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# Challenges of Biomass Utilization for Biofuels

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## Abstract

Lignocellulosic biomass materials are attracting increasing attention as renewable, economical and abundant resources to reduce dependency on petroleum resources. However, chemical and physicochemical properties of these materials (e.g., low density, moisture content, complex and rigid structure, etc.) limit their use. The contents and compositions of cellulose, hemicellulose and lignin polymers in biomass feedstock highly affect the efficiencies of conversion technologies. In aqueous-phase utilization processes, it is necessary to breakdown the starting biomass material into soluble components and release the carbohydrates into hydrolysate for an effective conversion. It is not economical to convert biomass hydrolysates into renewable fuels in high yields if they mostly contain large-sized molecules such as polysaccharides. The chapter describes challenges of lignocellulosic biomass materials usage in biofuel application such as their complexity and diversity, content and composition, low density, moisture content and dissolution difficulties, etc.

**Keywords:** biomass, utilization, conversion, biofuels, challenges

## 1. Introduction

Non-edible lignocellulosic biomass materials are attracting increasing attention as renewable, economical, and abundant resources to reduce dependency on petroleum resources and minimize energy and material feedstock costs. These resources do not cause additional increase in the carbon dioxide level in the earth's atmosphere compared to fossil-based energy fuels such as coal, gasoline or natural gas. The carbon dioxide captured in biomass growth mostly balances with the release of carbon dioxide from bioenergy/biofuel. Therefore, use of biomass energy has the potential to reduce greenhouse gas emissions.

Biomass materials are the largest carbon sources for production of various fuels, chemicals and platform compounds and bioproducts. Because of their heterogeneous, complex and rigid structures it is hard to breakdown these materials to smaller components and/or convert to a wide range of value-added products. Biomass has a relatively low energy density; therefore, it requires more biomass feedstocks to supply the same amount of energy as a traditional hydrocarbon fuel. High oxygen contents of biomass materials can also negatively affect their conversion to various products such as fuels. For instance, in order to produce hydrocarbon fuels that can be comparable with petroleum-based ones oxygen should be removed from biomass structure. Efficiency of conversion processes can also varied depending on the biomass types (hardwood, softwood, grass, etc.).

Following sections will focus on the challenges for conversion of biomass to biofuels in detail.

## **2. Challenges**

### **2.1 Moisture content**

Biomass materials with high moisture contents is not a suitable feedstock for conventional thermochemical conversion technologies such as gasification and pyrolysis. High moisture can reduce the effectiveness of conversion processes. Moisture in raw biomass materials is also undesired because fuel produced from these materials can contain moisture. The fuels, which have high moisture contents, cannot burn easily. Some part of energy in the fuel are consumed for vaporization of water, which is present in the fuel. In order to maximize the heating value of the fuel produced from these materials the moisture content of biomass should be less than 20%. Drying the materials before being used in the conversion process is not preferable because of high cost. On the other hand, some biomass conversion processes use biomass with high moisture contents. For instance, hydrothermal conversion processes, which use supercritical and subcritical water as reaction medium, and biological processes such as alcohol production from carbohydrates by biomass hydrolysis and fermentation can be applied to the biomass with high moisture content without the need for drying. In these processes, moisture in the biomass plays an important role in the conversion, either as a major reactant, or as a reaction environment.

High moisture content in biomass causes biological degradation, mold formation and losses in the organic contents (e.g., carbohydrates) during storage [1], that could reduce the yield of the fuel produced from these materials. Storing biomass at <10% can extend the conservation time of the materials and reduce major losses (sugars) in the biomass during the storage period [2]. The drawbacks of high moisture contents can be mostly solved by compressing the biomass material for more uniform properties that process is called densification. Increasing bulk density of biomass materials by densification reduces transportation costs and storage volume. However, this process increases the price of the end product.

### **2.2 Density**

The bulk density of lignocellulosic biomass materials is generally low (80–150 kg/m<sup>3</sup> for grass biomass and 160–220 kg/m<sup>3</sup> for woody biomass). This creates difficulties to handle such large quantities of feedstocks and increases their transportation and storage costs [3]. The bulk density of biomass should be between 190 and 240 kg/m<sup>3</sup> for efficient transport in various sizes of trucks with 25 ton loads [4].

The size, shape, moisture content, particle density, and surface characteristics are the factors affecting the bulk density of a material. The challenge for low density and different size and shapes of biomass can be overcome by densification process (**Figure 1**). In this process, biomass materials are mechanically compressed to increase their density and convert them to uniform shapes and sizes (briquetting, pelletizing, or cubing) [5, 6].

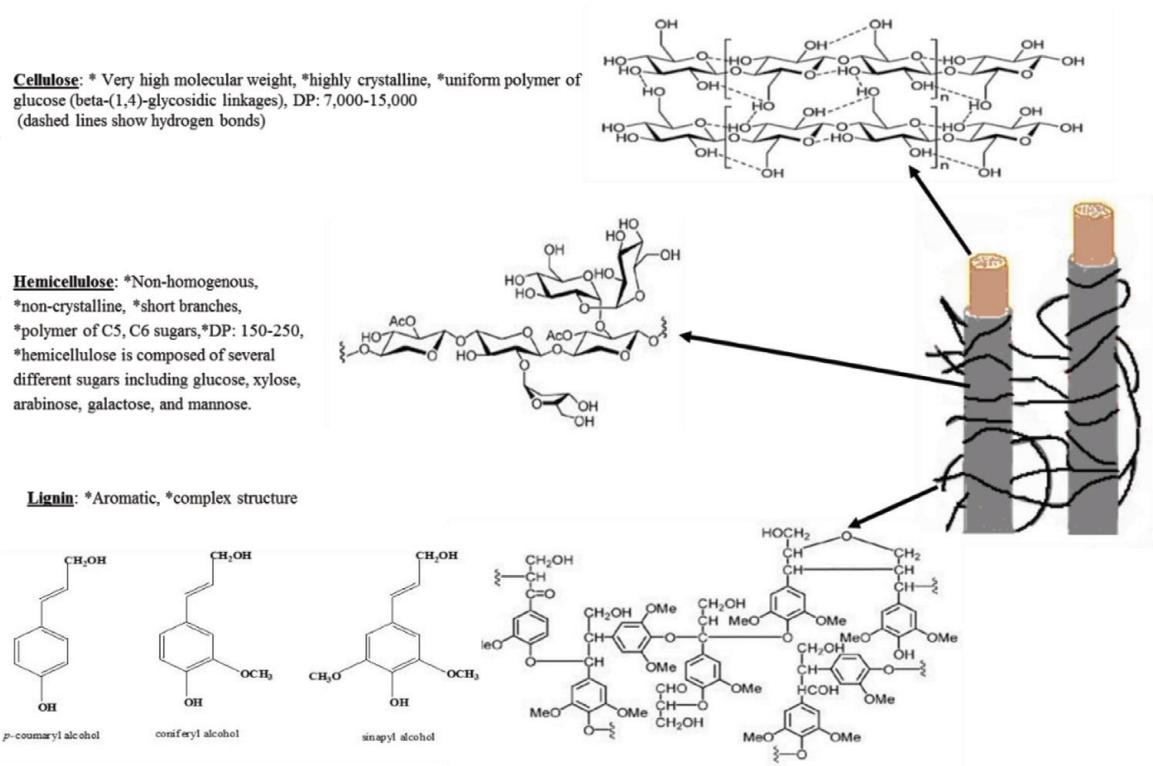
The density of biomass material can be increased ten-fold depending to biomass type, moisture content, processing conditions, etc. The costs of handling, transportation, and storage of resulted densified materials can be considerably reduced. Because of uniform sizes and shapes, the materials can be easily handled with standard machines or equipment [6].



**Figure 1.**  
*Increasing density of biomass.*

2.3 Complexity and diversity

Lignocellulosic biomass materials is mainly composed of three components which are lignin, cellulose, and hemicellulose (**Figure 2**). These polymers are organized in complex non-uniform three-dimensional structures and each one has different polymerization degrees. Polymerization degree and/or structures of these biopolymers can vary among biomass species. Cellulose is a linear structure composed of  $\beta(1-4)$  linked glucose subunits. Cellulose molecules determine the cell wall



**Figure 2.**  
*Structure of lignocellulosic biomass.*



framework. The inter- and intra- chain hydrogen bonding in the structure makes the cellulose to be crystalline and this portion of cellulose does not hydrolyze easily compared to amorphous cellulose structure [7, 8]. Hemicellulose has a random and amorphous structure, which is composed of several heteropolymers such as xylan, galactomannan, arabinoxylan, glucomannan and xyloglucan. Its polymerization degree is less than cellulose. The monomer units of hemicellulose polysaccharide include xylose, mannose, galactose, rhamnose, and arabinose units unlike only glucose in cellulose. Lignin is a complex aromatic substance of phenyl propane units. Three different phenyl propane building blocks p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, forms lignin structure.

Phenylpropanoid monomeric units in the lignin polymer are identified as p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively. The ratio of these units varies between plants; for example in hardwoods S and G forms dominate with minor amount of p-hydroxyphenyl (H), whereas softwood lignins contain only G units. On the other hand, lignins from grasses are composed of the three basic precursors (HGS) [9, 10].

Composition of lignin, cellulose and hemicellulose in biomass materials significantly differ among biomass species (**Table 1**). For instance, some biomass materials such as hardwoods contain more cellulose in their structures, while others such as straws have more of hemicelluloses. Hemicellulose fractions of softwoods mainly have D-mannose derived structures such as galactoglucomannans, while hemicelluloses in hardwoods have D-xylose derived structures such as arabinoglucuronoxylan [13]. This diversity among biomass materials can significantly affect the conversion processes for production of biofuel or other useful products from biomass materials.

2.4 Recalcitrance and dissolution difficulties

Despite their potential for the production of biofuels and chemicals alternative to petroleum, the complex and rigid structures of lignocellulosic materials limit their use in such applications. Success of using lignocellulosic biomass for biofuels and other useful chemical productions depends largely upon physical and chemical properties of the biomass, on pretreatment methods and optimization of the processing conditions. The compositional changes in plant cell wall and differences in ultrastructure greatly influence the pretreatment and hydrolysis (dissolution) efficiency of the biomass. Hydrolysis is a chemical reaction that releases sugars from biomass structures. Biomass dissolution involves both physical, chemical and/

Biomass material	Cellulose	Hemicellulose	Lignin
Switchgrass (grass)	33.8	28.4	16.6
Miscanthus (grass)	47.7	24.6	12.3
Poplar (hardwood)	52.1	27.4	15.9
Oak (hardwood)	40.4	35.9	24.1
Pine (softwood)	46.0	25.5	20
Spruce (softwood)	45.5	22.9	27.9
Corn stover (agricultural waste)	38.5	24.5	18.5
Rice husks (agricultural waste)	32.1	20.6	17.7
Corn bran (byproduct of milling)	20.5	65.3	1.6

**Table 1.**  
*Various lignocellulosic biomass materials and their chemical compositions [11, 12].*

or thermochemical treatment processes. The crystallinity of cellulose, hydrophobicity of lignin, and embedding the cellulose in lignin-hemicellulose matrix and difficulties in cleavage of some linkages (hydrogen bonding, ether linkages between the phenyl propane units, etc.) make biomass materials resistant to hydrolysis. It is relatively easy to hydrolyze hemicellulose into simple sugars compared to cellulose because hemicellulose fraction is more accessible compared to cellulose fraction which is embedded in the lignin matrix.

Biomass materials must first be broken down into components with smaller molecular weights (e.g., oligo- and monosaccharides) in order to be efficiently converted into a range of products. Hydrolysates from biomass can be used for producing a wide range of value-added products, including biofuels (ethanol, hydrogen, etc.), industrially important chemicals (e.g., solvents), and food products (sugar and sugar alcohols, etc.).

Significant existing challenges for hydrolysis of lignocellulosic biomass materials include the following:

- Existing hydrolysis methods are expensive and time consuming. Most of them are not environmentally friendly.
- Additional steps are required (pretreatment, neutralization, etc.)
- Released carbohydrates decompose in harsh hydrolysis conditions.

The major hydrolysis processes typically used for the solubilization of biomass require either use of toxic, corrosive, and hazardous chemicals (e.g., acid and alkali treatments) or longer retention times (e.g., enzymatic hydrolysis), which collectively make the process environmentally unsafe and/or expensive. Mineral acids are commonly used to dissolve hemicelluloses, whereas lignin is typically dissolved by alkaline or organosolv pretreatments [14, 15]. Recovery of the chemical catalyst is often crucial to the success of these processes [16]. On the other hand, generally harsh conditions (e.g., high temperatures and high acid concentrations) are needed to release glucose from biomass complex structures. Pyrolysis and other side reactions at higher temperatures become very important, and the amount of undesirable byproducts (tars) increases as the temperature is increased above 220°C [17].

Concentrated acid hydrolysis has been applied to breakdown lignocellulosic efficiently [18–20]. The hydrolysis of cellulose to its monomer sugar component occurs by degradation of chemical bonds in cellulose by the hydrolytic cleavage of  $\beta$ -1,4-glycosidic bond which is catalyzed by  $H^+$  ions of an acid. The reaction rate depends on the  $H_3O^+$  ion concentration, the reaction temperature, and the chemical environment of the glycosidic bond and the rate is increased with the increasing acid ion concentration and temperature. The acid hydrolysis process usually employs sulfuric acid and hydrochloric acid at concentrations of 1–10% using a moderate temperature (in the range of 100–150°C) [21]. A two-step sulfuric acid hydrolysis is a widely used technique for releasing sugars from biomass [18]. Biomass is first treated with concentrated sulfuric acid at a low temperature and then hydrolyzed with diluted sulfuric acid at an elevated temperature. Concentrated acid recrystallizes cellulose to less crystallized oligosaccharides followed by less concentrated and higher reaction temperature for converting recrystallized oligosaccharides to monosaccharides. Concentrated acid hydrolysis process can provide higher conversion from polysaccharides to monosaccharides with minimum formation of reaction by-products with careful control of reaction conditions.

The use of concentrated acid for biomass hydrolysis has several more drawbacks such as energy consumption, equipment corrosion, handling of non-safe chemicals,

an added necessary step of acid neutralization, the formation of byproducts that create an inhibitory effect in the fermentation [22, 23] and other negative environmental impacts. Thus, the current methods have undesirable processes and do not meet the needs.

Subcritical water ( $99.97^{\circ}\text{C} < T < 374.15^{\circ}\text{C}$ ;  $217.76\text{ atm} < P$ ) is an alternative way to hydrolyze lignocellulosic biomass in an environmentally friendly manner by only operating temperature and pressure conditions. Significant advantages of subcritical water over commonly used biomass breakdown methods—alkali, acidic, and enzymatic—are summarized in **Table 2**.

The chemical properties of water are greatly changed at high temperatures and pressures due to the reduction of hydrogen bonding, which causes changes in dissociation, solubility, diffusivity, and reactivity [24]. Subcritical water has a lower relative dielectric constant and a higher ionic product than ambient water. When the temperature of water increases from ambient temperature to  $250^{\circ}\text{C}$ , its relative dielectric constant decreases from around 80 to nearly 27, which is similar to that of acetone at ambient temperature [25, 26]. Furthermore, the ion product of subcritical water substantially increases with temperature; therefore, subcritical water can catalyze chemical reactions such as hydrolysis and degradation without the use of any additional catalyst [27, 28].

Ionic product numbers of water ( $K_w$ ) at various temperatures and pressures showed that when pressure is around 35 MPa and temperature is in sub- and supercritical regions under  $400^{\circ}\text{C}$ ,  $K_w$  values are always higher than  $1 \times 10^{-14}$ . The  $K_w$  increases to its maxima ( $\sim 10^{-11}$ ) between 200 and  $300^{\circ}\text{C}$  and does not respond to changes in pressure when in this temperature range. The molar concentrations of hydrogen ion ( $\text{H}^+$ ) and hydroxide ion ( $\text{OH}^-$ ) in these regions are almost 30 times higher than those under room temperature. Therefore, the hydrolysis yield in these regions is expected to be high, and biomass polymers could be broken down into their smaller molecular weight components efficiently [29–31].

The presence of a weak acid in subcritical water media can also improve hydrolysis of biomass materials. The use of carbon dioxide is as a pressurizing gas caused the formation of carbonic acid that plays a catalytic role in effective solubilization of biomass [32]. Some studies indicated that the addition of small amounts of hydrogen peroxide can enhance lignin removal and modify cellulose structure toward favoring enzymatic hydrolysis [33, 34].

Complexity and diversity of the biomass materials considerable affect the solubilization efficiency of these materials. The differences in the content and composition of resulted hydrolysates can change the yield of the biofuel or target compound produced from these biomass hydrolysates. The more degraded organics containing hydrolysates can positively affect the yield of certain various value-added products; for instance, production of gaseous products by hydrothermal gasification

Breakdown methods	Advantages and disadvantages
Alkali/acidic	Requires harsh conditions; uses corrosive, hazardous chemicals; high costs of chemicals; formation of inhibitory byproducts; recovery problem of chemicals; requires a neutralization step; decomposes released sugars.
Enzymatic	Ineffective unless coupled with an acid treatment; high cost; time consuming.
Subcritical water	Takes place in a safe solvent (water); no corrosive, hazardous, or toxic chemicals are needed; hydrolysis efficiency can be enhanced by operating temperature and pressure; use of recyclable heterogeneous catalysts can make the process more effective.

**Table 2.**  
*Comparison of alkali, acidic and enzymatic biomass breakdown methods with subcritical water treatment.*

processes. The maximum solubilization yield of wheat straw and kenaf biomass materials was 70–75%, which was achieved at 250°C in subcritical water medium [32, 35]. However, the hydrolysates obtained in this process had high molecular weight polysaccharides that were difficult to utilize for hydrogen production by aqueous-phase reforming [31]. For maximum usability, biomass components in hydrolysates should be further broken down into smaller molecular weight components with a suitable method.

## 2.5 Other challenges

Although energy demands are continuous, biomass materials are seasonal. Some biomass feedstocks have advantages in terms of production, harvesting, storage, and transportation compared to others. Non-food biomass such as energy crops (switchgrass, miscanthus, kenaf, etc.) have advantages over food crops (corn, sugarcane, sugar beet, sweet sorghum, etc.). Perennial energy crops such as switchgrass and miscanthus do not need to be replanted each year and they do not require special care and high maintenance to grow. On the other hand, agricultural biomass residues (corn stover, wheat straw, rice husk, crop peels, pulps, etc.) as promising low-cost feedstocks since they do not need additional land for biomass growth and the land used for agriculture belongs to these types of biomass materials. Forest biomass are also large source of materials for biofuels and other value-added products production. However, high costs of their harvesting and transportation limit their use. In addition to the advantage and disadvantage listed above, different sources of biomass feedstocks do not have same composition, uniform size and shape, etc., that considerable affect efficiency of conversion processes for a specific product. Therefore, biomass feedstocks for a bio-refinery needs to be standardized.

## 3. Conclusions

Biomass materials have some challenges that need to be overcome for their fully utilization for biofuel and other useful products. Availability, abundance, and requirements for growth, growth rate, etc., parameters considerably affect the feedstock selection for value-added products. Besides, the content of cellulose, hemicellulose, and lignin in biomass materials and accessibility of these fractions in the biomass structures play significant roles in biomass dissolution and biofuel production from the hydrolysate. Biomass material should be used in densified forms to overcome moisture, storage and handling problems. Biomass feedstocks delivered to a bio-refinery from different sources should be standardized for an effective conversion of a specific product.



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