MANUFACTURING OF ETHANOL AND CONVERSION OF AGRICULTURAL WASTE TO ETHANOL

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Abstract - Ethanol is an important commercial alcohol which is used in various industries. It can be produced by converting the sugar into alcohol under environmental conditions. Any starchy material can be used for production of ethanol. In this paper, we discuss the manufacturing process of ethanol and how we can use agricultural waste to produce ethanol.

Key Words: *Ethanol, Bio-Ethanol, Agricultural waste*

1. INTRODUCTION

Ethanol as most important alcohol can be produced by converting the sugar content of any starchy material into alcohol with the evolution of carbon dioxide (CO2) under controlled environmental conditions. The process is an anaerobic fermentation catalyzed by enzymes produced by bacteria and fungi. In this process yeast and heat are used to break down complex sugars into more simple sugars, producing ethanol. During the fermentation process, part of the sugar is assimilated by the yeast cells and part is transformed into glycerol, acetaldehydes and lactic acid. Production of ethanol from lignocellulosic materials such as corncob, cornstalk, cornhusk, sugarcane bagasse and sugarcane bark though faces challenges, but can substitute bio-ethanol production from edible food substances. The energy produced is both renewable and available in large quantities throughout the world. It would also allow agricultural land to be used more efficiently and at the same time prevent competition with food supplies. Until recently the problem was that the complex mixture of sugars that make up these left over materials could not be efficiently converted into ethanol by Saccharomyces cerevisiae because they have a very strong crystalline structure surrounded by lignin which makes it difficult for enzyme accessibility. However, these problems have been overcome through pre-treatments such as acid hydrolysis. Ethanol produced from agricultural waste using separate hydrolysis and fermentation also had problems as the higher concentration of reducing sugars inhibited the growth of yeast. This study reports on the production of ethanol from agricultural waste obtained from sugar cane and maize plant. The pH and the total reducing sugar of the final ethanol products were also determined. The world's present economy is highly dependent on various fossil energy sources such as oil, coal, natural gas, etc.

2. Manufacturing of Ethanol

2.1. Raw Material Required

Sugarcane: - grown in tropical and sub-tropical areas throughout the world. It is an important crop worldwide not only for sugar production, but also increasingly as a bioenergy crop due to its phenomenal dry matter production capacity. Most of worldwide bioethanol is produced from sugarcane and remaining bioethanol produced from other crops such as sugarbeet, sorghum, wheat, rice etc. Brazil is the largest producer of sugarcane (about 27% of global production) which is the main source of bioethanol production in World.

Sweet Sorghum: - is a perennial plant belongs to Phocaea family. Sweet sorghum reduces carbon emissions. Sorghum cultivated in temperate, subtropical and tropical climates. All components of the plant have economic value; the grain from sweet sorghum can be used as food, the leaves for forage, and the stalk (along with the grain) for fuel, the fiber (cellulose) either as mulch or animal feed. Its maturation period is 3-5 months which is shorter than that of sugarcane (10-12 months). It is also tolerance to salinity.

Potatoes: - Potatoes were introduced to Europe from the Americas in the second half of the 16th century by the Spanish. Today they are a food in many parts of the world and an integral part of much of the world's food supply. As of 2014, potatoes were the world's fourth-largest food crop after, wheat, and rice.

Sugar beet:- In European countries, beet molasses is the most utilized sucrose containing feedstock for bioethanol production. Sugar beet crop yields high amount of bioethanol than sweet sorghum and wheat. The advantage of sugar beet is shorter duration of crop production, high yield, high tolerance to broad range of climatic changes (e.g. drought and flood, etc.), low requirement of water and fertilizer.

2.2. Manufacturing process

Mechanical Methods:-
In this method involves the combination of chipping, grinding, shearing, or milling, which decreases the particle size and increases surface area thus facilitating the celluloses to attack on biomass surface and enhanced the conversion of cellulose to ethanol.

Chemical Methods:-
Chemical pretreatment involves the use of different chemical agents such as oxidizing agents (hydrogen peroxide and ozone), acids (H2SO4, HCl and organic acids etc.), alkalis (NaOH, Na2CO3, Ca(OH)2 and NH3 etc.), organic solvents, SO2, CO2 and other chemicals which degrades the hemicellulose and removes lignin from lignocellulose waste materials.

Acid Pretreatment:-
Acid pretreatment is a method in which agricultural waste is treated with dilute or concentrated acids (e.g. sulphuric acid,

hydrochloric, peracetic acid or nitric acid). This method hydrolyzes the polysaccharides, especially hemicelluloses to monosaccharides resulting in increased accessibility of cellulose to enzymatic hydrolysis. It can be done either under low concentration of acid and high temperature or under higher concentration of acid and lower temperature.

$$\underset{\text{Lignocelluloses}}{(C_6H_{10}O_5)} \xrightarrow[\text{Conc. } H_2SO_4]{+H_2O} \underset{\text{Reducing sugars}}{C_6H_{12}O_6}$$

Acid pretreatment have been utilized for many agriculture wastes. For instance, sorghum was pretreated with (0.5-4%) H2SO4. After enzymatic hydrolysis and pretreatment, 0.408g reducing sugars are produced. In another study, durian seed waste was pretreated with 0.6% sulphuric acid followed by enzymatic hydrolysis resulted in 50.0944g/L of glucose content. The disadvantage of using acid is causing corrosion to the equipment and formation of inhibitors (furans, carboxylic acids and phenolic compounds) which inhibits the fermentation process.

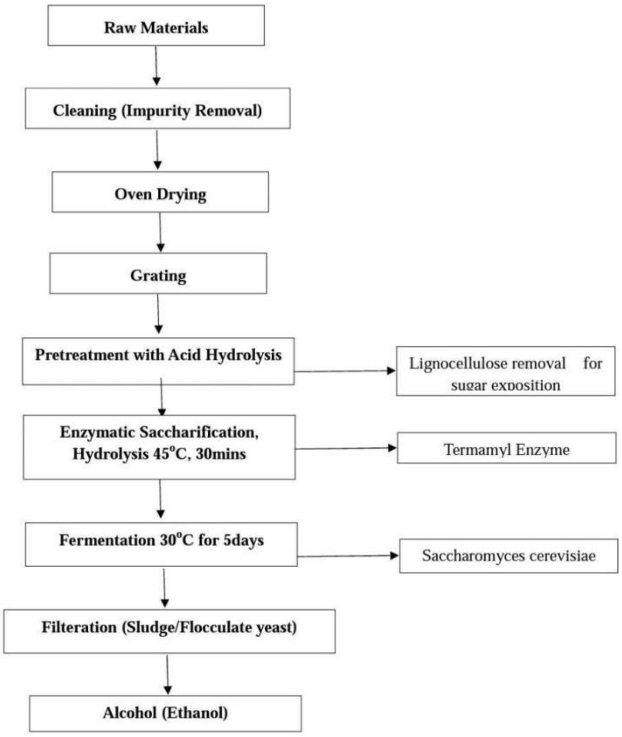


Fig -1: Flowchart of Manufacturing of Ethanol

Enzymatic Hydrolysis:-

Enzymatic hydrolysis is a process in which agriculture biomass hydrolytically break down into fermentable sugars by enzymes. Enzymatic hydrolysis is becoming more attractive as compared to acid hydrolysis because it avoids equipment corrosion, needed less energy and mild environment conditions, while fewer fermentation inhibitors are formed. Three major enzymes namely, endoglucanase, exoglucanase and cellobiase are used for the hydrolysis of cellulose. The endoglucanases attack and cleaved the cellulose chains into glucose, cellobiose and cellotriose. The exoglucanases attack the non-reducing end of cellulose and form the cellobiose units. Cellobiase converts calaboose units into D-glucose. Hemicelluloses structure is more complex therefore; several enzymes are needed for their degradation. For example, for xylan hydrolysis, the action of various enzymes is required such as endo-β- 1,4-xylanase, β-xylosidase, and accessory enzymes like α-Larabinofuranosidase, α-glucuronidase, α-galactosidase, acetylxylan esterase and feruloyl esterase. Hydrolytic enzymes obtained from both bacterial and fungal sources are used for hydrolysis of agricultural materials. Enzymes from the bacterial sources such as Clostridium, Cellulomonas, Bacillus, Thermomonospora, Ruminococcus, Bacteriodes, Erwinia, Acetovibrio, Microbispora and Streptomyces genera have been used extensively. Fungal enzymes obtained from P. chrysosporium, Trichoderma, Aspergillus, Schizophyllum, Humicola, Acremonium and Penicillium have been studied for production of hemicellulase and cellulases. Due to the limitations of bacterial species such as anaerobic nature of some bacteria and the generally low yields obtained from bacteria which attracted the scientists to the use of fungal strains for commercial enzyme preparations.

Fermentation:-

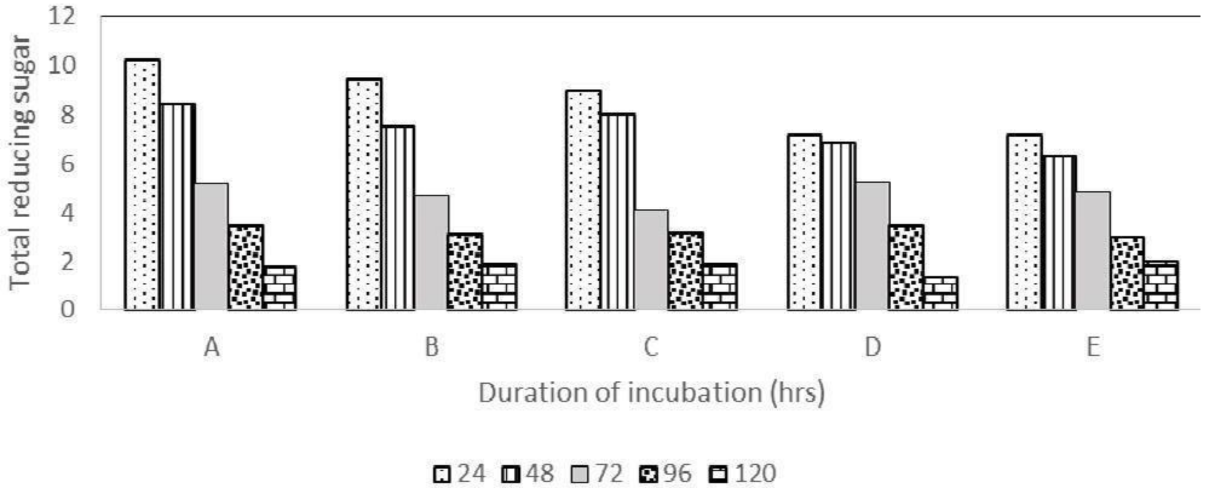
During fermentation, both pentose and hexose sugars (glucose) are fermented to bioethanol and carbon dioxide under aerobic/anaerobic conditions:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \rightarrow \underset{\text{Ethanol}}{2C_2H_5OH} + \underset{\text{Carbon dioxide}}{2CO_2}$$

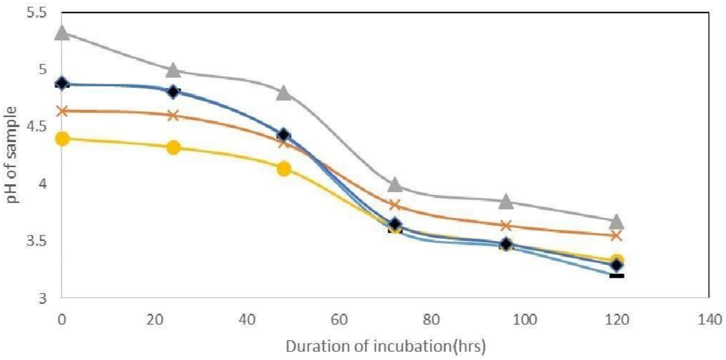
Saccharomyces cerevisiae (baker's yeast) is most commonly used for bioethanol production by fermenting the sugars (e.g. glucose, fructose, maltose and sucrose) obtained from first generation feedstocks. The main limitations of baker's yeast are that it is not capable of fermenting the pentose sugars. Therefore, genetically modified S. cerevisiae and non Saccharomyces yeasts are used for fermenting pentose sugars (e.g. xylose, arabinose) obtained from second generation feedstocks. Some other microorganisms such as Pichiastipitis, Candida shehatae and Pachysolantannophilus are also capable of fermenting both hexose and pentose sugars. Thermophilicbacteria (e.g. Thermoanaerobacterium saccharolyticum, Thermoanaerobacter ethanolicus) are of recent interest for bioethanol production from agricultural residues. These bacteria have several advantages for ethanol production such as:

1. Improved solubility of substrates,
2. Enhanced mass transfer due to decreased viscosity,
3. Increased rate of diffusion,
4. High bioconversion rates,
5. Use variety of low-cost biomass feed stocks,
6. Low risk of contamination,
7. Ferment both pentose and hexose sugars found in agriculture hydrolysates.

These bacteria also produce cellulose and hemicellulase enzymes which ferment biomass to ethanol without the addition of external hydrolytic enzymes results in decreased cost. Various systems are employed for processing and fermenting the agricultural waste. These include batch, fed batch, simultaneous saccharification and fermentation (SSF), simultaneous saccharification and co-fermentation (SSCF), separate hydrolysis and fermentation (SHF), consolidated bioprocessing (CBP).



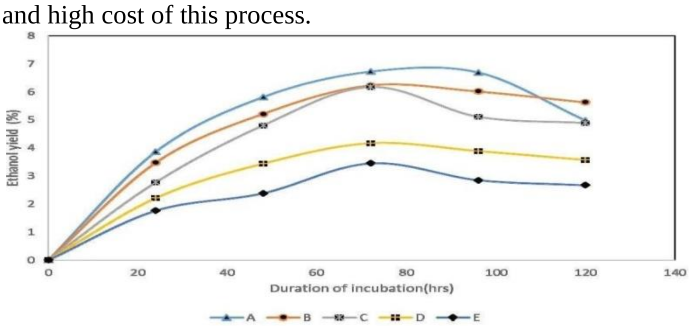
Graph 1: Total reducing sugar in fermentation.



Graph 2: pH of product during fermentation

Separation and Distillation:-

Distillation separates ethanol from water on the basis of the differences of volatilities. First, the mixture containing lignin, enzymes, unreacted cellulose and hemicellulose, yeast and various salts in the fermentation broth can be added to a distillation (beer) column to concentrate the ethanol in the overhead product and water. Solids removed from the bottom of the distillation device. Ethanol can then pass to a rectification column for concentration of the ethanol-water mixture to the azeotrope composition of about 95% by weight. The remaining product is added to the stripping column to remove extra water from this product. The bottoms solid from the first column can be further concentrated by centrifugation. If the ethanol is used as a hydrous fuel, the azeotropic mixture would be used. If anhydrous ethanol is blended with gasoline then utilize benzene or cyclohexane in distillation column. The main disadvantage associated with distillation is that impurity with similar boiling points to ethanol also recovered and high cost of this process.



Graph 3: Ethanol yield of samples.

2.3. Optimization

An efficient ethanol production requires four components: fermentable carbohydrates, an efficient yeast strain, a few nutrients and simple culture conditions.

Yeasts are most often used in the fermentation process and obtain energy from various carbon sources. Yeasts are the most common microorganisms for ethanol fermentation. Among the yeast kingdom, S. cerevisiae is one of the well known ethanol producers. Ethanol is an essential chemical which is used as a raw material for a vast range of applications including chemicals, fuel (bioethanol), beverages, pharmaceuticals and cosmetics. S. cerevisiae has short germination time and is easily cultured in large scale processes. The traditional method for optimization of parameters involves optimizing one parameter at a time. This is not only a time-consuming process, but often misses the alternative effects between components. Limitations of parameters of optimization can be eliminated by employing Response surface method (RSM) which is used to explain the combined factors in a fermentation process Generally, RSM defines the effect of the independent process variables, alone or in combinations, and generates a mathematical model that describes the entire process. Also, the RSM summarizes mathematical methods and statistical inference for an approximate functional relationship between a response variable and a set of design variables. The most popular RSM is the Central composite design (CCD) which is an efficient and flexible technique that provides sufficient information on the effects of process variables and overall experimental error with a minimum number of experiments In the purpose of present work, response surface methodology was used to optimize the culture conditions of Saccharomyces cerevisiae (MTCC 170) for maximizes the ethanol productivity.

2.4. Conversion of Agricultural waste to Ethanol

2.4.1. Composition of Agricultural Waste:-

Agricultural waste is composed of three main components: cellulose (35-50%) of the total dry weight, hemicellulose (20-35%) and lignin (10-25%). Cellulose and hemicelluloses are joined to lignin through hydrogen and covalent bonds which makes it resistant to degradation. The composition of common biomass is cellulose, hemicelluloses and lignin.

Table 1: Composition of different components of common biomass.

Agriculture Waste Feedstock	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Leaves	15-20	80-85	0
Nut shells	25-30	25-30	30-40
Softwoods stems	45-50	25-35	25-35
Grasses	25-40	35-50	10-30
Corn stover	40	29.60	23
Rice husks	36.70	20.05	21.30
Wheat straw	30	50	15
Barley husks	21.40	36.62	19.20
Rye straw	41.10	30.20	22.90
Oat straw	39.40	27.10	17.50
Rice straw	36.20	19.00	9.90
Corn stalks	35.00	16.80	7.00
Sugarcane bagasse	40.00	27.00	10.00

Cellulose:- Cellulose is a major component of agriculture biomass and found in plant cell wall. It is a linear, crystalline homopolymer polysaccharide made up of approximately 500-15,000 repeating units of D-glucose linked by β-1,4-glycosidic bonds . The structure of cellulose is rigid and compact so harsh treatment is required to obtain glucose. Cellulose chains are joined together by hydrogen and Vander Waal bonds and packed into microfibrils which make it crystalline in nature. Due to their crystalline nature cellulose becomes resistant to degradation into fermentable sugars (glucose, mannose etc.)

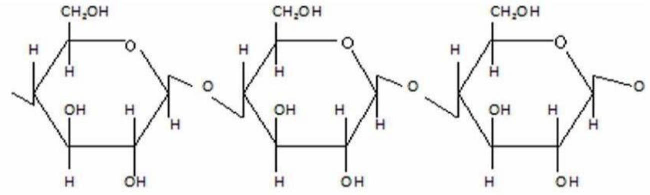


Figure 1: Cellulose

Hemicellulose: - Hemicellulose (C5H8O4)n is second major component of agriculture matter. It is a highly branched, long chain heteropolymer consist of pentose sugar (xylanose and arabinose) and hexose sugar (galactose and mannose) along with acetate units in its sidechains. It is less complex and easily converted into fermentable sugars such as pentose sugars and hexose sugars.

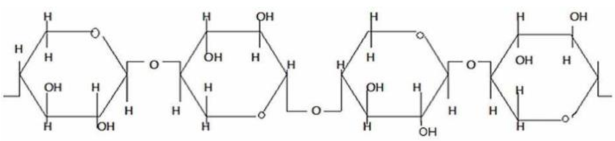


Figure 2: Hemicellulose

Lignin: - Lignin (C6H11O2) is the third major component of agriculture biomass. It is an aromatic polymer of phenyl propane units (p-coumaryl, coniferyl and sinapyl alcohol) are joined by C−O−C and C−C bonds. It is highly resistant to degradation. It is tightly linked to cellulose and hemicelluloses in agriculture biomass. Therefore, this strong linkage affects the enzyme degradation. Lignin is an amorphous heteropolymer which makes the cell wall water-resistant and protects from microbial attack. This property of lignin creates the hindrance for the conversion agriculture waste to bioethanol. Therefore, delignification of agriculture biomass should be done for efficient conversion into ethanol.

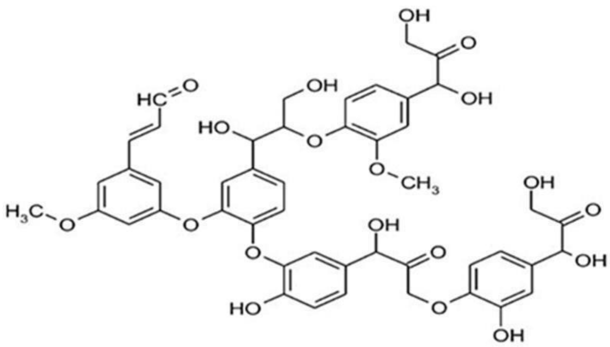


Figure 3: Lignin

2.5. Physicochemical Characteristic of Ethanol

Bioethanol is a transparent, colorless liquid with pleasant odor. The taste of ethanol is varies according to its concentration; when it is diluted has sweet flavor and has a burning taste if it is concentrated. It is the second member alcoholic group which contain hydroxyl group. The melting and boiling points of ethanol are -114.1oC and 78.5oC, respectively. The density of ethanol is 0.789 g/mL at 20oC. It forms homogeneous mixture with both types of solvents i.e. polar as well as non-polar solvents. It is also used as organic solvent and utilized in perfumes, paints, lacquer and explosive industry. Ether is formed after the dehydration of ethanol. It can be further oxidized to acetaldehyde and then into acetic acid. The detailed physico-chemical properties of bioethanol are shown in the Table. Alcoholic solutions containing non-volatile substances are called tinctures and solution having volatile substances is called spirit.

Table 2: Characteristics of Ethanol

Parameter	Characteristics
Molecular formula	C_2H_5OH
Molecular mass	46.07 g/mol
Appearance	Colorless liquid
Water solubility	Between –117°C and 78°C
Density	0.789 kg/l
Boiling temperature	78.5°C
Freezing point	–117°C
Flash point	12.8°C
Ignition temperature	lowest temperature of ignition
Explosion limits	Lower 3.5% (v/v) Upper 19%(v/v)
Vapour pressure at 38°C	50 mm Hg
Higher heating value (at 20°C)	29,800 KJ/kg
Lower heating value (at 20°C)	21,090 KJ/kg
Specific heat	Kcal/Kg 60°C
PKa	15.9
Viscosity	1.200 mPa.s (20°C)
Refractive index (*n*D)	1.36 (25°C)
Octane number	99

2.6. Comparative Account of Ethanol and Gasoline

Gasoline is a hydrocarbon used as fuel in transport sector. It is the by-product of crude oil which obtained after fractional distillation. It is hydrophobic and has a flash point of approximately -45oF, varying with octane rating. Vapour density lies between 3 and 4. It has a specific gravity of 0.72-0.76 and insoluble in water, due to these properties it floats on top of water. The gasoline internal combustion point lies from 280oC to 456oC. The boiling point of gasoline is varied from 37oC to 204oC. The high level of gasoline exposure for long time produced harmful effects to respiratory system. Bioethanol is an oxygenated fuel having 35% oxygen. Ethanol reduces particulate and nitrogen oxides (NOX) emission from combustion. Pure ethanol is polar solvent that is water soluble and has 55oF flash point. It is heavier than air vapour due to density of 1.59. The specific gravity of ethanol is 0.79, which means it is lighter than water. It is slightly soluble in water. The toxicity of bioethanol is less than gasoline and after blended with gasoline, utilized as automobile fuels. It reduces use of petroleum oil consequently it increases the oxygen in the fuel, which improve the combustion of gasoline consequently it produces less amount of greenhouse gas emission. The concentration of blending ethanol with gasoline is 10% bioethanol to 90% gasoline which is known as "E10" and commonly called "gasohol."

3. CONCLUSIONS

The potential for alcohol fuels in developing countries must be considered as part of a general biomass-use strategy that is, in turn, subverted by a broader energy supply and demand strategy. When sugarcane is the feedstock, for example, changing world demand for sweeteners, as well as the possible needs for diversification or integrated crop use, should be studied. The final strategies will necessarily reflect the needs, values and conditions of the individual nations, regions, and societies that developed them.

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