

Overview: Second Generation Bioethanol Process Technology

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Biofuels provide an attractive and sustainable energy option as they are considered to be clean fuels having 'very low to no sulphur' content. Biofuels therefore help in creating a positive environmental impact. Bioethanol is one such fuel that can be blended with gasoline. Typically and conventionally, bioethanol is extracted from sugars. Bioethanol can be produced at industrial scale through the sugar fermentation route. The bioethanol technology is termed as either first generation (1G) or second generation (2G) depending upon the origin of such sugars. While the 1G bioethanol technology uses starch as a source of sugar, the 2G bioethanol technology uses cellulose and hemicelluloses as a source of sugar. Starch required in 1G technology can be found in various feed stocks such as cereals (wheat, corn, sorghum barley, etc) and sugarcane. Feedstock such as wheat straw, corn, wood, agricultural residues or municipal solid waste are typically ligno-cellulosic materials and are used as a source of bioethanol in 2G technology. As compared to 1G technology, which use grain as feedstock, the 2G technologies use crop residues, a waste that otherwise would be of no value. This article provides an overview of the 2G bioethanol technology.

Advantages of Bioethanol:

There are number of advantages of using bioethanol as fuel. Some of the benefits are as below.

- Reduced dependency on crude oil imports: For oil importing countries like India, The major driving force is to reduce their dependency on fossil fuels. It benefits energy security as it can reduce crude oil by using domestically produced energy sources. Countries like India, having a limited access to crude oil resources, can grow crops for energy use and gain some economic freedom.
- Cleaner environment: Due to the fact that the exhausts from the automobile engines using bioethanol blended gasoline is more cleaner in nature, the second major benefit of using bioethanol is its ability to reduce the overall carbon footprint and their use help in reduction of greenhouse gas (GHG) emissions. It will also reduce the GHG emissions by reducing the of agriculture residues burning.
- Renewable energy source: Bioethanol is produced using plant materials such as corn, sugarcane, crop residues, etc. Since, all these are crops can be grown; bioethanol fuel is a renewable energy source.
- Financial benefit for farmers: Agricultural residues and wastes which otherwise are burnt by farmers can be utilized for producing bioethanol.

Raw material components:

As stated earlier, the 2G bioethanol technology uses ligno-cellulosic biomass as a feedstock. Lignocellulosic biomass is mainly composed of plant cell walls. It essentially contains three major components viz. Lignin, Cellulose, and Hemicelluloses. Cellulose and Hemicelluloses are the structural carbohydrates while lignin is heterogeneous phenolic polymer.

Cellulose is a polysaccharide made up of linear glucan chains held together by intra molecular hydrogen bonds and by intermolecular Van-der Waals forces. In order to obtain glucose, the crystalline cellulose must be subjected to some preliminary chemical or mechanical degradation.

Hemicellulose consists of short, highly branched chains of sugars. Hemicelluloses are highly amorphous and branched structures. It contains pentoses, hemicelluloses chains. Compared to cellulose, the hemicelluloses can easily be broken down to form their simple monomeric sugars. The exact sugar composition of hemicelluloses can vary depending on the type of plant.

Lignin is a non-sugar-based polymer. Lignin is not a suitable component for microbial fermentation process. It inhibits microbial growth and fermentation. However, lignin can be used as energy source as it yields

more energy when burned, and thus can be utilized for combined heat and power production in the bioethanol process.

Process Description:

The bioethanol process is carried out in following four major steps.

1. Pre treatment: Physical or chemical pre-treatment of the fibers to expose the cellulose so as to reduce its crystallinity.
2. Hydrolysis : Cellulose polymer is hydrolysed with enzymes or acids, to convert it into simple (glucose) sugars
3. Fermentation: Microbial fermentation of simple sugars to form ethanol.
4. Distillation and dehydration to produce 99.5% vol. fuel grade ethanol.

Pretreatment:

Due to the presence of lignin in 'Lignocellulosic' materials, and compared to the accessibility of sucrose in sugar cane and starch in grains, cellulose and hemicelluloses are not easily and readily available for saccharification and fermentation. A "pre-treatment" step is hence required to facilitate conversion of cellulose and hemicelluloses to fermentable sugars.

The pre-treatment process converts hemicellulose carbohydrates into soluble sugars (like glucose, xylose, etc.) by hydrolysis reactions in which acetyl groups in the hemicellulose are liberated in the form of acetic acid. Biomass feedstock is chemically treated by disrupting cell wall structures in the pre-treatment step which facilitates downstream enzymatic hydrolysis. This section is also termed as 'Delignification' section as the pre-treatment drives some lignin into solution. This step reduces cellulose crystallinity and chain length. Process parameters such as residence time, temperature, and catalyst loading affects the pre treatment process. The pre treated biomass is sent to the hydrolysis reactor.

Hydrolysis:

Hydrolysis process is used to convert hemicellulose and cellulose content of lignocellulosic biomass into fermentable monomeric sugars. This process can be carried out by two different routes. These routes are Acid hydrolysis and Enzymatic hydrolysis.

In acid hydrolysis process, mineral acids such as HCl, H₂SO₄, HNO₃, or HF are widely used for hydrolysing lignocellulosic biomass. In enzymatic hydrolysis, Cellulose is converted to glucose using cellulase enzymes. Enzymatic hydrolysis process is also termed as 'Enzymatic Saccharification' process. A cellulase enzyme is prepared from mixture of enzymes (catalytic proteins) which work together to break down cellulose fibers into glucose monomers.

For higher conversion and its suitability to the lower grade of metallurgy, enzymatic hydrolysis route is preferred over the acid hydrolysis route.

The glucose and other sugars obtained from hydrolysis of hemicelluloses are co-fermented to form ethanol in the next step.

Fermentation:

Fermentation process step is similar to the 1G ethanol technology. In this step, the hexoses and pentoses are converted into ethanol by employing variety of micro organisms, such as yeast, bacteria, fungi, etc.

Depending on how the enzymatic hydrolysis and fermentation steps are integrated, the technology can follow either of following route.

- Separate Hydrolysis and Fermentation
- Separate Hydrolysis and Co-fermentation
- Simultaneous Saccharification and Co-fermentation

Distillation and Purification:

Distillation and purification steps are also similar to the technology used in 1G bioethanol process. From fermented mash, fuel grade ethanol is produced through distillation and adsorption via molecular sieve. Ethanol and water forms an azeotropic mixture. Hence, the distillation can be used to obtain ethanol purity only upto 95.5 vol.% (corresponding to azeotropic composition) Desired fuel grade ethanol specification (of 99.5% vol.) is achieved by passing the 95.5 vol.% ethanol obtained from distillation through a molecular sieve.

Technology Selection Criteria:

There are various technologies presently available for manufacturing 2G bioethanol. The main parameters that influence the technology selection are discussed in brief.

- (1) Feedstock: Ability to process variety of feedstocks like rice straw, wheat straw, bagasse, corn cob, cotton stalk etc. Technology suitable to use mixed feedstock can be preferred.
- (2) Conversion Efficiency: This decides the quantity of feedstock required for the given ethanol throughput. Technology with higher conversion efficiency is preferred. Typical conversion efficiencies are 20%.
- (3) Conversion time: This varies from each technology. The hydrolysis, fermentation are batch processes and depending upon the technology used, the net conversion time will vary. Apart from start up time, this impacts capital costs and inventory costs.
- (4) Enzyme/Yeast Requirement: Quantity and cost of enzymes/yeast may affect overall economics of the technology selected.
- (5) Utility requirement: In general, the 2G ethanol technologies require significant amount of steam for removing water from the raw ethanol stream. The concentration of ethanol leaving the fermenter hence thus dominates the steam requirements; this is usually 5%.
- (6) Water recycle: Technology to be optimized and preferred when fresh water intake is minimized.
- (7) Turn down requirements: Ability of the technology to run on low turndown, say 25% is preferred.

Technological Challenges:

Since the 2G technology is not fully commercialized in India, few technological challenges still needs to be addressed. These issues need a detailed assessment and are briefed as below.

1. Commercial scale operation of 2G Ethanol Process: The commercial scale plant experience is available for one technology licensor. And others have demo or pilot scale experience.
2. Higher cost of production compared to first generation ethanol: The cost of ethanol production from lignocellulosic biomass is higher than first generation ethanol and there may be requirement of subsidy for economic viability and competitive ethanol pricing.
3. Commercial availability of lignin boiler: Lignin is recommended to be used as fuel in boiler and therefore the commercial availability of such applications needs to be ascertained.
4. Pretreatment forms a critical section and is the main process step that separates the 1G and 2G technologies. Commercial experience for pretreatment section is not available.
5. The availability of biomass round the year depends on proper pre planning and it is essential to build the ecosystem for ensuring biomass supply. Supply of secondary fuel for use in boiler is also to be addressed.
6. Biogas and Co₂ utilization: Finding the consumer and/or disposal of Biogas and Co₂ produced from 2G technology remains an open issue.

Indian Scenario:

The practice of blending ethanol in gasoline was started in India in 2001. Government of India, in 2003, mandated blending of 5% ethanol with gasoline in 9 States and 4 Union Territories. This was subsequently continued on an all-India basis in November 2006 (in 20 States and 8 Union Territories except a few North East states and Jammu & Kashmir). Indian Oil companies were asked to increase the ethanol blending target to 15% by Ministry of Petroleum and Natural Gas, on 1 September, 2015 and achieve this blend in as many states as possible.

At 10% blending, the projected ethanol demand is ~5500 million liters per annum by year 2021-2022. It would certainly require significant investments in near future. Presently, First few plants to produce bioethanol using 2G technologies are under consideration and are at various stages of planning and design.

Future Technology:

Third generation (3G) bioethanol technology is based on ethanol production from Microalgae. Currently, Microalgae is gaining increased attention as it is an alternative renewable source of biomass which can be used for 3G bioethanol production. The increased interest to use microalgae is also attributed to the fact that it can be produced all year along and does not require any pesticides or herbicides. It can be produced in sea water or brackish water and thus do not compete with agricultural land. Comparatively, microalgae have potential to reduce freshwater consumption as it requires less water than terrestrial crops.

Another technology to produce bioethanol from the CO₂ emission sources (Iron and steel producers) is also recently commercialized.

Concluding Remarks:

Bio-ethanol is considered as an important renewable fuel. The Indian economy is growing at a rate of approximately 7% to 7.5% resulting in the increased demand for energy. Bioethanol presents a sustainable source of energy. 2G Bioethanol technologies are being implemented in India.

TCE is associated with one of the first 2G bioethanol plants being installed in India and have first hand experience of commercializing such technology.