REVIEW

Reviving the carbohydrate economy via multi-product lignocellulose biorefineries

Y.-H. Percival Zhang

Abstract Before the industrial revolution, the global economy was largely based on living carbon from plants. Now the economy is mainly dependent on fossil fuels (dead carbon). Biomass is the only sustainable bioresource that can provide sufficient transportation fuels and renewable materials at the same time. Cellulosic ethanol production from less costly and most abundant lignocellulose is confronted with three main obstacles: (1) high processing costs ($/gallon of ethanol), (2) huge capital investment ($∼4–10/ gallon of annual ethanol production capacity), and (3) a narrow margin between feedstock and product prices. Both lignocellulose fractionation technology and effective co-utilization of acetic acid, lignin and hemicellulose will be vital to the realization of profitable lignocellulose biorefineries, since co-product revenues would increase the margin up to 6.2-fold, where all purified lignocellulose co-components have higher selling prices (>∼1.0/kg) than ethanol (∼0.5/ kg of ethanol). Isolation of large amounts of lignocellulose components through lignocellulose fractionation would stimulate R&D in lignin and hemicellulose applications, as well as promote new markets for lignin- and hemicellulose-derivative products. Lignocellulose resource would be sufficient to replace significant fractionations (e.g., 30%) of transportation fuels through liquid biofuels, internal combustion engines in the short term, and would provide 100% transportation fuels by sugar–hydrogen–fuel cell systems in the long term.

Introduction

Concerns pertaining to (1) increasing energy demands, especially for transportation fuels, (2) accumulating atmospheric CO_2 from the burning of fossil fuels, (3) depletion of fossil fuels, (4) national energy security, and (5) development of the rural economy are the main driving forces in the search for sustainable supplies of energy and renewable materials. The challenges of meeting human development needs and at the same time protecting the earth's life support systems confront scientists, technologists, policy makers, and communities from local to global levels.

Primary global energy consumption has increased 16-fold, as the human population has quadrupled in the twentieth century [1]. Total primary energy consumption is expected to rise to 27–42 from 13 TW with a world population increase from 6 billion people to 8∼11 billion by 2050 [1, 2]. Before the industrial revolution, the global economy mainly depended on carbon extracted directly or indirectly (via animals) from plants. Now the global economy predominantly depends on fossil fuels (dead carbon).

Now, fossil fuel burning is responsible for ∼82% of net greenhouse gas emissions, equaling ∼7.0 billion tons of carbon/year [3, 4]. Since the industrial revolution, nearly 270 billion tons of C from the combustion of fossil fuels

Y.-H. P. Zhang
Biological Systems Engineering Department,
Virginia Polytechnic Institute and State University,
Blacksburg, VA 24061, USA

Y.-H. P. Zhang (✉)
Institute for Critical Technology and Applied Science (ICTAS),
Virginia Polytechnic Institute and State University,
Blacksburg, VA 24061, USA
e-mail: ypzhang@vt.edu

has accumulated in the atmosphere [3]. The resulting atmospheric CO_2 level has increased from ~275 to ~380 ppm [5, 6]. Consequently, the global average near-surface atmospheric temperature has risen by 0.6 ± 0.2 °C in the twentieth century. The CO_2 level could easily pass 550 ppm by the middle of this century if no special actions are taken (i.e., at a current rate of ~3 ppm/year, assuming no artificial or natural carbon sequestration). Therefore, the 550 ppm target in the year 2100 would require a net carbon accumulation rate of 3.5 billion tons of C/year, far lower than the current emission rate (8.0 billion tons of C/year). Targets for controlling CO_2 levels at 450 ppm, and certainly 350 ppm, would require extraordinary efforts [1]. Therefore, a transition from a fossil fuel-based economy to the sustainable carbon-neutral bioeconomy will have to take place eventually.

Finite crude oil is believed to be a natural carbon reserve that has been stored and accumulated through billions of years. Approximately 1,010 billion barrels of crude oil is known to be the recovered reserve in the world; the total possible reserves might be as high as 2,000 billion barrels with new discoveries, expansion of existing fields, and new extracting technologies. Considering the current global oil consumption rate of ~30 billion barrels/year, the oil reserve could be depleted within 35~70 years. The use of oil is projected to peak in about 2007–2010, and the supply would become extremely limited within 40~50 years [7]. Approximately ~70% of crude oil consumption in the USA is used for transportation. Since new techniques typically take ~25 years to penetrate a market [8], development of alternative sustainable transportation fuels and renewable materials is urgently needed in order to meet developmental and environmental needs of present and future generations.

Biomass is the only known sustainable bioresource used for producing liquid transportation fuels [5, 9, 10]. However, locally produced biomass makes it impossible to establish monopoly. In his State of Union speech in 2007, President Bush projected that ethanol production in the US would achieve a level of 35 billion gallons per year by 2017 [11]. The US Department of Energy has proposed a scenario: producing 30% transportation fuels from biomass (i.e., ~60 billion gallons of biofuels) by 2030 [12]. The European Commission also has planned to replace 20 and 25% of conventional fossil fuels with alternative fuels in the transportation sector by 2020 and 2030, respectively [12, 13].

This article briefly reviews information about lignocellulose availability, its potential, and its recalcitrant structure. Furthermore, it stresses the urgent need for developing cost-effective lignocellulose fractionation technologies, promoting R&D for lignin and hemicellulose applications, and fostering their markets, which will be keys to the economic success of lignocellulose biorefineries, namely production of cellulosic ethanol for transportation and renewable materials, starting from lignin and hemicellulose.

Renewable, low cost, and abundant lignocellulosic biomass

Biomass is produced via photosynthesis, which converts light energy to chemical energy, stores it in carbohydrates as "$6 CO_2 + 6 H_2O \rightarrow C_6H_{12}O_6 + 6 O_2$", and fixes atmospheric carbon into biomass (living carbon). Lignocellulosic biomass is the most abundant renewable biological resource on earth, with a yearly production of $\sim 200 \times 10^9$ tons [14, 15], only 3% of which is used in non-food areas, such as the paper and pulp industries [16]. Current cellulose consumption is threefold higher than steel consumption and equals cereal consumption [17].

Lignocellulosic feedstock is far less costly than other feedstocks (crude oil, natural gas, corn kernels, and soy oil) based on energy content ($/GJ). For example, crude oil price varying from $40 to $80 per barrel (i.e., $7.1–14.2/GJ) is much higher than the price of lignocellulose ($0–3/GJ). Corn kernels with a price from $2.25 to 4.0 per bushel equals $6.3–11.5/GJ. During the past 2 years (2004–2006), corn kernel price has risen by >70% from a historically low price ($~2.25 per bushel) to ~$4 per bushel. With the high demand of corn kernels for ethanol production, the increasing price of corn kernels has resulted in rising prices for animal feed and human food. For instance, therefore, in 2006 the Chinese government banned building new ethanol production facilities based on grains. As expected, the less costly and most abundant feedstock, lignocellulose, makes production of biofuels and bio-based chemicals more appealing.

One key question for the future industry of biofuels and biobased products is whether the availability of lignocellulose is sufficient to meet both the basic demand for materials, animal feed, and secondary demand for fuels and biobased chemicals. The DOE and USDA report suggest that the USA has the potential to produce more than 1.3 billion dry tons of lignocellulose per year, including agricultural (933 million tons/year) and forest resources (368 million tons/year) [9]. Agricultural residuals or byproducts are annually renewable, abundantly available, and of limited value. Main lignocellulosic byproducts in considerable quantity are corn stover, the most abundant lignocellulose residue in the USA [14], wheat, rice, barley straw, sorgham stalks, coconut husks, sugarcane bagasse, and pineapple and banana leaves. Utilization of the crop residues would provide an additional revenue for farmers without adverse effect on soil fertility. Canada, the second largest supplier of woody lignocellulosic biomass, supplies

>200 million m^2 of lignocellulose annually through commercial operations [18]. China produces large amounts of agricultural and forest residues on a scale of about 1 billion tons/year [19]. If marginal lands (about 54–78 million hectares) are used for dedicated energy plants, another 1 billion tons could be produced yearly [19]. India yields at least 0.2 billion tons of agricultural residues yearly [17]. One billion dry tons of biomass theoretically equals ∼80–130 billion gallons of cellulosic ethanol. Therefore, the DOE of the USA has proposed to produce ∼60 billion gallons of biofuels from biomass to replace 30% of transportation fuel by 2030 [20].

Although the sunlight-to-chemical energy efficiency of photosynthesis is much lower than that of photovoltaic, photosynthesis is regarded as "the natural solar cell" that collects low-energy density solar radiation from large areas, fixes CO_2, and generates a chemical energy carrier, biomass, at nearly zero cost. On average, terrestrial net primary productivity of biomass equals only 0.3% of the average energy density of sunlight (180 W/m^2) [5]. The theoretical values of photosynthesis are estimated to be approximately 4% for C3 plants and 8% for C4 plants, respectively [1, 5]. Approximately 95% of global plants are C3 plants, including rice, wheat, barley, and most trees. Most C4 plants are tropical grasses, including corn and sugarcane. The above-ground productivities of corn plants (including kernel and stover) and sugarcane, probably two of the highest yielding land-based crops, are ∼19.5 ton/ha/year and 25∼32 dry ton/ha/year, with energy efficiencies of 0.6 and 0.8–1%, respectively [21].

With improvements in plant characteristics by modern biotechnology and cultivation technologies, a 10% increase in global photosynthesis efficiency for territorial plants would assimilate more than 8.8 billion tons of carbon from the atmosphere (not accounting for carbon re-emission), equaling current net carbon emission. Although the USDA expects corn kernel productivity to increase from the current level of 7.5 ton/ha/year (with 15% moisture) to 15 ton/ha/year by 2030 [22], it is not likely that practical maximal efficiencies of photosynthesis for recoverable terrestrial plant matter will exceed 2% of sunlight energy [5].

The ocean with its much greater surface area for marine biomass production (71% vs. 29%) has a great potential for biofuel production and CO_2 sequestration. The R&D costs for marine biomass collection and cultivation will be very high, but the potential returns should not be ignored. Microalgae and macroalgae are reported to produce 81∼150 dry ton/ha/year, close to the maximum theoretical yield (8%), if saturating levels of CO_2 are provided, perhaps from power stations [23]. Artificial fertilization of the oceans might stimulate marine phytoplankton growth, resulting in a great potential for CO_2 sequestration [24].

Lignocellulose recalcitrance

The major components of plant cell walls are cellulose, hemicelluloses, and lignin, which together form a complex and rigid structure (Fig. 1). The plant cell walls of different plant types vary greatly in appearance and property. The complicated structure of lignocellulose causes its resistance to biological and chemical degradation. For example, in nature, lignocellulose biodegradation is slow, requiring that a number of hydrolysis enzymes work together, including cellulases (endoglucanase, cellobiohydrolases, and beta-glucosidase), hemicellulases, and lignin-degrading enzymes [25]. Although biomass recalcitrance has been attributed to up to seven factors [12], two main root causes of the recalcitrance of lignocellulose to cellulase enzymatic hydrolysis are believed to be (1) low accessibility of (micro-) crystalline cellulose fibers, which prevents cellulases from working efficiently [26–28], and (2) presence of lignin (mainly) and hemicellulose on the surface of cellulose, which prevents cellulase from accessing the substrate efficiently [29, 30].

Cellulose is a linear biopolymer of anhydroglucopyranose, connected by β-1,4-glycosidic bonds. Coupling of adjacent cellulose chains by orderly hydrogen bonds and Van der Waal's forces leads to a parallel alignment and a crystalline structure, resulting in low accessibility to enzyme (Fig. 1). Recently, quantitative data of cellulose accessibility to cellulase (CAC) clearly suggest that only a small fraction of β-glucosidic bonds of cellulose are accessible by cellulase, ranging from 0.0023 to 0.041 [28]. The evidence from cell wall biophysics, biosynthesis, genomics, and AFM images suggests that elementary cellulose fibrils are synthesized by the cellulose synthase complex (CelS) locus that contains 36-glucan chains and that they have both crystalline and subcrystalline structures [31]. A number of elementary fibrils coalesce into much larger microfibrils; a number of microbrils form macrofibrils. Hemicelluloses are situated between the lignin and the collection of cellulose fibers underneath. Consistent with their structural chemistry and side-group substitutions, xylans seem not only to be interspersed, interweaved, and ester-linked at various points with the overlaying "sheath" of lignin, but also to produce a coat around underlying strands of cellulose via hydrogen bonds. The xylan layer with its covalent linkage to lignin and its non-covalent interaction with cellulose may be important in maintaining the integrity of the plant cell wall in situ and in helping protect the fibers against degradation by enzymes [32]. At least two types of covalent cross-links have been identified between hemicellulose and lignin: (1) diferulic acid bridges and (2) ester linkage between lignin and glucuronic acid attached to xylans [33].

Fig. 1 Recalcitrant ligno-cellulose structure containing cellulose, hemicellulose, and lignin
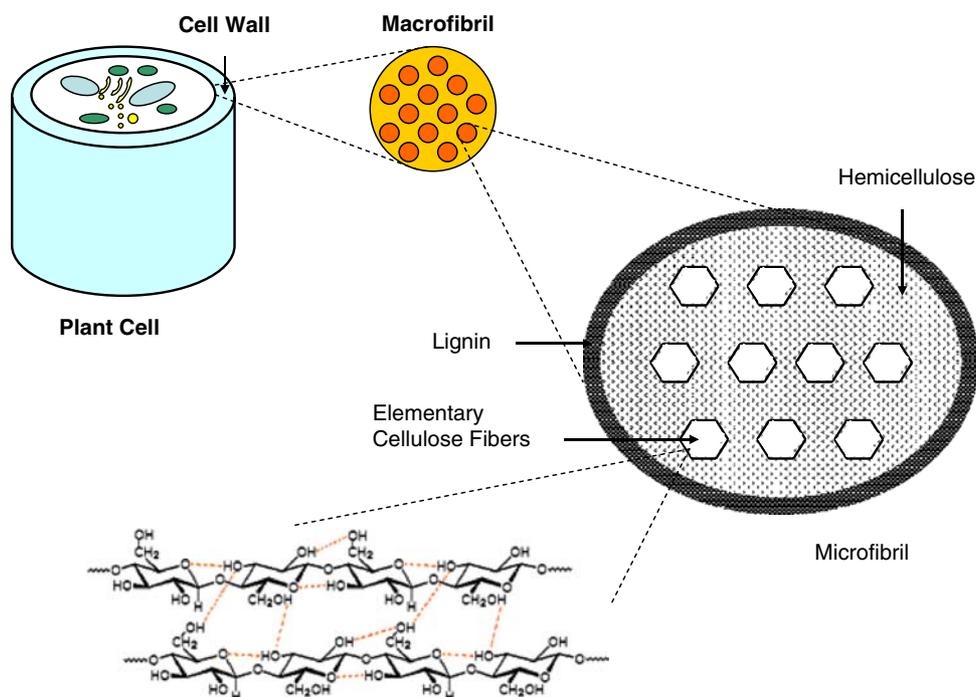
Multi-product lignocellulose biorefinery

In lignocellulose biorefineries, biological conversion of lignocellulose generally has three main steps: (1) lignocellulose pretreatment, which converts the recalcitrant lignocellulose structure to reactive cellulosic intermediates; (2) enzymatic cellulose hydrolysis, by which cellulases hydrolyze reactive intermediates to fermentable sugars (e.g., glucose); and (3) fermentation, which produces cellulosic ethanol or other bio-based chemicals (e.g., lactic acid, succinic acid) [25, 34, 36]. Effectively overcoming the recalcitrance structure of lignocellulose and releasing the locked polysaccharides is one of the most important and urgent R&D priorities for the emerging biofuel and bio-based product industry [37, 38], because lignocellulose pretreatment is among the most costly steps and has a major influence on the costs of both prior operation (e.g., lignocellulose particle size reduction) and subsequent operations (e.g., enzymatic hydrolysis and fermentation) [35, 39].

The typical lignocellulose refinery scenario is based on the product streams that (1) all isolated sugars are used to produce cellulosic ethanol or biobased products, and (2) all the residues, including lignin and residual cellulose, are used as burning fuels to generate steam and electricity. Therefore, the three large obstacles to profitable biomass biorefineries are (1) high processing costs, (2) huge capital investment ($4–10/gallon of annual ethanol production capacity), and (3) a narrow margin between feedstock and product prices [25, 40, 41].

Lessons useful to solve challenges associated with biomass biorefineries can be learned from successful industries. For example, in order to achieve high economic efficiency, petroleum refineries never produce a single product (e.g., gasoline), but produce multiple products (diesel, gasoline, heating oil, etc) because a one-product plant will have high risks for investors and poor performance in the face of market fluctuations. Recently, Dow Chemical has begun to fractionate ethylene from natural gas because the former has ∼20-fold the selling price of methane.

Biorefinery designers must take advantage of synergies between the production of both biofuels and high-value biobased products because the latter would enhance the economy of biomass biorefineries [10, 14, 16, 29]. Figure 2 shows the potential revenues for different lignocellulose biorefinery scenarios: (a) simple utilization (all sugars to ethanol and lignin as burning fuels), (b) partial utilization (all sugars to ethanol, half of lignin as burning fuels, the other half as polymeric materials, and acetic acid as a commodity), and (c) complete utilization (glucose to ethanol, xylose and other minor sugars for high-value products, all lignin used as polymeric materials, and acetic acid as a commodity), respectively. Taking simple utilization as an example (a typical lignocellulose biorefinery design), the potential revenues of biorefineries could be $145 per ton of corn stover. Considering $50/ton for feedstock, it is a great challenge that the narrow margin between cellulosic ethanol and feedstock ($∼95/ton, i.e., $1.20–1.30/gallon of ethanol) will pay off the sum of capital depreciation ($∼4–10 capital investment per gallon of annual ethanol production), processing costs (steam, enzyme, electricity, etc), and operating costs. A typical biomass biorefinery could have a minimum capacity of 2,000 dry tons per day considering
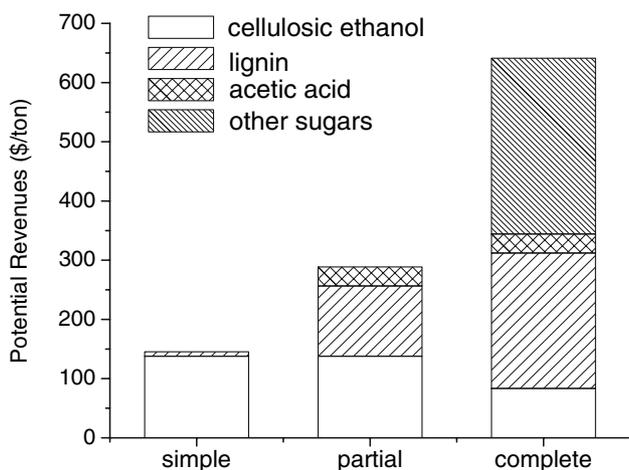
Fig. 2 Economic analysis for different lignocellulose biorefining scenarios based on corn stover containing 361 kg of glucose, 214 kg of xylan, 36 kg of arabinan (representing three other minor polysaccharides), 208 kg of lignin, and 32 kg of acetic acid. The overall sugar yields for pretreatment and hydrolysis yield are 90%; hextose and pentose fermentation yields are 90 and 85% of theoretical yields; ethanol = $1.50/gallon; acetic acid = $1.00/kg; high-value isolated lignin = $1.10/kg; burning lignin = 0.04/kg (based on $35 coal/short ton); and isolated xylose (including arabinose) = $1.20/kg

economy of scale, while transportation costs of the low-energy density feedstock limit the upper size of biorefineries, e.g., ~100 km of collection distance by trucks [5, 42].

Multi-product biorefineries would be more economically feasible, based on partial co-utilization ($288/ton) or complete co-utilization ($641/ton) if lignocellulose fractionation technology were well developed. Economic analysis based on product revenues suggests that co-utilization of lignocellulose components (lignin, acetic acid, and hemicellulose) would increase the net margin up to 6.2-fold (Fig. 2).

Availability of high-quality sulfur-free lignin in large quantities can stimulate development in new lignin applications, but such high-quality lignin is not available. More than 50 million tons of technical lignin from lignocellulose are produced annually by pulping industries; they can be classed into sulfur-containing lignins (kraft lignin and lignosulfonate lignin) and sulfur-fee lignins (alkali lignin and organosolv lignin) [43]. Kraft lignin (>90% of all isolated lignins), generated via kraft pulping, contains a small amount of the aliphatic thiol groups with a characteristic odor. Only a very small amount of kraft lignin is used for other applications; the majority is used as an in-house fuel for chemical recovery [44]. Lignosulfonate from a sulfite process contains 10% sulfur due to sulfonic acid groups. Alkali lignin is made from soda pulping from non-wood feedstocks, such as straw, bagasse, flax, etc. Oganosolv lignin is a high-purity, low molecular weight product [44–46].

Figure 3 shows potential lignin applications. High-quality lignin can be used as a substitute for polymeric materials: phenolic powder resins, polyurethane and polyisocyanurate foams, and expoxy resins. Phenolic powder resins (20% replacement) have been used as the binder in the manufacture of friction products, automotive break pads, and molding on a commercial scale by North American manufacturers. Polyurethane and polyisocyanurate foams with a lignin displacement of 17 and 26%, respectively, have a density of 24–32 kg per cubic meter. Expoxy resins containing approximately 50% lignin have been successfully prepared and applied to printed circuit board resins (PCB) [44]. Because it is a good adsorbent and has excellent adhesive, rheological, and collidial properties, lignin is used as a partial replacement for phenolic binders for oriented-strand board production [44]. Lignin is a raw chemical precursor for DMSO, vanilla, phenol, and ethylene [14, 44, 47], and can also be converted to value-added carbon fiber with a selling price ranging from $~5–20/kg [48–50]. Lignin has broad potential applications in agriculture. For example, lignin, a biodegradable UV-light antioxidant absorbent, is appropriate for release-controlled pesticides and slow-release fertilizers containing ionically or organically bound nitrogen or other fertilizers. Slow-release fertilizers are crucial for decreasing non-point groundwater pollution due to their ecological benefits. The largest scale utilization of lignin could be as a soil conditioner to aid in formation of humus [43]. Other unlimited low-value markets are synthetic diesel through lignin gasification, followed by the Fischer-Tropsch process as well as direct lignin burning. It is expected that the lignin applications for low-end lignin markets are considered after the high-end applications, such as polymer substitutions, carbon fiber, etc. Although lignin-based products did not compete with products derived from petrochemicals, now, technical and economic situations are changing rapidly.
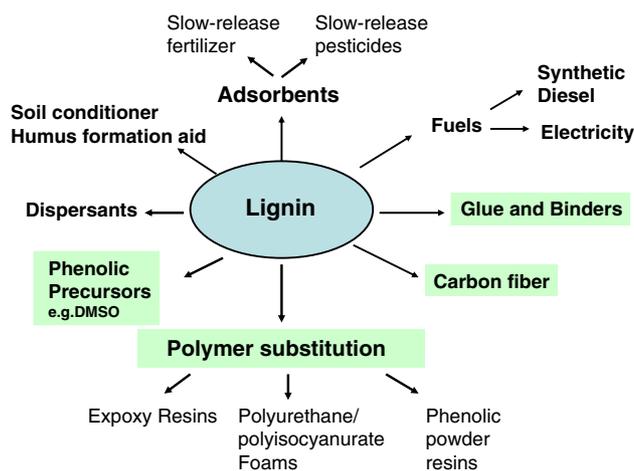

Fig. 3 A lignin utilization tree. The *shadowed boxes* represent high selling-price products

Figure 4 shows potential hemicellulose applications. Hemicellulose has been used as plant gum for thickeners, adhesives, protective colloids, emulsifiers, and stabilizers [16]. Recently, a very promising application is a biodegradable oxygen barrier films [51, 52]. Oligosaccharides may provide a source of higher value co-products, such as animal feed additives [53, 54]. Monomeric sugar, xylose, can be fermented to a sweetener, xylitol [55–57]. Xylitol, as a sucrose replacement for diabetes patients, leads to an impressive reduction in cavities incidence and an increase in oral health [58, 59]. Currently, furfural is profitably produced through chemical degradation of hemicellulose-rich lignocellulose (e.g., corncobs) in developing countries such as China. Furfural is a solvent used for lubricants, coatings, adhesives, furan resin, etc. [16, 60]. It was the starting material for the production of Nylon 6,6 and Nylon 6. Nylon was produced from furfural, but its production was abandoned in 1961 in the USA because of its inability to compete with petrochemicals. It might be time to revive Nylon production from hemicellulose because of (a) the rising price of crude oil and (b) an abundance of isolated hemicellulose or furfural [45]. Effective fermentation of xylose to ethanol or organic acids can solve the problem of limited market size for xylose and xylose derivatives [61–63].

Combinatorial pretreatment and fractionation of lignocellulosic biomass is very vital to the success of biorefineries [64]. A good lignocellulose pretreatment and fractionation method must have several or all of the following features:

(1) high sugar yields with little sugar degradation and high enzymatic cellulose digestibility;
(2) fractionate lignocellulose components for better economy (Fig. 2);
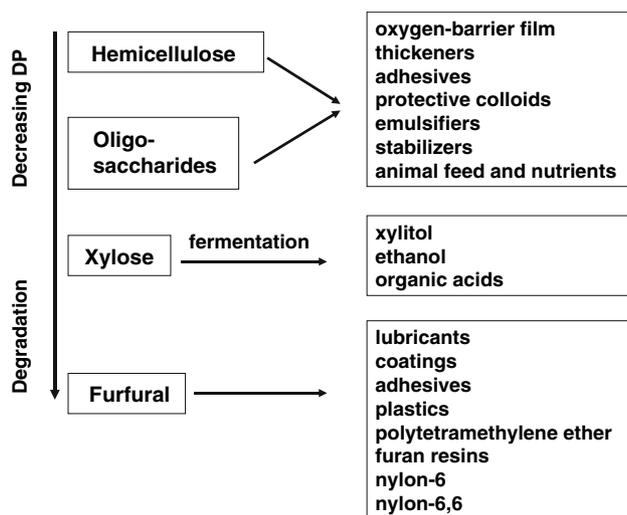(3) low-temperature reaction conditions with benefits, such as no or little sugar degradation, little inhibitor formation, low utility consumption, and decreased capital investment;
(4) amorphous cellulose generation from crystalline cellulose for fast hydrolysis rates, high sugar yields, lower enzyme use, and possibly efficient enzyme recovery; and
(5) broad substrate applicability for a variety of feedstock.

A number of lignocellulose pretreatment technologies are under intensive investigation on both laboratory scale and as pilot plants, including dilute acid, flow-through, ammonia fiber explosion (AFEX), ammonia recycle percolation (ARP), lime, steam explosion, and organosolv pretreatment [35, 40]. Considering the complicated chemical structure of lignocellulose (see "Lignocellulose recalcitrance"), it is relatively easy to address labile hemicellulose so as to break up the linkage among cellulose, hemicellulose and lignin. For example, with dilute acid, steam explosion, AFEX, ARP, lime, and organosolv pretreatment; it is relatively challenging to remove lignin (even partially) from the cellulose surface. With flow-through, ARP, and organosolv, it is rare to convert crystalline cellulose to amorphous cellulose, and it is nearly impossible to isolate lignocellulose components, except organosolv and cellulose solvent-based lignocellulose fractionation. Therefore, most of these technologies suffer from relatively low sugar yields, severe reaction conditions (high temperature and/or high pressure), large capital investment, high processing costs, and great investment risks [29, 41].

The idea of using cellulose solvents that break up the linkage among cellulose, hemicellulose, and lignin has a long history [65, 66], but technical challenges prohibit its practical applications. Recently, several groups have investigated the use of several cellulose solvents, including ionic liquids and concentrated phosphoric acid to converted crystalline cellulose to amorphous cellulose [27, 67–70]. The resulting amorphous cellulose can be hydrolyzed much faster [27, 68, 70]. Practical cellulose solvents for lignocellulose biorefineries must have most of the following features:

(1) able to dissolve cellulose at low temperatures;
(2) able to dissolve wet cellulose (i.e., avoid biomass drying);
(3) less costly or highly recyclable;
(4) nonvolatile;
(5) thermostable and chemostable;
(6) nontoxic to the sequential steps of enzymatic hydrolysis and microbial fermentation;
(7) high cellulose dissolution capacity (>10% weight cellulose/volume); and
(8) fast diffusion rate in solid lignocellulosic composite.

Sole cellulose solvent lignocellulose pretreatment cannot fractionate several lignocellulose components effectively.

Fig. 4 A hemicellulose utilization tree

The resulting cellulosic material with remaining lignin and hemicellulose cannot be hydrolyzed as fast as can amorphous cellulose. Recently, a new cellulose solvent- and organic solvent-based lignocellulose fractionation method has been invented; it sequentially uses a non-volatile cellulose solvent (concentrated phosphoric acid), a highly volatile organic solvent (acetone), and water under modest reaction conditions (50 °C and atmospheric pressure) [29]. This new technology isolates lignocellulose components based on their solubility and volatility in different solvents, and each unit operation for the separation is easy, e.g., solid/liquid separation. For example, cellulose is insoluble in water, but soluble in concentrated phosphoric acid. Hemicellulose is isolated from cellulose because it has high solubility in a mixture of acetone/water; a fraction of lignin is soluble in the organic solvent but insoluble in the aqueous phase so that it can be separated from other lignocellulose components. Nearly pure amorphous cellulose after lignocellulose fractionation has been obtained from herbaceous and hardwood lignocellulose. The highest sugar yields after enzymatic hydrolysis are attributed to no sugar degradation during the fractionation and the highest enzymatic cellulose digestibility (∼97% in 24 h) during the hydrolysis step. As compared to steam explosion, this new technology can produce at least 20% more sugar yields. Different from sole-cellulose solvent-based lignocellulose pretreatment technology, a second solvent, highly volatile acetone, was introduced between concentrated phosphoric acid (cellulose solvent) and water [29]. The use of acetone use has four goals: (1) to precipitate dissolved cellulose and hemicellulose to amorphous forms, resulting in an easy separation of solid saccharides from liquid cellulose solvent; (2) to dissolve partial lignin in acetone and recover solid lignin after removal of acetone because acetone-dissolved lignin is insoluble in acidic aqueous solutions; (3) to recycle concentrated phosphoric acid by avoiding acid dilution using water and easy acid re-concentration; and (4) to fractionate oligo-hemicellulose sugars from cellulose because the former has some solubility in the acetone/water mixture. Lignocellulose fractionation technology using combinatorial cellulose solvent and organic solvent is in its infant stage. It is anticipated that substantial advances will be made in cellulose-solvent-based lignocellulose fractionation and that the derived lignocellulose fractionation technologies will make great contribution to the realization of lignocellulose-based biorefineries.

Perspectives

At the dawn of the twenty-first century, a combination of economic, technological, political, and resource developments is driving the emergence of a new carbohydrate economy. We envision that renewable liquid biofuels (cellulosic ethanol and biodiesel) will replace significant fractions of fossil fuels within 30 years. In the long term, hydrogen-fuel cell systems will play more and more important roles in transportation section by replacing the internal combustion engines because carbohydrates (cellulose and starch) from biomass can be easily converted to hydrogen by a novel enzymatic technology and could be used as high hydrogen-density carriers (14.8 H_2 mass%) [71]. Development in lignocellulose fractionation technologies is urgently needed in order to make the most of each lignocellulose component, promote R&D of lignin and hemicellulose applications, and foster markets for lignin- and hemicellulose-derived products.

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