

A Review on Methods of Extraction of Various Kinds of Bio-Fuels

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Abstract: *There is an imperative need to improve the existing biodiesel production methods from both economic and environmental viewpoints and to investigate alternative and innovative production processes. Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning everyday because of the increase in the petroleum price and the environmental advantages. Different studies have been carried out using different oils as raw material different alcohol (methanol, ethanol, propanol & butanol,). Due to the increase in the price of the petroleum and the environmental concerns about pollution coming from the car gases, biodiesel is becoming a developing area of high concern. One of the advantages of this fuel is that the raw materials used to produce it are natural and renewable. All these types of oils come from vegetables or animal fat, making it biodegradable and nontoxic. When used in spark ignition engines alcohols have the potential to reduce NO_x , CO , HC and particulates. A test with E85 fueled Chevrolet Lumina showed that NMHC^[3] went down by 20-22%, NO_x by 25-32% and CO by 12-24% compared to reformulated gasoline.^[4] Toxic emissions of benzene and 1,3 Butadiene also decreased while aldehyde emissions increased (acetaldehyde in particular). Tailpipe emissions of CO_2 also decrease due to the lower carbon-to-hydrogen ratio of these alcohols, and the improved engine efficiency.*

Keywords: Methanol, Ethanol, Propanol, Bio-Fuel, MOC, RON

1. Introduction

Throughout history, alcohol has been used as a fuel. The first four aliphatic alcohols (methanol, ethanol, propanol, and butanol) are of interest as fuels because they can be synthesized chemically or biologically, and they have characteristics which allow them to be used in internal combustion engines. The general chemical formula for alcohol fuel is $C_nH_{2n+1}OH$. The above mentioned all four fuels coming under category of First Generation Bio fuels. First generation bio fuels are made from sugar, starch, or vegetable oil. They differ from "second generation bio fuels" in that their feedstock (the plant or algal material from which they are generated) is not sustainable/green or, if used in large quantity, would have a large impact on the food supply. First generation bio fuels are the "original" bio fuels and constitute the majority of bio fuels currently in use.

Most methanols are produced from natural gas, although it can be produced from biomass using very similar chemical processes. Ethanol is commonly produced from biological-material through fermentation processes. However, ethanol that is derived from petroleum should not be considered safe for consumption as the mixture contains about 5% methanol and may cause blindness or death. Bio butanol has the advantage in combustion engines in that its energy density is closer to gasoline than the simpler alcohols (while still retaining over 25% higher octane rating); however, bio butanol is currently more difficult to produce than ethanol or methanol. When obtained from biological materials and/or biological processes, they are known as bio alcohols (e.g. "bio ethanol"). There is no chemical difference between biologically produced and chemically produced alcohols. The raw energy-per-volume numbers produce misleading fuel consumption numbers however, because alcohol-fueled engines can be made substantially more energy-efficient. A larger percentage of the energy available in a liter of alcohol

fuel can be converted to useful work. This difference in efficiency can partially or totally balance out the energy density difference, depending on the particular engines being compared.

One advantage shared by the four major alcohol fuels is their high octane rating. This tends to increase their fuel efficiency and largely offsets the lower energy density of vehicular alcohol fuels (as compared to petrol/gasoline and diesel fuels), thus resulting in comparable "fuel economy" in terms of distance per volume metrics, such as kilometers per liter, or miles per gallon, Suitability as a fuel, based on flash point energy content, viscosity, combustion products and other factors

What is the use of Bio-ethanol?

The principle fuel used as a petrol substitute for road transport vehicles is bioethanol. It is mainly produced by the sugar fermentation process, although it can also be manufactured by the chemical process of reacting ethylene with steam. Fermented grain, fruit juice and honey have been used to make alcohol (ethyl alcohol or ethanol) for thousands of years. The Babylonians worshiped a wine goddess as early as 2700 B.C. In Greece, one of the first alcoholic beverages to gain popularity was mead, a fermented drink made from honey and water.

Why Alcohol Fuel?

- 1) Almost every country can become energy independent. Anywhere that has sunlight and land can produce alcohol from plants. Brazil, the fifth largest country in the world imports no oil, since half its cars run on alcohol fuel made from sugarcane, grown on 1% of its land.
- 2) We can reverse global warming. Since alcohol is made from plants, its production takes carbon dioxide out of the air, sequestering it, with the result that it reverses the

- greenhouse effect (while potentially vastly improving the soil). Recent studies show that in a perm culturally designed mixed-crop alcohol fuel production system, the amount of greenhouse gases removed from the atmosphere by plants and then exuded by plant roots into the soil as sugar can be 13 times what is emitted by processing the crops and burning the alcohol in our cars.
- 3) We can revitalize the economy instead of suffering through Peak Oil. Oil is running out, and what we replace it with will make a big difference in our environment and economy. Alcohol fuel production and use is clean and environmentally sustainable, and will revitalize families, farms, towns, cities, industries, as well as the environment. A national switch to alcohol fuel would provide many millions of new permanent jobs.
 - 4) No new technological breakthroughs are needed. We can make alcohol fuel out of what we have, where we are. Alcohol fuel can efficiently be made out of many things, from waste products like stale donuts, grass clippings, food processing waste—even ocean kelp. Many crops produce many times more alcohol per acre than corn, using arid, marshy, or even marginal land in addition to farmland. Just our lawn clippings could replace a third of the auto fuel we get from the Mideast.
 - 5) Unlike hydrogen fuel cells, we can easily use alcohol fuel in the vehicles we already own. Unmodified cars can run on 50% alcohol, and converting to 100% alcohol or flexible fueling (both alcohol and gas) costs only a few hundred dollars. Most auto companies already sell new dual-fuel vehicles.
 - 6) Alcohol is a superior fuel to gasoline! It's 105 octane, burns much cooler with less vibration, is less flammable in case of accident, is 98% pollution-free, has lower evaporative emissions, and deposits no carbon in the engine or oil, resulting in a tripling of engine life. Specialized alcohol engines can get at least 22% better mileage than gasoline or diesel. It's not just for gasoline cars. We can also easily use alcohol fuel to power diesel engines, trains, aircraft, small utility engines, generators to make electricity, heaters for our homes—and it can even be used to cook our food.
 - 7) Alcohol has a proud history. Gasoline is a refinery's toxic waste; alcohol fuel is liquid sunshine. Henry Ford's early cars were all flex-fuel. It wasn't until gasoline magnate John D. Rockefeller funded Prohibition that alcohol fuel companies were driven out of business.
 - 8) The byproducts of alcohol production are clean, instead of being oil refinery waste, and are worth more than the alcohol itself. In fact, they can make petrochemical fertilizers and herbicides obsolete. The alcohol production process concentrates and makes more digestible all protein and non-starch nutrients in the crop. It's so nutritious that when used as animal feed, it produces more meat or milk than the corn it comes from. That's right; fermentation of corn increases the food supply and lowers the cost of food.
 - 9) Locally produced ethanol supercharges regional economies. Instead of fuel expenditures draining capital away to foreign bank accounts, each gallon of alcohol produces local income that gets recirculated many times. Every dollar of tax credit for alcohol

generates up to \$6 in new tax revenues from the increased local business.

- 10) Alcohol production brings many new small-scale business opportunities. There is huge potential for profitable local, integrated, small-scale businesses that produce alcohol and related byproducts, whereas when gas was cheap, alcohol plants had to be huge to make a profit.
- 11) Scale matters most of the widely publicized potential problems with ethanol are a function of scale. Once production plants get beyond a certain size and are too far away from the crops that supply them, closing the ecological loop becomes problematic. Smaller-scale operations can more efficiently use a wide variety of crops than huge specialized one-crop plants, and diversification of crops would largely eliminate the problems of monoculture.
- 12) The byproducts of small-scale alcohol plants can be used in profitable, energy-efficient, and environmentally positive ways. For instance, spent mash (the liquid left over after distillation) contains all the nutrients the next fuel crop needs and can return it back to the soil if the fields are close to the operation. Big-scale plants, because they bring in crops from up to 45 miles away, can't do this, so they have to evaporate all the water and sell the resulting byproduct as low-price animal feed, which accounts for half the energy used in the plant.

2. Extraction of Methanol

Methanol fuel has been proposed as a future bio fuel, often as an alternative to the hydrogen economy. Methanol has a long history as a racing fuel. Early Grand Prix Racing used blended mixtures as well as pure methanol. The use of the fuel was primarily used in North America after the war. However, methanol for racing purposes has largely been based on methanol produced from syngas derived from natural gas and therefore this methanol would not be considered a bio fuel. Methanol is a possible bio fuel, however when the syngas is derived from biomass. In theory, methanol can also be produced from carbon dioxide and hydrogen using nuclear power or any renewable energy source, although this is not likely to be economically viable on an industrial scale Compared to bioethanol. The primary advantage of methanol bio fuel is its much greater well-to-wheel efficiency. This is particularly relevant in temperate climates where fertilizers are needed to grow sugar or starch crops to make ethanol, whereas methanol can be produced from lignocelluloses (woody) biomass. Methanol is the simpler molecule & derived from fossil fuels, industrially from nearly any bio mass or perhaps most simply, including animal waste, or from carbon dioxide and water or steam by first converting the biomass to synthesis gas in a gasifier. Methanol has most commonly been produced from synthesis gas, but there are more modern ways to obtain these fuels. Enzymes can be used instead of fermentation. It can also be produced in a laboratory using electrolysis or enzymes.^[1] Methanol at 109 RON (Research Octane Number), 89 MON (Motor Octane Number) (which equates to 99 AKI).^[2] When used in spark ignition engines alcohols have the potential to reduce NO_x, CO, HC and particulates. A test with E85 fueled Chevrolet Lumina showed that NMHC^[3] went down by 20-22%, NO_x by 25-32% and CO by 12-24% compared

to reformulated gasoline.^[4] Toxic emissions of benzene and 1,3 Butadiene also decreased while aldehyde emissions increased (acetaldehyde in particular). A liter of methanol 15.8 MJ or in other words, for the same energy content as one liter or one gallon of gasoline.

Methanol combustion is:
 $2\text{CH}_3\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O} + \text{heat}$

Methanol Production from Natural Gas Technology:

All commercial methanol technologies feature three process sections and a utility section as listed below:

- 1) Synthesis gas preparation (reforming)
- 2) Methanol synthesis
- 3) Methanol purification
- 4) Utilities

In the design of a methanol plant the three process sections may be considered independently, and the technology may be selected and optimized separately for each section. The normal criteria for the selection of technology are capital cost and plant efficiency. The synthesis gas preparation and compression typically accounts for about 60% of the investment, and almost all energy is consumed in this process section. Therefore, the selection of reforming technology is of paramount importance, regardless of the site.

Methanol synthesis gas is characterized by the stoichiometric ratio $(\text{H}_2 - \text{CO}_2) / (\text{CO} + \text{CO}_2)$, often referred to as the module M. A module of 2 defines a stoichiometric synthesis gas for formation of methanol. Other important properties of the synthesis gas are the CO to CO₂ ratio and the concentration of inert. A high CO to CO₂ ratio will increase the reaction rate and the achievable per pass conversion. In addition, the formation of water will decrease, reducing the catalyst deactivation rate. High concentration of inert will lower the partial pressure of the

active reactants. Inert in the methanol synthesis are typically methane, argon and nitrogen.

In the following a brief description is given covering technologies available for the three process sections.
 Synthesis Gas Preparation:

Several reforming technologies are available for producing synthesis gas:

- One-step reforming with fired tubular reforming
- Two-step reforming
- Auto thermal reforming (ATR)

In one-step reforming, the synthesis gas is produced by tubular steam reforming alone (without the use of oxygen). This concept was traditionally dominating. Today it is mainly considered for up to 2,500 MTPD plants and for cases where CO₂ is contained in the natural gas or available at low cost from other sources.

The synthesis gas produced by one-step reforming will typically contain a surplus of hydrogen of about 40%. This hydrogen is carried un-reacted through the synthesis section only to be purged and used as reformer fuel.

The addition of CO₂ permits optimization of the synthesis gas composition for methanol production. CO₂ constitutes a less expensive feedstock, and CO₂ emission to the environment is reduced. The application of CO₂ reforming results in a very energy efficient plant. The energy consumption is 5–10% less than that of a conventional plant [5]. A 3,030 MTPD methanol plant based on CO₂ reforming was started up in Iran in 2004. The two-step reforming process features a combination of fired tubular reforming (primary reforming) followed by oxygen-fired adiabatic reforming (secondary reforming). A process flow diagram for a plant based on two-step reforming is shown in Figure 1.

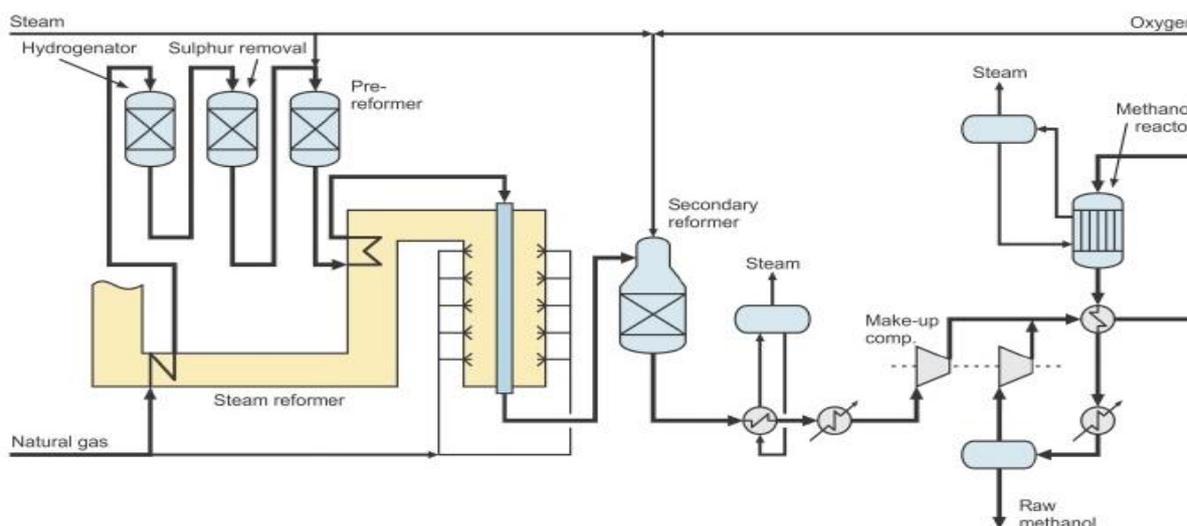


Figure 1: Methanol production by two-step reforming

The balance required to obtain a desired value of M depends on the natural gas composition. This is shown in Figure: 2 for two feed gas compositions: Pure methane (full lines) and a relatively heavy natural gas with the overall composition

CH_{3.6} (broken lines). The heavy gas requires more steam reforming and less oxygen compared to the requirements for lean gas. The same is true for gas containing CO₂. Curves for a feed containing 95 mol % CH₄ and 5 mol % CO₂ are

almost identical to the curves for the heavy natural gas in Figure: 2

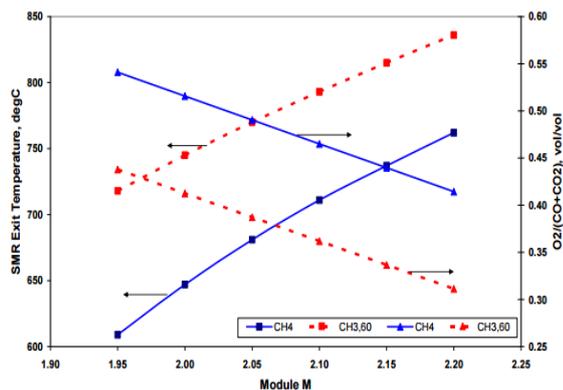


Figure 2: Correlation between steam reformer exit temperature, oxygen consumption and methanol module in two-step reforming

The secondary reformer requires that the primary reformer is operated with a significant leakage of unconverted methane (methane slip). Typically 35 to 45% of the reforming reaction occurs in the tubular reformer, the rest in the oxygen-fired reformer. As a consequence the tubular reformer is operated at low S/C ratio, low temperature and high pressure. These conditions lead to a reduction in the transferred duty by about 60% and in the reformer tube weight by 75 to 80% compared to one-step reforming.

The two-step reforming lay-out was first used in a 2400 MTPD methanol plant in Norway [1]. This plant was started up in 1997. A 5000 MTPD plant based on similar technology was started up in Saudi Arabia in 2008 [2]. Auto thermal reforming (ATR) features a stand-alone, oxygen-fired reformer. The auto thermal reformer design features a burner, a combustion zone, and a catalyst bed in a refractory lined pressure vessel as shown in Figure 3.

The burner provides mixing of the feed and the oxidant. In the combustion zone, the feed and oxygen react by sub-stoichiometric combustion in a turbulent diffusion flame. The catalyst bed brings the steam reforming and shift conversion reactions to equilibrium in the synthesis gas and destroys soot precursors, so that the operation of the ATR is soot-free. The catalyst loading is optimized with respect to activity and particle shape and size to ensure low pressure drop and compact reactor design. The synthesis gas produced by auto thermal reforming is rich in carbon monoxide, resulting in high reactivity of the gas. The synthesis gas has a module of 1.7 to 1.8 and is thus deficient in hydrogen. The module must be adjusted to a value of about 2 before the synthesis gas is suitable for methanol production. The adjustment can be done either by removing carbon dioxide from the synthesis gas or by recovering hydrogen from the synthesis loop purge gas and recycling the recovered hydrogen to the synthesis gas [6].

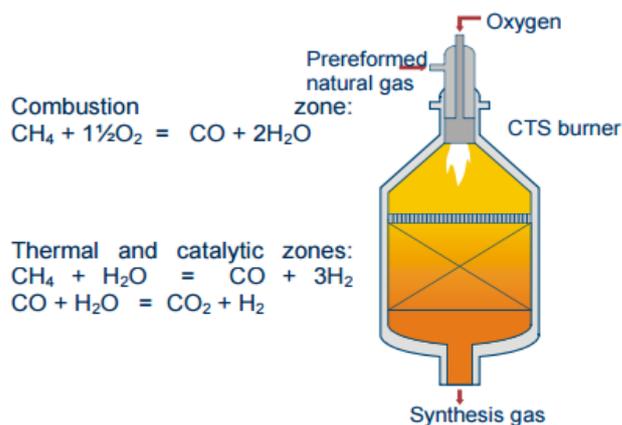


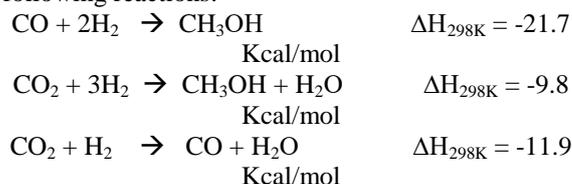
Figure 3: Auto thermal Reformer

When the adjustment is done by CO₂ removal, a synthesis gas with very high CO/CO₂ ratio is produced. This gas resembles the synthesis gas in methanol plants based on coal gasification. Several synthesis units based on gas produced from coal are in operation, this proves the feasibility of methanol synthesis from very aggressive synthesis gas. Adjustment by hydrogen recovery can be done either by a membrane or a PSA unit. Both concepts are well proven in the industry. The synthesis gas produced by this type of module adjustment is less aggressive and may be preferred for production of high purity methanol.

Methanol Synthesis and Purification:

In the methanol synthesis conversion of synthesis gas into raw methanol takes place. Raw methanol is a mixture of methanol, a small amount of water, dissolved gases, and traces of by-products.

The methanol synthesis catalyst and process are highly selective. A selectivity of 99.9% is not uncommon. This is remarkable when it is considered that the by-products are thermodynamically more favored than methanol. Typical byproducts include DME, higher alcohols, other oxygenates and minor amounts of acids and aldehydes. The conversion of hydrogen and carbon oxides to methanol is described by the following reactions:



The methanol synthesis is exothermic and the maximum conversion is obtained at low temperature and high pressure.

3. Extraction of Ethanol

Bioethanol could be one of the popular alternative automotive fuels used in the world. Ethyl alcohol (otherwise known as Ethanol). Brazil and USA are the world's top largest ethanol producers & Contributed to 65% and above worldwide ethanol production. Ethanol is a renewable, domestically produced alcohol fuel made from plant material, such as corn, potato, cassava, sugar cane, or grasses. Using ethanol can reduce oil dependence and

greenhouse gas emissions. Ethanol at 109 RON (Research Octane Number), 90 MON (Motor Octane Number), (which equates to 99.5 AKI) (Anti-Knock Index). Ethanol is an unclouded and colorless liquid, it can be blended together with gasoline so as to allow more oxygen into the fuel mixture, resulting in more complete combustion and less polluting emissions, biodegradable, - toxicity level is relatively low, therefore it is safe, and little environmental pollution caused if spilled.

4. Production of Bioethanol by Starch

Ethanol produced by fermentation, called bioethanol, accounts for approximately 95% of the ethanol production. It is recently widely used as an additive to gasoline. Ethanol is produced by fermentation. Fermentation process is a process to convert sugar to ethanol. Sucrose containing materials could simplify the ethanol production process.

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

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 (Rendleman and Shapouri, 2007). The schematic of dry milling is shown in Figure 4.

WET MILLING:

The components of grain are separated in wet milling before scarification. 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 (Rendleman and Shapouri, 2007). The schematic of wet milling is shown in Figure 5.

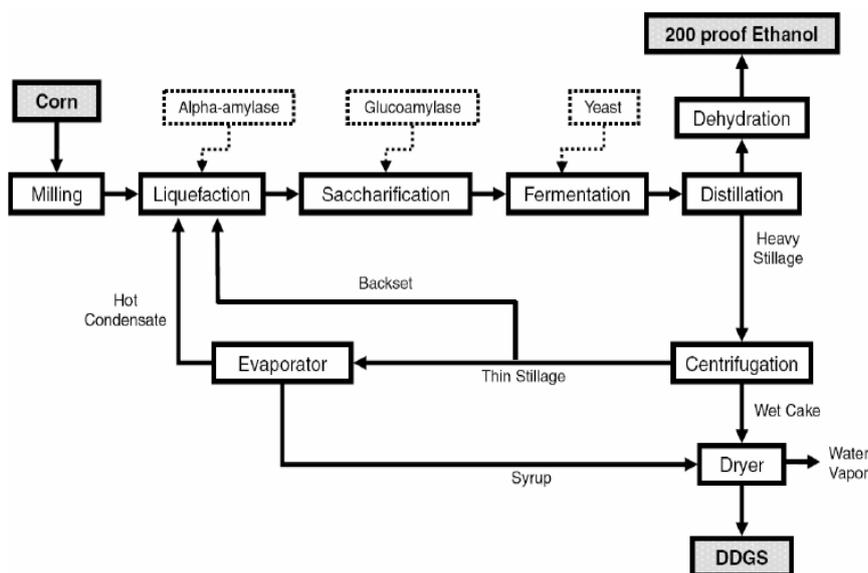


Figure 4: Schematic of dry milling ethanol production

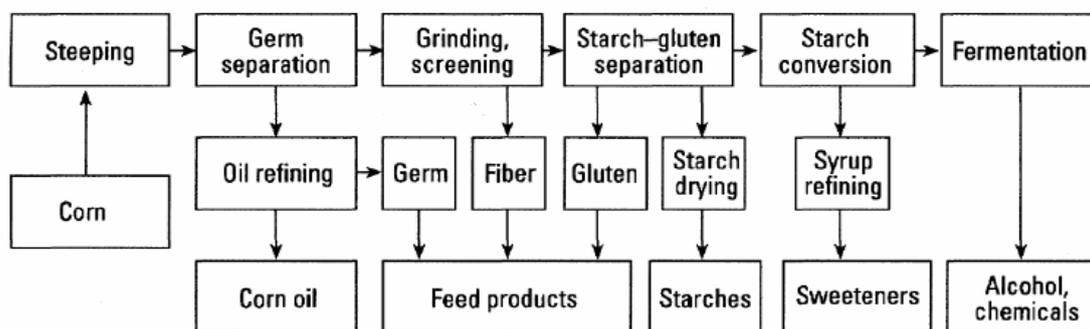


Figure 5: Schematic of wet milling ethanol production

Ethanol purification:

(a) 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.

(b) 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.

(c) 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.

(d) 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 (Demirbas et al., 2008) and activated alumina (Tripathy and Raichur, 2008) are the most expectable adsorbents.

(e) 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 (Bailey, 1982). 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.

(f) Gas stripping:

Gas stripping is a separation technique utilizing the differences of volatilities among compounds. The separation efficiency is simply governed by Henry's law constant (Alley, 2007).

$$H = P_{vap}/C_{sat}$$

Where H = Henry's constant (moles/L atm)

P_{vap} = the partial pressure of a pure compound (atm), and

C_{sat} = the saturation concentration of the pure compound in the liquid phase (moles / or mg/L)

5. Conclusion

This paper revealed successfully the various bio-fuels and methods of extracting them. In the short term, alcohol fuels will not replace hydrocarbon fuels. They will, however, be important additives to fuels for the foreseeable future. From gas stripping, Henry's law constant varies depending on the vapor and liquid phases. It is easily imagined that compounds with low boiling points can be stripped more easily such as acetaldehyde which is one of the major impurities in ethanol. If science continues to progress and the problem of compromising the food chain can be solved, then alcohol fuels may provide an excellent alternative to fossil fuels that allow us to better balance how much carbon dioxide we put into the atmosphere with how much plants remove.

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