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Pre-treatment of Wheat Straw: A Review.

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ABSTRACT

Wheat straw is an agricultural by-product which can be utilized to produce Bioethanol, an alternative source of energy for the depleting fossil fuel. The present work is dedicated to reviewing the methods which have been studied for pretreatment of wheat straws. Wheat straw contains high level of cellulose which can be used for production of reducing sugars, reducing sugars can be further converted into ethanol using various microorganisms like yeast. Important processes involved in conversion of wheat straw into ethanol: hydrolysis of lignocelluloses to produce reducing sugars and fermentation of sugars into ethanol. Pretreatment of wheat straws can enhance the process of hydrolysis by removing lignin and hemicellulose. Optimization of cellulose enzymes can improve hydrolysis process, Simultaneous saccharification and fermentation (SSF) is a combination of enzymatic hydrolysis and microbial fermentation inhibits reducing sugar and lead to maximum rate of enzymatic hydrolysis.SSF requires lower amount of enzyme and provide higher yield of alcohol from cellulose enzyme.

Keywords: Fermentation, Bioethanol, cellulose, pretreatment, cellulose, saccharification

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INTRODUCTION

With the increase in world population and modernization, energy consumption had increased tremendously leading to extensive use of fossil fuel ultimately resulting in depletion and increased prices of fuel. Since only few countries are blessed with natural reserves of fossil fuel, it is assumed that the world will run out of fuel by 2050-2065 with global energy demand increasing three times more than the present, China, India and Middle East contributing for 60% of the increase (international energy agency). Unlike fossil fuel Bioethanol is a renewable source of energy and can be produced from cheap biomass like wheat straw, husk, cane molasses, hard wood. Bioethanol is a eco-friendly fuel and produce negligible amount of toxic compounds like nitrogen oxides and carbon monoxides (Reijinders et. al., 2007). Bio-ethanol can be used for vehicles or industrial engines by blending it with petrol or using modified engines(Rudkin, 2002). Lignocellulosic biomass can be used for production of Bioethanol, current first generation Bioethanol production from corn-starch material is not practically possible as it competes for agricultural land needed for food. Second generation Bioethanol from lignocellulosic material may serve as a potential source for low-cost ethanol production and is beneficial for farmers as well as for state(sun and cheng, 2002). The conversion of cellulose to ethanol involves two processes: hydrolysis of cellulose present in wheat straw into fermentable reducing sugars and fermentation of the sugars to ethanol. The hydrolysis involves cellulase enzymes, and the fermentation is carried out by the use of microorganisms like yeast or bacteria (McMillan, 1994). Due to presence of lignin and hemicellulose, lignocellulosic biomass is not easily broken down into its components which makes access of cellulose to cellulase enzyme difficult, for the extraction of sugars an effective pretreatment is necessary for the liberation of polysaccharides from lignin and to access sugar components for hydrolysis step (Mosier et al., 2005). The contents of wheat straw is listed in table 1.

Table 1: Composition of wheat straw

Wheat straw composition	Percentage(%)
Dry Matter	89-94
Metabolizable energy mcal/lb	0.67
Crude protein	3.6
Acid detergent fibre	54
Hemicellulose	21-26
cellulose	33.7-40
Lignin	11-22.9
Ash	7-9.9
Calcium	0.18
Phosphorus	0.05
Relative Food Value	60

Source: Yasin et al. (2010

Various pretreatment processes can be performed to increase porosity, degrade lignin and hemicellulose and increase surface area for improvement of hydrolysis.

Pretreatment strategies

Pretreatment is performed in order to break the lignin-hemicellulose matrix to facilitate the access of cellulase enzymes to the cellulosic portion of the biomass for subsequent hydrolysis to glucose. Carbohydrate polymers in lignocellulose are bound to lignin with hydrogen and covalent bonds which act as hindrance in hydrolysis and ethanol production. Thus delignification is a crucial step prior to hydrolysis and fermentation which can significantly increase the rate of hydrolysis.

Physical Pretreatment

Mechanical Reduction

Mechanical reduction or comminution can be applied to increase surface area and pore size. A combination of chipping, milling and grinding can be used for effective reduction of cellulose crystallinity(Sun and Cheng, 2002). Vibratory ball milling has been found more effective in breaking down cellulose crystallinity than ordinary ball milling (Millet et al., 1976).

Pyrolysis

Pyrolysis is a convenient way to degrade lignocellulosic materials with heat in absence of air. In pyrolysis material is treated at temperature above 300°C due to which cellulose decomposes rapidly (Shafizadeh and Bradbury,1979).

Irradiation

Gamma rays, microwaves and electron beam can be used to improve hydrolysis process, combination of radiation with chemical methods can further accelerate hydrolysis. Irradiation above 100 MR, can lead to decomposition of oligosaccharides and glucose ring (Kumakura and Kaetsu, 1984). 20% of reducing sugar yield with 400 kGy Co-60 gamma radiation was observed by Yang et al.,2007 after 22 days.

Physio-chemical Pretreatment

Liquid-Hot water Pretreatment

Wheat straws can be cooked in liquid hot water as water under high pressure can penetrate into biomass, can remove lignin and hemicellulose (Zeng et al., 1997, 2007). High temperature e.g. 220°C for 2 minutes can remove hemicellulose completely and lignin without any use of chemicals(Sreenath et al.,1999).

Steam explosion(auto hydrolysis)

Steam Explosion involves steaming of wheat straw which helps in removal of hemicellulose and improves enzymatic digestion. In this process pressure is suddenly reduced which makes wheat straw to undergo an explosive decomposition. High pressure with high temperature (160-260°C) is applied to wheat straws for 30 seconds to 20 minutes (Baussaid et al.,1999, Kurabi et al.,2005). Steam explosion process is economically beneficial and serves all the requirement of pretreatment process. To achieve same size reduction mechanical methods require 70% more energy than steam explosion (Holtzapple et al., 1989).

Steam explosion with addition of SO_2

Sulfer dioxide can be used in steam explosion process to improve recovery of cellulose and hemicellulose. The process can be carried out with 1-4% Sulfer dioxide (w/w) at high temperature(160-230°C) for 10 minutes. Maximum results were obtained when was treated with 1% SO_2 at 200°C (Eklund et al., 1995).

Ammonia fiber explosion (AFEX)

It is a alkaline pretreatment process. In this process straws are exposed to liquid ammonia at high pressure (90-100°C) for a period of time e.g. 30 minutes, followed by reduction in pressure (Holtzapple et al., 1991). Ammonia fiber explosion process can significantly reduce lignin fraction while hemicellulose and cellulose remains intact (Sun and Cheng, 2002).

Sonication

Sonication is a physiochemical process which provide energy in the form of sound waves. Sound of frequency 16-100 kHz is produced by Ultrasound (kardos and Lunche, 2001). Ultrasound power intensity effects the cavitation process, Sonication alter the morphology of lignocelluloses and cause homolysis of lignin-carbohydrate bonds (Khanal et al., 2007, Li et al., 2012). Excess of sonication may lead to uneconomical process and formation of by-products (Montalbo-Lomboy et al., 2010a).

Chemical Pretreatment

Acid Hydrolysis

Wheat straws can be treated with strong acids at high temperatures which can significantly improve hydrolysis. Sulfuric acid is most used acid while HCL and nitric acid were also reported (Taherzadeh and Karimi, 2007). Acid pretreatment can be performed under high temperature with low acid concentrations which is dilute-acid pretreatment and under low temperature with high acid concentrations, called as concentrated-acid pretreatment. The glucose 86% yield using sulfuric acid can be achieved by treating straws at 200°C for 10 minutes (Bondesson et al., 2013). 49% of cellulose content was accessed afer dilute H_2So_4(2%v/v) pretreatment of wheat straws at 121°C for 120 minutes (Dhabai et al.,2012). Dilute-acid pretreatment have been more preferred as it can achieve high reaction rate and can improve cellulose hydrolysis (Esteghlalian et al., 1997). There are two types of dilute-acid hydrolysis: high temperature (T>160°C), for low solids loading (5–10% [weight of substrate/weight of reaction mixture]) and low temperature (T<160°C), for high solids loading (10–40%),(Sun and Cheng, 2002). Neutralization after acid hydrolysis is necessary for hydrolysis and fermentation process.

Alkaline hydrolysis

Alkali pretreatment is applied to straws to remove lignin, hemicellulose and to increase accessibility of cellulose for enzymatic hydrolysis, alkali hydrolysis is performed with alkaline solutions like NaOH, ammonia or $Ca(OH)_2$. Alkali pretreatment is performed at low temperature and pressure (Farid et al., 2010).Best results i.e. 61% delignification, 82% glucose yield from cellulose and 81% yield of total sugars can be achieved when pretreatment is performed at 80°C for 39 min with 0.18 g of sodium hydroxide and 0.06 g of lime per gram of biomass (Jaisamut et al., 2013). Ammonia can be used for removal of lignin. Ammonia with 2.5-20% concentration for 1hr reaction time can give significant results(Iyer et al., 1996).

Alkaline Peroxide

Alkaline peroxide pretreatment is a low cost and effective treatment for wheat straws. In this pretreatment process straws are soaked at room temperature in ph adjusted water (pH 11-12 by NaOH) containing peroxide (H_2O_2) for 6-24 hours(Saha and Cotta, 2006). In a two stage process with steam explosion(200-220°C at 15-22 psi) followed by alkaline peroxide treatment (2 % H_2O_2 at 50 °C for 5 h under pH 11.5) resulted in 80-88 % of delignification and significant loss of hemicellulose(Sun et al.,2005).

Ozonolysis

Preatreatment of wheat straws can be performed by using ozone, ozone can be degrade lignin and hemicellulose in wheat straws (Ben-Ghedalia and Miron, 1981). Ozonolysis is carried out at room temperature and do not form any inhibitory product(Vidal and Molidier, 1988). Ozonolysis is an expensive process(Sun and Cheng, 2002). Ozonolysis process during acid hydrolysis for 5, 10 and 15 minutes with ozone flow rate of 3.61mg/minute increased sugar yield by 3.59-5.22 mg/g (Gerulova and Blinova, 2011).

Organosolv process

Organosolv process can be performed to remove lignin and some parts of hemicellulose, organosalv process can be used to make pretreated cellulose suitable for enzymatic hydrolysis (Pan et al., 2006).

In the process organic liquid and water is mixed at different proportions with wheat straws, the mixture is heated to break lignin and some parts of hemicellulose, a catalyst can also be used to decrease operating temperature(Chum et al., 1985).

In organosolv pretreatment straws can be treated at temperatures of 150-200 °C with or without addition of catalysts such as oxalic, salicylic, and acetylsalicylic acid (Sun and Cheng, 2002). 99.5% sugar yield achieved by Araque et al.,2007 at 195°C for 5 min, pH 2.0 and 1:1 ratio of water and acetone.

Biological Pretreatment

Lignocellulosic materials like wheat straw can be treated with microorganism to enhance enzymatic hydrolysis. Applied microorganisms can degrade lignin and cellulose but little part of cellulose as cellulose show more resistance than other parts of lignocelluloses. Microorganism like white, brown, soft-rot fungi can be used to degrade wheat straws (Schurz, 1978). White rot fungi is most effective microorganism for biological pretreatment (Sun and Cheng, 2002).

Enzymatic Hydrolysis of wheat straw.

Enzymatic hydrolysis is a process by which cellulose can be converted into reducing sugars like glucose by cellulase enzymes. Enzymatic hydrolysis is conducted under mild conditions (pH 4.8 and temperature 40-45°C) which provide low corrosion, low toxicity and low utility consumptions (Duff and Murray, 1996). Cellulase enzymes are produced fungi, bacteria and protozoan that catalyze hydrolysis of cellulase(Lee,1997).

Cellulases

Cellulases are classified in glycosyl hydrolase family, cellulose is degraded into reducing sugars by action of three distinct enzymes. Endoglucanases, Cellobiohydrolases and b-glucosidases which can be easily produced by fungi and bacteria. Enzymatic hydrolysis takes place in three steps: adsorption of cellulase on cellulose, biodegradation of cellulose and desorption of cellulose (Converse et al., 1988). 10 FPU/g cellulase is used as it provides high glucose yield in a short time(48-72 hrs), concentration of cellulase enzyme vary from 7 to 33 FPU/g substrate (Gregg and Saddler, 1996).

End Product inhibition of cellulase activity

Activity of cellulase enzyme is affected by hemicellulose xylan, glucose, oligosaccharides and cellulobiose. Use of b-glucosidases,high enzyme concentration, b-xylosidase can significantly reduce such inhibition (Sun and Cheng, 2002; Kumar and Wyman, 2014). Cellulase inhibitors can be responsible for poor yields from enzymatic conversion (Kont et al., 2013). For preventing inhibition SSF (Simultaneous Saccharification and Fermentation) can be employed which ferment reducing sugar directly into ethanol and reduce product inhibition (Blotkamp et al., 1978). Fungus *T. reesei* and yeast *S. cerevisiae* are most commonly used micro organisms in SSF which can perform at optimum temperature of 38°C for hydrolysis and 30°C for fermentation. (Philippidis, 1996).

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