EB 0810

FUEL ALCOHOL

FUEL ALCOHOL: ALCOHOL FROM BIOMASS

Biomass, regardless of its source, contains three principal ingredients: cellulose, hemicellulose, and lignin. The composition of typical agricultural residue is 30-40% cellulose, 25-35% hemicellulose, and 20-35% lignin. The purpose of biomass conversion is to break down (hydrolyze) the cellulose and hemicellulose into sugars that can be fermented into alcohol.

Cellulose consists of a linear chain of linked monosaccharides (D-glucose). Hydrolysis is a process by which this linkage is broken using either enzymes or acid, yielding individual sugar molecules (glucose). Cellulose is difficult to hydrolyze due to its crystalline nature. Hemicellulose is represented by two major types, glucomannans and xylans, neither of which is crystalline in nature. Both are linear chains of monosaccharides (D-glucose, D-xylose), but additional monosaccharide units are bonded to the chain (D-mannose, L-arabinose). Currently, xylans are not fermentable. Lignin is a polyphenolic macromolecule that functions as a reinforcing material in plant cell walls and infrastructure.

The principle behind biomass conversion is the hydrolysis of cellulose and hemicellulose into the sugars, glucose, and pentoses. Hydrolysis is the process by which the bond between the monosaccharides is broken by using either hydronium (hydrogen) ions or enzymes as catalysts. These reactions must be carried out by bringing the catalytic agent into intimate contact with the molecular surfaces (topochemical reactions). Hemicellulose is readily hydrolyzed to yield pentose. Cellulose is not readily hydrolyzed because of its crystalline structure and its close association with lignin which acts to seal and protect it.

Presently there are two methods commonly used for the hydrolysis of biomass: acid hydrolysis and enzymatic hydrolysis. Only acid hydrolysis has been developed and employed on a commercial scale. Two general types of industrial processes have been used—dilute acid hydrolysis and concentrated acid hydrolysis. Dilute acid hydrolysis employs a dilute acid concentration at high temperatures (above 150°C) to hydrolyze the polysaccharides. Concentrated acid hydrolysis is carried out at ambient temperatures and requires an efficient recovery system of the acid to be economically feasible. Enzymatic hydrolysis has been the subject of intensive research to overcome the difficulty involving the inaccessability of the polysaccharide molecules to the enzymes required for the catalytic reaction. Research is underway to develop pretreatment techniques (mechanical, chemical, or enzymatic) that will increase the accessibility and yields, and reduce processing time.

Three proposed techniques for the commercial production of alcohol from biomass are summarized. They represent investigations and research into the two processes described above. They are: (1) Purdue Process as developed at the Laboratory of Renewable Resources Engineering, Purdue University; (2) USFPL Hydrolysis-Wet Oxidation-Fermentation Process, of the University of California Forest Products Laboratory; and (3) Direct Cellulose to Ethanol-Gulf Enzyme Process, University of Arkansas.

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Purdue Process

A conversion process for corn residue was recently reported by Dr. George Tsao and Michael Ladish of the Laboratory of Renewable Resources Engineering, Purdue University. A brief description of the process follows. Although originally designed for corn residue, the techniques are applicable to any cellulose biomass. Basically the technique consists of: hydrolysis of the hemicellulose, separation and pretreatment of the remaining ligno-cellulose, cellulose hydrolysis, separation of the lignin component, fermentation and distillation.

1. Hemicellulose hydrolysis: Crop residues are mixed with dilute sulfuric acid (0.45% at 95°C for 5 to 6 hours), which hydrolyzes the hemicellulose into pentosans. The remaining material consists mostly of cellulose and lignin (ligno-cellulose).
2. Dewatering: The pentosans are filtered out and can be processed into industrial chemicals and plastics. Excess water is removed from the ligno-cellulose pulp with a roller press.
3. Solvent pretreatment: Concentrated sulfuric acid (70-80%) and a tumbler are then employed to break the cellulose-lignin bond with minimum breakdown of the cellulose. The cellulose can then be reprecipitated from the solvent by either adding water or methanol.
4. Cellulose hydrolysis: The cellulose can now be easily hydrolyzed by dilute sulfuric acid or enzymes. The lignin can be filtered off and burned for its heating value.
5. Fermentation: The glucose is easily fermented into ethanol using traditional technology.

Disadvantages of the acid hydrolysis are the need for expensive corrosion-proof equipment and, because of the acid concentration needed, the decomposition of the resulting sugar. Glucose yields of approximately 50% of the weight of cellulose used have been obtained commercially. Purdue estimates a 90% conversion efficiency for their process, yielding 90 gallons of ethanol from 1 ton of biomass.

UCFPL Hydrolysis-Wet Oxidation-Fermentation Process

A process has been designed based on experimental work carried out at the University of California Forest Products Laboratory for dilute acid hydrolysis of biomass to produce sugars for fermentation. Basically the process consists of: hydrolysis in steps to produce the solutions of sugar; fermentation of the sugar solutions to produce ethanol; methanation to convert soluble organic products not isolated from the water solutions to methane; and wet oxidation to convert solids produced in the process to soluble organic products that can be methanated, carbon dioxide, and thermal energy.

The basic hydrolysis and fermentation are similar to the Purdue technique except that lower acid concentrations and higher temperatures are employed in hydrolysis. Added is the production of methane from the byproduct of the process and wet oxidation of the ligneous residue and organic solids. Yields of about 57 gallons of ethanol per ton of residue are projected.

Direct Cellulose to Ethanol Process-Gulf Enzyme Process

This process can be broken down into five steps: feedstock pretreatment, enzyme production, yeast production, simultaneous saccharification/fermentation, and ethanol recovery.

1. Pretreatment includes mixing with water to obtain a uniform mixture and moisturization followed by pasteurization or sterilization as necessary.
2. The Gulf process utilizes an enzyme from a mutant strain of *Trichoderma resei* to break down the crystalline cellulose to glucose. The optimum temperature for the cellulose enzyme system is 45 to 50°C.
3. The third step is the production of yeast necessary for converting glucose to ethanol. Since most yeasts have a temperature optimum lower than that of the cellulose system

(30-35°C), a temperature of 40°C is used as optimum for the combined system.

4. The fourth step is considered to be the key to the economic viability of cellulose-to-ethanol conversion. The pretreated cellulose slurry is simultaneously converted to glucose and the glucose to ethyl alcohol in the same vessel in a continuous or semi-continuous mode. There is a 25-40% increase in yield over a two-step process of saccharification and then fermentation. This improvement results from the removal of products formed during saccharification which inhibit the enzyme system.
5. The last step is recovery of the ethanol. To accomplish this, Raphael Katzen Associates designed a stripping column in which the mash is pumped and the alcohol stripped off with an upward flow of steam. The resulting ethanol-water mixture can then be further concentrated through a normal distillation system.

Advantages of this system are that conversion takes place at essentially ambient temperatures and pressures with no corrosive chemicals. Disadvantages are the low production rate and low concentration. The economic viability of this technique is determined by the ability to manage or overcome these limitations.

A proposed commercial process envisions the conversion of 1,000 tons per day of cellulosic wastes into 75,000 gallons of ethanol (190 proof). In addition, 267 tons per day of by-product animal feed would be produced.

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