Chapter 1
Background and General Introduction

Abstract Owing to the increasing demand for energy, the hunt for alternative sources of energy generation that are inexpensive, ecofriendly, renewable, and can replace fossil fuels is on. One approach in this direction is the conversion of plant residues into biofuels wherein lignocellulose, which forms the structural framework of plants consisting of cellulose, hemicellulose, and lignin, is first broken down and hydrolyzed into simple fermentable sugars, which upon fermentation form biofuels. A major bottleneck is to disarray lignin which is present as a protective covering and makes cellulose and hemicellulose recalcitrant to enzymatic hydrolysis. A number of biomass pretreatment processes have been used to break the structural framework of plants and to depolymerize lignin. In this chapter, background and general introduction on pretreatment of lignocellulosic biomass for biofuel production are presented.

Keywords Energy · Biofuels · Lignocellulose · Cellulose · Hemicelluloses · Lignin · Fermentation · Biomass · Pretreatment · Enzymatic hydrolysis

Development of sustainable energy systems based on renewable biomass feedstocks is now a universal effort. Biofuels produced from various lignocellulosic materials, such as wood, agricultural, or forest residues, have the potential to be a valuable substitute for, or complement to, gasoline. Liquid biofuels, such as ethanol, can be produced from biomass via fermentation of sugars produced from the cellulose and hemicellulose within the lignocellulosic materials. Ethanol produces slightly less greenhouse emissions than fossil fuel (carbon dioxide is recycled from the atmosphere to produce biomass); can replace harmful fuel additives (e.g., methyl tertiary butyl ether), and produces jobs for farmers and refinery workers (Bajpai 2013). It is easily applicable in present-day internal combustion engine vehicles (ICEVs), as mixing with gasoline is possible. Ethanol is already commonly used in a 10 % ethanol/90 % gasoline blend. Adapted ICEVs can use a blend of 85 % ethanol/15 % gasoline (E85) or even 95 % ethanol (E95). Ethanol addition increases octane and reduces carbon monooxide, volatile organic carbon and particulate emissions of gasoline. And, via on-board reforming to hydrogen, ethanol is

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also suitable for use in future fuel cell vehicles (FCVs). These vehicles are believed to have about double the current ICEV fuel efficiency.

Use of lignocellulosic biomass as a feedstock is seen as the next step toward significantly expanding ethanol production. Lignocellulosic biomass includes the following:

- Forestry wastes (e.g., wood chips, and sawdust)
- Agricultural residues (e.g., corn stover (cob and stalk), rice straw, bagasse, cotton gin trash, etc.)
- Bioenergy crops (sweet sorghum, switchgrass and common reeds)
- Industrial wastes (e.g., paper sludge, recycled newspaper)
- Municipal solid wastes.

Unlike food-based (starch-derived) biomass, it shows a series of advantages such as, low cost, abundant supplies, non-competition with grain as food (Sathisuksanoh et al. 2009).

Lignocellulose, a natural complicated composite basically consists of cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are tangled together and wrapped by lignin outside (de Vries and Visser 2001). Depending on sources and cell types, the dry weight typically makes up of around 35–50 % cellulose, 20–35 % hemicellulose, and 10–25 % lignin (Demirbas 2005). Cellulose, the most abundant natural carbon bioresource on the earth, is a homopolysaccharide of anhydroglucopyranose linked by ß-1, 4-glycosidic linkages (McMillan 1997). Adjacent cellulose chains are coupled via orderly hydrogen bonds and Van der Waal's forces, resulting in a parallel alignment and a crystalline structure (Zhang et al. 2007). Several elementary fibrils gather, forming much larger microfibrils, which are further bundled into larger macrofibrils, leading to the rigidity and strength of cell walls. Efficient conversion of cellulose into glucose has been a central topic for long. Hemicellulose, the second main polysaccharide, is a polymer containing primarily pentoses (xylose and arabinose) with hexoses (glucose and mannose), which are dispersed throughout and form a short-chain polymer that intertwines with cellulose and lignin like a glue (Wilkie 1979). Lignin is a polymer consisting of various aromatic groups. It can be converted into numerous chemical products that are made from fossil-based chemical industry, including coal, oils and natural gas. The production of cellulosic ethanol holds promise for an improved strategic national security, job creation, strengthened rural economies, improved environmental quality, nearly zero net greenhouse gas emissions, and sustainable local resource supplies (Demain et al. 2005; Lynd et al. 1991, 1999, 2002; Zhang 2008). So far, more companies are working on reducing costs of cellulosic ethanol production, such as Iogen Corporation, Abengoa Bioenergy, Dupont, British Petroleum, Mascoma (Biotechnology Industry Organization 2008). The price of E85 is still as high as $1.81 per gallon (DOE 2009).

Lignocellulosic biomass can be converted into soluble sugars via a large number of approaches. Conversion for lignocellulose is much more complicated and difficult, considering their complex and recalcitrant structures (Jorgensen et al. 2007; Yang and Wyman 2008). The biological conversion of cellulosic biomass into bioethanol is based on the breakdown of biomass into aqueous sugars using chemical and biological means, including the use of hydrolytic enzymes. From that point, the fermentable sugars can be further processed into ethanol or other advanced biofuels. Therefore, pretreatment is required to increase the surface accessibility of carbohydrate polymers to hydrolytic enzymes. The goal of the pretreatment process is to break down the lignin structure and disrupt the crystalline structure of cellulose, so that the acids or enzymes can easily access and hydrolyze the cellulose. Pretreatment can be the most expensive process in biomass-to-fuels conversion but it has great potential for improvements in efficiency and lowering of costs through further research and development. Pretreatment is an important tool for biomass-to-biofuels conversion processes. Numerous lignocellulose pretreatment approaches have been developed, which are reviewed by many researchers (Chandra et al. 2007; Dale 1985; Eggeman and Elander 2005; Himmel et al. 2007; Ladisch et al. 1992; Lin et al. 1981; Lynd 1996; Lynd et al. 2003, 2008; McMillan 1994; Mosier et al. 2005; Office of Energy Efficiency and Renewable Energy and Office of Science 2006; Ragauskas et al. 2006; Sun and Cheng 2002; Vertès et al. 2006; Wyman 2007; Wyman et al. 2005a, b; Bensah and Mensah 2009; Zheng et al. 2009; Chaturvedi and Verma 2013; Agbor et al. 2011; Kumar et al. 2009; Avgerinos and Wang 1983). Most notably, a collaborative team called consortium for applied fundamentals and innovation (CAFI) funded by the Department of Energy and Department of Agriculture has formed and focused on several "leading pretreatment technologies," including dilute (sulfuric) acid pretreatment, flow-through pretreatment, ammonia fiber expansion (AFEX), ammonia recycle percolation (ARP), and lime pretreatment for the past several years (Moxley 2007).

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