

## Advantages and Significance of Acid and Alkali Pretreatment of Lignocellulose Biomass in Biorefining Process

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Biomass can be defined as the organic materials obtained from green plants. Lignocellulose biomass is mentioned as the fourth largest energy source after coal, oil and natural gas. In addition, it is the most vital renewable energy source today and can generate various forms of energy [1]. Energy obtained from biomass resources is considered to be carbon neutral owing to the fact that the quantity of carbon dioxide (CO<sub>2</sub>) released in biomass combustion is the same amount absorbed during the plant-photosynthesis process [2]. Lignocellulose biomass is considered as an eco-friendly and available energy source for bio-refinery, which signifies it as an economical and sustainable bioenergy source [3]. Bio-refinery is one of the best solutions to maximize socio-economic benefits, while minimizing environmental pollution and decreasing overall costs of the disposal of landfilling wastes. Currently, a wide array of value-added products from lignocellulose biorefinery include bioethanol, biogas, biodiesel, drop-in fuel, platform chemical, food additive and biopolymer [4], [5].

Lignocellulose biomass contains three major biopolymer components: cellulose, hemicellulose and lignin. Cellulose is a glucose polymer containing β (1-4) linked D-glucose subunits. It is a straight-chain polymer obtained from the dehydration of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) molecules. Hemicellulose is composed of pentose and hexose molecules such as mannose, xylose, arabinose and glucose. Lignin is a phenyl propane

polymer connected with ester bonds that acts as a binder with the structure of hemicellulose and cellulose [2].

Pretreatment of lignocellulose biomass is inevitable for bioconversion because it promotes the hydrolysis reaction to release carbohydrate monomer and oligomer. The mechanisms of pretreatment include increasing surface area for the cellulase accessibility, removing inhibitory compound of hydrolysis reaction, and modifying the crystalline structure of cellulose to be more susceptible to hydrolysis. The pretreatment methods used for lignocellulose biomasses are commonly grouped into chemical, physical, physicochemical and biological techniques [6], [7].

Chemical pretreatment of biomass is a common and promising process for the lignocellulose biorefinery. Conventional chemical pretreatment involves the usage of bases and acids in biomass hydrolysis [8]. It tends to solubilize lignin and hemicellulose to depict the cellulose to acid and/or enzymatic hydrolysis. Chemical pretreatment of lignocellulose to alter the biomass structure to make cellulose more accessible is done by interaction with intra- and inter-polymer bonds of organic components [9]. Among the chemical pretreatment techniques acid and alkaline pretreatments are most commonly used methods due to their efficiency. Alkali pretreatment processes mainly affect the elimination of lignin and partially solubilization of hemicellulose content [10]. The reactivity of remaining

polysaccharides is enhanced after the removal of lignin via the cleavage of the lignin-carbohydrate linkages in a biomass [11]. Depolymerization and cleavage of lignin-carbohydrate bonds results from solvation and saponification induced by alkali hydrolysis [12]. Compared to wood materials, alkali pretreatment is more effective on agricultural biomass [13]. Sodium hydroxide (NaOH), calcium hydroxide (Ca(OH)<sub>2</sub>) and potassium hydroxide (KOH) are the commonly used alkaline solution utilized for lignocellulose biomass pretreatment [14]. Alkaline pretreatment causes the delignification and enables more surface area, reduction in the degree of polymerization and porosity of lignocellulose biomass [15]. Alkali pretreatment eliminates uronic acid and acetyl group in hemicellulose for providing accessibility to hemicellulose. The effect of alkali pretreatment depends on the lignin component present in the biomass and increases the accessible surface area. The base treatment of biomass considerably diminishes the amount of inorganic ash, alkali metals and other impurities.

As a result of the processing of alkali pretreatment at lower pressure and temperature, it is a favorable pretreatment technique of lignocellulosic biomass relative to other techniques that is dependent mainly on the lignin content concentration [16]. In comparison to acid pretreatment, alkali pretreatment results in low solubility of cellulose and hemicellulose [17]. Alkali pretreatment presents the most efficient method of breaking the ester bonds in lignocellulosic materials [18]. It also prevents fragmentation of hemicellulose. Increase in enzymatic saccharification and ethanol production are observed with the pretreatment of lignocellulosic biomass like wheat and sorghum straws with alkaline [18].

Owing to the strong effect of acids on hemicellulose and lignin compared to crystalline cellulose, they are applied as catalysts in pretreatment of lignocellulosic biomass [19]. Acid pretreatment is aimed mainly at solubilizing the hemicellulose portion of lignocellulosic biomass thus, making inherently present cellulose accessible to enzymes [19]. The efficacy of acid pretreatment could be ascribed to the acid concentration, particle size of biomass, liquid-to-solid ratio and reaction temperature [20]. Primary acidic agents involved in biomass pretreatment include hydrochloric acid (HCl), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and nitric acid (HNO<sub>3</sub>). The advantages of acid pretreatment include

converting hemicellulose into sugars and solubilization of lignin with minimal degradation [10]. Dilute sulfuric acid is commonly used for the pretreatment of biomass. In dilute acid pretreatment, the structure of the lignocellulose materials is cracked and enhances the enzymatic digestibility and porosity of biomass [21]. The acid pretreatment process allows converting hemicellulose into xylose, acetic acid, glucose, mannose, etc. This may prevent hemicellulase addition for enzymatic hydrolysis [9]. However, phenolic compounds are formed due to the partial degradation of lignin. Acid pretreatment interrupts covalent bonds, Van der Waals and hydrogen bonded together in the biomass [22]. The key benefit of the acid treatment method lies in solubilizing lignin and hemicellulose to make more cellulose content. Acid and alkali pretreatment of lignocellulose biomass increases the product yield during biomass conversion into useful energy. In the future, further research is essential to make eco-friendly and economical pretreatment techniques for efficiently converting biomass into bioenergy.

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