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Conversion of Lignocellulosic Biomass in to Mixed Alcohol Fuels

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Abstract—*The negative impact of fossil fuels on the environment has put pressure to find renewable fuel alternatives. Ethanol comparatively being a cleaner fuel is produced from sugar or grain; however, this leads to the argument that whether to use food as a biofuel or not. This has given rise to the thought of finding alternative nonfood sources. As a consequence, industrial research efforts have become more focused on low cost and large scale processes for lignocellulosic feedstocks that originate mainly from agricultural and forest residues and municipal wastes. Lignocellulosic biomass can be utilized to produce ethanol. The two main processes involved: cellulosic hydrolysis in the lignocellulosic biomass to produce reducing sugars, and fermentation of the sugars to ethanol. Although cellulosic-derived biofuel is a promising technology, there are some obstacles to make it cost effective. The ethanol production from lignocellulosic materials is costly, the major challenges being the low yield and high cost of the hydrolysis process. This review explains the current methods on lignocellulosic-derived bioconversion of biofuel and an overview on the major steps involved in cellulosic-based bioethanol processes are provided; also the problems that are faced during such operations. Solutions to these problems along with the possibilities in the future are also explained.*

1. INTRODUCTION

It is a well-known fact that utilization of renewable energies and resources such as wind, hydroelectricity, solar and biomass is being stimulated globally as an essential priority. Presently, out of the total consumption of fossil fuels about 75 percent is for heat and power generation, while remaining 25 percent for transportation and fuel, and only a few percent for materials and chemicals. Currently, biomass is the singular resource that can give us renewable liquid fuels. In the chemical industry, it can also be considered as a vital feedstock. Wheat straw, palm, rice straw, corncobs, corn stems and husks etc. are the different types of lignocellulosic raw materials available in abundance in nature. Lignocellulose is rather strenuous to convert than starches, oils and sugars. It is fibrous in nature and is found in the cell walls of the plant architecture. It mainly contains three components:

1. CELLULOSE

It is made up of polymers of glucose which are bundled together for material strength and thus have high molecular weight. It accounts for around 40 weight% of lignocellulose.

2. Hemicellulose

It is made up of shorter polymers of different sugars that help in binding the cellulose bundles. It accounts for around 25 weight% of lignocelluloses.

3. Lignin

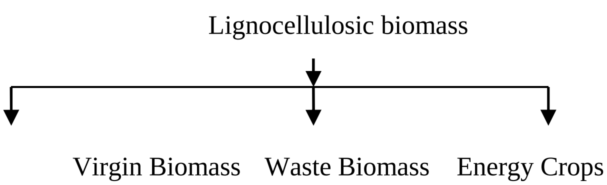
It is a propyl-phenol polymer, tridimensional in nature and rooted to hemicellulose. It is estimated that global produce of lignocellulosic wastes (3-5 gross tonnage/year) could supply energy of about 50-85 exajoule/year, which accounts for 10-20% of current energy demand. Thus, producing bioethanol through bioconversion of lignocellulosic biomass has a potential demand in the field of energy generation. The current review emphasizes on technologies used presently and their shortcomings. Future prospects are also discussed.

2. HISTORICAL AND CURRENT TRENDS

The ancient fabrication of alcohol and fermented beverages in INDIA can be traced back to Indus valley civilization which appeared in the chalcolithic era, while production of ethanol as a fuel is a comparatively recent event which began about 70 years ago. Sugars obtained from different sources are biologically fermented for manufacturing bioethanol. Since the inception of automobile, alcohol has been employed as a fuel. And the oil crisis of 1970's led to the establishment of ethanol as a substitute fuel. This need led to the research and evolution of bioethanol from the available matter. Bioethanol manufactured from sugar feedstock such as corn (in USA) and molasses (in INDIA) are termed as 'First Generation Bioethanol'. It is estimated that manufacture of bioethanol will increment to more than 100 billion liters by 2022 through 'first generation technologies', but the required raw materials compete with food and thus have an anti-impact on biodiversity; also they are inadequate to encounter the ever expanding demand. Hence, these growing concerns have grabbed the attention of the world to enhance ‘Second Generation Bioethanol’ from non-food lignocellulosic biomass which consists of paper, wood, agricultural remnants, dedicated energy crops and municipal solid wastes, all of which compose the inexhaustible organic constituent of the biosphere. As for the current trends, about 67 crore liters of bioethanol was procured by the public sector oil marketing firms in INDIA for the crop year 2014-2015, while it is estimated to reach about 120 crore liters by the end of crop year 2015-2016.

3. SOURCES OF LIGNOCELLULOSIC BIOMASS

Lignocellulose refers to plant dry matter hence called lignocellulosic biomass. From where the lignocellulose biomass comes can be divided into 3 broad categories:



1. Virgin Biomass
It includes everything naturally occurring such as trees, bushes and grass.

2. Waste Biomass
It is the waste from various industrial sectors such as sugarcane bagasse, straw etc. from the agricultural industry and saw mill and paper mill discards from the forestry industry. Energy crops: Crops like poplar trees and sugarcane are used due to their ability to provide high yields of biomass and the fact that they can be harvested multiple times a year. Focusing on India, a study in the North East of India found that nut husk, moj and bonbogori are also potential sources of biofuel production.

4. COMPOSITION OF LIGNOCELLULOSE

Lignocellulose is mainly composed of carbohydrate polymers which are cellulose and hemicellulose and an aromatic polymer lignin. The carbohydrate polymers contain different sugar monomers and they are tightly bound to lignin. 15-25% of lignocellulose consists of lignin whereas hemicellulose makes up 23-32% and 38-50% is cellulose. The cellulose and hemicellulose make up 70% of the entire biomass and covalent, hydrogen bonds are used for tight linkage to lignin component.

1. Cellulose
The major structural component in the plant cell wall, it is highly crystalline, insoluble, and resistant to enzyme attack.

2. Hemicellulose
Hemicellulose is a short, highly branched polymer. The role of hemicellulose is to provide a linkage between lignin and cellulose.

3. Lignin
Lignin is an amorphous, heterogeneous and cross-linked aromatic polymer. In plant cell wall it varies from 2 to 40 %.

5. FORMATION OF BIOETHANOL FROM LIGNOCELLULOSIC BIOMASS

The bioethanol formed from lignocellulosic biomass is called “second generation” bioethanol.

Initially when the feedstock is delivered to the plant, it needs to be stored carefully to prevent early fermentation and contamination. Following are the main steps involved in the formation of second generation bioethanol.

1. Pre – Treatment
This step involves removal of lignin from the feedstock so that the cellulose can be easily accessible in the hydrolysis step. The most common methods to do this are steam explosion and dilute acid pre - hydrolysis, after which enzymatic hydrolysis is performed. To improve the solubilization of hemicellulose and to reduce the amount of inhibitors formed, Sulphuric acid and carbon dioxide are added.

2. Hydrolysis
In this step glucose is produced from the released cellulose of the biomass. It is either catalyzed by dilute acids, concentrated acids or by cellulose enzymes. The cellulose and hemicellulose conversion can be expressed as:

$$(C_6H_{10}O_5)_n + nH_2O \longrightarrow nC_6H_{12}O_6$$
$$(C_5H_8O_4)_n + nH_2O \longrightarrow nC_5H_{10}O_5$$

3. Fermentation
Modern lignocellulose to ethanol processes are still in the pilot stage and the pilot plants are capable of producing a couple of hundred thousand liters of ethanol per year.

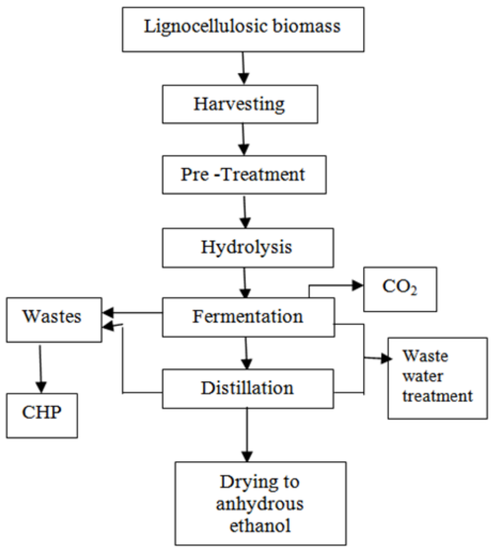
So fermentation is the biological process of formation of ethanol from hexoses and pentoses by using microorganisms such as bacterial, yeast or fungi. The reaction for the same is as follows:

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$
$$3C_5H_{10}O_5 \longrightarrow 5C_2H_5OH + 5CO_2$$

4. Purification
Typically, we get ethanol concentrations in the region of 3-6% by volume, while we can get 12-15% from 1st generation feedstock. Immaterial of the type of feedstock used, the alcohol produced from fermentation cannot be used in industrial and fuel applications. Hence the ethanol must still be purified. Fractional distillation is one method which we can

be used for further purification. The ethanol so produced is 95.6% concentrated by volume.

The formation process can be represented in more detail by the following flowchart.



6. CURRENT ISSUES AND APPROPRIATE SOLUTIONS

With the development of the lignocellulosic bioconversion technology for treating waste effectively, there are certain issues for which solutions have to be found out. Some of those current issues are as follows:

1. The cost of the enzymes used
For the enzymatic hydrolysis of lignocellulosic biomass to be commercialized, cost of the enzymes hinders the process. Approximately 50% of the total hydrolysis cost is represented by the cost of the enzymes.

2. The recalcitrant behavior of the lignocellulosic biomass
Though lignocellulosic biomass is being used as a feed for bio-refineries, its recalcitrant behavior and complex nature create an obstacle economically and technically for biofuel production. The composition and physical chemistry of the lignocellulosic materials make them highly resilient.

3. Water availability for the bioconversion system
Although water plays a vital role in the sustainability of the bio-refineries, there is limited information on water requirement. Water availability is not a serious issue in countries like Brazil, Canada, Russia and some African nations, but other countries like China, India, South Africa and Turkey are already facing water issues even without considering estimated water consumption for biofuel production. Water availability could become an issue for the United States if proper agricultural practices to sustain water are not adopted. Till today, lignocellulosic-based ethanol in the United states is only produced at a small scale and is not yet available commercially.

6. Commercial Investments
In the coming times, as per the increasing demand for liquid fuel for transportation lignocellulosic biomass can be considered as a captivating inexhaustible resource. An appropriate pretreatment system will make the bioconversion of lignocellulosic biomass into bioethanol an efficient and economically beneficial method. The establishment of the initial commercial bioethanol manufacturing plants making use of lignocellulosic biomass is just beginning. It is estimated that investment in the range of USD 125-250 M will be required to venture a new second generation biofuel plant for a moderate scale plant manufacturing about 50-150 Ml/year, in its initial stage of growth and development.

1. Investment Costs

Based on the usage of different pretreatment techniques, no pretreatment techniques and 'ideal' pretreatment technique the capital investment for various lignocellulosic bioethanol plants will vary. The cost of almost all the pretreatment techniques is higher than the ideal estimation. Though decreasing the cost of pretreatment methods is an essential factor in reducing the capital costs, there is not much difference in the capital costs between different systems. Thus feedstock characteristics, application costs and required expertise at hand are considered as basic criteria for selecting a suitable pretreatment technology.

2. Operating Costs

To make the process of bioconversion of lignocellulosic biomass to bioethanol financially beneficial, the cost of lignin co-products have proven to be an important factor. This follows because an increment in the value of lignin co-product causes a remarkable reduction in costs of bioethanol production. It is estimated that the process can be rendered economically neutral by high lignin values of around 50% more than the usual bioethanol manufacturing costs. On the other hand, the process cost can also increase to 200% depending on current economic conditions, if the biomass feedstock value is incremented. As for now efforts must be made to increment the value of lignin co-products. Since the past decade has seen doubling of the prices of gas and electricity, the impact of lignin as a substitute fuel for heat and power generation will be important.

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4. Inhibitors of enzymatic catalysts

Substances that may act as inhibitors are phenolic compounds and other aromatics, aliphatic acids, furan aldehydes, inorganic ions, and bio-alcohols.

5. Other inhibitions

S. cerevisiae's viability, growth, glucose transport systems, and proton fluxes is inhibited by ethanol generated during fermentation. The permeability, organization, and lipid composition of the yeast plasma membrane is affected.

Some solutions to problems caused by inhibitors

1. The feedstock and the pretreatment conditions affect the concentrations of inhibitors and sugars in hydrolysates; one way is to select feedstocks which have low recalcitrance and to use pretreatment conditions that are mild.

2. We should design the fermentation process so that we can avoid inhibition problems; example. SSF can be used for cellulolytic enzymes to avoid their inhibition by sugars.

8. CONCLUSION-FUTURE PROSPECTS

The Lignocellulosic based biofuel (second generation biofuel) has turned out to be an alternative over bioethanol derived from food (first generation biofuel); it being originated from mainly sugarcane and cornstarch. A few advantages of the second generation biofuel over the one of the first generation are as follows:

1. They are more efficient and environment friendly.

2. The by-products that are produced can be used in other processes or can be burned for effectively achieving heat and power.

3. The greenhouse gas effect was reduced by 78% by the carbon footprint of first generation biofuels while the greenhouse gas was reduced by 94% by the second generation biofuels when compared to the greenhouse gas effect caused by fossil fuels.

The high recalcitrant behavior of lignocellulosic materials is responsible for the concerning expense of the pretreatment of the the feedstock. It is necessary to design a combination of pretreatment methods that would prove to be highly effective for a large range of lignocellulosic material, thus dealing with the variability in feedstock. SSCombF and CBP being technologies that are beginning to create an impact as the operation steps and chemical inhibitors are reduced. Companies like DDCE (DuPont Danisco Cellulosic Ethanol), Butalco, etc. use conventional strains that are genetically engineered, example S. cerevisiae and ethanol genic Z. mobilis for their capability of tolerating higher alcohol and yield. To achieve optimal second-generation biofuel performance a combination of advanced systems analysis and techniques that are economical and designed to cope with the versatility of the feedstock are required.

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