LIGNOCELLULOSIC BIOMASS PRETREATMENT FOR BIOFUEL PRODUCTION

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ABSTRACT

The energetic crisis of recent years, as well as the increasing greenhouse gas emissions, have created premises for identification and exploitation of new, non-polluting and economic energy sources. Thus, have appeared concerns in the field of biofuel production from renewable materials. Worldwide, biomass is considered the most valuable source of alternative energy to fossil fuels. Lignocellulosic biomass, consisting of agricultural and forest residues, animal manure and energy crops, is considered the main substrate for the production of second-generation biofuels (biogas, bioethanol etc).The main components of lignocellulosic materials are cellulose, hemicelluloses and lignin which is the most recalcitrant component of the plant cell wall (the higher the proportion of lignin, the higher the resistance to chemical and enzymatic degradation).

In this paper there are presented the main pretreatment methods of lignocellulosic biomass, including mechanical, biological, chemical and thermal pretreatment, with the focus on the principles, advantages and disadvantages of each method for biofuels production.

INTRODUCTION

Lignocellulosic biomass is the most abundant available plant material on our planet and consists of agricultural and forest residues, municipal organic wastes animal manure and energy crops (eg.corn stalks, wheat straw, rice straw, switchgrass, hardwood stems, *Miscanthus*) [4].

Lignocellulosic materials mainly consist of 40–50% cellulose, 25–30% hemicellulose, 15–20% lignin, traces of pectin, nitrogen compounds and inorganic ingredients. Bioconversion of lignocellulosic biomass is limited by the protective structure of recalcitrant lignin [3].

Cellulose is a linear polymer of β-glucose that provides structure to plants. Cellulose has both an amorphous and a crystalline section. Amorphous sections are more disordered and allow water to penetrate, thus increasing the enzymatic hydrolysis, unlike the crystalline sections that have hydrogen bonds between the polymers that make it more resistant to enzymatic hydrolysis. Hemicellulose is more easily hydrolyzed than cellulose because of its amorphous structure. It is mainly composed of pentoses and hexoses. Lignin is a phenyl-propane polymer that acts as a glue to hold hemicellulose and cellulose together. Lignin is highly resistant to biological degradation and is the main physical barrier among plant cell wall polymers [10, 16].

The (enzymatic) hydrolysis of lignocellulose is limited by several factors, such as: crystallinity of cellulose, degree of polymerization, moisture content, available surface area and lignin content [7]. Pretreatment is required to to make cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars [13].

In this case, lignocellulose must be pretreated to degrade the network structure of lignin and improve the efficiency of cellulose utilization. In experimental researches, physical, chemical, biological and thermal pretreatment methods have been tested in order to break down the lignin and increase the biodegradation of cellulose and hemicelluloses.

MATERIAL AND METHOD

Pretreatment is the crucial step in the conversion of energy from lignocelluloses, which consists in the separation of the complex components of lignocellulose. Thel pretreatment methods can be classified into mechanical, biological, chemical, thermal and their combinations (Fig. 1) [3].

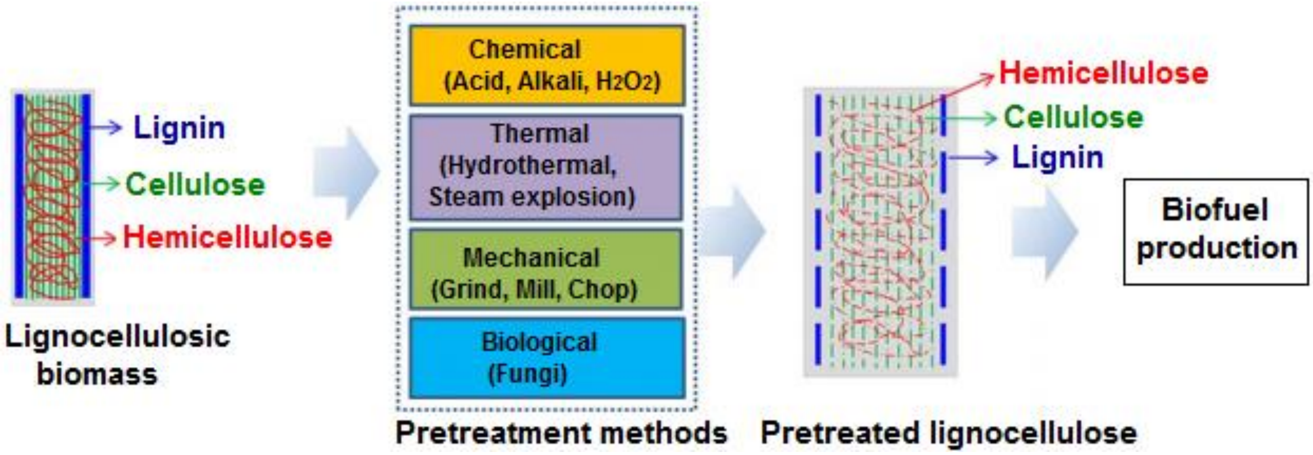

Fig. 1. Lignocellulosic biomass pretreatments [16]

RESULTS AND DISCUSSIONS

Mechanical pretreatment

The mechanical size reduction procedures include chipping, size reduction, grinding, shredding and milling. The main purpose of a mechanical pretreatment is the reduction of particle size and crystallinity, leading to an increase of available specific surface and a reduction of the degree of polymerization [7]. Also, mechanical treatment is an important step to improve the digestibility and the conversion of saccharides during enzymatic hydrolysis and bioconversion [9]. Chipping implies to decrease the size in range of 10–30 mm, while the size reduction for milling and grinding is usually 0.2–2 mm [1]. These processes often have high energy and capital costs.

Zhang R. and Zhang Z. [20], reported that size reduction is more efficient when is combined with other pretreatment methods. A combination of grinding, heating and ammonia treatment (2%) resulted in the highest biogas yield from rice straw.

Hajji A. and Rhachi M. [6], studied the influence of particle size on the performance of anaerobic digestion of municipal solid waste, in order to improve the efficiency of biogas process. They tested the particle size of 10 mm, 20mm, 30mm and 100 mm in diameter. The obtained results showed a high correlation between particle size and the production of biogas, with optimum production recorded for small particle sizes (Fig. 2).

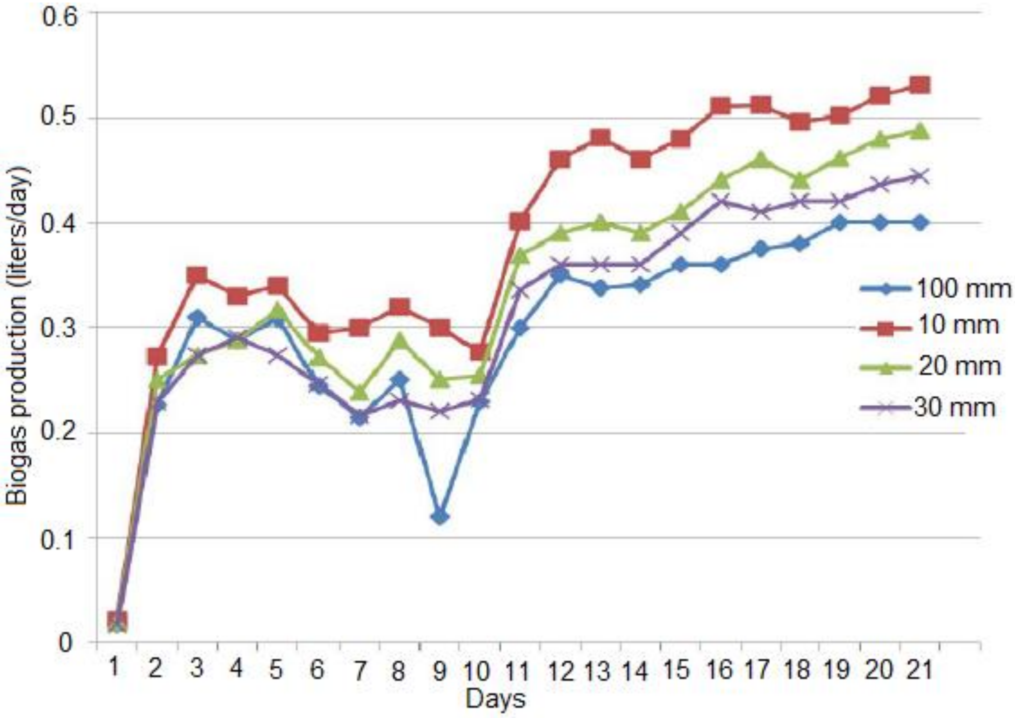

Fig. 2. Biogas production as a function of time and particle size [6]

Chemical pretreatment

Chemical pretreatment uses a variety of acids, alkalis or oxidants to extract or break down organic compounds present in biomass [16]. Some common chemical or physico-chemical pretreatment techniques include acid, alkaline, steam explosion, liquid hot water, ammonia fiber, carbon dioxide explosion, ionic liquids, organosolv, ozonolysis and wet oxidation [2].

Acid pretreatment involves the use of concentrated and diluted acids to break the rigid structure of the lignocellulosic material. The most commonly used acid is sulphuric acid (H_2SO_4), which has been used for a wide variety of biomass types. Acid pretreatment (removal of hemicellulose) followed by alkali pretreatment (removal of lignin) results in relatively pure cellulose [12].

Alkaline pretreatment involves the use of bases, such as sodium, potassium, calcium, and ammonium hydroxide, for the pretreatment of lignocellulosic biomass. The use of an alkali causes the degradation of ester and glycosidic side chains resulting in structural alteration of lignin, cellulose swelling, partial decrystallization of cellulose and partial solvation of hemicellulose [12].

Carbon dioxide can also be used for the pretreatment of lignocelluloses. Under the high pressure, CO_2 penetrates the biomass and results in increasing digestibility of biomass [5].

Narayanaswamy et. al. [14] investigated supercritical CO_2 (SC-CO_2) pretreatment of corn stover and switchgrass at various temperature and pressure. The biomass was hydrolyzed after pretreatment using cellulase and β-glucosidase. Glucose yields were used to measure the efficiency of the tested pretreatment method. The authors reported that glucose yields from corn stover samples pretreated with supercritical CO_2 were higher than the untreated sample. The highest glucose yield of 30% was achieved with supercritical CO_2 pretreatment at 3500 psi and 150 °C for 60 min, compared with 12% for untreated biomass (Fig. 3).

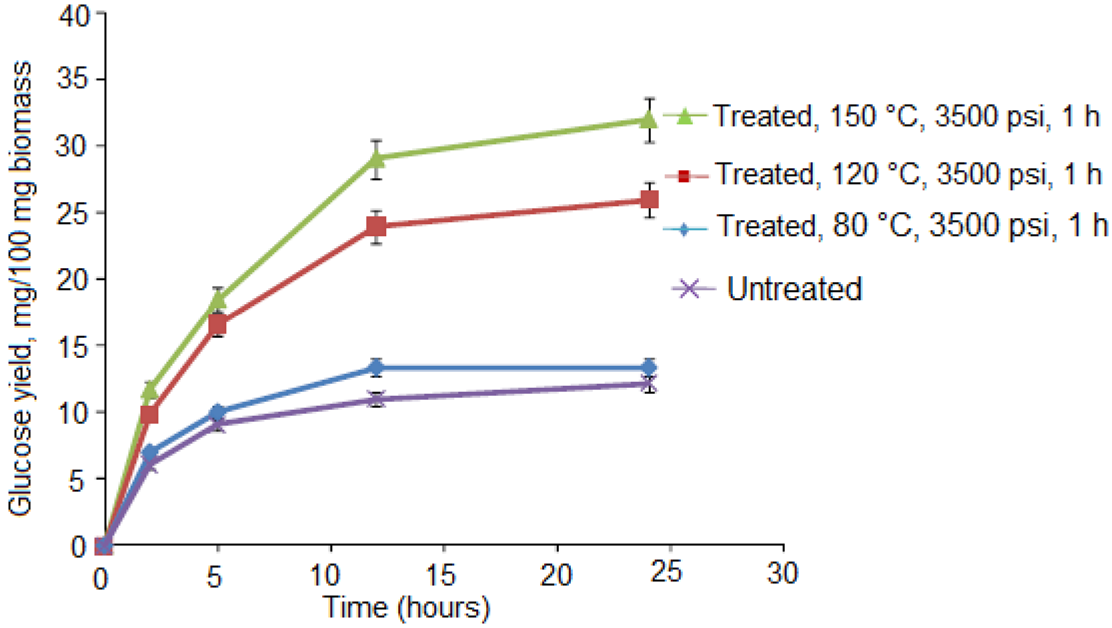

Fig. 3. Effect of temperature on SC-CO_2 pretreatment of corn stover [14]

Wet oxidation is an oxidative pretreatment where oxygen or air is employed as a catalyst at temperature above 120 °C. The main reactions that occur in this case are oxidative reactions as well as the formation of acids.This process is effective in separation of the cellulosic fractions from lignin and hemicelluloses [8, 11].

Biological pretreatment

Biological methods has an advantage over mechanical and chemical methods in pretreating biomass. Biological pretreatment is environment-friendly and can be carried out under mild conditions, consumes low energy, and requires simple procedures and equipments [18]. The organisms predominantly responsible for lignocellulose degradation are fungi. White-rot fungi are the most effective lignin-degrading microorganisms in nature. Lignin biodegradation by white-rot fungi is an oxidative process and phenol oxidases are the key enzymes. The most studied enzymes produced by the white-rot fungi are lignin peroxidases, manganese peroxidases and laccases [17].

Wan C. and Li Y. [19], tested the microbial pretreatment of corn stover with *Ceriporiopsis subvermispora* for ethanol production. They investigated the effects of particle size (5–15 mm), moisture content (45–85%), pretreatment time (18–35 d), and temperature (4–37 °C) on lignin degradation. The results showed that *C. subvermispora* selectively degraded lignin up to 31.59% with a limited cellulose loss of less than 6% during an 18-d pretreatment. The authors concluded that higher ethanol yields were obtained with extended pretreatment time. As can be seen in Fig. 4, untreated corn stover presented an ethanol yield around 15.91%. The samples treated for 18 d, 28 d and 35 d, have registered an ethanol production of about 50.68%, 54.26%, and 57.80%.

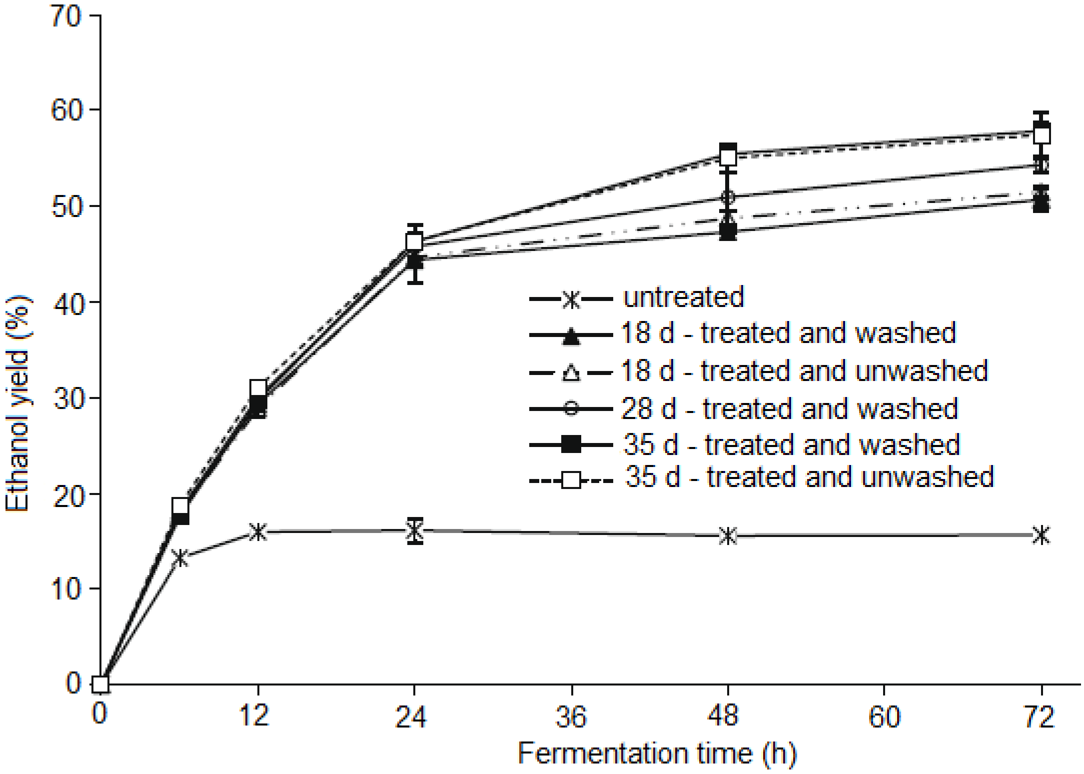

Fig. 4. Ethanol yield of corn stover pretreated by C. subvermispora [19]

Sun F.h. et al. [18], studied the biological pretreatment of corn with *Trametes hirsuta yj9* in order to enhance enzymatic digestibility. They reported that the pretreated corn stover showed a significant decrease in lignin and hemicellulose contents, and a small increase in cellulose content. After 42-day pretreatment, lignin content decreased from 14.65% to 7.45%, hemicellulose content decreased from 29.44% to 11.32%, whereas the cellulose content increased from 49.41% to 59.14% (Fig. 4).

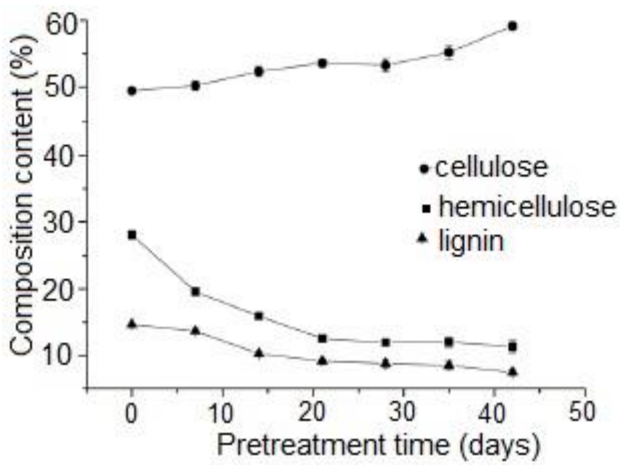

Fig. 4. The composition of the corn stover during 42-day pretreatment [18]

Thermal pretreatment

During this pretreatment the lignocellulosic biomass is heated at high temperatures. If the temperature is above 150–180 °C, parts of the lignocellulosic biomass, firstly the hemicelluloses and after that lignin, will start to solubilize. During thermal processes, a part of the hemicellulose is hydrolysed and forms acids which are responsible to catalyze the further hydrolysis of the hemicellulose [7].

Steam explosion is a pretreatment method which is also used for treating the lignocellulosic biomass. During the treatment, the biomass is treated with steam at a high temperature for few minutes in order to facilitate the enzymatic hydrolysis of cellulose and hemicellulose to monomeric hexose and pentose sugars. Steam explosion is performed at a temperature of 160-260 °C for several seconds to a few minutes and after that the material is exposed to atmospheric pressure [2, 12]. Steam explosion method has some limitations, such as incomplete disruption of the lignin–carbohydrate matrix and generation of some compounds that might be inhibitory to microorganisms used in fermentation processes [15].

Liquid hot water pretreatment is similar to steam explosion, except for the use of water in the liquid state at high temperatures (160–240 °C) instead of steam. This kind of treatment results in hydrolysis of lignocelluloses and removal of lignin. However, complete delignification is not possible by liquid hot water because of the recondensation of soluble components originated from lignin [2].

CONCLUSIONS

Lignocellulosic residues constitute a renewable resource from which many products can be obtained. The biodegradability of lignocellulosic biomass is limited by several factors such as crystallinity of cellulose, available surface area and lignin content.

Pretreatment technologies for lignocellulosic biomass include mechanical, biological, chemical, thermal and various combinations of these. Mechanical methods reduce crystallinity and particle size, biological pretreatments use microorganisms that degrade lignin and hemicellulose and chemical pretreatments that use ozone, organic solvents are focussed on lignin removal, this leading to a good enzymatic degradability of cellulose.

Pretreatments improve access to the lignocellulosic parts of the biomass (cellulose, hemicelluloses and lignin) that are otherwise difficult or impossible to degrade.

Different feedstocks contain different amount of lignin that must be removed via pretreatment to enhance biomass digestibility. However, the effect of the pretreatments is dependent on the biomass composition and operating conditions.

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