Bioethanol from Lignocellulosic Biomass

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***Abstract* — We have to come up with a source of energy that is renewable and has the potential to meet our energy demands. One such source of energy is derived from the biomasses, these are called Biofuels. In this paper we shall review Bioethanol which the Planning Commission of India has considered as one of the primary biofuel. We review the innovative technologies and strategies to generate it from Lignocellulosic biomass and conclude with the economic and financial benefits it will provide for India.**

***Keywords*—Lignocellulosic biomass, Bioethanol, Technologies, Economic and Financial Benefits, Renewable Energy.**

I. INTRODUCTION

Two of the major challenges that India and several other nations are facing are the Population Explosion and the need to meet the increasing Energy demands. Up until now, we have been relying on the conventional sources of energy like coal and petroleum for fulfilling it but data shows that the world population is likely to increase from 6.7 billion to 8 billion by 2030 while the global oil production is anticipated to turn down from 25 billion barrels to 5 billion barrels by 2050[1]. This will create a dearth which will have catastrophic implications on our future. [2]

USA and Brazil are considered to be foremost producers of bioethanol. These countries utilize molasses obtained from sugarcane and corn as the feedstocks for ethanol production. However, there is a major problem with these feedstocks and that is their food value. Since, feeding the population will be the priority of any economy utilizing these food sources would clash with this priority and at the same time it will also increase the cost of food sources which will eventually bring bioethanol in bad light. Hence, in order to prevent this we have to find alternative sources of producing bioethanol which will not have an adverse effect on food sources of a country. One such resource is the Ligno-cellulosic biomass obtained from agricultural wastes. Agricultural wastes are perhaps the most undervalued source of energy. It is generated in abundance and hence is also one of the cheapest sources of energy [2].

II. LIGNOCELLULOSIC BIOMASS

Lignocellulosic material has 3 major components:

- Cellulose (about 30-50%)
- Hemi-cellulose (accounting for 15-35%)
- Lignin (estimated to be 10-20%)

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Table I
Composition of Lignocellulosic Biomass

Component	Constitution	Structure	References
Hemicellulose	Hexoses- D-glucose, D-galactose and D-mannose Pentoses-D-xylose and L-arabinose	β-(1/4)-linkages that include D-xylose-90% L-arabinose-10%	[3]
Cellulose	β-D-glucose	1,4-glycosidic bonds	[3]
Lignin	Phenyl propane units - Syringyl, Guaiacyl and p-Hydroxy phenol	β -aryl ether bonds	[2] [3]

III. PRODUCTION STEPS

There are 4 steps involved in the preparation of lignocellulosic derived bioethanol:

- Preliminary treatment,
- Hydrolysis,
- Fermentation
- Distillation

IV. PRE-TREATMENT

Pretreatment involves solubilisation and separation of one or more components of biomass. The lignocellulosic complex is composed of cellulose and lignin bonded by hemicelluloses chains. Pretreatment breaks the matrix to reduce the degree of crystallinity of the cellulose and increase the portion of amorphous cellulose which is apt for enzymatic attack during the hydrolysis process [2].

The recalcitrance of lignocellulose hinders economical production of bioethanol. Inefficient pre-treatment results in residue which is not easily hydrolysable by cellulase enzyme and may lead to production of toxic inhibitors for microbial metabolism.

A. Mechanical Size Reduction

Involves milling, grinding, and chipping of the lignocellulosic feedstock. The size of the materials is usually 10–30 mm after chipping and 0.2–2 mm after milling or grinding. Some of the milling operations include:

- Wet milling
- Dry milling
- Vibratory ball milling
- Compression milling

Size Reduction increases the reactive surface area and reduces the crystallinity of cellulose.

However, very fine particles may generate clumps involving liquid and may lead to channelling. Specific energy consumption also increases. These operations are time consuming, energy intensive and expensive.

B. Steam Explosion Pre-treatment

High pressure and high temperature steam is passed into a sealed chamber filled with lignocellulosic material in the form of chips. After 1–5 min, when pressure is released, resulting in steam to expand within the lignocellulosic matrix thereby separating the individual fibers and causing an explosive decomposition. Temperature maintained is 433–533 K and pressure 0.69–4.83 MPa before the material is opened to atmospheric pressure for cooling. Addition of acids like H_2SO_4 (or SO_2), CO_2 during steam explosion can reduce time and temperature, improve hydrolysis, reduce the generation of inhibitory compounds, and lead to complete removal of hemicellulose.

45-65% of xylose recovery makes steam-explosion pre-treatment economically attractive. There is evidence that this process promotes delignification. Less hazardous chemicals are used. Less negative environmental impact. Complete sugar recovery [4].

But it is highly energy intensive and less efficient than SPORL and Organosolv pre-treatment [5].

C. Ammonia Fiber Explosion

Pre-wetted lignocellulosic material having moisture content of 15–30% is kept in a pressure vessel and is subjected to liquid ammonia at high temperature and pressure, and a subsequent fast decompression. Temperature is between 60-100 ˚C and residence time may vary from low (5-10 min) to intermediate (30 min) depending on the degree of saturation of the biomass. 1-2 kg ammonia per kg of dry substrates is the ammonia loading. Pressures exceeding 12 atm are required. No inhibitors are produced and very fine size of feed is not required.

It is simple with a less time required. Is inefficient for biomasses having high lignin content (e.g. softwood newspaper). [8]

D. Acid Pretreatment

Operates either at high temperature with low acid concentration (dilute acid pre-treatment) or at low temperature with high acid concentration (concentrated acid pre-treatment).

- Dilute acid: 5–10% [w/w], T>433 K and is continuous process.
- Concentrated acid: 10–40% [w/w], T < 433 K and is batch process.

With higher pre-treatment temperatures and shorter reactor residence times, higher xylose recovery and enzymatic cellulose digestibility is observed. [6]

By-products like furfural (pentose sugars by-product), and hydroxyl methyl furfural (HMF; hexose sugar by-product), phenolic acid (lignin by-product) and acetate (diacetylation product of hemicellulose). Concentrations of 5 mM or above have considerable inhibitory effect in the fermentation process.

Use of concentrated acid

- Yields very high levels of sugar (90%)
- Can handle diverse feedstock
- Is relatively rapid (10 to 12 hours)
- Leads to less degradation

But it needs more expensive corrosion resistant equipment and the hydrolysate has to be neutralized by the addition of lime and contaminants are removed by treating it using activated charcoal [1].

E. Alkaline Pretreatment

Alkaline solutions are used to remove lignin and various uronic acid substitutions on hemicellulose which lower the enzyme access to the hemicellulose and cellulose. It increases the surface area hence permitting penetration of water molecules to the inner layers therefore breaking the bonds between hemicellulose and lignin carbohydrate. Works at lower temperatures and pressures compared to other pre-treatment methods. This method presents hindrances in the process economy for obtaining fuels. Sodium, potassium, calcium and ammonium hydroxide are appropriate chemicals for pre-treatment. [8]

F. Organosolv Pretreatment

The use of organic solvent and water mixture removes the requirement of burning the liquor as it permits the separation of lignin (by distillation of the organic solvent). 40 to 60% of organic solvent at 160 to 190°C for 30 to 60 min is needed [1]. Examples include use of 90% formic acid and pressurized CO_2 in combination. Other solvents which can be used are methanol, ethanol, acetic acid, performic acid and peracetic acid, acetone, etc. The advantages of these methods include recovery and recycling of organic solvents as they can be easily distilled out. But, Inhibitory compounds are formed and expensive high pressure equipment is needed.

G. SPORL

Sulphite Pretreatment to Overcome Recalcitrance of Lignocellulose (SPORL) uses aqueous sulphite or bisulphite solutions over a wide range of pH and temperatures to weaken the chemical structure. The pH of pre-treatment liquor can be adjusted using re-agent. This reduces the energy consumption needed in mechanical processes by more than 10 times. It has excellent scalability to commercial production. [10]

V. HYDROLYSIS

Molecules of cellulose and hemicelluloses are cleaved by water molecules. The carbohydrate polymers are converted to simple sugars.

A. Chemical Hydrolysis

Chemical hydrolysis involves exposure of lignocellulosic materials to a chemical for a period of time at a specific temperature.

1) Dilute Acid Hydrolysis

Dilute acid hydrolysis takes place in 2 stages. The first stage occurs at low temperature with 0.7% H_2SO_4 and 463K to increase the hemicellulose yield, while the 2nd stage occurs at higher temperature of 488 K with 0.4% H_2SO_4 to optimize hydrolysis of the cellulose.

The fast rate of reaction facilitates continuous processing.

However, the challenge is to raise glucose yield by more than 70% economically while ensuring a high cellulose hydrolysis rate and minimal glucose decomposition. For rapid continuous processes, in order to allow adequate acid penetration, feedstocks must also be reduced in size to mm.

2) Concentrated Acid Hydrolysis

It utilizes 70% H_2SO_4 at 313–323K for 2–4 h in the reactor. The low temperatures and pressure ensure minimal sugar degradation. The solid residue from first stage is de-watered and drenched in 30–40% concentration sulphuric acid for 50 minutes at 373K for further cellulose hydrolysis.

Compared to dilute hydrolysis this gives minimal degradation and yield upto 100%. Inhibitor generation is less however; it requires large quantities of acid as well as costly acid recycling, which makes it commercially less attractive.

B. Enzymatic Hydrolysis

When hydrolysis is catalysed by enzymes, the process is known as enzymatic hydrolysis.

1) Cellulose

Cellulase, produced by bacteria and fungi, involves synergistic actions by (EG) endo-1,4-β-D-glucanases, exoglucanases(CBH) or 1,4-β-D-glucan cellobiohydrolases and β-glucosidases (BGL) or cellobiases. The enzymatic action is:-

- EG hydrolyses accessible intramolecular β-1,4-glucosidic bonds randomly to produce new chain ends.
- CBH cleaves cellulose chains at the ends to release soluble cellobiose.
- BGL hydrolyses cellobiose to glucose to avoid cellobiose inhibition. BGL completes the hydrolysis process.

Cellobiose, at higher concentrations decreases the rate of cellulose hydrolysis. It has been a hindrance in enzymatic hydrolysis because commercially used cellulase generating microorganisms make very little β-glucosidase which can lead to accumulation of cellobiose and increase the amount of cellulose required. Rate of hydrolysis is affected by

- Molecular structure of cellulose
- Crystallinity of cellulose
- Surface area of cellulose fiber
- Degree of swelling of cellulose fiber
- Degree of polymerization
- Associated lignin or other materials

2) Hemicellulose

Water, methanol, methanoic acid, ethanoic acids, propanoic acids, hydroxy-1-propanone, hydroxy-1-butanone and 2-furfuraldeyde are 8 major products that are formed by xylan degradation. Under high temperature and pressure xylose is further degraded to furfural. The enzymes include α-glucoronisidase, acetyl xylan esterase, ferulic acid esterase endoxylanase,, α-arabinofuranosidase, exoxylanase, and ß-xylosidase. Working:-

- The endoxylanase attacks the main chains of xylans and β-xylosidase hydrolyses xylooligosaccharides to xylose.
- The α-arabinofuranosidase and α-glucuronidase remove the arabinose and 4-o-methyl glucuronic acid substituents, respectively.
- Acetyl esterases hydrolyse acetyl substitutions present on xylose moieties and feruloyl esterases hydrolyse ester bond between the arabinose substitutions and ferulic acid.
- Feruloyl esterases help to release hemicellulose from lignin and leave free polysaccharide product more open to degradation by hemicellulases.

Accessibility to the substrate is easier than cellulose as xylan does not form inaccessible crystalline structures.

3) Advantages of Enzymatic Hydrolysis

- Utility cost of enzymatic hydrolysis is low compared to others as enzyme hydrolysis is conducted under mild conditions and has no corrosion problem.
- The enzymatic hydrolysis has currently high yields (75–85%)and is environment friendly.[8]

Lignin has adverse effect on enzyme working.

VI. FERMENTATION

This process requires presence of microorganisms to ferment sugars into ethanol and other end products. The types of fermentation process include:-

- Batch culture which is a closed culture system containing limited quantity of nutrients inoculated with microorganisms.
- Fed Batch reactors are commonly used for industrial usage. These have the ability to enhance viable cell concentration, prolong lifetime of culture and higher concentration products.
- In the continuous process, feed is pumped continuously in an agitated vessel where microbes are active. The product is taken from the top of bioreactor.

The performance parameters of fermentation are:

- Temperature range
- pH range
- Alcohol tolerance
- Growth rate
- Productivity
- Osmotic tolerance
- Specificity
- Yield
- Genetic stability
- Inhibitor tolerance

The microorganisms responsible for fermentation are S.Cerevisiae, Z.Mobilis, K.Oxytoca, Thermophilic Bacteria. [8]

VII. NEW TECHNIQUES

A. Simultaneous Saccharification and Fermentation

The enzymatic hydrolysis and fermentation process can be carried out together in a single step called simultaneous SSF. It increases the hydrolysis rate by converting the sugars that inhibit the cellulase activity. It reduces the enzyme requirement, gives high product yield, Reduce sterile

requirements as glucose is removed immediately and bioethanol is produced.

Disadvantage is the different optimal requirements for the process. In many cases, the low pH, e.g., less than 5, and high temperature, e.g., 4313 K, may be apt for enzymatic hydrolysis, but the low pH will inhibit the lactic acid production and the high temperature will adversely affect fungal cell growth. [2][8]

B. Simultaneous Saccharification and Co- Fermentation

The pre-treated mass is neutralized and directly exposed to different enzymes and microorganisms capable of hydrolysing cellulose and hemicelluloses to fermentable sugars as well as ferment sugars to ethanol.

The enzymatic hydrolysis releases hexose sugars continuously, which increases the rate of glycolysis in a way the pentose sugars are fermented faster and with higher yield. [2][8]

C. Consolidated Bioprocessing(CBP)

A strategy in which cellulase production, hydrolysis of substrate, and fermentation are accomplished in a single step and in one reactor. Only one microbial group is used for cellulose production and fermentation. Has the potential to lower production costs due to simpler material processing and less energy inputs, higher conversion efficiencies than SSF or SSCF based processes. But natural microbes exhibiting all the desired features for CBP are not easily available, although, a number of microorganisms, both bacteria and fungi, have been identified. [2][8]

VIII. DISTILLATION

The boiling point of water (100 ˚C) is more than ethanol (78.3 ˚C)so it will be converted to steam before water. Hence water is separated and ethanol distillate is obtained at 95% concentration. Many large-scale industries and refineries use continuous distillation column system with multiple effects.

IX. CONCLUSION

Developing countries like India import oil from the foreign countries for meeting their energy demands. This puts a lot of pressure on the country as the costs are exorbitant. Bioethanol one can put a halt on this money drain regime as the raw material required for its production is inexhaustible, abundant and hence cheap. This technology opens up a new market for all the savvy investors looking for reliable and lucrative sources of energy. This harbingers setting up of new Industries and new trade outlets, which demands human resources thereby increasing the employment opportunities. This will curb the most burning issue our country is facing today-Unemployment. Development of any new technology beckons a healthy competition between the countries for developing an optimized approach and this can be a money-spinner. Enterprises would invest a large amount of money if it helps in the production of a widely acceptable commodity since it can be profitable for them. Hence I conclude that advancement and promotion of this technology will be beneficial.

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