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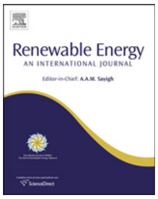

Technical Note

# Status and barriers of advanced biofuel technologies: A review

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ABSTRACT

Development of biofuels from renewable resources is critical to the sustainability of the world's economy and to slow down the global climate change. Currently, a significant amount of bioethanol and biodiesel are produced as biofuels to partially replace gasoline and diesel, respectively, in the transportation sector worldwide. However, these biofuels represent a tiny portion ($<4\%$) of the total fuels consumed. Furthermore, bioethanol is produced predominantly from sugarcane and corn, and biodiesel from crop and plant oils. Production of these raw materials is competing for the limited arable land against food and feed production. It is not feasible to tremendously increase biofuel production using the current technologies. Therefore, it is critical to investigate advanced or 2nd generation biofuel production technologies. This article is trying to summarize the current status of the 2nd generation biofuel technologies including bioethanol from lignocellulosic materials and biodiesel from microalgae. The summary includes the descriptions of the technologies, their advantages and challenges, feedstocks for the 2nd generation biofuels, the key barriers to their commercial applications, and future perspectives of the advanced technologies.

## 1. Introduction

Biofuels are generated from renewable resources such as agricultural crops, woody and herbaceous biomass, and waste materials which are renewable annually or in several years. Although the combustion of biofuels releases $CO_2$, which is believed as a major greenhouse gas (GHG) to cause global climate change, the $CO_2$ is utilized for biosynthesis during the reproduction of renewable feedstocks for biofuels. Currently, the major forms of biofuels include bioethanol and biodiesel. Energy production from biofuels is currently a tiny portion of the total worldwide energy production.

Bioethanol is a major biofuel on the market worldwide. It is used to partially replace gasoline to make gasoline-ethanol mixtures, E15 (15% ethanol and 85% gasoline) and E85 (85% ethanol and 15% gasoline). The current commercial fuel ethanol is produced mainly from sugarcane and corn, depending on the climate conditions of the producers' locations. The feedstock used for fuel ethanol production is mainly sugarcane in tropical areas such as Brazil and Columbia, while it is dominantly corn in other areas such as the United States, European Union, and China. In 2008, the total fuel bioethanol production worldwide is 17.34 billion gallons [1].

Bioethanol can also be produced from lignocellulosic materials, which is commonly called 2nd generation bioethanol. The feedstocks for the second generation bioethanol include agricultural residues, grasses, and forestry and wood residues. There have been tremendous research efforts in developing cost-effective 2nd generation or advanced technologies for fuel ethanol production in the literature. However, there are some challenges for the commercial applications of the advanced technologies.

Biodiesel is another major biofuel, which 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 or rapeseed, sunflower, and palm oil. There are research activities on using alternative oils such as waste oils from kitchens and restaurants and microalgal oils for biodiesel production.

The primary objective of this study is to understand the status of advanced biofuels technologies and key barriers to their commercial application. This study aims to analyze in detail the status of various technologies such as: (i) Lignocellulosic ethanol and microalgal biodiesel, and (ii) feedstock for 2nd generation biofuels (e.g., grasses, agricultural residues, forestry and wood residues, waste materials, and microalgae).

## 2. Lignocellulosic ethanol production

Bioethanol can be produced from different natural materials: sugar-, starch-, and lignocellulose-based materials. Currently,

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bioethanol is produced predominantly from sugarcane and corn. However, production of these raw materials is competing for the limited arable land against food and feed production. It is not feasible to tremendously increase bioethanol production using the current technologies. Lignocellulosic materials are abundant almost all over the world and they 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 or starch-rich materials. The conversion of lignocelluloses to ethanol involves three steps: pretreatment, hydrolysis, and fermentation.

## 2.1. Lignocellulosic ethanol technology

### 2.1.1. Lignocellulose

Lignocellulose is composed of mainly cellulose, hemicelluloses, and lignin. 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. 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). 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

Pretreatment is the process to prepare the ligocellulosic materials for the enzymatic hydrolyses of cellulose and hemicelluloses to generate fermentable sugars. The purpose of the pretreatment is to separate the lignin from cellulose and hemicelluloses in the lignocellulose, reduce cellulose crystallinity, and increase the porosity of the material, so the hydrolytic enzymes can access their substrates (cellulose and hemicellulose) in the following enzymatic hydrolysis. Pretreatment technologies have been extensively investigated in the last three decades, including physical, chemical, and biological processes for lignocellulosic materials [2].

*2.1.2.1. 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 0.2–2 mm and reduce the crytallinity of the materials. Steam explosion applies high-temperature (160–260 °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 °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 °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 [2].

*2.1.2.2. Chemical pretreatment.* Commonly used chemical pretreatment technologies include acid and alkaline hydrolyses. Dilute sulfuric acid pretreatment applies high temperature (140–190 °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. Most hemicelluloses are degraded into sugars which stay in the liquid portion, while cellulose remains in the solid portion. 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 °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 [2]. 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.

*2.1.2.3. Biological pretreatment.* Biological pretreatment processes use microbes such as brown-, white- and soft-rot fungi to degrade lignin and hemicellulose in lignocellulosic materials. 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 [3]. 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 [4].The enzymatic hydrolysis is usually carried out at mild conditions (pH 4.8 and temperature 45–50 °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.

## 2.2. Feedstocks for lignocellulosic ethanol production

Lignocellulosic materials can be 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.