Research & Reviews: Journal of Microbiology and Biotechnology

Key Methods for Pretreatment of Lignocellulosic Biomass - An Overview

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Research Article

Received: 01/08/2016

Accepted: 21/09/2016

Published: 28/09/2016

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Keywords: Pretreatment, Lignocellulosic Biomass, cellulose, Hemicellulose, Lignin

ABSTRACT

Biofuels can be produced from almost all types of lignocellulosic materials, such as forest residues, wood or agricultural. Lignocellulosic biomass can be the potential substitute to gasoline. There are many factors that cause hindrance to hydrolysis of cellulose present in biomass to fermentable sugars that can further be used to produce biofuel. The goal of pretreatment is to make the cellulose accessible to hydrolysis for conversion to fuels. There are several pretreatment methods that modify the physical and chemical arrangement of the lignocellulosic biomass and improve the rate of hydrolysis. From the past few decades a huge number of pretreatment methods have been evolved including acidic pretreatment, ammonia explosion, alkaline pretreatment etc. In this review, different pretreatment methods have reported.

INTRODUCTION

In past few decades, due to the rapid increase in world's energy demand and ambiguity in supply, increasing fossil fuels prices, increased environmental pollution, it has become imperative to develop alternate sources of energy that can replace natural fossil fuels [1-5]. Burning of fossil fuels release CO_2, that is a major cause of global warming. United States comprise of only 4.5% of world's population is consuming 25% of global energy and emit 25% of total CO_2 [6-9]. To compensate the increasing demand of natural fossil fuel biofuel are the most promising alternative source of energy with minimum emission of pollutants such as carbon dioxide, sulphur, carbon monoxide and nitrous compounds [10-15].

Lignocellulosic biomass is the most abundant and available renewable feedstock present on earth with the globally annual production of 1x1010 MT. The biofuels produced from lignocellulosic biomass resources have the potential to reduce greenhouse gas emissions by 86% [16-18]. Lignocellulosic biomass can be agricultural waste such as wheat straw, sugarcane bagasse, corn Stover, and dedicated energy crops, forestry wastes such as hardwood and softwood, municipal solid waste, animal manures etc. However byproducts of biofuels can also be utilized as biological manure, reducing the use of chemical fertilizers [19-25].

Lignocellulosic biomass is a crystalline structure, mainly comprised of cellulose, hemicellulose, lignin and pectin. Composition of every component varies depending on the origin of lignocellulosic material. Among these cellulose and hemicelluloses are sugar polymers and can be further hydrolyzed to fermentable sugar [26-28]. Major structural component of cell wall is Cellulose and provides mechanical and chemical stability to plants. Lignin forms outer covering of cellulose and hemicellulose, which prevents the availability of cellulose and hemicellulose to various fungi and bacteria for biofuel production [29]. To convert biomass to biofuel breakdown of cellulose and hemicellulose to its monomers is must, so that it can be utilized by microorganisms. Therefore, a pretreatment is required for destruction of lignin prior to conversion of cellulose and hemicellulose into simple sugars [30-33].

Pretreatment is the most expensive steps for the conversion of lignocellulosic biomass to fermentable sugar. Various Methods of pretreatment has been developed for different varieties of lignocellulosic biomass and have varying results based on composition of cellulose, hemicellulose and lignin in raw material used biofuel production [34-37]. Pretreatment alters/damage the structure of lignocelluloses and remove lignin and expose cellulose and hemicellulose for hydrolysis for conversion to fermentable sugars. The main focus of the pretreatment process is to disrupt the structure of lignin and cellulose, so that it can be accessible by acids or enzymes for hydrolysis [28,38-43].

STRUCTURE OF LIGNOCELLULOSIC BIOMASS

Lignocellulosic biomass refers to waste obtained from plants that mainly consist of cellulose, hemicellulose and lignin.

Cellulose $C_6H_{10}O_5)_n$

Cellulose is an organic polymer made up of linkage of small monomers of anhydroglucose by β-1,4)-glycosidic bonds that forms a linear-chain polymer [44-47]. Various characteristics properties of cellulose rely on the degree of polymerization that is the number of glucose monomers which make one polymer molecule. The nature of linkage between the molecules of glucose leads to the arrangement of polymer in long linear chain [48-52].

Hemicellulose

Hemicellulose is a physical barrier covering the cellulose fibers and prevents enzymatic hydrolysis of cellulose. Disintegrating the hemicellulose increases substrate pore size and increase exposure of cellulose for hydrolysis [53]. Unlike cellulose, hemicellulose does not only comprise of glucose units, but also contain pentose and hexose monosaccharides. Hemicelluloses are water insoluble at low temperature. Hydrolysis of hemicellulose initiates at temperature lower than that of cellulose [54-59].

Lignin

Lignin is the complex natural polymer that is second abundant and important organic compound in the plant cell. Lignin is a polymer made up of phenolic crosslinking that provide structural integrity to cell wall of plant cell [60-63]. Lignin is a three-dimensional polymer that is made up of phenyl propane monomers as the predominant building blocks. Lignin in wood is an insoluble three-dimensional structure [64,65]. It plays vital role in the cell's development and endurance, as it helps in transportation of nutrients, metabolites and water in the plant cell [66-68].

PRETREATMENT OF LIGNOCELLULOSIC BIOMASS

Pretreatment is an important and most expensive step in production of biofuel. Several pretreatment methods have been developed till now to solubilize, fractionate, separate and hydrolyze cellulose, hemicellulose, and lignin components of plant cell [69,70-75]. Pretreatment changes the structure of lignocellulosic biomass which increases the accessibility of cellulose to enzyme that converts it into fermentable sugar Figure 1) [76-78].

Pretreatment methods are mainly categorized into four major types:

- Physical Pretreatment
- Chemical Pretreatment
- Physiochemical pretreatment
- Biological Pretreatment

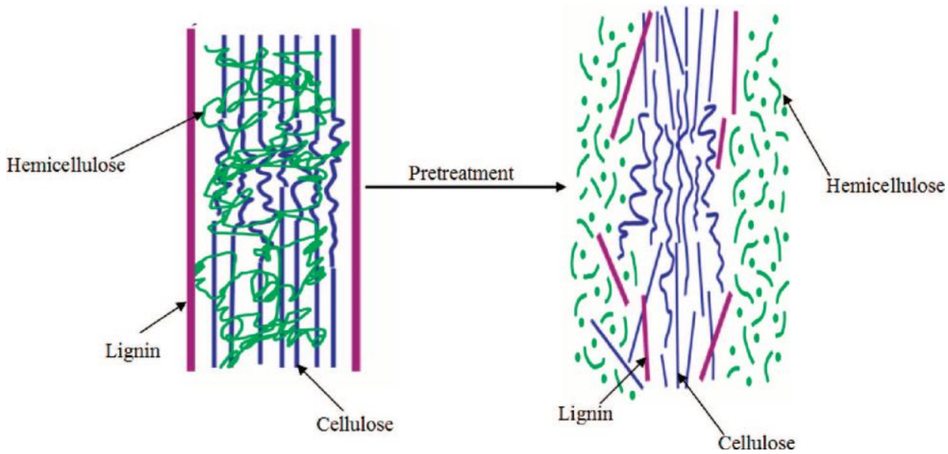

Figure 1: Effect of pretreatment on lignocellulosic pretreatment.

Physical Pretreatment

Mechanical pretreatment

The main objective of mechanical pretreatment is to decrease the size and crystallinity of lignocellulosic biomass that increases the surface area of cellulose for hydrolysis. Mechanical pretreatment can be performed by grinding, milling or milling as per requirement to get the desired particle size of the biomass [79-80].

Extrusion

In Extrusion process biomass is treated at very high temperature more than 300⁰C followed by shearing and mixing of biomass which leads to chemical modification of cellulose [81-83]. The barrel temperature and screw speed are considered to disintegrate the structure of lignocellulosic biomass causing shortening, defibrillation, and fibrillation of the fibers that increases exposure of cellulose to enzymatic attack [84-86].

Chemical Pretreatment

Acidic Pretreatment

Acid pretreatment can be performed either with concentrated or diluted acid but concentrated acid is less used due to the formation of inhibiting compounds. Concentrated acids are mild, corrosive and hazardous, so to corrosive resistant vessels should be used to perform concentrated acid pretreatment [67-68,87-89]. Acidic pretreatment results in chemical hydrolysis of lignocellulosic biomass which disintegration hemicellulose and lignin which increases the exposure of cellulose to enzyme. Most commonly used acids are Sulphur acid H_2SO_4), Hydrochloric acid HCL), Nitric acid, Phosphoric acid, oxalic acid, acetic acid etc. Dilute acid pretreatment method is the mostly used for industrial scale pretreatment process [28,90-91].

Alkaline Pretreatment

Alkaline Pretreatment is performed by treating lignocellulosic biomass with alkali potassium, Sodium, ammonium and calcium hydroxides) at normal pressure and temperature. The process efficiently removes lignin from the biomass and exposes cellulose for enzymatic hydrolysis. Alkali pretreatment can also be performed at lower pressure, temperature and time ranging from various hours to days. Alkali pretreatment is more effectively expose cellulose's internal surface area to enzyme and reduce crystallinity of structure [43,92-94].

Ozonolysis

The lignocellulosic biomass is treated with ozone O_3), a powerful oxidizing agent that degrades lignin by breaking aromatic rings structure and causes no harm to hemicellulose and cellulose. This method is effective on different kinds of lignocellulosic biomass Sugarcane bagasse, wheat straw, rice husk, corn stover, sawdust etc.). Ozonolysis pretreatment is performed at room temperature and normal pressure and do not have any toxic byproduct that can effect hydrolysis and fermentation [95,96].

Ionic Liquids

Ionic liquids are those salts those are in liquid phase at room temperature. There are a large number of salts that possess the same characteristic and another characteristic theses salts share is they have inorganic anions an organic cation which forms a heterogeneous structure of these salts. This pretreatment process is not practiced at industrial scale and there is not much study done on the effects of this pretreatment on lignocellulosic biomass [88,90,97].

Physiochemical Pretreatment

Steam explosion

Steam explosion is common and cheap method used for the treatment of the lignocellulosic biomass. In this method biomass is treated with steam under high pressure for few seconds 35 s) to minutes 25 min) and followed by sudden decrease in pressure which leads to explosive shock decompression of the biomass. Biomass is treated at 161⁰C to 261⁰C under pressure of 0.70-4.82 MPa and then exposed to atmospheric pressure. The pretreatment leads to the degradation of hemicellulose and transformation of lignin due to high temperature and pressure, thus explosion cellulose for hydrolysis [76,84,98].

Ammonia fiber explosion AFEX)

The process is similar to steam explosion. Ammonia fiber explosion is pretreatment method in which lignocellulosic biomass is treated with liquid ammonia at high pressure and temperature for time period followed by sudden decrease in pressure. In this process 1 to 2 kg liquid ammonia is used per kg of dry biomass at temperature of 90^0C-95^0C for time period of 30 min to 35 min. The AFEX pretreatment method has been used for the treatment of large number of lignocellulosic biomass such as wheat straw, wheat chaff and alfalfa etc.

CO_2 explosion

The process is similar to steam explosion and ammonia fiber explosion. This pretreatment method is mostly employed to hydrolyze hemicellulose and cellulose. In this method supercritical CO_2 explosion is used at low temperature that also reduces the expense of the process. It was observed that CO_2 produces carbonic acid when reacts with water and increase the hydrolysis of cellulose. CO_2 explosion yields less as compare to Steam explosion and ammonia fiber explosion, but it yields more when compared to enzymatic hydrolysis [23,56,67,82,99].

Biological Pretreatment

Biological Pretreatment is a safe and eco-friendly method of pretreatment, as it does not requires expensive equipment's and also does not need much energy. In biological pretreatment various microorganisms such as white rot fungi, soft rot fungi and brown rot fungi are used. Brown rot fungi only hydrolyze cellulose, whereas soft rot fungi and white rot fungi attacks both on hemicellulose and lignin. White rot fungi produces enzymes peroxidases and laccase that help in degradation of the lignin and is most effective in biological pretreatment [92,100].

CONCLUSION

The increasing use of biofuels leads to development by reduction of greenhouse-gas emissions and the use of natural fossil fuel resources. Lignocellulosic biomass, including forestry residues and agricultural can be ideal, inexpensive and easily available source of sugar for biofuels production. Crystallinity of cellulose, available surface area, covering by lignin, and Wrapping by hemicellulose are resistance to cellulose hydrolysis. Pretreatment od biomass and its intrinsic structure are initially responsible for its hydrolysis. Therefore, pretreatment of lignocellulosic biomass is very important step in the production of biofuels from lignocellulosic biomass, and it is very important to understand the basics of different pretreatment methods, that can be helpful in making right choice depending on the chemical and physical characteristics of the biomass and the hydrolysis agent.

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e-ISSN: 2320 - 3528
p-ISSN: 2347-2286

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