from water, solids, and other chemicals produced in pretreatment.

Finally, feedstock versatility is another factor to consider when choosing pretreatment. Feedstock is a major cost factor in cellulosic ethanol production [11], which shares about 30% of the total cost. 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. Currently, many pulp mills must use whatever is available from a lumber mills because lumber is more valuable than fiber (paper). Pulp mills do not have the luxury to choose specific tree species or a particular section of a tree 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 at this time. It is expected that cellulosic ethanol refineries will have even less flexibility and choice in selecting feedstocks. Therefore, the pretreatment process must be versatile, i.e., effective on different feedstocks. Processes that are only effective on certain feedstocks, such as dilute acid and AFEX that only work for agricultural residues, will have limited applications in commercial production of cellulosic ethanol.

3. CONCLUSIONS

One of the key barriers in cellulosic ethanol production is pretreatment. For woody biomass, physical pretreatment through size reduction is critical. Limited attention has been paid to size reduction by the biorefining community. To address intensive energy consumption by size reduction of woody biomass, chemical pretreatment should be carried out prior to size reduction. The need for chemical pretreatment before size reduction, as well as questions regarding scalability of new processes has so far ensured that there are few viable or potentially viable processes for commercial cellulosic ethanol production, especially from woody biomass.

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