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Review

A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass

Jun Seok Kim [a], Y.Y. Lee [b], Tae Hyun Kim [c,*]

[a] Department of Chemical Engineering, Kyonggi University, Suwon 443-760, Gyonggi-do, Republic of Korea
[b] Department of Chemical Engineering, Auburn University, Auburn, AL 36849, USA
[c] Department of Environmental Engineering, Kongju National University, Cheonan 330-717, Chungnam, Republic of Korea

HIGHLIGHTS

- Leading alkaline pretreatments technologies and their features are described.
- Advantages, mechanisms, and effects of alkaline pretreatment are discussed.
- Desirable pretreatment process and alkaline process options are reviewed.
- Various barriers and inhibition mechanism in biomass utilization are discussed.
- Application of alkaline pretreatment in biorefinery is presented.

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ABSTRACT

The native form of lignocellulosic biomass is resistant to enzymatic breakdown. A well-designed pretreatment that can promote enzymatic hydrolysis of biomass with reasonable processing cost is therefore necessary. To this end, a number of different types of pretreatment technologies have been developed with a common goal of making biomass more susceptible to enzymatic saccharification. Among those, a pretreatment method using alkaline reagent has emerged as one of the most viable process options due primarily to its strong pretreatment effect and relatively simple process scheme. The main features of alkaline pretreatment are that it selectively removes lignin without degrading carbohydrates, and increases porosity and surface area, thereby enhancing enzymatic hydrolysis. In this review, the leading alkaline pretreatment technologies are described and their features and comparative performances are discussed from a process viewpoint. Attempts were also made to give insights into the chemical and physical changes of biomass brought about by pretreatment.

1. Introduction

Lignocellulosic biomass is composed of carbohydrates (cellulose and hemicellulose), lignin, and other extraneous components (proteins, lipids, and inorganic substances) (Kim, 2013). It is a renewable and abundant resource suitable for production of bio-based products such as biofuels and chemicals. Bio-based products produced from renewable sources are desirable alternatives to conventional petroleum-based fuels and chemicals; such bio-based products are also the backbone of the biorefinery concept. According to the International Energy Agency (IEA) report (IEA Bioenergy, 2009), biorefinery is defined as the process for sustainable processing of lignocellulosic biomass into various bio-based products (food, feed, chemicals, and materials) and bioenergy (biofuels, power and/or heat). The biorefinery concept calls for lignocellulosic biomass to be processed with one of two end goals: (1) to be fractionated into three main components for further conversion to bio-based products with maximal added-value, or (2) to produce primarily biofuels, with residues as co-products. The US Department of Energy (DOE) (Werpy and Petersen, 2004) reported that as many as twelve important building block chemicals can be produced from sugars through either biological or chemical conversions (Holladay et al., 2007). It is anticipated that biorefining technology will play a leading role in creating a new bio-based industrial sector to replace fuels and chemicals currently produced from fossil oil, and to reduce greenhouse gas emissions (Mabee and Saddler, 2010; Park and Kim, 2012).

Commercialization of cellulosic ethanol production, the first step toward biorefinery, still remains challenging because of technical

* Corresponding author. Tel.: +82 41 521 9426; fax: +82 41 552 0380.
E-mail addresses: thkim@kongju.ac.kr, hitaehyun@gmail.com (T.H. Kim).

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and economic barriers (Holladay et al., 2007; Kim and Kim, 2014). Conversion of cellulose and hemicellulose biologically using enzymes and microbes requires five main unit processes: (1) mechanical size reduction (chopping/grinding), (2) pretreatment to make the cellulosic parts more amenable to enzymatic reaction, (3) enzymatic saccharification to hydrolyze cellulose/hemicellulose into monomeric sugars (fermentable sugars), (4) microbial fermentation to convert monomeric sugars into fuels and chemicals, and (5) product recovery and purification. In an integrated biomass conversion process, pretreatment becomes a key element because the design of the subsequent saccharification and fermentation processes rely strongly upon the result of pretreatment. The ultimate goal of pretreatment is to improve the enzymatic hydrolysis of carbohydrates (cellulose and hemicellulose) consequently increasing overall bioconversion efficiency for production of sugars.

In order to achieve this goal, various pretreatment methods, most involving chemical pretreatment, have been proposed, and various reagents and catalysts for different substrates developed. The known methods are: steam/steam explosion (Liu and Chen, 2015), grinding/milling, hot water/autohydrolysis (Timung et al., 2015; Garrote et al., 2002; Vaquez et al., 2001), acid treatment (Jacobsen and Wyman, 2000; Kim et al., 2001), alkali treatment (Ferrer et al., 2000; Choi et al., 2013; Kim et al., 2003; Yoo et al., 2011), and other methods. The outcome of each pretreatment varies widely in terms of its physical and chemical characteristics (Kim, 2013).

Among aforementioned pretreatment options, alkaline pretreatment has emerged as one of the front runners because it has a number of desirable features. Alkaline methods utilize mostly non-polluting and non-corrosive chemicals such as ammonia (aqueous, liquid, and gaseous), sodium hydroxide, sodium carbonate, and calcium hydroxide (lime). Alkaline pretreatment is carried out under milder conditions than those needed for acid pretreatment. Alkaline reagents interact primarily with lignin; therefore, they are more efficient for lignin removal. In this paper, various alkaline pretreatment technologies are reviewed. These include: ammonia recycle percolation (ARP), ammonia fiber explosion/expansion (AFEX), soaking in aqueous ammonia (SAA), low-liquid ammonia (LLA), low-moisture anhydrous ammonia (LMAA), and other alkaline technologies using NaOH, and $Ca(OH)_2$. Reaction mechanisms, major effects, background, processing schemes, and the advantages and disadvantages related to alkaline pretreatment technologies are discussed. Overall, the paper reviews the role of pretreatment technologies using alkaline reagents in biorefinery, which can produce high value products from lignocellulosic biomass.

2. Lignocellulosic biomass

Lignocellulosic biomass is categorized into four major groups based on its source: (1) woody biomass, (2) agricultural residues (rice/wheat/barley straws, corn stover, sugarcane bagasse), (3) energy crops (switchgrass, miscanthus, short rotation hardwood specifically grown for biofuel production), and (4) various types of cellulosic wastes (municipal solid waste, pulp mill and lumber mill wastes). Regarding plant taxonomy, these sources are simply classified as hardwood or softwood tree species, or grass species. However, some agricultural residues and some energy crops such as switchgrass, miscanthus, and elephant grass (*Pennisetum purpureum*), are considered herbaceous plants. The softwoods (gymnosperms) are a group of seed-producing, non-flowering plants, mostly conifers and cycads. The deciduous flowering plants that have broad leaves are called hardwood.

Lignocellulosic biomass is heterogeneous polymeric material comprised of carbohydrates (cellulose and hemicellulose), lignin, and other components. Many factors affect biological conversion of lignocellulosic biomass, and these include chemical and physical barriers that inhibit its enzyme hydrolysis (Kim et al., 2003; Kim, 2013). Carbohydrates, particularly plant cellulose, has a highly crystalline, recalcitrant structure, which makes the enzymatic hydrolysis of cellulose extremely difficult (Kim, 2013). The presence of lignin has also been proven to a major factor hindering enzymatic reaction and microbial fermentation (Brown, 2003; Wyman, 1996; Yang and Wyman, 2006; Kim and Lee, 2006). Lignin is a hydrophobic hetero-polymer of three monomers (coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol), which is resistant to microbial attack. Lowering the lignin content is desirable during pretreatment because this enhances enzyme saccharification and microbial fermentation.

3. Desirable pretreatment process and process options

The purpose of pretreatment is to make lignocellulosic biomass amenable to enzymatic reactions (saccharification) with reasonable processing cost. Some commonly observed outcomes of pretreatment include decrease of lignin content, increase of surface area, and decrease of crystallinity of the biomass; all of which result in enhanced enzymatic hydrolysis rate and yield (Kim et al., 2003; Kim, 2013). Pretreatment is an essential element in the biorefining of lignocellulosic substrates. Kim (2013) described that pretreatment plays a major role in the economics of the overall bioconversion process because all of the subsequent processes (enzymatic saccharification, fermentation, and the downstream processes) are tailored to the pretreatment results. Ideally, a pretreatment process should (1) improve the enzymatic hydrolysis reaction, (2) produce minimal/no inhibitory compounds, and (3) require reasonable capital and operating costs (with low energy input and minimal waste) (Drapcho et al., 2008; Kim, 2013).

Pretreatment can effectively overcome both chemical and physical barriers and enhance the enzymatic digestibility of biomass if proper chemical reagents/catalysts are applied. For selection of optimal treatment reagent/catalyst, a strategy must be set for the removal of lignin and/or hemicellulose. Pretreatment at high temperature with short reaction time (e.g., by dilute sulfuric acid, ARP, or steam explosion), could improve the enzymatic digestibility of the treated solid significantly by removing some of the carbohydrates, mostly hemicellulose. Unfortunately, such a process also degrades sugars into inhibitory compounds. High temperature processes induce high pressure, thus requiring high-pressure materials and vessels and high energy inputs. These lead to high capital and operating costs of the biomass processing facility. Pretreatments designed to operate at low or moderate temperature (e.g., SAA, AFEX, LMAA, LLA, lime treatment) require longer reaction time to compensate for the less severe conditions. During pretreatment, partial degradation of carbohydrates (hexose and pentose), lignin, and other components takes place, producing furfural, 5-HMF, phenols, and various acids. If the reaction conditions (temperature, time, and reagent concentration) are severe enough to remove lignin and hemicellulose, breakdown of the sugars and other soluble components also occurs. Therefore, the selection of proper treatment conditions is necessary, and is the key to effective conversion of lignocellulosic biomass into sugars with minimal formation of inhibitory compounds. For selection of a pretreatment method, not only effective enzymatic hydrolysis, but also undesirable side reactions, especially degradation of carbohydrate and lignin to inhibitory components, must be taken into consideration.

4. Alkaline pretreatment

4.1. Description of alkaline pretreatment technologies

Alkaline pretreatment technologies applying various reagents have been investigated for the common purpose of improving

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