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# Fuel Ethanol from Cane Molasses: A Review of Feedstocks, Technologies, Opportunities and Challenges

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### ABSTRACT

In current scenario, Ethanol especially bioethanol (produced from biomass) has potential to substitute conventional energy sources like coal, gasoline etc. This study reviewed the literature on production of ethanol through the fermentation of molasses for its potential to replace petroleum fuels and different techniques available for the separation of ethanol from fermented wash. Metrics include: feedstocks, fermentation process, separation techniques and comparison of various techniques on the basis of their heat integration, energy consumption, cooling water requirement and pollution reduction pertaining to economics of the ethanol production. The key findings are that an agreement exists among the literature that multi pressure distillation is considerably good as compared to other techniques to warrant large-scale production but multi pressure distillation in combination with molecular dehydration is even better from the energy consumption point of view. When these findings are considered along with the marginal improvement in  $CO_2$  emissions and other pollutants, it appears that the techniques for the treatment of production waste are well developed. In summary, considering all the facts associated with the latest ethanol production technologies, it is found that still there is a large scope for the improvements. It is observed that the domain of energy and environmental impacts of the production technologies had so far been neglected.

#### 1. Introduction

Currently, most of the energy in use is produced from fossil fuels such as coal, oil and natural gas. Finite nature of fossil-fuel reserves and increasing price of crude oil; demands exploration of other alternatives. There is a strong consensus amongst the scientific community across the world about the environmental impact of greenhouse gas emissions and world-wide warming trends caused by anthropogenic greenhouse gas emissions, primarily carbon dioxide. In fact, the expected warming trends can already be observed in recent measurements - 11 of the last 12 years are among the hottest on record since 1850. The combination of these factors has motivated the need for research and development of alternative energy sources ranging from solar, wind, and hydrogen to biomass. Since the transportation sector is one of the largest consumers of energy, it is necessary to find viable options to reduce the amount of harmful emissions produced from vehicles as well as the emissions produced from the production of fuel [1]. From the vast literature survey, it is found that biofuels are the only alternative to have potential to cater the need of transportation sector with minimal impact on the environment.

One of the major advantages of biofuel is that the biomass has direct effect with respect to carbon sequestration. The plants naturally absorb carbon from the atmosphere, aiding in the sequestration of carbon dioxide. The current state of knowledge on biomass fuels is limited due to differences in the literature and the still developing technology for biomass fuels. Ethanol is found to have a great potential to come up as an environmentally clean transportation fuel. Traditionally, ethanol can be produced by catalytic conversion of ethylene and microbial fermentation. But because of scarcity of petroleum feed stock and in abundance availability of renewable raw materials for fermentation, the fermentation process is more attractive than catalytic conversion process [2]. The aim of this paper is to bring together the various sources of data and to produce a comprehensive study of feed stocks, fermentation process, separation techniques and comparison of various techniques required for the production of ethanol. This comparison will focus on the basis of heat

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integration, energy consumption, cooling water requirement and pollution reduction pertaining to economics of ethanol production.

#### 2. Experimental Methods

#### 2.1 Feedstock

Ethanol can be produced from any biological feed stock that contains simple sugars (monosaccharide). All ethanol feed stocks contain sugars that are linked together in structures that differ in complexity and reactivity. Through a variety of treatments, feed stocks are reduced to their component sugars which further converted into ethanol. Feed stocks used in the production of ethanol are classified as sugary, starchy and cellulosic feed stocks.

#### 2.1.1 Sugary Feed Stock

Sugary feed stocks for production of ethanol includes Sugar Cane, different grades of molasses, Beet and Sweet Sorghum etc. The sugars in these feed stocks are easy to extract and ferment, making large-scale ethanol production affordable. Molasses is an abundant byproduct of the sugar industry that is at present one of the cheaper sources of sugar, and in contrast to grain, it does not require hydrolysis of starch [3]. Sugar cane molasses is the main feedstock for ethanol production in India; cane juice is not presently used for this purpose [4]. Table 1 indicates the properties and composition of molasses whereas Table 2 indicates the properties and composition of fermented wash produced from the fermentation of molasses.

#### 2.1.2 Starchy Feed Stock

Starchy feed stocks include Grains like Wheat, Corn, Rice, Millet, Sorghum, Rye, Barley, Triticale and Tubers such as Tapioca (Cassava/Mandioca) [5], Potato, etc. Amongst above corn is the major feed stock available for production of ethanol. Corn ethanol is derived from the sugars contained in corn starch, a carbohydrate that comprises the bulk of the dry weight of a kernel of corn. Starch is a polymer of glucose, a simple six carbon sugar (hexose), which can readily be fermented using commercially available microorganisms. Before fermentation, the starch must be broken down by treatment with dilute sulfuric acid, enzymes, or both [6, 7].

#### 2.1.3 Cellulosic Feed Stock

Cellulosic feed stocks are made up of three key components: cellulose, hemicellulose, and lignin. These feed stocks also contain small quantities of ash, proteins and lipids. Cellulose accounts for 35–50% of the dry weight of cellulosic biomass and is made up of long chains of glucose that can be separated by the hydrolysis reaction with water using enzymes or diluted acid as a catalyst. Processing of cellulose is more difficult than starch because of strong hydrogen bonds that hold the glucose chains together in a highly organized structure. Hemicellulose comprises 20–35% of the dry-weight of cellulosic biomass and is a polymer of several sugars including some five carbon sugars or pentose.

Amorphous structure of hemicelluloses makes it easier to convert to sugar than cellulose. Lignin accounts for 12–20% of the dry-weight of cellulosic biomass and is not a sugar-based material. But lignin is important because of its energy value; power is often generated from lignin at the ethanol plant through combustion with steam generation or via gasification [8-10]. Cellulosic feed stocks are classified into four nonfood based general categories based on the sources as: agricultural residues, forestry residues, municipal solid wastes, and energy crops. Agricultural wastes are typically plowed back into the soil, composted, burned, or taken to landfills. For information on forestry residues, municipal solid wastes, and energy crops, readers are advised to see [11, 12, 13]. Demirbas [14] reported that in the production of ethanol from cellulosic biomass, a pretreatment process is necessary to reduce the sample size, break down the hemicelluloses to sugars and open up the structure of the cellulose component.

The cellulose portion is hydrolyzed by acids or enzymes into glucose sugar that is fermented to ethanol. The sugars from the hemicelluloses are also fermented to ethanol. The comparative study of these feed stocks reveals that cellulosic feed stocks offer many advantages over starch and sugar based feed stocks. They are available in abundance and can be used to produce more substantial amounts of ethanol. They are waste products or trees and grasses grown specifically for ethanol production, can be grown on marginal lands not suitable for other crops. Less fossil fuel energy is required to grow, collect, and convert them to ethanol, and they are not used for human food. But there are challenges with harvesting, collecting, and delivering cellulosic feed stocks. Researchers are studying these challenges in order to formulate the feasible solutions to them.

#### 2.2 Fermentation

In a distillery, ethanol is produced by the fermentation of molasses. Several microorganisms, including Saccharomyces cerevisiae [15-17], Kluyveromyces marxianus [18], and Zymomonas mobilis [19-22] are the well-known ethanol producers but the yeast, Saccharomyces cerevisiae, is largely employed in ethanol production using renewable biomass molasses as the main carbon source [3]. The properties and characteristics of molasses shown in Table 1 are determined from the various methods like spectrophotometric method for dextrose sugar analysis, refractometer for brix degree measurement etc. For detail study on analysis of molasses, growth kinetics, mathematical model of ethanol formation, substrate consumption and inhibition readers are advised to refer Ghorbani and Younesi [23]. The ethanol fermentation can be carried out in batch, fed-batch or continuous mode. Ethanol produced via batch mode is the basis for fermentation research to investigate and collect the information about yeast growth, sugar concentration, and yield. In fermentation process initially molasses are diluted with water in 1:5 (molasses: water) ratio by volume. The resulting solution is then received in a large tank and yeast is added to it at 30 °C and kept for 24-36 hours.

Fermentation of molasses is a two-step process, in the first step sucrose present in the molasses is hydrolyzed to glucose and fructose; in the second step glucose and fructose is converted into ethanol and carbondioxide. The enzymes invertase and zymase present in the yeast Saccharomyces cerevisiae acts as a catalyst for the first and second reaction respectively [24]. These yeasts cannot sustain at a higher alcohol concentration of 10-15% which acts as an important rate limiting factor. The fermented wash produced as a product of reaction consists of ethanol, dissolved solids, suspended solids, unfermentable sugar, sludge etc. The produced fermented wash is then sent for distillation where the alcohol content of the wash is stripped of and ethanol of approximately 95.5%(w/w) concentration is recovered. Further concentration of ethanol using distillation is not possible because ethanol and water forms an azeotrope at this composition (95.6% ethanol). No number of distillations, however, will ever result in a distillate that exceeds the azeotropic ratio. Further enrichment of ethanol must obviate azeotropic point.

$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6 \\ C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2 \end{array}$$

Table 1 Composition and properties of molasses

Sr. No.	Parameter	Units	Concentration Range
1	Density of Molasses	kg/m <sup>3</sup>	1350
2	Color	-	Dark Brown
3	Odor	-	Sugary
4	Total Solids %	w/w	73 - 80
5	Total Reducing Sugar %	w/w	48.5 - 52
6	Un Fermentable Sugar %	w/w	4.0 - 4.5
7	Fermentable Sugar %	w/w	44.5 - 47.5
8	F/N Ratio	-	1.46 - 1.56
9	Sludge %	w/w	1.96 - 3.1
10	Total Volatile Acidity	mg/lit	2500 - 4000
11	pH at 40°Bx	-	4.6 - 5.0
12	Total Viable Count	cfu/gm	5.5x10 <sup>2</sup> - 2.4x10 <sup>4</sup>
13	Butyric acid	mg/lit	4.5 – 95
14	Iso-Butyric acid	mg/lit	105 - 212
15	FAN	mg/lit	4500 - 5000

Table 2 Composition and properties of fermented wash

Sr. No.	Parameter	Units	Concentration Range
1	Density of Fermented Wash	kg/m <sup>3</sup>	1050
2	Color	-	Dark Brown
3	Odor	-	Sugary
4	Ethanol %	v/v	12 - 15
5	Water %	v/v	80 - 85
6	Total Solids	mg/lit	52000 - 86000
7	Total Suspended Solids	mg/lit	3000 - 5000
8	Total Dissolved Solids	mg/lit	49000 - 81000
9	рН	-	5.0 - 5.5

#### 2.3 Techniques for Ethanol Separation

The ethanol concentration in the fermentation broth is about 10%. Different techniques are available for the recovery of ethanol from fermentation broth. In this study, the possibilities of various techniques for the removal of water from ethanol-water azeotropic mixture are explored. The objectives of this work are to minimize the water content in the final ethanol product at a lower capital and energy cost compared to conventional technologies. One of the major costs contributing in the production of anhydrous ethanol is the energy cost. These techniques can be classified as follows:

A) The techniques/processes like reverse osmosis [25] that can be directly employed for the recovery of ethanol from fermentation broth in order to produce commercial ethanol.

B) The techniques/processes like ultrafiltration, pervaporation [26, 27] that cannot be employed directly but can be employed in combination for the recovery of ethanol from fermentation broth in order to produce commercial ethanol.

C) The techniques/processes like azeotropic distillation, catalytic distillation [28], adsorptive distillation [29], molecular sieve dehydration, that cannot be employed directly but can be employed after simple distillation for recovery of ethanol from fermented wash in order to produce fuel ethanol. The aforementioned techniques have their own merits and demerits.

#### 2.4 Reverse Osmosis

Reverse osmosis is basically a water purification technology that uses a semi permeable membrane in which applied pressure is used to overcome osmotic pressure, a colligative property, that is driven by chemical potential, a thermodynamic parameter. In reverse osmosis the solute is retained on the pressurized side of membrane and pure solvent is allowed to pass to other side of the membrane. Years back this technique was used for the separation of ethanol from fermented wash with the prime objective of replacing the conventional distillation approach in order to make the process less energy intensive. Choudhury et al. [25] concluded that Permeability and separation efficiency are the two most important factors governing the performance of membrane in terms of separation. It is observed that increase in operating pressure causes both the flux and separation efficiency to increase. But increases in alcohol concentration in the feed causes a considerable drop in permeate flux. Using reverse osmosis the separation of ethanol up to the maximum concentration of 93 % is possible, but the separation efficiency decreases with increase in alcohol concentration in the feed.

#### 2.5 Pervaporation

Pervaporation is a membrane process for liquid separation in which two components are separated with a nonporous polymeric or inorganic membrane through the combination of different permeation rates of the components. Commonly, vacuum is applied on the downstream side of the membrane for an evaporative phase change to occur [26]. According to the vapor-liquid equilibrium curve of ethanol-water, the mass fraction of ethanol in vapor is much higher than its mass fraction in liquid when the ethanol concentration in liquid is between 0 to 20%. Moreover, pervaporation has an inherent selectivity for ethanol from fermentation broth as it is produced thus reducing the inhibitory effect of high ethanol concentration. This approach would also allow for a continuous fermentation. The separation membrane is the key element in pervaporation equipment. The pervaporation performances of membrane are generally characterized with flux and selectivity.

There are two steps of the process: permeation through membrane by permeates, and its evaporation into the vapor phase. The membrane acts as a selective barrier between the two phases: the liquid-phase feed and the vapor-phase permeate. It allows the desired component of the liquid feed to transfer through it by vaporization. Separation of components is based on a difference in transport rate of individual components through the membrane. Typically, the upstream side of the membrane is at ambient pressure and the downstream side is under vacuum to allow the evaporation of the selective component after permeation through the membrane. Driving force for the separation is the difference in the partial pressures of the components on the two sides. Years back this technique was used for the separation of ethanol from fermented wash with the prime objective of replacing the conventional distillation approach in order to make the process less energy intensive. But the major concern in this technique is of membrane materials.

Peng et al. [27] reported that though the lot of membrane materials is available for recovery of ethanol from dilute fermentation broths, the material with good ethanol-permselective properties are few and their pervaporation performances do not meet the demands of industrialization at this stage. They further reported that Polydimethylsiloxane (PDMS) commonly Known as silicone rubber is found to be the most suitable alcohol-permselective membrane material for the removal of alcohol from aqueous solutions at low alcohol concentrations because of its hydrophobic nature. Beaumelle et al. [30] in his review paper reported that the fluxes of unmodified PDMS membranes ranged from 1 to 1000 g/m<sup>2</sup>h and the separation factors were less than 10 for the removal of ethanol by the pervaporation process. O'Brien et al. [31] after analyzing the fermentation-pervaporation processes of a commercial-scale fuel ethanol plant, concluded that a coupling system would be cost-competitive if the performances of pervaporation membranes could be improved modestly so as to exhibit the flux of 150 g/m<sup>2</sup>h and separation factor of 10.3 for ethanol to water. But the general disadvantage of this process is its relatively high energy consumption in comparison to pressure-driven membrane processes such as reverse osmosis and ultrafiltration where no phase transition occurs. The pervaporation process consumes an amount of energy which is at least equal to the heat of vaporization of the complete pure product that has to be separated [32]. Another disadvantage of the process is that it should be used in combination with ultrafiltration; application of pervaporation process directly to the fermentation broth will result in the chocking of membrane.



Fig. 1 Symbolic diagram of Ultrafiltration + Hybrid pervaporation process

Mulder et al. [32] reported that considerable cost saving can be achieved by using various membrane processes, such as ultrafiltration, reverse osmosis and electro dialysis in combination with distillation. The combination of ultrafiltration and pervaporation makes it possible to remove and concentrate ethanol during a continuous fermentation process. Fig. 1 shows the symbolic diagram of ultrafiltration + hybrid pervaporation process. In the first step fermentation broth from fermenter is sent for ultrafiltration where the cell mass is retained on the feed side and permeate having ethanol concentration of about 5 to 10 % by weight is obtained at the other side of membrane. The cell mass is recycled back to the fermenter while the permeate is sent for Pervaporation-I having ethanol selective membrane Ultrafiltration can be used as a cell recycle system, where the rejected cells are returned to the fermenter and the ethanol is removed. Thus, the rate of ethanol production remains high. The ethanol concentration in the ultrafiltration permeate will be about 5 to 10 % by weight. In order to keep the energy consumption of this process as low as possible, the ethanol concentration in the feed must be high. To get the high ethanol concentration in the feed, the water should be preferentially removed. It results into two-stage pervaporation process with ethanol-selective membranes which gives permeate having ethanol concentration up to 40 % in the first stage and water-selective membranes in the second stage. But from a commercial point of view, the purification of ethanol from 5% to 99% by pervaporation alone is not attractive [32]. Besides this, necessary reheating of the feed stream and cooling of permeate makes pervaporation, the much costlier than its rivals.

#### 2.6 Distillation

The concentration of ethanol in fermentation broth is approximately 10% by weight. The recovery of ethanol from fermentation broth and its enrichment up to 95% by weight is achieved solely by distillation; further enrichment of ethanol up to 99.5% by weight to produce commercial ethanol is not possible by distillation since the ethanol water mixture form homogeneous azeotrope at this composition which limits the separation by simple distillation. Further enrichment of ethanol must obviate the azeotrope point. To overcome this limitation and to obtain anhydrous ethanol, hybrid processes coupling simple distillation, adsorptive distillation, multi-pressure distillation, membrane processes, or adsorption [33] are often used.

#### 2.6.1 Azeotropic Distillation

Azeotropic distillation is a technique in which a third component known as an entrainer is added to break up the binary ethanol-water azeotrope. The third component could be benzene, cyclohexane, or pentane. Azeotropic distillation followed by simple distillation completely removes the water from the mixture to produce anhydrous ethanol of 99.5% by weight. However, azeotropic distillation seems to be a very energy intensive process because ethanol must be distilled twice to recover the added third component. Parkinson [34] in his paper reported that the energy required to enrich the ethanol from 95% at azeotropic point to 100% (pure anhydrous ethanol) requires about half the energy required in enriching ethanol from an initial 10% ethanol mixture to 95% at azeotropic point. This process is also proved to be capital intensive because of the need for additional distillation columns. Also the use of carcinogens like benzene makes it a second choice.

#### 2.6.2 Extractive Distillation

Extractive distillation is a technique employed to separate systems which are either impossible (due to the existence of an azeotrope) or uneconomical (due to excessively low relative volatility) to separate by normal distillation. It is quite similar to that of azeotropic distillation. In extractive distillation a third component is fed to the column, where its molecules form an association complexes in the liquid phase with the molecules of the two feed components, thus lowering both of their volatilities. The separating agent is chosen in such a way that its molecules will associate preferentially with the molecules of the less volatile feed component over those of the other. As a result, the volatility of the less volatile component will be lowered by an amount greater than that of the more volatile component, thus raising the relative volatility of the system and thereby reducing the number of ideal stages required to achieve the separation. Further [35] reported that extractive distillation is costly as compared to that of normal fractional distillation, a consequence of both increased capital costs and increased energy costs arising largely from the requirement for recovery and recycle of the separating agent, which normally must be used at very high concentration to achieve its desired effect.

#### 2.6.3 Extractive Distillation by Salt Effect

Salt effect distillation is a novel variation on extractive distillation in which the agent added to the column to effect the separation is a salt rather than a liquid. This technique offers the major energy savings over conventional processing, primarily in the dehydration of ethanol. In certain systems where solubility considerations permit, it is possible to use a salt dissolved into the liquid phase as the separating agent in place of the normal liquid additive. The attraction of this technique lies in its potential for greatly reduced energy requirements compared with conventional extractive and azeotropic distillation processes. The salt, which must be soluble to some extent in both feed components, is fed at the top of the column by dissolving it at a steady rate into the boiling reflux just prior to entering the column. Further [35] concluded that the salt, being nonvolatile, flows entirely downward in the column, residing solely in the liquid phase. Therefore, no knockback section is required above the separating agent feed point to strip agent from the overhead product. Recovery of the salt from the bottoms product for recycle is by either full or partial drying, rather than by the subsequent distillation operation required with liquid separating agents.

#### 2.6.4 Catalytic Distillation

Catalytic distillation, which has been proven to be a very high efficiency process to produce ether oxygenates [36], seems to be very promising for the removal of water from ethanol water mixture. It's a process in which a heterogeneously catalyzed chemical reaction and separation of the products from reactants occur simultaneously in a single distillation column [37]. The combination of reaction and separation in a single column brings the significant reduction in capital and energy costs. Inside the column, solid catalyst is surrounded by boiling liquid, therefore the heat released by exothermic reactions can be efficiently utilized in the generation of more vapor, thus reducing the reboiler duty. Catalytic distillation is most suitable for equilibrium-limited reactions because the reaction products formed can be distilled away from reactants, thus shifting the chemical equilibrium toward 100% conversion. Till date, no detailed experimental and simulation results have been reported on the removal of water from ethanol by catalytic distillation. In a catalytic distillation column water can be removed by reacting it with olefins. The olefin used in this work was isobutylene [2].

#### 2.6.5 Adsorptive Distillation

Al-Rub et al. [29] reported that adsorptive distillation is a process for the separation of liquid mixtures in which inert packing material in a packed distillation column is replaced by active packing material. The active packing material affects the intermolecular forces among the system components and thus alters its vapor-liquid equilibrium (VLE). The VLE of the ethanol-water system at 1 atm was studied using a circulation still in the absence and in the presence of different amounts of 4 Å molecular sieves. Further he concluded that the VLE of the system was altered in the presence of the molecular sieves, the azeotropic point of the system was eliminated and considerable separation of azeotropic mixture was achieved and the alteration in the VLE of a given binary mixture is a function of the pore size and the amount of the molecular sieves. These results prove the feasibility of using active packing materials to alter the VLE of binary mixtures.

#### 2.6.6 Atmospheric Distillation

Atmospheric distillation is the technique used for the production of ethanol from fermented wash in a distillery. It is a seven column system, in this technique all the columns are operated at atmospheric pressure. In this process each distillation column is supplied with saturated steam to meet its heat requirement. The vapor coming from the top of each column are get condensed by using condenser with the help of cooling water from cooling tower. The energy consumption in this process is quite a high as there is no heat integration in the process. For the process to be work on the atmospheric distillation the size of the boiler is quite a high as each column in the process is supplied with steam, also the size of the cooling tower required is nearly a double as compared to that of multi-pressure distillation technology as condensers are provided on the top of the each column. The major concerned about atmospheric distillation is its high steam consumption. Another concerned is its high cooling water requirement to remove the latent as well as sensible heat from top vapors of the each column. Moreover there are chances of scaling due to invert solubility of certain precipitating inorganic salts. All these things make the operation uneconomical.

#### 2.6.7 Multi-Pressure Distillation (MPRD)

MPRD is a latest technique employed in the bioethanol production. It is a seven column system, in which two columns are operated at pressure, three at vacuum and two at atmospheric pressure. Only two columns operating at pressure are supplied with saturated steam to meet its steam requirement. Vapor coming from the top of these two columns are used as a source of heat for three columns operating under vacuum and one columns operating at atmospheric pressure. Heat requirement of remaining one column is met by the flash steam generated from the steam condensate. The energy consumption in this process is quite a low as compared to that of atmospheric distillation process (Table 3). Patil et al. [38] further exercises the rigorous analysis of energy (steam) consumption in MPRD and found that application of MPRD lowers the energy (steam) consumption from 5.8 to 3.2 kg/litre of produced ethanol. He further reported that process integration is a key for reducing costs of bioethanol production and increasing bioethanol competitiveness to conventional fossil fuels. For the process to be work on the multi-pressure distillation the size of the boiler is also reduced as only two columns are supplied with steam, also the size of the cooling tower required is nearly half the size required for atmospheric distillation process as only few condensers are provided on the top of the column. This technique is useful only for the production of potable grade alcohol i.e. 96.5% V/V.

Pribic et al. [39] reported that vapor recompression is probably the best known arrangement for energy savings in distillation. It consists of taking the overhead vapors of a column, condensing the vapor to liquid, and using the heat liberated by the condensation to reboil the bottoms liquid from the same column. The temperature driving force needed to force heat to flow from the cooler overhead vapors to the hotter bottoms product liquid is ascertained by either compressing the overhead vapor and condense at a higher temperature, or by lowering the pressure on the reboiler liquid to make it boil at a lower temperature and subsequently compressing the bottoms vapor back to the column pressure. But vapor recompression is not suitable for all separation applications. It is attractive for applications involving near-boiling point products and in particular applications with a small temperature differential between the bottom and top of the column. As a part of energy conservation in conventional distillation system, Bhole et al. [40] also developed a new single stage distillation technique with artificial irrigation by external re-circulation pump. After successful testing of technique for methanol-water system, he concluded that irrigation in stage by external re-circulation pump offers significant enhancement in rectification and is clearly observed in terms of increased MVC (Methanol) concentration in distillate. Patil and Patil [41] in their paper discussed the comparative performance of various types of trays and concluded that movable valve trays (valve tray with movable flapper) offer better operating characteristics over conventional trays. They perform great when As far as the domain of efficiency, capacity, turndown and maintenance is considered; movable valve tray performs great at slightly higher cost.

#### 2.7 Molecular Sieves Dehydration

Jeong et al. [42] suggested that molecular sieve dehydration is a promising alternative to conventional dehydration processes and a good attempt in reducing the energy consumption over conventional dehydration processes. Molecular sieve technology operates on the principle of pressure swing adsorption (Fig. 2) [43]. The process consists of two absorber beds filled with 3 Å zeolite molecular sieves that are subjected to adsorption and desorption of water alternately. 3 Å zeolite based on its specific pore size retains the water molecules from vapors of ethanol water mixture, preventing the ethanol molecules to pass through it, since the micro pores are too small to be penetrated by alcohol molecules. During the pressurized adsorption step water vapor is adsorbed on the molecular sieve and ethanol is condensed after exiting the adsorption column.



Fig. 2 Symbolic diagram of molecular sieve dehydration

During regeneration of the column water is removed by depressurizing the column and purging the bed with a portion of the purified ethanol vapor. This process is characterized by low steam and power consumption but also requires high capital investment. In this case, electrostatic interactions and polarity are the main forces between the adsorbent and the mixture. Although both ethanol and water are polar, only water molecules (diameter 0.28 nm) are able to pass through the pores as the diameter of ethanol molecules is too large (diameter 0.44 nm) to pass through the pores (diameter 0.3 nm) of zeolite. Thus the water molecules enter through the pores and are trapped in the cages of the zeolite. The ethanol passes through the column and is collected. Both liquid and vapor-phase adsorption are technically possible, but vapor-phase adsorption is usually preferred, which involves the evaporation and superheating of the ethanol water mixture prior to its exposure to the molecular sieve bed [44].

Adsorption of water on the zeolite is a strongly exothermic process. As soon as ethanol water vapor enters the bed, rapid water adsorption followed by significant heat generation takes place. Cote et al. [45] reported that a basic difference in membranes and molecular sieves used for water removal is that the productivity of a membrane system increases with water concentration, while the productivity of molecular sieves decreases with water concentration. This is so because the flux through the membrane is proportional to the water concentration in the feed while the water holding capacity of a molecular sieve is finite.

#### 2.8 Environmental, Economic and Social Aspects of Ethanol Production

Production of ethanol from any feedstock is associated with the emission of pollutants. When feedstock is delivered to the plant, handled and milled, tiny particles (diameter less than 10 microns) are released in the air. These particulate matters also get released in the air when residual solids are dried in the dry mill process. During fermentation and distillation, volatile organic compounds (VOCs) are released in the air. Carbon monoxide and dioxide (CO and  $CO_2$ ), nitrogen oxides (NOX), and sulfur oxides are generated from combustion in the boilers of plant. In average, 73% of ethanol produced worldwide corresponds to fuel ethanol, 17% to beverage ethanol and 10% to industrial ethanol [46]. Ethanol is the most employed liquid biofuel used either pure, or mixed with petrol or as an oxygenated fuel additive [47]. Moreover ethanol has greater octane booster properties, it is not toxic, and does not contaminate water sources. Also the production cost of ethanol production is less than its competitor MTBE [48].

Most of the countries in the world are dependent on gulf countries for oil; in view of being independent form this dependency, it is necessary to undertake certain efforts. One of the parts of these efforts is to minimize the import of oil resulting in the remarkable increase in fuel ethanol production. Moreover increase in fuel ethanol production would causes increase in infrastructural setup in a country. The increase in fuel ethanol production would result in generation of employment in the rural areas boosting the economy of these areas. Availability of employment at the rural area itself; prevents the migration of the youths from the areas towards the cities. The prevention of migration results in the reduction of Availability of unfeasible load on the urban facilities available. employment at the rural area prevents the youths from earning the money from criminal means. Sheehan and Himmel [49] reported that, diversification of fuel portfolio could bring the money and jobs back into the economy. Among the new research trends in this field, process integration is the key for reducing costs in ethanol industry and increasing bioethanol competitiveness related to gasoline [50]. Also the great concern of the environmental pollution gets addressed satisfactorily since the burning of fuel ethanol results in the less pollution as compared to that of conventional fuels.

#### 3. Results and Discussion

Ethanol can be produced from any biological feed stock that contains simple sugars (monosaccharides). These feedstocks are further classified as sugary feedstocks like Sugar Cane, different grades of molasses, Beet and Sweet Sorghum, starchy feedstocks like Wheat, Corn, Rice, Millet, Sorghum, Rye, Barley, Triticale and Tubers such as Tapioca, Potato and cellulosic feedstocks like agricultural residues, forestry residues, municipal solid wastes, and energy crops. All ethanol feed stocks contain sugars that are linked together in structures that differ in complexity and reactivity. Through a variety of treatments, feed stocks are reduced to their component sugars that can then be converted into ethanol. Out of these feedstocks sugary feedstocks are easy to extract and ferment, making large-scale ethanol production affordable. The complexity of production process depends on the feedstock and the spectrum of designed and implemented technologies extends from simple conversion of sugars by fermentation, to the multi-stage conversion of lignocellulosic biomass to ethanol. In a distillery, ethanol is produced by the fermentation of molasses. Out of the capable microorganisms yeast, Saccharomyces cerevisiae are largely employed in ethanol production using molasses as a main carbon source. The fermentation of molasses which is a two-step process can be carried out in batch, fed-batch or continuous mode but the later is preferred for large scale production. The enzymes invertase and zymase associated with the yeast acts as a catalyst for the fermentation reactions. Ethanol concentration in fermented wash is about 10 % and acts as an important rate limiting factor.

Different techniques are available for the recovery and concentration of ethanol from fermented wash and have their own merits and demerits. However, combination of multi-pressure distillation and molecular sieve dehydration seems to be most reliable, convenient and economically optimized choice. Multi-pressure distillation alone concentrates the ethanol approximately upto 95.5% (w/w). Since ethanol and water forms an azeotrope at this composition (95.6% ethanol), further concentration of ethanol using distillation alone is not possible therefore molecular sieves are employed and further dehydration of ethanol upto 99.5% is achieved. Production of ethanol from any feedstock is associated with the emission of pollutants. At every stage of the plant operation different pollutants like tiny particles (diameter < 10 microns), volatile organic compounds, carbon monoxide and dioxide, nitrogen and sulfur oxides are released in the atmosphere. But even these pollutants are justified as compared to carcinogens released in the burning of fossil fuels. Due to the biotechnological production of ethanol, the great concern of the environmental pollution gets addressed satisfactorily since the burning of fuel ethanol results in the less pollution as compared to that of conventional fuels.



Fig. 3 Steam consumption/litre ethanol



Fig. 4 Cooling water requirement

In average, 73% of produced ethanol worldwide corresponds to fuel ethanol, 17% to beverage ethanol and 10% to industrial ethanol. The domain of ethanol applications is wide ranging from fuel, fuel additive, gasoline enhancer to cosmetics. Moreover ethanol has greater octane booster properties, it is not toxic, and does not contaminate water sources. Also the production cost of ethanol production is less than its competitor MTBE. Most of the countries in the world are dependent on gulf countries for oil; in view of being independent form this dependency, they are remarkably undertaking the efforts to establish the infrastructural setup for the production of bioethanol. It results in the generation of employment in the rural areas boosting the economy of these areas. Establishment of infrastructural setup for bioethanol production emerge as a solution to lot of sevier social problems like unemployment, boosting of rural economy, youth migration towards urban areas, reduce the load of migrants on facilities available for the natives. In short, diversification of fuel portfolio could bring the money and jobs back into the economy. Moreover, the development of energy crops dedicated to the biofuels production would imply a boost to agricultural sector.

Table 3 shows the comparative study of atmospheric distillation and multi-pressure distillation from energy consumption point of view. It is observed that the no of columns required for desired duty are same in both

the cases. In case of atmospheric distillation, steam must be supplied to all the columns at 1.5 +/- 0.05 kg/cm<sup>2</sup>(g) at 128 °C whereas in case of multipressure distillation only two columns has to be supplied with steam at 3.5 +/- 0.05 kg/cm<sup>2</sup>(g) at 148 °C. Heat integration and flash steam generation is not achieved in case of atmospheric distillation whereas it is achieved in case of multi-pressure distillation. Fig. 3 graphically shows that steam consumption for ATD and MPRD is 6.60 and 3.40 kg/litre of ethanol produced respectively.

Table 3 Comparison of operating parameters

C. N.	. Parameter	Atmospheric	Multi-Pressure
Sr. NO.		Distillation	Distillation
1	Distillation Column	07	07
2	Reboilers	06	06
2	No. of Column Supplied by	07	02
3	Steam		
4	Flash Steam Generation	NO	YES
5	Heat Integration	NO	YES
<i>(</i>	Steam Requirement/Litre	6.06 kg	3.40 kg
6	Ethanol		
7	Cooling Water Requirement	700 m <sup>3</sup> /hr	450 m <sup>3</sup> /hr
0	Steam Properties Requirement	1.5 +/- 0.05	3.5 +/- 0.05
0		kg/cm <sup>2</sup> (g) at 28°C	kg/cm <sup>2</sup> (g) at 48 °C

In case of atmospheric distillation, cooling water must be supplied at 700 m<sup>3</sup>/hr at 32 °C whereas in case of multi-pressure distillation cooling water should be supplied at 450 m<sup>3</sup>/hr at 32 °C. Fig. 4 graphically shows that cooling water requirement for ATD and MPRD is 700 and 450 m<sup>3</sup>/hr respectively.

#### 4. Conclusion

Considering all the facts associated with technologies available for the biotechnological production of ethanol, it is observed that the complexity of production process depends on the feedstock and the spectrum of designed and implemented technologies extends from simple conversion of sugars by fermentation, to the multi-stage conversion of lignocellulosic biomass to ethanol. Besides different technologies, multi-pressure distillation and molecular sieve dehydration seems to be the most reliable, convenient and economically optimized choice. Multi-pressure distillation alone concentrates the ethanol approximately upto 95.5% (w/w) and molecular sieves dehydrates ethanol upto 99.5%. Though these technologies are associated with the emission of pollutant; these pollutants are justified as compared to carcinogens released in the burning of fossil fuels. Due to the biotechnological production of ethanol, the great concern of the environmental pollution gets addressed satisfactorily since the burning of fuel ethanol results in the less pollution as compared to that of conventional fossil fuels. There is a wide range of ethanol applications ranging from fuel, fuel additive and gasoline enhancer to cosmetics. The less production cost of bioethanol makes it more attractive fuel additive as compared to its rivals MTBE. Establishment of infrastructural setup for bioethanol production emerge as a solution to lot of severe social problems like unemployment, boosting of rural economy, youth migration towards urban areas, reduce the load of migrants on facilities available for the natives. In short, diversification of fuel portfolio could bring the money and jobs back into the economy. Moreover, the development of energy crops dedicated to the biofuels production would imply a boost to agricultural sector.

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