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FACULTY OF ENGINEERING &
TECHNOLOGY

INDUSTRIAL ALCOHOL PRODUCTION

•Ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$ (synonyms: ethanol, methyl carbinol, grain alcohol, molasses alcohol, grain neutral spirits, cologne spirit, wine spirit), is a colorless, neutral, mobile flammable liquid with a molecular weight of 46.47, a boiling point of 78.3 and a sharp burning taste.

•Although known from antiquity as the intoxicating component of alcoholic beverages, its formula was worked out in 1808. It is rarely found in nature, being found only in the unripe seeds of *Heracleum giganteum* and *H. spondylium*.

•Ethyl alcohol undergoes a wide range of reactions, which makes it useful as a raw material in the chemical industry.

•Some of the reactions are as follow:

(i) Oxidation: Ethanol may be oxidized to acetaldehyde by oxidation with copper or silver as a catalyst

(ii) Halogenation: Halides of hydrogen, phosphorous and other compounds react with ethanol to replace the $-\text{OH}$ group with a halogen:

- (iv) Haloform Reaction: Hypohalides will react with ethanol to yield first acetaldehyde and finally the haloform reaction
- (v) Esters: Ethanol reacts with organic and inorganic acids to give esters
- (vi) Ethers: Ethanol may be dehydrated to give ethers
- (vii) Alkylation: Ethanol alkylates (adds alkyl-group to) a large number of compounds

Uses of Ethanol

- (i) Use as a chemical feed stock: In the chemical industry, ethanol is an intermediate in many chemical processes because of its great reactivity as shown above. It is thus a very important chemical feed stock.
- (ii) (ii) Solvent use: Ethanol is widely used in industry as a solvent for dyes, oils, waxes, explosives, cosmetics etc.
- (iii) (iii) General utility: Alcohol is used as a disinfectant in hospitals, for cleaning and lighting in the home, and in the laboratory second only to water as a solvent.
- (iv) (iv) Fuel: Ethanol is mixed with petrol or gasoline up to 10% and known as gasohol and used in automobiles.

Denatured Alcohol

- All over the world and even in ancient times, governments have derived revenue from potable alcohol. For this reason when alcohol is used in large quantities it is denatured or rendered unpleasant to drink.
- The base of denatured alcohol is usually 95% alcohol with 5% water; for domestic burning or hospital use denatured alcohol is dispensed as methylated spirit, which contains a 10% solution of methanol, pyridine and coloring material.
- For industrial purpose methanol is used as the denaturant. In the United States alcohol may be completely denatured (C.D.A. – completely denatured alcohol) when it cannot be used orally because of a foul taste or four smelling additives.
- It may be specially denatured (S.D.A. – specially denatured alcohol) when it can still be used for special purposes such as vinegar manufacture without being suitable for consumption.

Substrates The substrate used will vary

- In Brazil sugar cane, already widely grown in the country, is the major source of fermentation alcohol, while it is planned to use cassava and sweet sorghum. In the United States enormous quantities of corn and other cereals are grown and these are the obvious substrates.
 - Cassava grows in many tropical countries and since it is high yielding it is an important source in tropical countries where sugar cane is not grown. It is recognized that two important conditions must be met before fermentation alcohol can play a major role in the economy either as gasohol or as a chemical feedstock.
 - First, the production of the crop to be used must be available to produce the crop without extensive and excessive deforestation.
 - Secondly, the substrate should not compete with human food.
 - Ethanol is produced from various kinds of substrates. The substrate used for ethanol production is chosen based on the regional availability and economical efficiency
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1. Sucrose containing materials

Ethanol is produced by fermentation. Fermentation process is a process to convert sugar to ethanol. Sucrose containing materials could simplify the ethanol production process.

(a) Sugarcane

Brazil is the world second biggest ethanol producer. In Brazil, sugarcane is the major substrate for ethanol (Goldemberg et al., 2008). Countries in Central America and Caribbean are suitable for sugarcane cultivation, and their ethanol production is increasing recently.

(b) Sugar beet

Sugar beet is mainly cultivated in European countries (Power et al., 2008) since it grows under cold climate.

(c) Sugar sorghum

Sugar sorghum is also a sucrose containing crop. It yields large amount of biomass and sugar due to its high photosynthetic efficiency (Giorgis et al, 1997).

2. Starchy materials

Starch is converted to sugar by saccharification followed by fermentation. Today, saccharification and fermentation are done simultaneously (SSF: simultaneous saccharification and fermentation).

•*Corn*

It is relatively easy to obtain high purity starch from corn. As the world biggest corn producer, the United States mainly produces ethanol from corn, and this also makes the United States the world biggest ethanol producer.

•*Other starchy materials*

Any kind of starch containing crop can be used to produce ethanol. Many researches on ethanol production from various starchy materials, such as potato, sweet potato, cassava, and wheat.

3. Lignocellulosic biomass

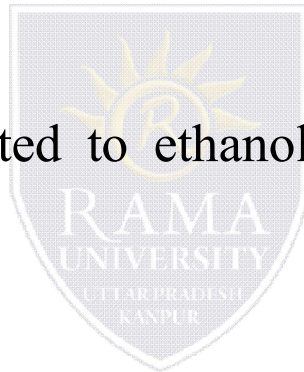
Many studies are going on for ethanol production from lignocellulosic biomass.

Lignocellulosic materials include maize silage, barely hull, and paper sludge. The difficulties of using lignocellulosic materials are there poor porosity, high crystallinity, and lignin contents.

Various kinds of pretreatment techniques have been investigated, such as steam, acid, and alkali treatments.

Production process

Starchy materials are converted to ethanol by two major processes, dry milling and wet milling.



(a) Dry milling

Dry milling the dominant and more efficient ethanol production process than wet milling. It produces about 2.8 gallons of ethanol per bushel of corn. The schematic of dry milling is shown below (Figure 1).

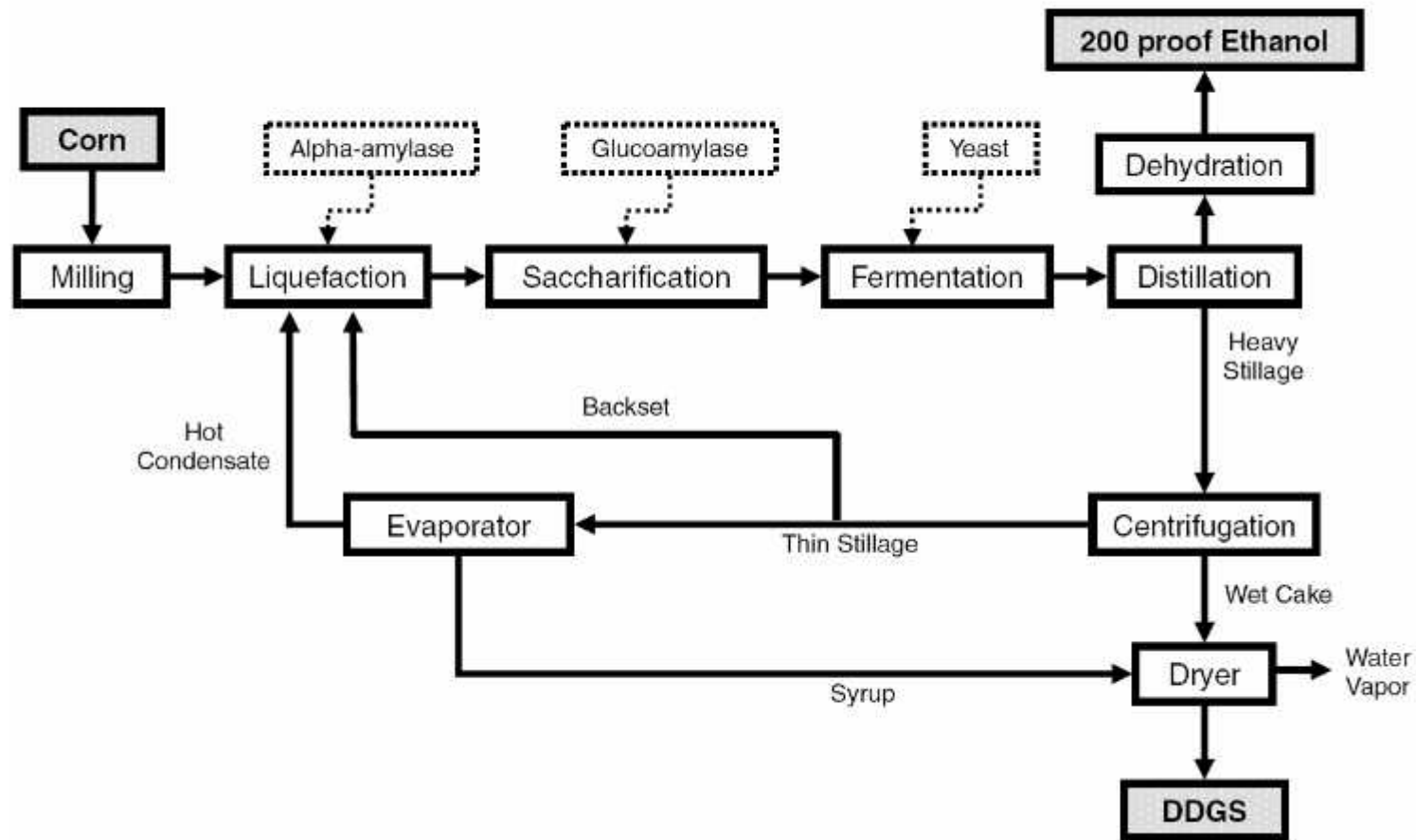


Figure 1. Schematic of dry milling ethanol production

(b) Wet milling

The components of grain are separated in wet milling before saccharification. Produces various high value products such as corn gluten meal (CGM) and corn gluten feed (CGF) are produced through wet milling. It produces about 2.7 gallons of ethanol per bushel of corn. The schematic of wet milling is shown below (Figure 2).

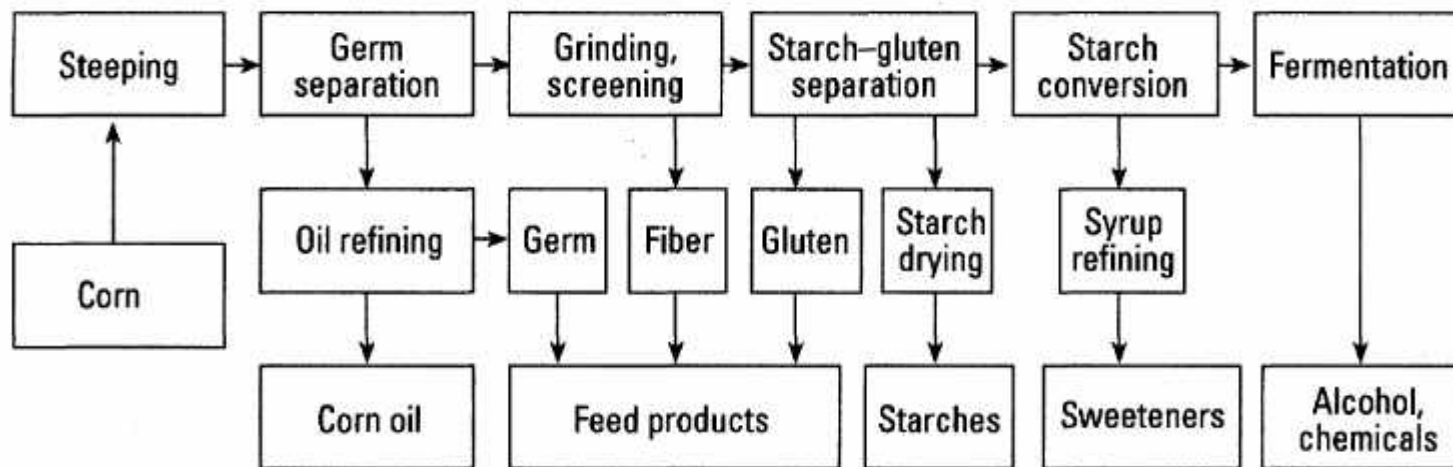


Figure 2. Schematic of wet milling ethanol production

Ethanol purification

Fermentation by-products Ethanol is produced by yeast fermentation. Although yeast mainly produces ethanol, it also produces by-products. These by-products need to be removed to obtain pure ethanol. There are mainly two kinds of by-product sources, starch and lignin.

Starch derived by-products include esters, organic acids, and higher alcohols. Lignin derived by-products include cyclic and heterocyclic compounds. Purification techniques Fermentation by-products are mostly removed by distillation.

However, volatile by-products tend to lodge more in ethanol. Also, especially for drinking or pharmaceutical purpose, high concentration of ethanol is not required. In this case, further distillation is just waste of energy and money. Many studies have done to find a new purification technique of ethanol which can take place of distillation.

(a) Distillation

Distillation is the most dominant and recognized industrial purification technique of ethanol. It utilizes the differences of volatilities of components in a mixture.

The basic principle is that by heating a mixture, low boiling point components are concentrated in the vapor phase. By condensing this vapor, more concentrated less volatile compounds is obtained in liquid phase.

Distillation is one of the most efficient separation techniques. However, it contains several problems. One is separation of volatile compounds. In ethanol production, a distillation tower is designed to separate water and ethanol effectively.

Water is obtained from the bottom of the tower and ethanol is obtained from the top of the tower. It is expected that impurities with similar boiling points to ethanol lodges in ethanol even after distillation. Second is its cost. Distillation is a repetition of vaporization and condensation. Therefore, it costs a lot.

(b) Adsorption

- Adsorption is a separation technique utilizing a large surface area of adsorbent. Compounds are simply adsorbed on the adsorbent depending on their physical and chemical properties.
- In general, bigger particles tend to be adsorbed more due to their low diffusivities. Also, compounds with the similar polarity to the adsorbent surface tend to be adsorbed more.
- When purification of ethanol is considered, non-polar surface and wide ranging pore distribution are favorable since ethanol is polar compounds and various sizes of particles could be contained in ethanol as impurities.
- From water treatment, activated carbon and activated alumina are the most expectable adsorbents.

(c) Ozonation

- Ozone is a tri-atomic molecule consisted by three oxygen atoms. Ozone could decompose various kinds of compounds using its strong oxidation potential. Decomposition of compounds could result in changes in physical and chemical properties of compounds such as increases in volatility, biodegradability, and a decrease in toxicity.
 - Although oxidation of ethanol could be expected with oxidation, it does not happen under the atmospheric condition. Thus, ozone can remove impurities without a significant damage on ethanol.
 - There are still some problems, non-oxidizable compounds and ozonolysis by-products. It is expected that some compounds cannot be oxidized by ozone. These compounds will remain after ozonation. Also, ozonation is an oxidation process and not remove compounds physically.
 - Thus, ozonation could generate new compounds, ozonolysis by-products. These compounds should be removed after ozonation by post-ozonation treatments.
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