

Removal of Furfural from Lignocellulosic Hydrolysates for Improved Bioethanol Production: Current Trends and Challenges

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Abstract— Over the years, tremendous research has been ongoing to find cost effective ways to produce bioethanol on a large scale as it serves as a form of renewable energy. Second-generation materials also referred to as lignocellulosic materials, form inedible feedstocks for bioethanol production as they are composed of agricultural residues such as oil palm empty fruit bunch, rice straw, corn straw, municipal solid waste, waste paper and forest residues. However, the use of acid for pretreatment or hydrolysis of lignocellulosic biomass leads to the formation of inhibitors that affect the fermentation process and subsequently reduce bioethanol yield. In this paper, an overview of the various methods that have been employed in the removal of furfural, a major inhibitor is discussed. Current trends and challenges faced have also been identified. An effective and low-cost method for removal of one of the major fermentation inhibitors is also presented.

Keyword— Bioethanol, Fermentation inhibitors, Lignocellulosic biomass, Palm empty fruit bunch (EFB)

INTRODUCTION

In order to cope with increasing energy demands and reduce emission of greenhouse gases, research has been ongoing to discover alternative sources of energy that are renewable so as to reduce dependence on fossil fuel. Global focus on the use of bioethanol as a renewable alternative has increased greatly in recent years [1]. Currently, bioethanol is being used to power automobiles as additives or extender because of its high-octane rating. For example, E85 is a blended fuel of 85% bioethanol and 15% gasoline [2]. The world's largest producer and consumer of ethanol is the United States, followed by Brazil [3]. In 2015, the US alone accounted for 15 billion gallons of the total production. Together, the U.S. and Brazil produce 85% of the world's ethanol [4]. A large amount of U.S. ethanol is produced from corn, while Brazil primarily uses sugar. Figure 1.1 shows global ethanol production by country or region, from 2007 to 2015. Global production peaked in 2015 after a dip in 2012 and 2013. Production of bioethanol can be done using various feedstocks. These feedstocks can be divided into three categories: sucrose-rich crops, starch rich crops and lignocellulosic materials [5]. Sucrose-rich crops and starch-rich crops include food resources such as corn and sugarcane and can be further classified as first-generation materials. However, due to the growing concern that the use of these materials would affect food supply, focus was shifted to the use of lignocellulosic materials as they form inedible feedstocks. Lignocellulosic materials are classified as second-generation materials [6] and can be categorized based on type of resource into four groups: crop residue resources, waste paper, municipal solid waste and forest residues [5]. Presently, attention is on the production of bioethanol from highly abundant crop residues such as oil palm empty fruit bunch, rice straw, corn straw, wheat straw etc. as it avoids the existing competition of food

versus fuel caused by food-based feedstocks [7]. This paper gives an overview of the various methods that have been used for removal of furfural from lignocellulosic biomass and presents the use of activated carbon as a cheaper and more effective method.

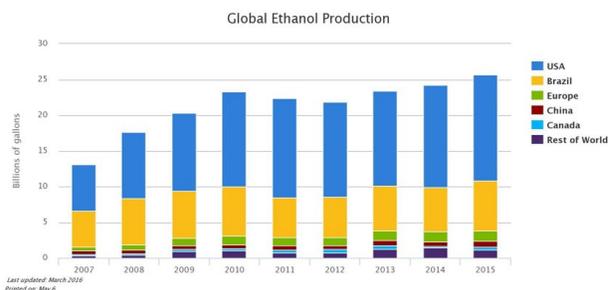


Figure 1.1 Global Ethanol Production by Country [1]

The rest of this paper is organised as follows. In Section 2, the current trends in bioethanol production from lignocellulosic biomass is discussed. Section 3 discusses the open issues in fermentation inhibitors. Section 4 presents the future direction and Section 5 concludes the paper.

1 CURRENT TRENDS IN BIOETHANOL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS

In recent times, the focus has been on the use of lignocellulosic biomass for bioethanol production as it does not interfere with food availability and because it is the largest renewable resource in the world. About 442 liters of bioethanol is produced from lignocellulosic biomass per year [8]. The basic components of all lignocellulosic materials are: cellulose (30-50%),

hemicellulose (15-35%), and lignin (10-20%) [9, 10]. The two ways of converting lignocellulosic biomass into bioethanol are: biochemical conversion and thermochemical conversion [11]. They both have to do with breaking lignocellulosic biomass' resistant cell wall structure into its basic components; cellulose, lignin and hemicellulose, which undergo hydrolysis to form sugars and are eventually converted into bioethanol then purified [11].

Nevertheless, the two conversion methods have different procedures. Thermochemical conversion has to do with gasification of the biomass at 800°C along with a catalytic reaction. The use of a very high temperature ensures the conversion of the biomass into synthesis gas (syngas) like carbon monoxide, hydrogen and carbon dioxide. The syngas formed can be used to form ethanol and water by microorganisms, using catalysts. Distillation can then be used to separate them [12].

Biochemical conversion begins with the pretreatment step which could be physical, thermo-chemical or biological pretreatment [13]. The purpose of pretreatment is to break the recalcitrant structure of the material and provide a larger surface area for easy accessibility of the cellulose to cellulase [13]. After pretreatment, cellulosic materials undergo enzymatic or acid hydrolysis (cellulolysis) and hemicellulose conversion (saccharification) to form monomeric free sugars. The next step involves biological fermentation of sugars into ethanol and final purification using distillation [12]. The most recalcitrant material among the components of cell walls; lignin, undergoes combustion to produce electricity and heat [14]. The biochemical conversion process is made up of four-unit operations: pretreatment, hydrolysis, fermentation and distillation [15] and it is the most commonly used technique for production of bioethanol.

Cellulose, the main constituent of plant biomass, is a structural polysaccharide with glycosidic linkages and additional hydrogen bonding which makes it rigid and hard to break. During hydrolysis, cellulose is broken down into its component sugar molecules [16]. The product formed is a six-carbon sugar called glucose. The process is called saccharification. Hemicellulose is a second major constituent made up of five-carbon (pentoses) and six-carbon (hexoses) sugars. Hemicellulose comprises of xylose and arabinose (five-carbon sugars), and galactose, glucose and mannose (six-carbon sugars). Due to the amorphous nature of hemicellulose, they are more easily broken down during hydrolysis compared to cellulose [17]. The main five-carbon sugar gotten from hardwood and agricultural residues hemicellulose is xylose while mannose is gotten from the hemicellulose of softwood [18].

2 INHIBITORS

Pretreatment of lignocellulosic materials can lead to the formation of various inhibitory substances that slow down the action of fermenting microorganisms. These substances have different sources and are broadly divided into three, namely: furan derivatives, weak acids and phenolic compounds [19]. Lately, a lot of research has been carried out to determine the effect of a single inhibitor on the growth and fermentation of yeast [20]. Results have

shown that the presence of these inhibitors in the fermentation process can reduce the specific growth rate [21], reduce biomass production [21] and also reduce specific and volumetric productivity of ethanol [22].

When methods like acid pretreatment, acid hydrolysis and sulfite pulping are used for the hydrolysis of hemicelluloses, the pentose and uronic acids formed go through dehydration, leading to the generation of 2-furaldehyde (furfural). The six-carbon sugars that are also formed from hemicelluloses hydrolysis go through dehydration to form 5-hydroxymethyl-2-furaldehyde also referred to as HMF [23]. Furfural and HMF are the furan derivatives. HMF can undergo further degradation to form formic and levulinic acids when exposed to conditions such as high temperature and acid concentration, and extended time of reaction [24]. Another acid formed due to hydrolysis of hemicelluloses' acetyl group during acidic treatment of biomass is acetic acid. Levulinic acid, formic acid and acetic acid are the weak acids formed. Phenolic compounds are formed when the β -O-4 ether and acid-labile linkages in lignin are split during acidic treatments. When the concentration of these compounds in the biomass hydrolysate is above threshold concentration, they affect the fermentation process and subsequently the ethanol yield. Therefore, for effective fermentation to take place, the removal of these inhibitors from biomass hydrolysate is necessary.

Based on previous studies, furfural has been identified as a major inhibitor found in most hydrolysates of lignocellulosic biomass [25]. Furfural inhibits growth and alcohol production by *Saccharomyces cerevisiae*, which is commonly used during the fermentation process. It was suggested that the inhibition of glycolysis and reduced ethanol production were caused by the action of furfural on important glycolytic enzymes such as triosephosphate dehydrogenase and alcohol dehydrogenase [26]. Therefore, there has been more focus on the removal of furfural leading to improved bioethanol production.

Various processes such as membrane separation, distillation, over-liming, nanofiltration, solvent extraction, adsorption etc. have been applied for the removal of furfural from a solution. Azeotropic distillation at a temperature of 180-200°C and a pressure of 8-10 atm was used to remove furfural from an aqueous solution. During distillation of aqueous solution of furfural at atmospheric pressure, a heteroazeotrope containing 35% by weight of furfural is produced. This makes it difficult to fully remove furfural by distillation as 84.1% by weight of furfural is contained in the organic phase and 18.4% is in the water phase when condensation occurs [27]. The use of organic solvents such as toluene, methyl isobutyl ketone (MIBK) and isobutyl acetate (IBA) for extraction of furfural from aqueous solution has also been studied [28]. In as much as the use of toluene was less expensive compared to MIBK and IBA, and there was less solvent loss during the extraction process, toluene was found to be more toxic than the other two solvents. The use of supercritical carbon dioxide for extraction of furfural at high temperature (298-333K) and high pressure (80-340 bar) has also been studied [29]. It was noticed that with decrease in temperature and increase in pressure, the solubility of furfural increased.

The application of organic solvent extraction on an industrial scale is limited by the large amount of solvent that will be used.

The use of flat sheet hydrophobic polyurethane urea membranes for pervaporative separation of furfural/water mixtures was investigated and the process was seen to be diffusion-limited [30]. The membranes showed selectivity for furfural as the separation factor between furfural and water was 638 and the permeate flux was 44.7g/m²h. With an increase in the feed temperature and the feed's furfural content, there was a corresponding increase in the partial flux of furfural. Although the polyurethane membranes were seen as appropriate for the separation process, the pretreated biomass consists of various chemicals that could cause membrane fouling if the process were to be applied industrially. Nanofiltration was also applied for removal of furfural [31]. It was found that increasing the operating temperature tended to increase the pore size of the membrane, causing a decrease in retention of sugars.

Different adsorbents such as zeolite, polymeric resins, activated carbon etc have been used for the removal of furfural from lignocellulosic hydrolysates by adsorption. The use of Amberlite polymeric resin XAD-4 (polystyrene-divinylbenzene copolymer bead) for adsorption of furfural from water was investigated [32]. At an equilibrium solution concentration of 2g/l of furfural, 90mg of furfural was adsorbed per gram of the adsorbent (XAD-4). The results obtained using XAD-7 (methacrylic ester bead) as adsorbent were similar to that of XAD-4. Different types of zeolites have been studied as adsorbents of HMF, furfural, and xylose [33]. The use of hydrophobic zeolites with the same pore size but different Si/Al ratios for adsorption, has been examined. The results showed the same adsorption isotherms for these zeolites as they selectively adsorbed the inhibitors at 298K. The results also established that zeolites containing large amounts of silica perform more efficiently in the removal of furfural and HMF.

Application of coconut-based commercial activated carbon for furfural removal was investigated [2]. The equilibrium adsorption was attained in six hours and the adsorption kinetics followed the pseudo-second order rate. The use of two types of activated carbon (commercial activated carbon and polymer-derived activated carbon) for adsorption of furfural from an aqueous solution was studied [3]. The results showed effective removal of furfural from the biomass hydrolysate, that led to efficient fermentation. However, the use of adsorption for removal of furfural sometimes leads to removal of some of the fermentable sugars and might affect final ethanol yield [2].

4 FUTURE DIRECTION

Current technologies used for production of bioethanol from lignocellulosic biomass are quite expensive and the high cost of the hydrolysis process and low yield are major problems [35]. For the biomass-to- bioethanol conversion process to be economical, all the sugars present in the cellulose and hemicellulose must be efficiently converted as the feedstock accounts for greater than 40% of all process costs [35-37]. The use of dilute acid for pretreatment and hydrolysis has been well established for low

cost production of fermentable sugars because it promotes the effective hydrolysis of hemicelluloses [38]. However, the major disadvantage of using dilute acid for pretreatment is that it leads to the formation of different compounds (e.g. furfural, hydroxymethyl furfural, phenolic compounds etc.) which act as fermentation inhibitors.

To make the process economically viable and attractive to industries, it must have low production cost and high yield. Activated carbon is the most widely used and cost-effective sorbent in industrial application [39] due to its porous structure and huge internal surface area for adsorption. Hence, recent investigations have been focused on the use of activated carbon for adsorption of furfural from lignocellulosic hydrolysates by varying various experimental parameters such as temperature, contact time, pH and adsorbent dose [40, 41].

5 CONCLUSION

In this paper, a review of the removal of furfural from lignocellulosic hydrolysates for improved bioethanol production has been presented. The various methods that have been employed in the removal of some of inhibitors which are formed from the use of acid for pretreatment and hydrolysis was discussed and future direction identified. From our review, the use of activated carbon for adsorption of furfural from lignocellulosic hydrolysates will continue to attract more research interest due to its economical benefits.

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