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Advanced Biofuel Technologies

Status and Barriers

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Abstract

Large-scale production of crop based (first generation) biofuels may not be feasible without adversely affecting global food supply or encroaching on other important land uses. Because alternatives to liquid fossil fuels are important to develop in order to address greenhouse gas mitigation and other energy policy objectives, the potential for increased use of advanced (non-crop, second generation) biofuel production technologies has significant policy relevance. This study reviews the current status of several advanced biofuel technologies. Technically, it would be possible to produce a large portion of transportation fuels using advanced biofuel technologies, specifically those that can be grown using a small portion of the world's land area (for example, microalgae), or those grown on arable lands without affecting food supply (for example, agricultural residues). However, serious technical barriers limit the near-term commercial application of advanced biofuels technologies. Key technical barriers include low conversion efficiency from biomass to fuel, limits on supply of key enzymes used in conversion, large energy requirements for operation, and dependence in many cases on commercially unproven technology. Despite a large future potential, large-scale expansion of advanced biofuels technologies is unlikely unless and until further research and development lead to lowering these barriers.

This paper—a product of the Environment and Energy Team, Development Research Group—is part of a larger effort in the department to analyze economic, social and environmental impacts of biofuels. Policy Research Working Papers are also posted on the Web at http://econ.worldbank.org. The author may be contacted at gtimilsina@worldbank.org.

Advanced Biofuel Technologies: Status and Barriers[#]

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Key words: Advanced biofuels, cellulosic ethanol, biodiesel, Fischer-Tropsch fuels.

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Advanced Biofuel Technologies: Status and Barriers

1. Introduction

Biofuels can be produced using various feedstocks and conversion technologies. The most common biofuels include bioethanol produced from sugar or the starch portion of plants (e.g., corn, wheat, sugarcane, sugar beet and cassava) and biodiesel produced from vegetable oils (e.g., rape seed, sunflower, soybean and palm oil). Bioethanol can also be produced from lignocellulosic materials, and biodiesel can also be produced from animal fats and microorganisms, such as microalgae. We refer these emerging biofuel technologies (i.e., cellulosic ethanol and microorganism based biodiesel) as advanced biofuel technologies. Synthetic fuels produced from biomass through Fischer-Tropsch (FT) process[1] are also included in this category.

Numerous research efforts have been spent on technological advancement and cost reduction of the cellulosic ethanol production. Boateng et al. (2007) studied the conversion of Bermudagrass to bioethanol and effect of genotypes on pyrolysis product yield. Kadam and McMillan (2003) investigated the availability of corn stover as a sustainable feedstock for bioethanol production. Kim and Dale (2004) summarized the global potential of bioethanol production from wasted crops and crop residues. Sassner et al. (2008) evaluated the techno-economic feasibilities of bioethanol production from different lignocellulosic materials. Most of the recent research activities in cellulosic bioethanol production have been focused on more cost-effective pretreatment technologies for lignocellulosic materials, low-cost and high-efficiency cellulase enzymes, and co-fermentation of 6-carbon and 5-carbon sugars for ethanol production.

Biodiesel, another major biofuel, is produced using vegetable oil, plant oil, and animal fat. Obviously, biodiesel is an alternative fuel for diesel and most diesel engines can use 100% biodiesel. The main feedstock currently used for biodiesel production includes soy bean, canola seed, rapeseed, sunflower, and palm oil. A great challenge of using vegetable oils for biodiesel production is the availability of crop land for oil production to produce enough biodiesel that

[1] It refers to a chemical process that converts a mixture of hydrogen and carbon monoxide – derived from biomass– to liquid fuels.

significantly replaces the current fossil fuel consumption. Chisti (2007) estimated that it would take 24% of the existing crop land in the US to grow oil palm that is considered as a high-yield oil crop or over 3 times of the current cropland in the US to grow soybean to produce enough biodiesel that would replace 50% of the transportation fuel in the US. There are research activities on using alternative oils such as waste oils from kitchens and restaurants and microalgal oils for biodiesel production. Miao and Wu (2006) studied biodiesel production from heterotrophic microalgal oil. Shah et al. (2007) investigated the utilization of restaurant waste oil as a precursor for sophorolipid and biodiesel production. Zhang et al. (2003) evaluated the Biodiesel production from waste cooking oil including economic analysis. A great advantage of using microalgal oil over vegetable oils for biodiesel production is that the production of algal oil does not necessarily need cropland and has much higher oil yield per acre of land because the microalgae can been grown in three dimensions in photo-reactors. However, a big challenge of biodiesel production using algal oil is that the cost of algal oil production is prohibitively high.

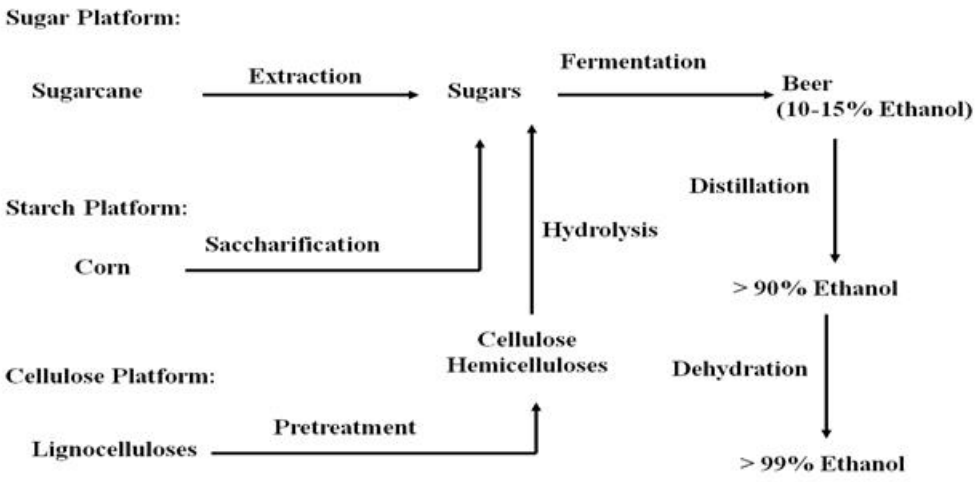
The primary objective of this paper is to examine the status of advanced biofuels technologies and key barriers to their commercial operation. This study aims to analyze in detail the status of various technologies such as: (i) Lignocellulosic ethanol; Microalgal biodiesel; Biomethanol and Fischer-Tropsch (FT) fuels; and (ii) feedstock for second generation biofuels (e.g., switch grass, jatropha, agricultural residues, forestry and wood industry residues, animal wastes, and microalgae).[2]

2. Lignocellulosic Ethanol Production

Bioethanol can be produced through physical, chemical, and biological processes from different natural materials: sugar-, starch-, and lignocellulose-based materials. The general processes for bioethanol production from different materials are shown in Figure 1.

[2] A companion paper (Carriquiry, Du and Timilsina 2010) explores the economic potential and barriers to increased use of second-generation biofuels.

Figure 1. General processes for bioethanol production from different renewable materials



Sugar-platform bioethanol production: The main natural materials that can be converted to bioethanol through the sugar-platform processes include sugarcane, sugar beet, and sweet sorghum. These materials are rich in sugars, mainly sucrose, that are readily fermented by yeasts or bacteria to bioethanol. Releasing of sugars from the materials can be achieved through simply mechanical extraction or squeezing. Sugarcane grows in warm temperate to tropical regions and accumulates biomass and sugars at a very high rate. Brazil is the largest sugarcane producing country in the world, with an annual production of 514,080,000 tons in 2008. After the extraction, the juice is used for bioethanol production through fermentation and the bagasse is usually dried and burned to provide energy for the distillation of the fermentation beer. Surplus bagasse is used for producing steam which is then utilized for electricity generation and industrial heating. Brazil produced 5.96 billion gallons of bioethanol from sugarcane in 2007. Sugar beet is a plant whose root contains a high concentration of sucrose. It normally grows in cool temperatures and produces a large (1–2 kg) storage root whose dry mass is 15–20% sucrose by weight during its growing season. Sugar beet is widely grown in European Union, Russia, and North America. Sweet sorghum is a sorghum that has a high sugar (sucrose) content and grows well under dry and warm conditions. It is widely grown in the US, mainly for syrup production.

Starch-platform bioethanol production: The biomaterials that can be converted to ethanol through the starch-platform processes including starch-rich grains (corn, wheat, rice, barley, and grain sorghum), potatoes, and sweet potatoes. The starch content is in the range of 60

to 75% in the grains, and 10-30% in potatoes and sweet potatoes. Conversion of starch to ethanol involves one additional step, saccharification of starch to produce fermentable sugars (mainly glucose), compared to the sugar-to-ethanol process. The saccharification of starch is normally performed through enzymatic reactions catalyzed by amylases. The main product of the saccharification is glucose which is readily fermented to ethanol by yeasts or bacteria. Among the starch-rich materials, corn is widely used for commercial fuel ethanol production in US, China, and Europe. The US produced 6.49 billion gallons of fuel ethanol from corn in 2007. Note that this amount is higher than ethanol produced from sugarcane in Brazil in the same year.

Cellulose-platform bioethanol production: Lignocellulosic materials can be used for bioethanol production because they have a high content of cellulose and hemicelluloses. However, the conversion of lignocellulosic materials to ethanol is much more difficult than that of sugar-rich (e.g. sugarcane) or starch-rich (e.g. corn) materials. This is because the cellulose and hemicelluloses molecules are tightly tangled together and the structure is firmly wrapped up by lignin. The conversion of lignocelluloses to ethanol involves three steps: pretreatment, hydrolysis, and fermentation. Pretreatment is necessary because of the unique compact structure of lignocellulosic materials. The main purpose of the pretreatment is to remove lignin from the material, and reduce the crystallinity and increase the porosity of the material, so the cellulose and hemicelluloses are accessible for hydrolysis to produce fermentable sugars. The complex processes for the conversion of lignocellulosic materials to ethanol make the conversion more expensive than the conversion of either sugars or starch to ethanol. With the rapid increase of the prices of the sugar and starch feedstocks and limitation of cropland for the feedstock production, the abundant and inexpensive lignocellulosic materials have a great potential in substantial expansion of fuel ethanol production.

2.1. Description of lignocellulosic ethanol technology

2.1.1. Lignocellulose

Lignocellulose is composed of mainly cellulose, hemicelluloses, and lignin (Figure 2A. Cellulose is a long-chain homogenous polysaccharide of D-glucose units linked by β-1,4 glycosidic bonds and contains over 10,000 glucose units (Figure 2B). Hemicellulose is a complex, heterogeneous polymer of sugars and sugar derivatives which form a highly branched network and the monomers include hexoses (glucose, galactose, and mannose) and pentoses (xylose and arabinose) (Figure 2C). It consists of about 100-200 sugar units. Lignin is a very

complex heterogeneous mixture of mainly phenolic compounds and their derivatives. It is a main component in plant cell walls. Lignin holds the cellulose and hemicellulose fibers together and provides support to the plants.

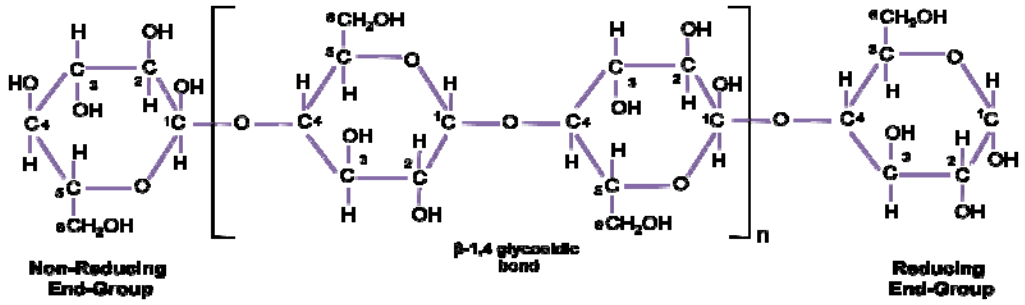
2.1.2. Pretreatment

A diagram of pretreatment process is shown in Figure 3. Pretreatment technologies

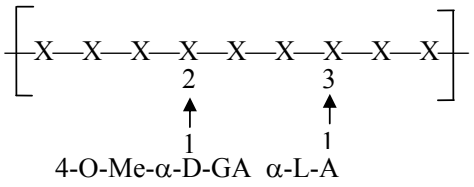
Figure 2. Structures of (A) lignocelluloses, (B) cellulose, and (C) hemicelluloses

A.

B.

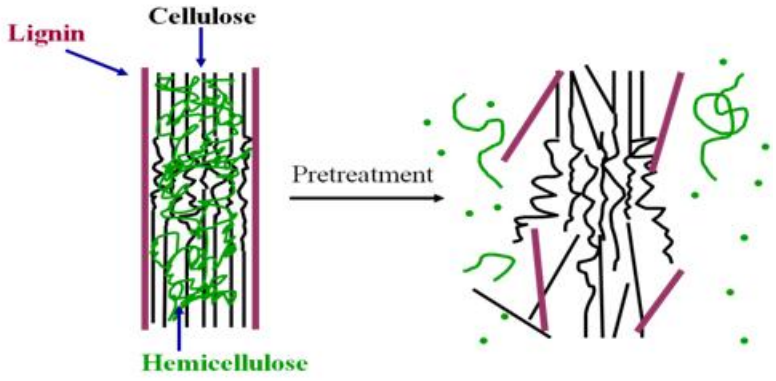


C.



X—X: β-1,4-linked D-xylopyranose units
Me: methoxy group
GA: glucuronic acid
A: esterified-α-L-arabinofuranose side chain

Figure 3. A pretreatment process for lignocellulosic materials



have been extensively investigated in the last three decades, including physical, chemical, and biological processes for lignocellulosic materials (Sun and Cheng, 2002).

Physical Pretreatment: Physical pretreatment includes mechanical comminution, steam explosion, ammonia fiber explosion, and pyrolysis. Mechanical comminution combines chipping, grinding, and milling to break the lignocellulosic materials down to 0.2 to 2 mm and reduce the crytallinity of the materials. Steam explosion applies high-temperature (160-260 ^{o}C) and high-pressure saturated steam to steep the lignocelluloses and swiftly release the pressure to atmospheric, causing explosive decompression which separates lignin from the carbohydrates and degrade the hemicelluloses. Similar to steam explosion, ammonia fiber explosion uses liquid ammonia to soak the lignocellulosic materials at high temperature (around 100 ^{o}C) for a period of time and then the materials are swiftly flashed to a low pressure, breaking the chemical bonds between lignin and cellulose and hemicelluloses and substantially increasing the porosity of the materials. In pyrolysis, the lignocellulosic materials are exposed to a high temperature (over 220 ^{o}C). At that temperature, the hemicelluloses and some lignin and cellulose will be degraded to gaseous and tarry compounds and the tight structure of the lignocelluloses will be broken. Physical pretreatment can effectively break the structure of the lignocellulosic materials and substantially improve sugar yield in the following enzymatic hydrolysis. However, physical pretreatment usually involves high energy input (Sun and Cheng, 2002).

Chemical Pretreatment:

Commonly used chemical pretreatment technologies include acid and alkaline hydrolyses. Dilute sulfuric acid pretreatment applies high temperature (140 – 190 ^{o}C) to the

mixed slurry of the lignocelluloses and the acid. The acid decomposes the hemicelluloses at that temperature, resulting in a breakup of the lignocellulosic structure. Dilute acid pretreatment has been used in pilot-scale lignocellulosic ethanol production because the technology is quite mature and breaks the lignocellulosic materials very efficiently. After the pretreatment, the lignocellulosic materials can be easily separated into a liquid portion and a solid portion. Most hemicelluloses are degraded into sugars which stay in the liquid portion, while cellulose remains in the solid portion. The separated cellulose is then hydrolyzed in the following enzymatic hydrolysis to produce fermentable sugars for ethanol production. The main disadvantage of dilute acid pretreatment is the formation of chemicals such as furfurals during the degradation of hemicelluloses that inhibit the following enzymatic hydrolysis and microbial fermentation.

Alkaline hydrolysis is another chemical pretreatment method at high temperature (100 – 170 ^{o}C). During the alkaline pretreatment, there are saponification reactions of intermolecular ester bonds crosslinking hemicellulose and cellulose or lignin in the lignocellulosic materials. Alkaline pretreatment can also disrupt lignin structure, decrease crystallinity of cellulose and degree of sugar polymerization (Sun and Cheng, 2002). Although alkaline pretreatment could cut the bonds between lignin and cellulose or hemicelluloses, a significant portion of lignin still remains mixed with cellulose after the pretreatment. The existence of lignin may inhibit cellulase enzymes during the following enzymatic hydrolysis.

Biological Pretreatment: Biological pretreatment processes use microbes such as brown-, white- and soft-rot fungi to degrade lignin and hemicellulose in lignocellulosic materials (Schurz, 1978). Brown rots mainly attack cellulose, while white and soft rots attack both cellulose and lignin. White-rot fungi are the most effective basidiomycetes for biological pretreatment of lignocellulosic materials (Fan et al., 1987). Biological pretreatment is probably the most economical pretreatment technology for the lignocellulosic materials. However, it is also a very time consuming process. The pretreatment usually takes a few weeks.

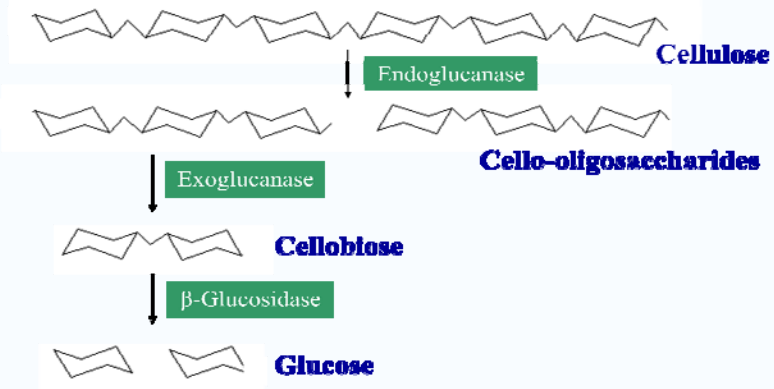
2.1.3. Enzymatic hydrolysis

Enzymatic hydrolysis of pretreated lignocellulosic materials involves enzymatic reactions that convert cellulose into glucose and hemicellulose into pentoses (xylose and arabionose) and hexoses (glucose, galactose, and mannose). The conversion of cellulose and hemicellulose is catalyzed by cellulase and hemicellulase enzymes, respectively. The enzymes are highly specific

(Béguin and Aubert, 1994). The enzymatic hydrolysis is usually carried out at mild conditions (pH 4.8 and temperature 45 to 50 °C).

Cellulases or β-(1-4) glycoside hydrolases are a mixture of several enzymes and at least three major groups of cellulases are involved in the hydrolysis of cellulose: endoglucanase, exoglucanase, and β-glucosidase. After the pretreatment, most of lignin is removed from the lignocellulosic materials, the crystallinity of the materials is significantly reduced, and the porosity is substantially increased, which allows the enzymes to penetrate into the materials and access the substrates. Endoglucanase randomly attacks regions of low crystallinity in the cellulose fiber and hydrolyze the β-(1, 4) glycosidic bonds of cellulose to produce cello-oligosaccharides with free-chain ends. Exoglucanase can hydrolyze the β-(1, 4) glycosidic bonds from the non-reducing ends of the cello-oligosaccharides to generate cellobiose which is further hydrolyzed by β-glucosidase to glucose. The joint hydrolysis of the three groups of enzymes completes the conversion of cellulose into glucose, as shown in Figure 4.

Figure 4. Enzymatic hydrolysis of cellulose to glucose



2.1.4. Fermentation process for ethanol production

During the enzymatic hydrolysis, the cellulose from the lignocellulosic materials is converted to glucose which is then fermented by yeast to ethanol and carbon dioxide:

$$\text{Glucose} \xrightarrow{Yeast} \text{Ethanol} + \text{CarbonDioxide} + \text{Heat} \quad (1)$$

In yeast fermentation, the glucose solution obtained from cellulose hydrolysis is mixed with acclimated yeast culture under aseptic conditions. The optimum temperature for yeast fermentation is around 32^{o}C. Glucose in the solution penetrates into yeast cells and is converted by a group of enzymes created by yeast cells through a series of enzymatic reactions to eventually ethanol, CO_2, and energy. Some of the released energy and glucose are utilized by the yeast cells to support their growth during the fermentation. The rest of the energy becomes heat to the fermentation broth and may increase the temperature if not taken out of the system. Both ethanol and CO_2 penetrate out of yeast cells. CO_2 readily dissolves in water, but can be easily saturated in fermentation broth. The excess CO_2 bubbles out of the liquid and can be collected for food and soft drink preparation. Ethanol dissolves in water at any ratio and the CO_2 bubbling helps the transportation of ethanol from around the yeast cells to the bulk fermentation broth, avoiding the occurrence of high ethanol concentration in local areas that may be toxic to yeast cells. The overall biochemical reactions to convert glucose to ethanol and CO_2 in yeast fermentation can be expressed as:

$$C_6H_{12}O_6 + 2\,ADP \xrightarrow{Enzymes} 2\,C_2H_5OH + 2\,CO_2 + 2\,ATP + 10.6\,kJ \qquad (2)$$

where ADP and ATP represent adenosine diphosphate and adenosine triphosphate, respectively. The process involves a series of enzymatic reactions carried out by the enzymes generated by yeast cells under anaerobic conditions.

2.1.5. Ethanol purification

When the fermentation process is completed, ethanol concentration in the fermentation broth is usually 10-15% (w/w). To have a fuel-grade ethanol, ethanol needs to be purified to over 99%. The purification process normally takes place in two steps: fractional distillation and dehydration.

Fractional distillation is a thermal physical process, based on phase equilibrium of the ethanol-water mixture. The process is performed in a fractionation column with plates or packing materials. Ethanol can be mixed with water to form a solution at any ratio. The boiling point of pure ethanol and water is 78.4 and 100 °C, respectively. However, the ethanol-water solution is a non-ideal solution. At certain ethanol concentration between 0 and 93% (w/w), the solution has a higher dew point than a boiling point. In the fractionation column, the ethanol-water mixture is at the boiling status, which generates an up-flow vapour with higher ethanol content

and a down-flow liquid with lower ethanol content. Thus, the effluent collected from the top of the column has much higher ethanol content than that from the bottom of the column. Theoretically, if there are enough plates in the fractionation column, the effluent collected from the top of the column can be close to 93% (w/w) ethanol and the ethanol content in the bottom effluent can be close to 0%. Ethanol concentration of 93% (w/w) is the theoretical maximum for fractional distillation because of the azeotropic characteristics of ethanol solution at 93 to 100% (w/w). Normally, ethanol concentration can be increased through fractional distillation to around 90% (w/w) from the fermentation broth.

To further remove the rest of the water, dehydration is necessary to increase ethanol content to over 99% for being used as automobile fuel. A commonly used technology for the dehydration of ethanol-water mixture is molecular sieve adsorption. The fundamental principle is based on the different sizes of water and ethanol molecules. The diameters of water and ethanol molecules are approximately 0.28 and 0.40 nm, respectively. The molecular sieves used in the dehydration to produce anhydrous ethanol usually have pores with a diameter of 0.3 to 0.35 nm which adsorb water molecules but not ethanol, so ethanol can be separate from water.

2.2. Feedstocks for lignocellulosic ethanol

Lignocellulosic materials can be derived from wood, grasses, agricultural residues, and waste materials. They usually contain quite high cellulose, hemicelluloses, and lignin. The contents of the compounds in common lignocellulosic materials are listed in Table 1.

2.2.1. Wood

Woods are divided into softwood and hardwood. Softwood is the dominant source of lignocellulosic materials in the northern hemisphere. 92% of the world's softwood forests are in North America, Russia, and Europe. Hardwood, in contrast, is widely distributed in the world.

Among the different types of woods, poplar is of particular interest because of its rapid growth. Poplar is typically grown for 2-5 years and then harvested (annual yield of 5-6 dry tons per acre). Hardwood is generally a better material for ethanol production because of its structural advantages over softwood. First, hardwood has significantly less lignin than softwood. As discussed previously, lignin is a major component of lignocellulosic materials that hinders the hydrolysis of cellulose. In addition, the hemicelluloses of hardwood are mainly composed of hexoses, while the hemicelluloses of softwood are mainly composed of pentoses. Hexoses, e.g.

glucose, are much easier to be fermented to ethanol than pentoses, e.g. xylose, using the current technologies. Details will be discussed later in this paper.

Table 1. Contents of cellulose, hemicellulose, and lignin in common lignocellulosic materials.

Lignocellulosic Materials	Cellullose, %	Hemicellulose, %	Lignin, %
Hardwoods stems	40-55	24-40	18-25
Softwood stems	45-50	25-35	25-35
Switch grass	45	31.4	12-20
Miscanthus	40	18	25
Coastal Bermuda grass	25	35.7	9-18
Corn stover	35-40	17-35	7-18
Wheat straw	30	50	15
Rice straw	36-47	19-25	10-24
Cotton seed hairs	80-95	5-20	0
Newspaper	40-55	25-40	18-30
White paper	85-99	0	0-15

Sources: Reshamwala et al., 1995; Cheung and Anderson, 1995; Boopathy, 1998; Dewes and Hünsche, 1998; Sorensen et al., 2008.

2.2.2. Grasses

Herbaceous lignocellulosic materials are among the high yield biomass in the world. The promising candidates for biofuel production include switchgrass, Bermudagrass, and *Miscanthus*. Switchgrass is a warm-season perennial grass native to North and Central Americas (Subbendieck et al., 1997). It can also be found in Africa and South America. It can grow to a height of more than 3 m and have a root depth of more than 3.5 m (Weaver, 1968). Switchgrass can grow on a wide variety of soils including marginal land areas with limited fertilizer requirement. Its yield varies with the growing conditions, but the annual biomass production is generally 6 – 15 dry tons per acre. *Miscanthus* is originally a native grass in Southeast Asia. It was introduced to Europe as an ornamental garden grass. It is now considered as a promising energy crop in Asia and Europe. *Miscanthus* can reach a height of over 2 m during the establishment year and up to 4 m in subsequent years in Europe and as tall as 7 to 10 m in China, with root penetration of over 1 m into the soil (El Bassam, 1998). Similar to switchgrass, the annual production rate of *Miscanthus* can be 6 – 15 dry tons per acre. It grows well in marginal

land with low nutrients, but application of fertilizers could improve the production yield. Coastal Bermudagrass is another herbaceous crop widely grown in the United States. It is a warm-season perennial crop and is currently grown on 10 to 15 million acres in the southern US for forage and hay production (Boateng et al., 2007). Although coastal Bermudagrass can grow on different soil conditions, it requires fertilization (especially Nitrogen) to achieve a good annual biomass yield (6 – 10 dry tons per acre).

2.2.3. Agricultural residues

Corn stover is normally left in a field after corn kernel is harvested, including stalks, leaves, cobs, and husks. Corn stover is usually produced at a rate of 1 kg (dry) per kg of corn grain or 4 dry tons per acre per year (Kim and Dale, 2004; Heaton et al., 2008). The United States generates about 80-100 million dry tons of corn stover per year (Kadam and McMillan, 2003).

Wheat straw is the leftover for wheat grain production and it is generated at a rate of 1-3 tons per acre per year under intensive farming conditions (Reitz, 1976). The annual wheat straw generation in the United States is approximately 82 million dry tons (Kadam and McMillan, 2003). In addition to cellulose, hemicelluloses, and lignin, wheat straw also contains a significant amount of pectin and proteins (Schmidt and Bjerre, 1997).

Rice straw is generated from rice production all over the world. It has similar contents of cellulose, hemicelluloses, and lignin compared to other cereal crop residues, but it has higher silica content than most other cereal straw. The annual worldwide rice straw generation rate is about 731 million dry tons in 2007, including Africa - 20.9 million tons, Asia - 667.6 million tons, Europe - 3.9 million tons, North America - 37.2 million tons, and Oceania - 1.7 million tons.

Several factors need to be considered in selecting an appropriate lignocellulosic feedstock for bioethanol production, including ethanol yield, local availability, environmental impact, competition for arable land against food and feed production, and transportation of the biomass. The average ethanol yields and annual field production rates of common lignocellulosic feedstocks are listed in Table 2 (the data are calculated based on the yields from USDA National Agricultural Statistics Service, 2008). According to the data in Table 2, herbaceous biomass, especially switchgrass and *Miscanthus*, has much higher annual ethanol yield per acre of land

than woody biomass or agricultural residues. It is also environmentally friendly to grow herbaceous biomass and convert it to ethanol fuel because the whole cycle has almost balanced carbon dioxide, which is greatly helpful in mitigating global climate change. However, growing herbaceous biomass may compete for arable land for food and feed production. Although herbaceous biomass can be grown on marginal land with little fertilization and/or irrigation, their annual production rate per acre would be at the low end in that situation. Another disadvantage of the herbaceous biomass is its low density, which makes the transportation of the biomass to the processing facility quite expensive.

Table 2. Ethanol yields and field production rates of common lignocellulosic feedstocks

Feedstock		EtOH Yield (liter/dry ton)	Production Rate (dry ton/acre/year)	EtOH Yield (liter/acre/year)
Wood	Poplar tree (hardwood)	360	5 – 6	1,980
	Pine tree (softwood)	345	3 – 4	1,208
Grasses	Switchgrass	310	6 – 15	3,255
	Miscanthus	305	6 – 15	3,203
	Bermudagrass	300	6 – 10	2,400
Agricultural Residues	Corn stover	345	3 – 5	1,380
	Wheat straw	333	1 – 3	666
	Rice straw	335	3 – 4	1,173

The main advantage of woody biomass is its high density, which makes its transportation cost much cheaper than herbaceous biomass or agricultural residues. Woody biomass has a modest annual production rate, especially the fast growing hardwood such as poplar. Utilizing wood processing wastes such as tree thinning or wood chips for bioethanol production would be a desirable process because it does not require new arable land. If trees are grown as a special energy crop for bioethanol production, a comprehensive study needs to be conducted to compare the advantages and disadvantages of trees with herbaceous grasses.

Agricultural residues are a big source of lignocellulosic feedstock for bioethanol production. Corn stover, wheat straw, and rice straw are probably the most abundant agricultural residues in the world. Many farmers used to burn these residues in the fields after harvesting the grains. Because of the concern of air pollution, burning agricultural residues has been banned in the United States. Therefore, it will cost the farmers to manage these agricultural residues or wastes. For example, California rice farmers must pay $25 to $45 per acre to have the rice straw baled and removed from their fields. Although using these agricultural residues for bioethanol production would not have a high annual ethanol yield per acre of land, compared to special energy crops such as switchgrass or *Miscanthus*, it does not require any additional land for bioethanol production. In addition, there is no cost for growing the lignocellulosic feedstock for bioethanol production. Instead, taking the agricultural residues or wastes away from the grain farming fields could get paid, resulting in a negative cost of the feedstock for bioethanol production. For example, Colusa Biomass Energy Corp., a company which is building its first plant to process rice straw for bioethanol production in California, has made some deals to take the rice straw off the farmers' fields for a $15 per acre. Conversion of agricultural residues to bioethanol is just like "one stone kills two birds". A main disadvantage of agricultural residues is their low density, just like the herbaceous biomass, which makes the transportation cost relatively expensive compared to high-density biomass such as wood.

2.3. Research and development activities on lignocellulosic ethanol in the world

The main disadvantages of lignocellulosic ethanol production include, in comparison with sugar-based or starch-based or 1st generation ethanol production, the low accessibility of cellulose and hemicelluloses due to a complex tight structure of the lignocelluloses, low activities of cellulase enzymes, and difficulty to ferment 5-C sugars from the hydrolysis of hemicelluloses to ethanol. Research on lignocellulosic ethanol production has been focused on developing cost-effective pretreatment technologies, improved cellulase enzyme activities, and co-fermentation of 6-C (e.g. glucose) and 5-C (e.g. xylose) sugars to ethanol.

Cellulose fibers are embedded in a covalently joined matrix of pectin, lignin, and hemicellulose. Each cellulose macrofiber is composed of crystalline bundles of individual chains of cellulose (Clarke, 1997). The release of soluble sugars from cellulose can be achieved by a combination of physical and chemical processes or a combination of physical and enzymatic processes (Ingram et al., 1999). Chemical hydrolysis using weak mineral acids releases glucose,

pentose, acetate, and other organic monomers. This process, however, generates toxic substances, such as acetate, for ethanol fermentation (Ingram et al., 1999). The ideal approach for releasing soluble sugars from lignocellulose is to use cellulase enzymes. Enzymatic hydrolysis of cellulose includes a series of biochemical reactions catalyzed by the synergistic action of endoglucanase, exoglucanase and β-glucosidase (Sharrock, 1988). Endoglucanase is an important cellulase that degrades regions of amorphous cellulose to cellobiose and cellotriose. Exoglucanase or cellobiohydrolase degrades the molecules further by removing cellobiose units from the free-chain ends. These oligosaccharides need to be broken down to glucose by β-glucosidases before they can be used for ethanol fermentation by yeasts *Saccharomyces* spp. and bacteria *Zymomonas* spp., two commonly used microorganisms. These microorganisms cannot ferment pentose, another sugar that can be obtained from biomass. Hemicellulose is hydrolyzed into pentose and hexose sugars. Yeasts *Candida* spp. that ferment cellobiose to ethanol cannot ferment pentose, either (Freer and Detroy, 1982). Enteric bacteria such as *Escherichia coli* can ferment pentose and hexose sugars derived from hemicellulose. A soil bacterium *Klebsiella oxytoca* not only is capable of fermenting hemicellulose-derived sugars but also can use cellobiose andcellotriose as substrates. These bacteria, however, do not produce ethanol as the major fermentation product. Ingram and colleagues have constructed a PET operon containing alcohol dehydrogenase (adhB) and pyruvate decarboxylase (pdc) genes of *Z. mobilis* under the control of the *E. coli lac* promoter (Ingram et al., 1987). When the PET operon was introduced into *E. coli* and *K. oxytoca* strains, the organisms shifted their fermentation mainly to ethanol production. The alcohol dehydrogenase gene also makes the host ethanol tolerant. The genetically engineered K. oxytoca P2 strain has been shown to ferment monosaccharides and oligosaccharides including cellobiose and cellotriose from lignocellulose hydrolysates to ethanol (Lawford and Rousseau, 1991; Barbosa et al., 1992; Beall et al., 1992; Wood and Ingram 1992).

Traditionally, pretreatment of lignocellulosic materials has been accomplished through several physical processes such as mechanical comminution, steam explosion (Playne, 1984; Taylor, 1981), ammonia fiber explosion and carbon dioxide explosion, and chemical methods such as acid or alkaline hydrolysis (Knappert et al., 1980; Goldstein et al., 1983; Weimer et al., 1986; Playne, 1984) and ozonolysis. Mechanical comminution and steam explosion techniques are favorable because they do not generate hazardous wastes. Steam explosion is an explosive decompression of chipped biomass induced by the exposure to high-pressure, saturated steam

and subsequent flashing. Steam explosion is typically carried out between 160 and 260°C, with corresponding pressures between 0.69 and 4.83 Mpa, and before rapid exposure to atmospheric pressure. Grous et al. (1986) reported that poplar chips pretreated by steam explosion could result in 90% enzymatic hydrolysis of cellulose after 24 hours compared to only 15% hydrolysis of untreated chips. Time, temperature, chip size, and chip moisture content are important parameters in steam explosion (Duff and Murray, 1996). Effective hemicellulose solubilization and hydrolysis has been achieved with high temperatures and short residence times (e.g. 270°C, 1min) or low temperatures and long residence times (e.g. 190°C, 10min). Most recent work favors lower reaction temperatures and longer residence times (Wright, 1998). The addition of H_2SO_4, SO_2, or carbon dioxide in steam explosion could improve carbohydrate survival, decrease the production of inhibitory compounds and achieve more complete removal of hemicellulose.

There is substantial evidence that white-rot fungi can be used to selectively upgrade lignocellulosic materials to an industrial feedstock containing less lignin and hemicellulose and having an expanded structure. The key feature that makes the lignocelluloses bio-upgrading feasible is the ligninolytic enzyme system of the white-rot fungi. These enzymes, secondary metabolites that are produced under conditions of nutrient deprivation, depolymerize lignin to allow fungal attack of the polysaccharides of the materials. This biological process replaces pretreatment steps such as steam explosion or other energy-intensive pulping methods with a lower-energy consuming compost-like system that reduces energy consumption and waste. This bio-upgrading method can be performed on-farm at low cost and with minimal labor. Finally, on-farm bio-upgrading will allow value to be captured at the farm gate.

In nature, fungi remove lignin using peroxidative delignifying enzymes (Boominathan and Reddy, 1992; Thompson et al., 1998). There is considerable potential for the use of these organisms or their enzymes in processes of industrial importance, including fungal pretreatments and biopulping/biobleaching of paper pulps (Myers et al., 1988; Messner and Srebotnik, 1994), decolorization of pulp bleaching effluents (Boominathan and Reddy, 1992; Michel et al., 1991), and biotransformation of lignin into chemical feedstocks and related applications (Eriksson, 1994). The major lignin degrading fungi are white-rot basidiomycetes (Boominathan and Reddy, 1992). These fungi degrade lignin more rapidly and extensively than other microbial groups. They grow into the lumens of cell walls, where they secrete extracellular enzymes, including cellulases, hemicellulases, and peroxidases (Boominathan and Reddy, 1992). These fungi do not utilize lignin

as a growth substrate but remove the protective lignin barrier and open up the structure of the matrix so that over time, near complete degradation of the lignocellulose is possible (Blanchette et al., 1989). Ligninolytic enzymes are produced by the fungus during secondary metabolism as a result of carbon and/or nitrogen limitation, allowing the fungus to utilize cellulose and hemicellulose as substrates for growth and other metabolic functions (Boominathan and Reddy, 1992). Some white-rot fungi, including several members of the genus *Pleurotus*, attack lignin and hemicellulose in wheat straw without extensive cellulose removal (Valmaseda et al., 1990; Moyson and Verachtert, 1991). Thus, it is likely that white rot fungi could upgrade wheat straw and other substrates to a more desirable feedstock. This process would meet the goals of the agriculture industry by providing a higher quality feedstock with less energy and waste, while capturing the value on site.

Increasing the dosage of cellulases in the process, to a certain extent, can enhance the yield and rate of the hydrolysis, but it would significantly increase the cost of the process. Cellulase dosage of 10FPU/g cellulose is often used in laboratory studies because it provides a hydrolysis profile with high levels of glucose yield in a reasonable time (48-72h) at a reasonable enzyme cost (Gregg and Saddler, 1996). Cellulase enzyme loadings in hydrolysis vary from 7 to 33 FPU/g substrate depending on the type of substrates.

Enzymatic hydrolysis of cellulose consists of three steps: adsorption of cellulase enzymes onto the surface of the cellulose, the biodegradation of cellulose to fermentable sugars, and desorption of cellulase. Cellulase activity decreases during the hydrolysis. The irreversible adsorption of cellulase on cellulose is partially responsible for this deactivation. Addition of surfactants during hydrolysis was capable of modifying the cellulose surface property and minimizing the irreversible binding of cellulase on cellulose. The surfactants used in the enzymatic hydrolysis include nonionic Tween 20, 80, and 81, Emulgen 147, polyoxyethylene glycol, amphoteric Anhitole 20BS, cationic Q-86W, sophorolipid, rhamnolipid, and bacitracin. The rate of enzymatic hydrolysis was improved by 33% using Tween 80 as surfactant in the hydrolysis of newspaper (Castanon and Wilke, 1981).

Use of cellulase mixture from different microorganisms or the mixture of cellulases and other enzymes in the hydrolysis of cellulosic materials has been extensively studied (Beldman et al., 1988; Excoffier et al., 1991; Xin et al., 1993). The addition of β-glucosidases into the *T. reesei* cellulases system achieved better saccharification (Excoffier et al., 1991; Xin et al., 1993).

β-glucosidases hydrolyze the cellobiose which is an inhibitor of cellulase activity. A mixture of hemicellulases or pectinases with cellulases exhibited a significant increase in the extent of cellulose conversion (Ghose and Bisaria, 1979; Beldman et al., 1984). Baker et al. (1994) found a new thermostable endoglucanase, *Acidothermus cellulolyticus* E1, and another bacterial endoglucanase, E5 from *Thermomonospora fusca*, exhibiting striking synergism with *Trichoderma reesei* CBH1 in the saccharification of microcrystalline cellulose.

2.4. Main challenges for commercialization of lignocellulosic ethanol production

A great progress has been achieved in developing lignocellulosic ethanol production in the last decade. The achievements include more efficient and lower-cost cellulase enzymes production, high efficient pretreatment, and co-fermentation of glucose and xylose to ethanol. However, the ethanol production costs need to be further reduced for the commercial application of the advanced technologies for ethanol production.

Most pretreatment processes produce an increase in glucose yield from enzymatic hydrolysis, indicating expansion of the matrix and/or varying degrees of removal of hemicellulose and lignin (Thompson et al., 1992). However, the high cost of some pretreatments and the low bulk densities of most lignocellulosic materials make them uneconomical to pretreat or to transport to centralized facilities for processing. Reducing these costs before reaching the processing stage is desirable to allow use of these annually renewable materials.

Although pretreatment could significantly increase the yield of glucose and soluble sugars in the enzymatic hydrolysis, the key to successful hydrolysis is the cellulase enzymes. Industrial preparations of the cellulase enzymes are normally obtained from fungal and bacterial origins (Ohmiya et al., 1997). These enzymes are usually very expensive, which makes the ethanol production from lignocellulosic biomass not economically competitive (Himmel et al., 1999). It is critical to develop low-cost cellulase production systems to reduce the cost for lignocellulosic ethanol production.

Another challenge for the commercialization of lignocellulosic ethanol production is to efficiently utilize the lignocellulosic materials. In the sugar- and starch-based ethanol production technologies, almost all the sugars and starch are converted to ethanol. However, the conversion rate of lignocelluloses to ethanol is much lower, in the range of 30-60% depending on the technologies. Among the three major components of lignocelluloses, cellulose has the highest

conversion rate to ethanol, 85-90%; hemicelluloses 30-85%; lignin; 0%. The main products of hemicellulose hydrolysis include hexoses and pentoses. The former can be readily fermented to ethanol by yeast or bacteria, but the latter is difficult. To make the lignocellulosic ethanol production economically feasible, it is necessary to utilize the hemicelluloses, which is about one-third of the biomass. In other words, it is critical to develop cost-effective technologies to ferment both hexose and pentose into ethanol. Lignin is very tough to be converted to ethanol, but it can be used as a fuel in the fractional distillation in ethanol purification.

To overcome the barriers of lignocellulosic ethanol production, more research is needed in feedstock, pretreatment, cellulase enzyme production, and new fermentation technologies. The research in developing cost-effective technologies for the cellulosic ethanol production need to be focused on the following areas:

(1) Feedstock Development: Lignocellulosic materials such as corn stover, switchgrass, and poplar trees can be genetically modified for lower lignin and higher cellulose contents. Lower lignin content in the lignocellulosic materials could substantially reduce the severity of the pretreatment process or even eliminate the process. Some success has been reported in genetically reducing lignin content in aspen trees, but more research is necessary to have stable low lignin woody biomass production of the trees in the field.

(2) Pretreatment Technology: Current pretreatment technologies usually involve high temperature or high pressure, which result in a high cost of the process. Low-cost low-temperature pretreatment is a promising technology for the pretreatment of lignocellulosic materials and need more research and development.

(3) Enzyme Cost Reduction: Although the cellulase enzyme cost has been significantly reduced in the last decade, it is still high in comparison with amylases (the enzymes used in starch to ethanol process). Microorganisms that have high-efficiency in cellulase enzyme generation need to be explored to improve the enzyme fermentation process. Novel technologies may be needed to significantly reduce the cost of cellulase enzymes.

(4) Co-Fermentation of Glucose and Xylose: Glucose is the main product of enzymatic hydrolysis of cellulose, while xylose is a main product of hemicellulose hydrolysis. Fermentation of glucose to ethanol is a mature technology, but converting

xylose to ethanol is quite complicated. There have been some efforts in developing genetically engineered microorganisms (yeast and bacteria) that can efficiently convert both glucose and xylose to ethanol, but more research needs to be done in this area.

Besides, technical challenges discussed above, costs of production is another main challenge for commercialization of second generation biofuels. Currently, the cost of fuel ethanol produced from lignocellulosic materials is much higher not only than gasoline but also than corn- or sugarcane-based ethanol, mainly because of the more complicated processing associated with the lignocellulosic ethanol production. Although the main cost advantage of lignocellulose-based ethanol as compared to starch-based ethanol is the feedstock, the higher costs of capital and supplies causes lignocellulose-based ethanol production significantly expensive than the starch-based ethanol production (Sassner et al. 2008). Note that ethanol production using lignocelluloses as a feedstock needs an additional step, i.e. pretreatment, before enzymatic hydrolysis or saccharification. The pretreatment is a high cost process as it usually requires a high temperature or high pressure. In addition, cellulase enzymes used in the hydrolysis of lignocelluloses are much more expensive than the amylases used in the saccharification of starch for fermentable sugar production. Fortunately, the cost of cellulase enzyme production has substantially reduced in the last decade, but its current price is still significantly higher than that of amylases. For more details on economic analysis of second generation biofuels, please see Carriquiry et al. (2010).

2.5. Pilot-scale lignocellulosic ethanol production

Although there are still some barriers for commercial production of advanced bioethanol from lignocellulosic materials, there are a few pilot-scale lignocellulosic ethanol production facilities by pioneer industrial companies in Asia, Europe, and North America. Table 3 shows some of the pilot-scale cellulosic ethanol production facilities.

The **SEKAB**'s pilot lignocellulosic ethanol plant in Örnsköldsvik, Sweden was established in 2004 and has been continuously operated to produce 300-400 liters of ethanol per day. Wood chips from pine trees are used as the raw material for ethanol production in the facility. Acid pretreatment is used in the process, followed by enzymatic hydrolysis and yeast fermentation. This pilot project is funded by European Union to optimize the process of converting lignocellulosic materials into fuel ethanol. Other lignocellulosic materials such as

bagasse from sugarcane, wheat and corn stover, energy grass and recycled waste will also be evaluated as raw materials for bioethanol production.

Table 3. Pilot-scale cellulosic ethanol production facilities using lignocellulosic materials as feedstocks in the world

Company	Location	Raw Materials	Capacity
SEKAB E-TECHNOLOGY	Örnsköldsvik, Sweden	wood chips from pine trees	300-400 liters of ethanol per day
Arkenol	Izumi, Japan Irvine, California, USA	Mixed waste wood chips of cedar, pine, and hemlock	100-300 liters of ethanol per day
Iogen	Ottawa, Ontario, Canada	Wheat straw	Process 40 tons of wheat straw to ethanol per day

Arkenol's pilot cellulosic ethanol plant was established in Izumi, Japan in 2002. This facility is generating 100-300 liters of ethanol per day, using mixed waste wood chips of cedar, pine, and hemlock. This facility is unique because it uses Arkenol's concentrated sulfuric acid hydrolysis to convert the carbohydrates in the wood chips into sugars which are then fermented by bacteria or yeast to ethanol. Recombinant bacterium, *Z. mobilis* developed by National Renewable Energy Laboratory (NREL) of US Department of Energy in fixed bed and yeast, *S. cereviscae* are used in fermentation process. The pilot system involves the following operation units:

1. Feedstock preparation;
2. Sulfuric Decrystallization/Hydrolysis Reaction Vessel;
3. Solids/Liquid Filtration;
4. Separation of the acid and sugars;
5. Fermentation of the sugars; and,
6. Product purification (distillation and dehydration).

Stable cellulose conversion efficiency of 70% has been achieved, with optimization to 80%. Sulfuric acid recovery has been over 97%. Lignin combustion is conducted to provide heat

during the distillation process. A membrane distillation and ethanol purification system, which has a lower operating cost than a conventional system, is used to produce fuel-grade ethanol from the fermentation beer. Another Arkenol's pilot system was demonstrated in Irvine, California, USA.

Iogen Corporation has developed a proprietary process to produce fuel ethanol from lignocellulosic materials. The company has established a pilot demonstration facility using wheat straw as the feedstock in Ottawa, Ontario, Canada. The facility has been designed and built to process 40 tons of wheat straw per day into ethanol using enzymes made in its adjacent enzyme manufacturing facility. The company delivered its first shipments of cellulosic ethanol into the marketplace in 2004. Iogen has produced cellulosic ethanol at this demonstration facility, for use in a variety of international demonstrations, including fueling the leaders' vehicles at the 2005 G8 Summit in Gleneagles, Scotland. The company also provides cellulosic ethanol to flexible fuel fleets within the Government of Canada. Iogen is currently working with the US and Canadian Energy Agencies to build a larger scale lignocellulosic plant using a variety of feedstocks.

Other industrial pioneers who are involved or planning to establish pilot-scale lignocellulosic ethanol plants include BlueFire Ethanol and Colusa Biomass Energy Corporation (CBEC) in California, USA, Brelsford Engineering in Montana, USA, and Masada Resource Group, LLC in Alabama, USA. The industrial companies that are involved in developing more economical cellulase enzymes and the cost-effective technologies for enzymatic hydrolysis of lignocelluloses include Novozymes, Abengoa Bioenergy, Iogen, Mascoma, Dyadic, Verenium, and Genencor.

3. Biodiesel Production

Biodiesel is a mixture of fatty acid alkyl monoesters derived from vegetable oils and fats. It can be used as a replacement of petrodiesel because of their structural similarity.

3.1. Biodiesel production technology

Biodiesel is produced through chemical transesterification of triglycerides from oils and fats with alcohol. The chemical reactions are shown in Figure 5. A general biodiesel production process is shown in Figure 6.

Figure 5. Chemical reactions for biodiesel production

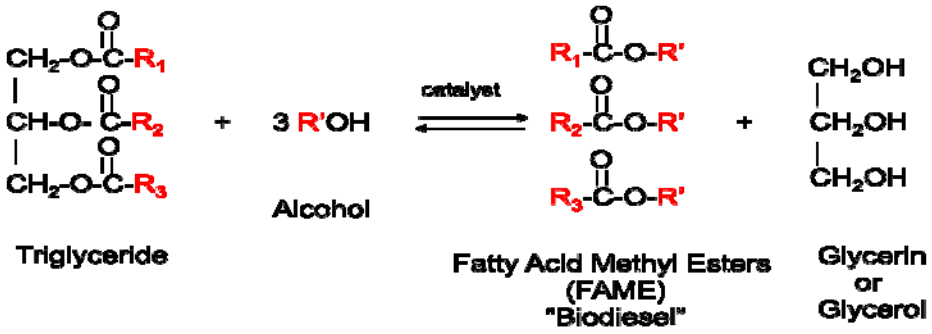
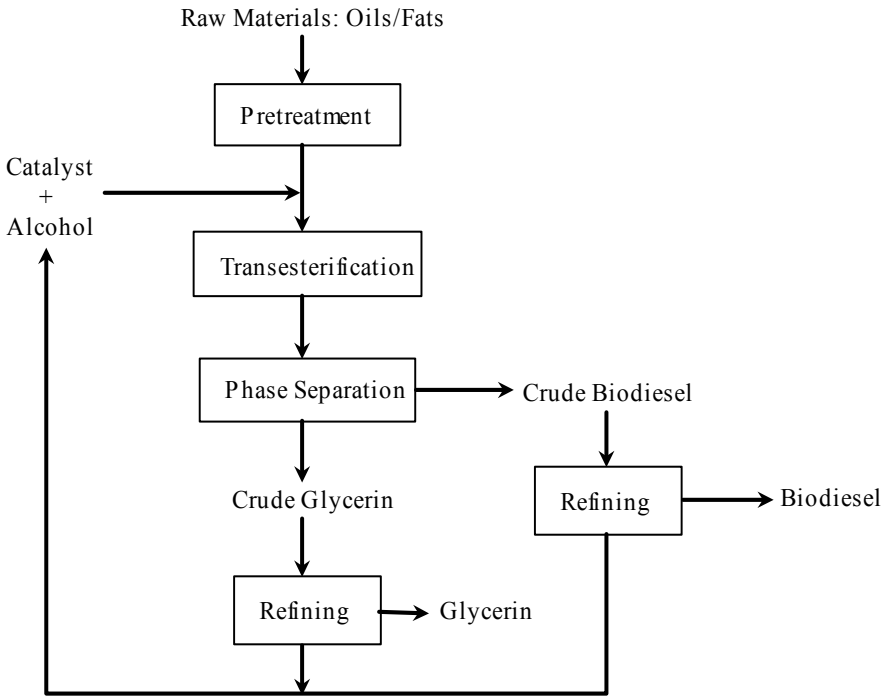


Figure 6. A general process for biodiesel production.



The process starts with oils or fats from vegetable or animal origins. Some oil or fats may need a pretreatment for degumming, deacidification, bleaching, and dehydration, depending on the compositions of the materials. Degumming is to remove phosphatides from most feedstocks because phosphatides cause turbidity of oil during storage, promote accumulation of water in oil, and increase catalyst consumption. Deacidification is to remove free fatty acids (FFAs) which form soap with alcohols. The FFAs can also be converted to esters with alcohols with an acid as catalyst. Bleaching removes pigments and trace metals and reduce oxidation products in raw materials. Dehydration removes water from the oils or fats because water is toxic to transesterification and reduces oil to biodiesel conversion efficiency.

Alcohol is the other reactant for the transesterification to produce biodiesel. Either ethanol or methanol can be used for the transesterification, but methanol is commonly used mainly because it is cheaper. According to the stoicheometry of the chemical reaction, converting one mole of triglyceride requires three moles of alcohol. Since the chemical reaction is reversible, alcohol is usually overdosed to improve the biodiesel production efficiency.

Transesterification can be catalyzed by alkalines (NaOH), acid (H_2SO_4), or enzymes (lipase). Alkaline is commonly used as catalyst for oils with high triglycerides content. Acid is usually used in pretreatment of the oils or fats with high FFAs which can be converted to esters. The esters are then converted to biodiesel through transesterification to improve the conversion efficiency. Lipase can convert both triglycerides and FFAs to biodiesel, but it is much more expensive than alkalines or acids.

The main products of transesterification are biodiesel and glycerin which can be separated through settling, filtration, and decantation. Centrifugation can speed up the separation process, especially when significant amount of soap is present in the products.

Refining of both biodiesel and glycerin improves the quality of the biodiesel and the glycerin. It also makes it possible to recycle the unreacted alcohol back for reuse to improve the biodiesel production rate and the economics.

3.2. Feedstock for biodiesel production

The main feedstock for biodiesel production worldwide includes oils from soybean, rapeseed, canola, sunflower, corn, palm kernels, animal fats, and recycled oil. Jatropha has also been used for biodiesel production in tropical areas such as India and Africa. Vegetable oils from soybean, rapeseed, canola, sunflower, and corn are considered high-quality materials for

biodiesel production because of their high triglyceride content (92-99%) and low FFAs (< 2%). Soybean and rapeseed oils are the most commonly used feedstock for biodiesel production in the United States and Europe, respectively.

Soybean is an annual plant that has been used as a food source for centuries. The dominance of soybean as a global oilseed resource can be attributed to its characteristics of high oil protein contents, which makes the soybean an advantageous feedstock for food, fuel, and feed production. The soybean seed contains 40% proteins, 34% carbohydrates, 21% oils, and 5% ash. Other minor components of the seed include phospholipids, sterols and minerals. The top five producers of soybean in the world and their annual production in 2007 are: the US - 70.7 million tons, Brazil – 58.2 million tons, Argentina – 45.5 million tons, China – 15.6 million tons, and India – 9.4 million tons (FAO, 2008).

Rapeseed is widely grown in Europe for animal feed and vegetable oil. It prefers a cool and moist climate. **Canola** is from the same family as the rapeseed but prefers a warm climate for growth. Rapeseed and canola together have become the third leading source of vegetable oil in the world in the last two decades. Their annual production worldwide was 49.5 million tons in 2007. China was the leading producer of canola and rapeseed with the annual production of 10.4 million tons, followed by Canada with 8.9 million tons, India with 7.1 million tons, Germany, and France in 2007 (FAO, 2008). Compared to soybeans, rapeseeds and canola contain twice as much oil (38-50%, dry basis), slightly less protein (36%), soluble carbohydrates such as sucrose (7.4%) and stachyose (2.5%), and the insoluble carbohydrates such as cellulose (4-5%), pectins (4-5%), hemicellulose (3%), and starch (1%) (Salunkhe et al., 1992).

Oil palm is a tropical plant widely grown in Africa, Asia, and Central and South Americas as a food oil source. Palm oil is a semi-solid at room temperature. It is composed primarily of neutral lipids with a small amount of phospholipids and glycolipids. Unlike the vegetable oils discussed earlier, palm oil contains equal amounts of saturated and unsaturated fatty acids. The major fatty acids in palm oil are oleic acid (39-40%, dry basis), palmitic acid (44-45%), linoleic acid (10-11%) and linolenic acid (small amount) (Lin, 2002). Malaysia is the largest palm oil producer in the world, followed by Indonesia, Nigeria, Colombia, Thailand, Papua New Guinea, Ivory Coast, and Ecuador (Gunstone, 2002).

Jatropha is a tropical plant or shrub originally from Central America. It is now widely grown in Africa, Asia, and Americas for biofuel production because of its high oil yield.

Jatropha produces seeds in an annual rate of 1,500 to 2,000 kilograms per hectare and seeds contain 27-40% oil (Achten et al., 2007). It can be grown on marginal land without competition for arable land against food and feed crops. In India there are 306 million hectares of jatropha growing for biofuel production, of which 133 million hectares are classified as either eroded farmland or non-arable wasteland (Fairless, 2007). The jatropha shrubs can live up to 50 years, fruiting annually for more than 30 years. They are resistant to drought and pests and quite easy to grow. Jatropha oil can be used for biodiesel and jet fuel. The railway line between Mumbai and Delhi is planted with Jatropha and the train itself runs on 15-20% biodiesel. Air New Zealand successfully completed a two-hour test flight using a 50/50 mixture of jatropha oil and Jet A1 in one of the four Rolls-Royce RB211 engines of a 747 jumbo jet on December 30, 2008. A week later, Continental Airlines successfully completed a two-hour test flight using a 50/50 mixture of algae/jatropha oil and Jet A in one of the two CFM56 engines of a Boeing 737-800 New Generation jet. Currently, jatropha oil is also used for biodiesel production in other countries such as Brazil, China, Mali, Paraguay, Philippines, and Thailand. India is currently the leading producer of jatropha in the world. China had 2 million hectares of jatropha under cultivation in 2007 and plans to plant an additional 11 million hectares across its southern states by 2010.

Waste oil is a recycled used oil in restaurants, food industry, and households. It contains substantially more free fatty acids and water and less triglycerides than fresh vegetable oils. A typical fatty acid profile for waste oil from restaurants includes linoleic acid (53%), oleic acid (28%) and palmitic acid (11.73%) (Shah et al., 2007). Because of its high FFAs and water contents, waste oil usually needs a pretreatment before the transesterification for biodiesel production. During the pretreatment, water is removed and FFAs either removed or transformed to esters. Annual waste edible oil generation worldwide is significant. In 2007, more than 15 million tons of waste edible oil is generated in the world with the US accounting for 10 million tons, followed by European Union, China, Canada, Japan, and Malaysia (Gui et al., 2008).

The biggest challenge of biodiesel production from vegetable oils is the availability of crop land for oil production to produce enough biodiesel that significantly replaces the current fossil fuel consumption. Chisti (2007) estimated crop land requirement to replace 50% of the transportation fuel in the United States based on the oil production rates of various crops. The

conclusion was that it would take 24% of the existing crop land in the US to grow oil palm that is considered as a high-yield oil crop. If growing soybean, it would take more than 3 times of the current cropland in the US. In addition, growing oil crops for biodiesel production would compete for arable land against food and feed production. To sustainably produce biodiesel without using a huge portion of the cropland that is critically needed to produce food and feed, it is necessary to explore alternative feedstocks for biodiesel production.

3.3. Second-generation biodiesel production from microalgae

3.3.1. Feedstock production systems

Microalgae have a great potential as a future feedstock for biodiesel production because of their high growth rates and high oil content of some species. Microalgae generally double their biomass within 24 hours under normal growing conditions. The doubling time during the exponential growth phase for microalgae can be as short as 3.5 hours. The oil content of microalgae ranges from 15 to 75% (dry weight). Other major components of microalgae include carbohydrates and proteins. Some high-oil microalgal species are listed in Table 4.

Table 4. The oil content of some high-oil microalgae

Microalgae	Oil Content (% dry wt)
Botryococcus braunii	25–75
Cylindrotheca sp.	16–37
Isochrysis sp.	25–33
Nannochloris sp.	20–35
Nannochloropsis sp.	31–68
Neochloris oleoabundans	35–54
Nitzschia sp.	45–47
Schizochytrium sp.	50–77

Source: Source: Chisti, 2007.

Annual oil production from high-oil microalgae can be in the range of 58,700 to 136,900 liters per hectare (Chisti, 2007). If this microalgal oil is used for biodiesel production, it would take

approximately 1.0-2.5% of the current cropland in the US to meet 50% of the US transportation fuel needs, which looks much more feasible than the current oil crops.

Commercially growing microalgae for value-added products is usually conducted in open ponds or closed photobioreactors under autotrophic or heterotrophic conditions at relatively warm temperature (20-30^{o}C). In autotrophic microalgal cultivation, the microalgae need sunlight (energy source), carbon dioxide (carbon source), and nutrients (N, P, and minerals) for their photosynthesis and generate oxygen. The main difference of growing heterotrophic microalgae from autotrophic ones is the carbon source. The former requires organic carbon such as glucose to support its growth. Normally autotrophic microalgae are grown for biodiesel production, mainly because they use carbon dioxide as their carbon source for growth. Therefore, the whole cycle of growing microalgae for biodiesel production and combustion of biodiesel as fuel would generate zero net carbon dioxide emission to the atmosphere. In addition, carbon dioxide emitted from the existing power plants can be used for growing microalgae. However, sometimes heterotrophically grown microalgae can make much more oil than autotrophic ones. Miao and Wu (2006) reported the heterotrophic growth of *Chlorella protothecoides* resulted in a significant increase of oil content of the microalgae from 14.5% under the original autotrophic growth to 55.2% (dry wt).

In a photobioreactor microalgal growth system, pure high-oil microalgae are grown in closed plastic or glass tubular bioreactors. Nutrient water is circulated in the bioreactors for the growth of the microalgae and for keeping the microalgae from settling. Natural sun light is usually the energy source for microalgal growth. Although artificial illumination to the photobioreactors is feasible, it is much more expensive than natural illumination. Pure microalgal culture can be maintained in the photobioreactors. Heat exchanger is usually necessary to maintain an adequate temperature in the photobioreactors. A high concentration of microalgal biomass can be achieved in photobioreactors. In that case high dissolved oxygen may inhibit the microalgal growth, so degassing system is usually necessary to release oxygen from the water.

In an open pond microalgal growth system, microalgae are usually grown in shallow ponds (0.3-0.5 m) with water containing adequate nutrients. Wastewaters from municipalities and animal operations can also be used for growing microalgae. Water recirculation or stirring is also necessary to keep the microalgae from settling. Microalgal biomass concentration in the

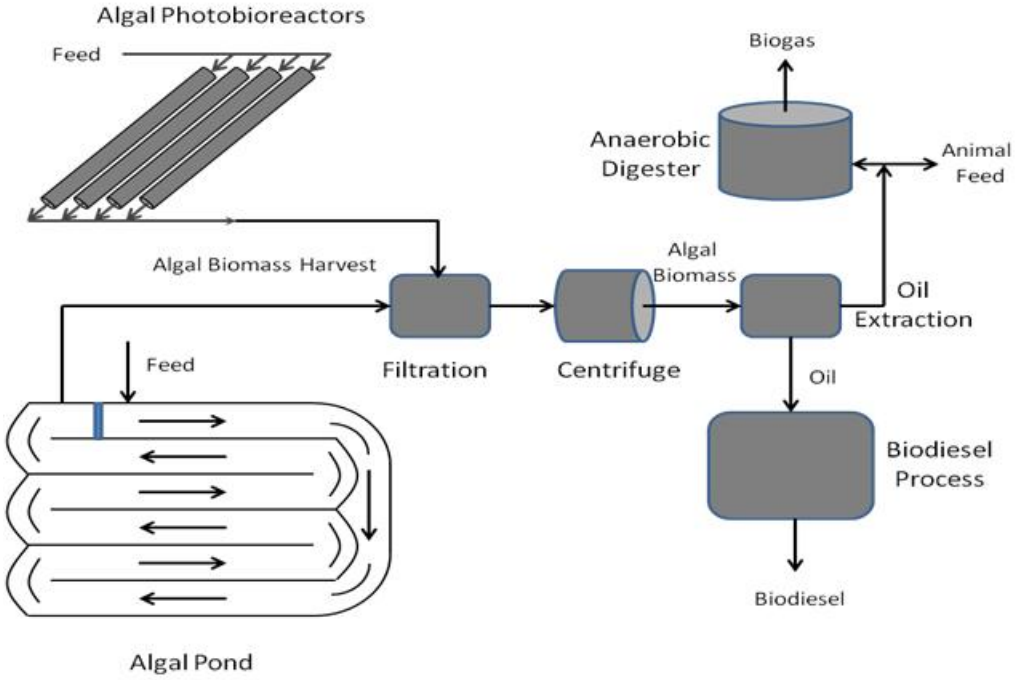
ponds is normally low compared to the photobioreactors. Wild algae and/or bacterial contamination is usually challenging in the open ponds. A comparison of growing microalgae in open ponds and photobioreactors is shown in Table 5.

Table 5. A comparison of growing microalgae in open ponds and photobioreactors

Open ponds	Photobioreactors
High volumetric productivity	Low volumetric productivity
High algal biomass concentration	Low algal biomass concentration
Pure algal culture can be maintained	Easy contamination from wild algae and/or bacteria
Low area requirement	Higher area requirement
High equipment and operational costs	Low equipment and operational costs

Microalgal biomass from the open ponds or photobioreactors can be harvested through filtration and centrifugation, after which oil is extracted for biodiesel production. The residues can be either used for animal feed production or processed in anaerobic digestion for biogas production. A flow chart of biodiesel production from microalgae is shown in Figure 7.

Figure 7. Biodiesel production from microalgae and byproducts.



3.3.2. Pilot-scale production

There are several pilot-scale biodiesel production facilities using microalgal biomass in operation in the last few years. Aurora Biofuels, Inc., a bioenergy firm in California, USA, has operated a pilot microalgal biodiesel production facility in Florida, USA since 2007 (www.americanfuels.info/2009/03/aurora-biofuels-pilot-algae-plant.html). In this facility, microalgae with high oil content have been grown on seawater in open ponds on non-arable land. The company has developed efficient technologies in microalgae harvesting and oil extraction.

Scientists and engineers at Old Dominion University built an algal farm to produce biodiesel in Virginia, USA in 2008. A one-acre open algal pond has been established to produce algal biomass for biodiesel production. Treated wastewater has been utilized to grow microalgae in the pond. Algal oil has been extracted from the biomass to produce 3,000 gallons of biodiesel fuel per year (www.odu.edu/ao/news/index.php?todo=details&id=12031).

Renewable Energy Group (REG), a biodiesel production company based in Iowa, USA developed a pilot-scale biodiesel production technology using the oil from a variety of microalgae in 2008. The pilot plant can produce a large amount of high-quality biodiesel from microalgae. The company has developed a pretreatment technology that cleans the crude oil from microalgae. The clean oil is then used for tranesterification to produce biodiesel (www.hydrocarbons-technology.com/projects/algae-biodiesel/).

3.3.3. Challenges for commercialization

Technically, producing biodiesel from microalgae has been proven feasible. The land area required to produce the same amount of oil from microalgae is only a small portion of that for oil crops. Biodiesel production from microalgal biomass or the advanced biodiesel technology has a potential for biofuel production to replace fossil fuel without serious competition for arable land against food and feed production. However, the biggest challenge of the advanced biodiesel production is its high cost. The current microalgae production and the separation of the microalgal biomass from the growing media are too expensive. An estimated cost to produce a kilogram of microalgal biomass with an average oil content of 30% is $2.95

and $3.80 for photo bioreactors and open pond, respectively, assuming that carbon dioxide is available and free (Chisti, 2007). Taking account of 30% oil content in the microalgal biomass and the cost of oil extraction from the microalgae, the cost to produce a kilogram (approximately 1.14 liters) of crude microalgal oil is more than three times of that of producing a kilogram microalgal biomass. This cost is much higher than vegetable oil production, e.g. the market price for crude palm oil which is probably the cheapest vegetable oil was only $0.52/liter in the US in 2006. It would be more discouraging if compared to petrodiesel production cost (the retail price of petrodiesel including taxes in the US in 2006 was only between $0.66 and $0.97 per liter). Another challenge in microalgae production in open ponds is the contamination by wild algae and bacteria.

3.3.4 Future perspectives of microalgal biodiesel production

To improve the economics of microalgal biodiesel production, more research and development are necessary to reduce the costs of growing microalgae and the separation of microalgal biomass from the growth media, and to efficiently control culture contamination when grown in open ponds. The research and development efforts probably need to focus on the following areas (Chisti, 2007):

(1) Selection and development of high-yield, oil-rich microalgae: Oil-rich microalgal species can be improved through cultivation and genetic engineering to increase the oil content in their biomass without compromising the biomass production rate.

(2) Improvement of the tolerance oil-rich microalgae to high and/or low temperatures: Most microalgae prefer to grow at the temperatures of 20-30^{o}C. When the temperature is higher than 30^{o}C, which happens very often during the sunny days in photobioreactors, heat exchangers have to be operated to cool down the microalgal culture to maintain a high microalgae growth. Installation and operation of the heat exchangers significantly add cost to the whole microalgal biomass production. Selection and modification of microalgae to enable them grow fast at high temperatures would probably eliminate the heat exchangers and contribute to the cost reduction of microalgal biomass production.

(3) Improvement of the tolerance of oil-rich microalgae to the high concentration of oxygen: When microalgae grow under autotrophic conditions, they produce oxygen that dissolves in water to result in a super saturated dissolved oxygen concentration in the media, sometimes 4-5 times of the air saturation value. A combination of high dissolved oxygen

with intense sunlight inhibits the growth of the microalgae and damages the microalgal cells. To prevent the inhibition and damage to the microalgae, a degassing system is necessary to keep the dissolved oxygen at an adequate level in the growth media. Increasing the tolerance of the microalgae to the high dissolved oxygen concentration in the media could also reduce the cost of microalgal biomass production.

(4) Improvement of the competitiveness of oil-rich microalgae against wild algae and bacteria: In open pond microalgae production, the contamination of wild algae and bacteria is very challenging. If the growth media is contaminated by wild algae and/or bacteria, the wild algae and bacteria will consume the nutrients in the media and significantly reduce the yield of the desired microalgae. Improving the competitiveness of the oil-rich microalgae against the wild algae and bacteria and inhibiting the wild algal and bacterial activities in the media for growing the microalgae also has a potential to reduce the cost of microalgal biomass production.

(5) Enhancement of the engineering of the microalgae growth systems: Both microalgae growing systems currently used for microalgal biomass production, photobioreactors and open ponds have rooms for improvement. When microalgae grow in tubular photobioreactors, some of them stick on the wall of the tubes, significantly reducing the penetration of light to the growth media and resulting in a lower yield of the microalgal biomass. Cost-effective materials which prevent the microalgae from attaching the surface should be explored to maintain a high growth rate of the microalgae. The main disadvantage of growing microalgae in open ponds is contamination. Greenhouse ponds can be an effective system to prevent contamination and to increase the microalgal density in the growth media.

(6) Development of cost-effective microalgae harvesting systems: Harvesting microalgal biomass contributes substantially to the total costs of the biomass production. Current technologies usually involve coagulation, filtration and centrifugation, which are costly. Innovative cost-effective harvesting systems need to be explored to significantly lower the cost of microalgal biomass harvesting.

(7) Application of the biorefinery concept to microalgal biodiesel production system: Microalgal biomass contains lipids (oil), carbohydrates, proteins, and other minor components such as minerals and vitamins. Oil is obviously used for biodiesel

production. Other components can also be processed into value-added products. After oil extraction, the residues which are rich in carbohydrates, proteins, and minor nutrients can be utilized to produce animal feed (Figure 7). They can also be utilized for biogas production through anaerobic digestion (Figure 7). Special high-value organic chemicals could be extracted from the residues and should be explored to increase the revenue of the microalgae-to-biodiesel process. All these byproducts have potentials to improve the economics of the microalgae-to-biodiesel process.

4. Biomethanol and Fischer-Tropsch (FT) Fuels

In the processes for bioethanol and biodiesel production, only a portion of the plant biomass is utilized for fuel production. For example, when switchgrass is used for bioethanol production, only cellulose and possibly hemicelluloses of the grass biomass is utilized, while lignin and other components are most probably wasted. Similarly, in biodiesel production using soybean oil as feedstock, only the oil is used in fuel generation and rest of the seeds is probably used as animal feed, by the straw is most probably wasted in the field. These solid waste materials can be converted into gaseous fuel through gasification process.

4.1. Gasification

Gasification is a partial oxidation process that converts solid organic materials into gases usually called synthetic gases or syngas, including hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4). The syngas can be directly combusted for energy production. They can also be utilized for syntheses of liquid fuels such as methanol and Fischer-Tropsch fuels.

Gasification was initially used to convert coal through partial oxidation into gases (H_2, CO, CO_2, and CH_4) in early 1800s. It is usually performed at high temperature (750-900^oC) with limited oxygen or air. Gasification is now extensively studied for converting organic biomaterials such as wood chips, grass hales, and agricultural residues into syngas. Normally gasification takes four steps: heating and drying, pyrolysis, gas-solid reactions, and gas phase reactions.

During the first step or heating and drying, heat is transferred to the solid particles to drive the moisture out of the biomaterials. The temperature of the solid particles increases to 100^oC and remains at that temperature until all the water in the biomass has evaporated. At this

step no chemical reaction occurs in the process. The heating and drying process is an endothermic one and requires energy input.

Pyrolysis is the chemical decomposition of the organic biomass in the absence of oxygen. The various biomass components decompose at different temperatures. Hemicellulose is the easiest one to be decomposed, followed by cellulose. Lignin is the most difficult component for decomposition. The break-down temperatures for hemicellulose, cellulose, and lignin are 225-325^{o}C, 300-400^{o}C, and up to 500^{o}C, respectively. The main products of pyrolysis are volatile gases (H_2, CO, CO_2, CH_4, and other light hydrocarbons) and char (porous carbonaceous residue). Pyrolysis is a rapid process, taking a few seconds to a few minutes. The ratio of volatile gases to char is a complex interaction of temperature, heating rate, particle size, and catalysts.

The volatile gases and the char generated during the pyrolysis can react with each other in the gas-solid reaction step and the reactions convert the solid carbon into gases (CO, CO_2, H_2 and CH_4). The major chemical reactions during the gas-solid reaction step include:

$$C + \frac{1}{2} O_2 \leftrightarrow CO \qquad \Delta H = -110 \text{ kJ} \qquad (3)$$

$$C + O_2 \leftrightarrow CO_2 \qquad \Delta H = -394 \text{ kJ} \qquad (4)$$

$$C + 2H_2 \leftrightarrow CH_4 \qquad \Delta H = -75 \text{ kJ} \qquad (5)$$

$$C + CO_2 \leftrightarrow 2CO \qquad \Delta H = 172 \text{ kJ} \qquad (6)$$

$$C + H_2O \leftrightarrow H_2 + CO \qquad \Delta H = 131 \text{ KJ} \qquad (7)$$

As more gases are formed during the gas-solid reaction step, the gases are reacting each other in the last step, gas phase reactions. The major gas-gas chemical reactions in this step include:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad \Delta H = -41 \text{ kJ} \qquad (8)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H = -206 \text{ kJ} \qquad (9)$$

The final gas composition after the gasification process will be determined by the amount of oxygen and steam added to the system, as well as the residence time and temperature in the gasifier. The reaction of the CO with water to from H_2 and CO_2 or water-gas shift reaction (Rxn 7) is favored at high temperatures, while methane formation or methanation (Rxn 8) is favored at low temperatures and high pressure.

In addition to major gases of CO, H_2, H_2O, CO_2, N_2, and CH_4, gasification also produces small quantities of higher hydrocarbons, NH_3, H_2S, HCl, and tars. The components in syngas that are useful for fuel generation include CO, H_2, H_2O, CO_2, and CH_4. Before the utilization of

the syngas for the production of biofuels such as biomethanol or Fischer-Tropsch fuels, the syngas has to be cleaned up to remove the "contaminants" such as NH_3, H_2S, HCl, and tars. Tars are oxidized aromatic compounds and can be removed through condensation by cooling the syngas. The dust, HCl, alkali metals, sulfur oxides and tars can be removed by spraying water into the syngas stream with a Venturi scrubber so the contaminants can be condensed on the water droplets. Particulates can be removed from the syngas with cyclones, filters, and electrostatic precipitators.

4.2. Biomethanol production

One of the important applications of syngas is the synthesis of biomethanol which can be used directly as liquid fuel or for biodiesel production. Biomethanol can also be used for the production of dimethyl ether (DME) that can be used in diesel engines as fuel. Biomethanol is produced through synthetic reactions of CO and H_2 with steam and a copper-zinc oxide as catalysts at 260^{o}C and 100psi. The overall reaction is shown as following:

$$2H_2 + CO \rightarrow CH_3OH \quad (9)$$

The process actually involves two steps: water-gas shift and hydrogenation which are shown in Rxns 10 and 11, respectively:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (10)$$

$$3H_2 + CO_2 \rightarrow CH_3OH + H_2O \quad (11)$$

The reaction for chemical synthesis of DME is shown as follows:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (12)$$

The chemical reaction takes place with aluminum oxide or silicate as catalyst at temperatures between 200-300^{o}C.

4.3. Fischer-Tropsch (FT) fuel production

Syngas, specifically CO and H_2, can be utilized to produce fuels through Fischer-Tropsch (FT) process in which CO and H_2 react to form organic compounds, mainly alkanes such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8), etc. The synthetic chemical reactions take place at high temperature (150-300°C) and high pressure (5-50 atm) and are catalyzed by transition metals such as cobalt (Co), iron (Fe), ruthenium (Ru), and nickel (Ni). A general chemical reaction of the FT process can be expressed as follows:

$$(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ H_2O \quad (13)$$

Synthetic fuels such as gasoline, diesel, and jet fuel (a variety of long-chained alkanes) can be produced through the FT process. In addition to alkanes, the FT process also produces a small amount of byproducts such as alcohols and alkenes. A major product of the FT process is determined by the chemical reaction conditions (temperature and pressure) and selection of the catalyst. Higher temperatures lead to higher reaction and conversion rates, but also favor methane formation. Relatively lower temperatures favor the production of higher molecule alkanes such as gasoline, diesel, and jet fuel. High pressure also favors formation of long-chained alkanes and leads to higher conversion rate. Cobalt and iron are commonly used catalysts in FT process for long-chained alkane production. Nickel, as a catalyst, usually favors the formation of methane.

The FT process was invented by German researchers, Franz Fischer and Hans Tropsch to convert coal into liquid fuels in 1920s. It has to be refined to convert natural gas and biomass into liquid fuels.

Currently, commercial FT fuel productions use mainly coal and natural gas to generate liquid fuel. Shell produces low-sulfur diesel from natural in Bintulu, Malaysia. Sasol in South Africa produces different synthetic petroleum products including diesel using coal and natural gas as a feedstock. Several FT fuel production plants using coal and natural gas as feedstocks are in operation in China, Germany, and the US. Recently, there are developments in using biomass as a feedstock for FT fuel production. UPM, a Finish paper company is trying to produce biodiesel through the FT process using the waste biomass from its paper and pulp manufacturing processes.

4.4. Main challenges for biomethanol and FT fuel production

Biometahnol and FT fuel production processes are usually a combination of gasification of biomass and synthesis of the biofuels from the syngas generated in the gasification. Gasification and biomethanol and FT fuel syntheses all involve high temperature and/or high pressure, thereby implying high capital costs and high operation and maintenance costs. Improving energy efficiency, the ratio of energy output of the syngas to energy input in gasification, is critical for commercial operation of the gasification technology. Although gasification and FT fuel (including methanol) production processes are established technologies to convert coal and natural gas into liquid fuels, their applications to use biomass as a feedstock still need further research. Compared to coal, biomass has a much lower energy density, which

means that the costs of transporting the biomass to the FT fuel plant would be significantly higher. Natural gas pipeline network has been well established and makes the transportation of natural gas quite economical in comparison with biomass transportation. Another big challenge is related to the complex compositions of the biomass which result in many impurities in the syngas after the gasfication of the biomass. These impurities include NH_3, H_2S, HCl, tars, and higher hydrocarbons which need to be removed before the synthetic chemical reactions in the FT process for biofuel production, because the catalysts such as cobalt and iron for the chemical reactions are very sensitive to the impurity chemicals.

Biomethanol and other Fischer-Tropsch (FT) fuel productions from biomass involve gasification of the biomass and catalytic syntheses of the syngas to produce the fuels.

5. Conclusions

The advanced biofuel production technologies including lignocellulosic ethanol, microalgal biodiesel, and Fischer-Tropsch (FT) fuel have a good technical potential to substantially replace fossil fuels in the future. Lignocellulosic materials such as agricultural residues, woods, and grasses are abundant in most land areas of the world and their generation does not necessarily compete for arable land against food and feed production. Microalgae can produce a huge amount of oil on a small footprint, hundreds or thousands of times higher yield than most oil plants. It is technically possible to produce a high volume of biodiesel that is equivalent or higher than the current level of diesel consumption using microalgae as a feedstock that are grown on a small portion of land areas (not necessary arable land) in the world. However, advanced biofuel technologies face serious barriers for their commercial applications. The main challenge for all the advanced biofuel technologies is their high production costs.

All advanced biofuel technologies have a number of technical constraints. For example, the commercialization of lignocellulosic ethanol production is constrained with high costs of pretreatment, enzymes used in hydrolysis, and conversion of 5-C sugars to ethanol. Research is necessary to improve the efficiencies in those areas and explore new technologies to convert lignocelluloses to ethanol. Similarly, the major challenge for microalgal biodiesel production is the high cost of producing microalgal biomass. The key issues to be solved are cost-effective algae harvesting, and protection of the high-oil microalgae from the contamination of wild algae. Another important issue for both lignocellulosic ethanol and microalgal biodiesel processes is

byproducts development. Both processes utilize only a portion of the raw materials for biofuel generation: only cellulose and hemicelluloses are used in ethanol production, while lipids are the only materials used for biodiesel production. The residues need to be processed for byproducts through biorefinery to improve the economics of the whole process. The FT fuel technology has a big advantage of converting almost all carbons of a biomass to biofuel. However, the two main components of the technology, gasification and fuel synthesis, both require a high energy input. Unfortunately, almost all of the current FT fuel technologies have a negative net energy yield, or the energy input in the FT fuel production is higher than the energy content of the FT fuel itself. It is critical to improve the energy efficiency of FT fuel production. Research efforts should include more efficient gasification and low-cost, high-efficiency catalysts in the FT fuel syntheses.

While barriers related to economics of advanced biofuels could be addressed through financial incentives, dealing with technological barriers is not straightforward. The main policy instrument to address the technological barriers could be to provide financial supports to research and development (R&D) activities. However, R&D activities possess large uncertainties and technological breakthrough, by virtue, might take a long lead time. It is therefore commercial deployment of advanced biofuel technologies, despite having enormous technical potential, might take time.

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