# CHAPTER I

# INTRODUCTION

## 1.1 Background

Waste vegetable oil is considered a second generation bio-fuel as it can't be reused for food, in fact recycling it for fuel can also improve the overall environmental impact. Automative bio-diesel has been a very important issue to attract the researchers, since it uses a renewable energy and considered as an alternative energy for petrol oil; so we need the production of bio-diesel basically for living (Wood and Parrott 2013) . Waste vegetable oil (WVO) was chosen in this plant design because of the following reasons. First, it doesn't threaten the food chain. Second, it is readily available. Third, easy to convert to bio-diesel. Forth, it has low sulfur content. And in general, restaurants will usually dispose the used cooking oil and replace it by a new one. At this point we might take the advantage of using the used cooking oil to make bio-diesel in a more economical way, as we don't need to pay much for waste vegetable oil and at the same time will decrease the environmental pollution by (WVO) disposal. However, the one disadvantage of WVO is that it can decrease engine life if it wasn't properly refined.

The advantages of vegetable oils as diesel fuel are A. liquid nature-portability, B. heat content (80% of diesel fuel), C. ready availability and D. Renewability. The disadvantages are A. higher viscosity, B. lower volatility and C. The reactivity of unsaturated hydrocarbon chains (Pryde 1983).

In the process of bio-diesel production will result (glycerin) byproduct density of 10.5 per gallon as bio-diesel production will generate about 10% (w/w) glycerol as the main byproduct , to simplify it , every gallon of bio-diesel produced generates around 1.05 pounds of glycerol, for example a plant that produces 30 million gallon per year will generate around 11.5 tons of 99.9% pure glycerin, glycerin is considered a very basic material for any factory that produces cosmetics as it is a high moisture for the skin (Pachauri 2006).

Catalyst is a substance that functions to speed up the reaction rate under a specific temperature degree without being involved in the reaction, in bio-diesel production of these papers will use sodium methoxide (NaOH) catalyst, which functions in the reaction process to speed up the reaction rate, it reacts with triglycerides and break them apart so that the methanol can bond with the fatty acid and make bio-diesel. NaOH tends to be hard to dissolve in methanol and will need more time compared to other basic catalysts as KOH for an instant, KOH will dissolve faster and that is the reason why KOH is mostly used instead of NaOH. However, KOH is considered more expensive than NaOH which is around $2.50/lb for KOH and $1.27/lb for NaOH. In addition, the Amount of KOH catalyst to make bio-diesel is considered more than the amount of NaOH catalyst, and according to these reasons NaOH catalyst was chosen for these research papers (Hossain and Mazen 2010).

The basic purpose of this plant design is to design a bio-diesel plant which uses Ultrasonic agitation in reactor and to determine economic feasibility for plant establishment.

**The Designed Production Capacity**

The term production capacity can be defined as the maximum amount of production done within a particular unit of time; a manufacturer should have an optimal production capacity in which the quantity and the type of the product manufactured should have a maximum profit with minimal costs.

**a. Biodiesel need in Indonesia**

In contrast with the stagnant condition of Indonesian FE, Indonesia's biodiesel sector maintained healthy growth in 2013. Biodiesel production increased from 2.2 billion liters in 2012 to 2.45 billion liters in 2013. Growth is attributable to an ambitious new bio-fuel mandatory program. The program will continue driving Indonesian biodiesel production through 2014 and 2015, despite unfavorable biodiesel markets overseas. Indonesian biodiesel production is expected to reach 3.65 billion liters in 2014, and it will further increase to 4.15 billion liters in 2015.

Table 1. 1 Comparative view of minimum biodiesel mandatory program in Indonesia, 2008 – 2025 (Slette 2013)

| Sector | 2008 | 2009 | 2010 | 2015 | 2020 | 2025 |
|---|---|---|---|---|---|---|
| Transportation (public service PSO) | 1% (existing) | 1% | 2.5% | 5% | 10% | 20% |
| Transportation Non PSO | | 1% | 3% | 7% | 10% | 20% |
| Industry | 2.5% | 2.5% | 5% | 10% | 15% | 20% |
| Electricity | 0.1% | 0.25% | 1% | 10% | 15% | 20% |

If the new bio-fuel mandatory program is successful, Indonesian Ministry of Energy and Mineral Resources (MEMR) expects Indonesia will face biodiesel supply shortages starting in 2016. MEMR is therefore encouraging industry to expand production capacity from the current level of 5.67 billion liters per year. Business-as-usual biodiesel supply expansion growth, according to MEMR calculation, will result in the situation of annual excess demand for biodiesel at 2 billion liters within 2016 – 2020 timeframe.

**b. The need for biodiesel overseas**

The expansion of bio-fuels worldwide has been primarily state-driven. Mandatory bio-fuel-blending policies and economic incentives (such as tax breaks and direct subsidies) have not only incentivized production and reduced its costs but also created great market demand for these fuels. Leading roles can be attributed to Brazil, the United States, and the EU in the advancement of these supportive policies internationally. The US and Brazil together account for about three-quarters of all bio-fuel production in the world and recently have been expanding not only their own production but also engaging with other countries through research and development trade agreements, and pro-bio-fuel partnerships (Peters 2011).

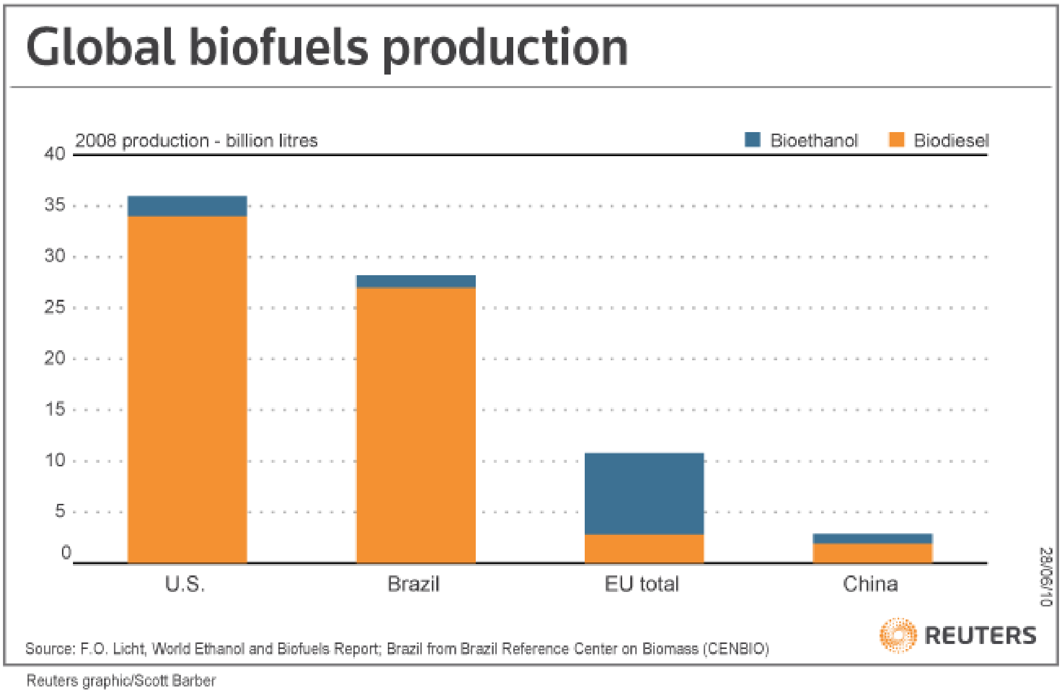


**Figure 1. 1 Diagrammatic figure of global fuel production ( (World Ethanol and biomass Report 2008))**

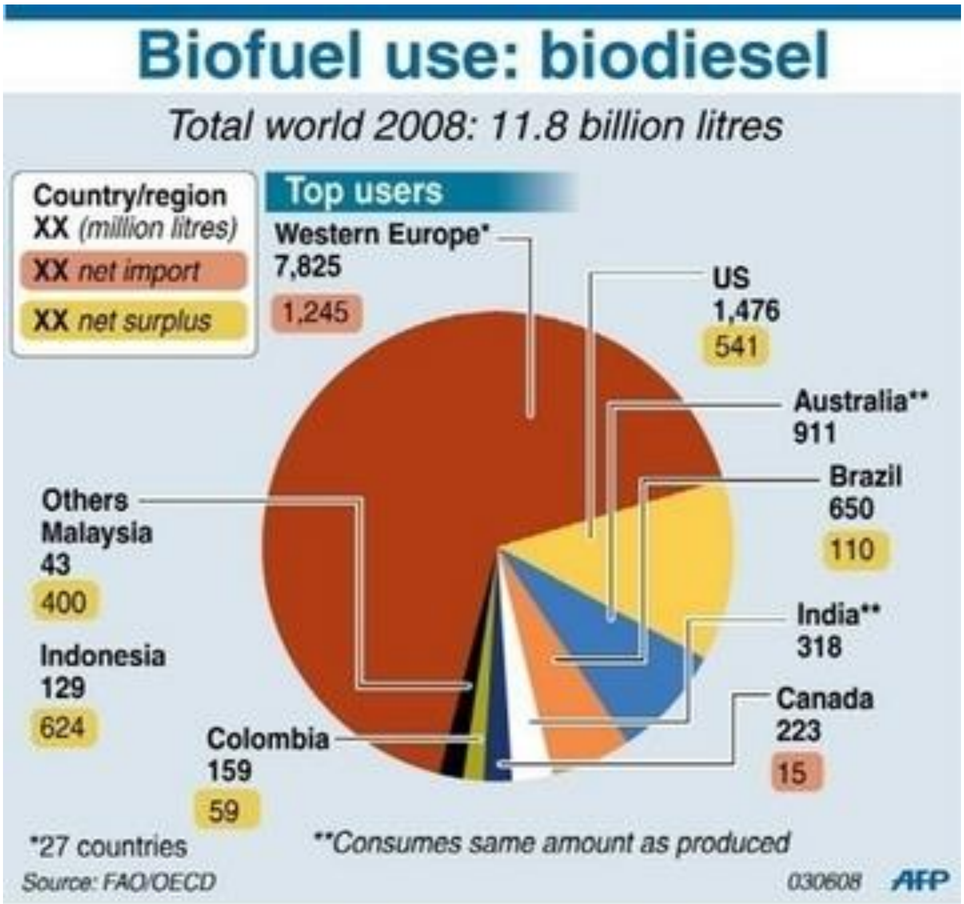


Figure 1. 2 World consumption of biodiesel ( (World Ethanol and biomass Report 2008))

As we can see in Figure 1.1 and 1.2 above, 27 Western Europe countries are the top users of the world biodiesel followed by the USA, some countries as Australia and India consumes the same amount of their produced biodiesel (Global energy network institue GENI 2010).

Indonesia isn't a high fuel producer and that's why we consider this plant design.

**c. Availability of Raw Materials**

Since Indonesia has significant land area in different forest types that could be used to produce bio-fuels, the potential to collect and convert forest materials to methanol for use in energy production is pretty high. Using the annually available above ground forest biomass, from 40 to 168 billion of bio-methanol could be produced for use as a transportation fuel and/or to supply fuel cells to produce electricity.

By generating electricity using bio-methanol/fuel cells instead of from fossil fuels, from 9 to 38% of the total carbon currently emitted each year in Indonesia could be avoided. In contrast, substituting this same amount of bio-methanol for gasoline could provide all of the annual gasoline needs of Indonesia and contribute towards reducing their carbon emissions by about 8–35%. So we might conclude that Indonesia is a very qualified place to make Biodiesel because it won't face problems to provide methanol raw material from its forests for the biodiesel production process. As for the catalysts KOH or NaOH can be obtained with a price of US $900-1100 / Metric Ton (FOB Price)90% purity.

### d. Minimum/Maximum design capacity

**Table 1. 2 Data import of biodiesel in Indonesia (Biodiesel Import in Indonesia 2005)**

| No | Year | Capacity Ton/year |
|---|---|---|
| 1. | 2005 | 200,565.796 |
| 2. | 2006 | 435,148.64 |
| 3. | 2008 | 10,866.304 |
| 4. | 2009 | 5,580.205 |
| 5. | 2010 | 24,365,814 |

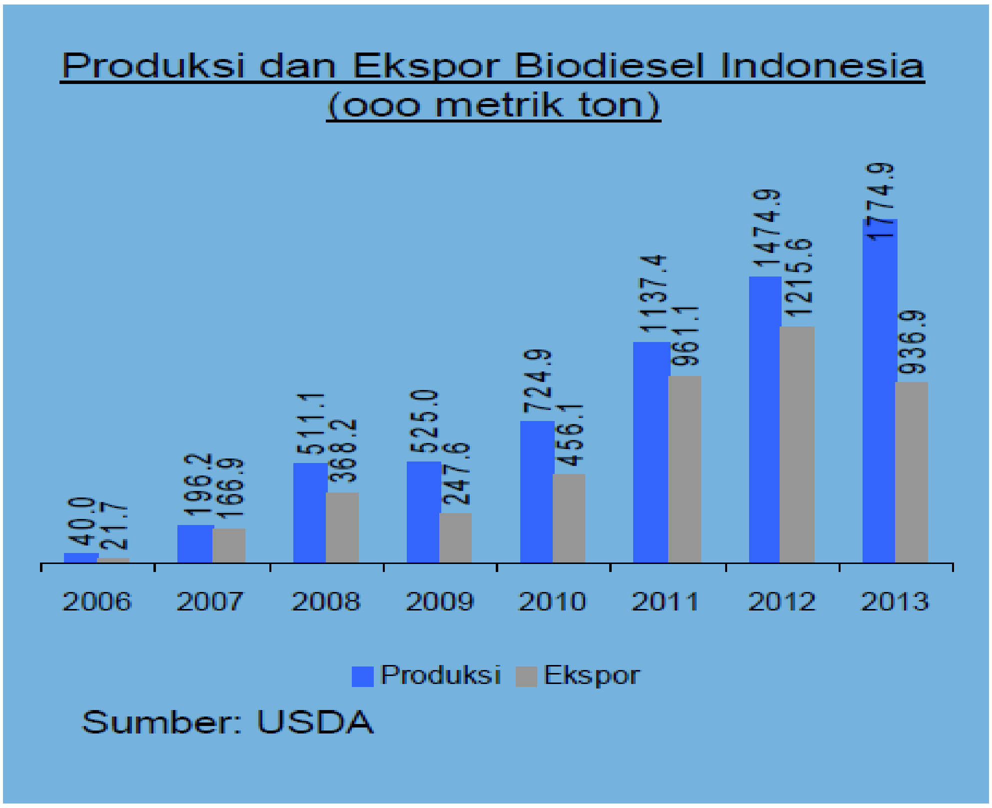


**Figure 1. 3 Production and export of biodiesek in Indonesia from 2006-2013( (USDA Production and Export in Indonesia 2006-2013))**

As observed in figure 1.3 above, Indonesia production of biodiesel from 2006 until 2013 is more than it exports, or in another way, Indonesia exports most of its biodiesel production.

Table 1. 3 Capacity data of biodiesel in Indonesia( **(Indobiofuel 2006-2013)**)

| No | Plant name | Capacity |
|---|---|---|
| 1. | BBKK Departemen Perindustrian, Jakarta | 300 liter/day |
| 2. | Pondok Pesantren Uswatun Hasanah Kayeli, Pulau Buru, Ambon | 300 liter/day |
| 3. | PLN Mataram, NTB | 1 ton/day |
| 4. | POLITEKNIK Lampung | 300 liter/day |
| 5. | PT.PN IV Tebing Tinggi,Sumut | 5 ton/day |
| 6. | Penda Riau, Pekanbaru | 8 ton/day |
| 7. | PT.Multukimia Intipelangi, Cibitung | 20 ton/day |

The chosen capacity for this plant is 15.000 ton/year, this capacity might be changed in future, and that depends on the consumption of products. If the consumption of biodiesel increased then it's possible to use the expansion area and increase the capacity.

## 1.2 Site Selection for the Plant

It has been decided that the plant will be based in Bontang/East Kalimantan. With the following considerations:

1. Sources of the Raw Materials

The Plant of Biodiesel belongs to the process of cost reduction and thus the plant should be built near the sources of raw materials. The main raw materials include methanol from PT. Kaltim methanol industry in bontang and KOH/NaOH (catalysts) from PT. Tjiwi Kimia in Surabaya.


**Figure 1. 4 Location of methanol plant in Bontang (Pt.kaltim methanol industry (Google maps 2015)**

2. Location (with respect to the marketing area): A site should be selected so that it is close to at least two major forms of transport: road, rail, waterway or a seaport. Road transport is being increasingly used, and is suitable for local distribution from a central warehouse.
3. Transportation: the plant is located in *Bontang*. To supply the raw materials, it can be carried out using land transportation which is by *Jl. Samarinda-Bontang* for the transportation of methanol from *PT.Kaltim* methanol to *Bontang*, where KOH/NaOH can be transported from Semarang using airplane to *Banjar masin*, from there to *Bontang* via *Jl. Ahmad Yani*.
4. Water Facilities: *Bontang* is one of the industrial areas in Indonesia that its main utility supply is water; the availability of water is not a problem since it is located near Java Sea.
5. Labor Force: The labor force of the plant is required to be from Bontang population and its surrounding areas, in which the population in this area is high, making it a potential source of labor force.
6. Society: In relation to the social conditions, society here has already been familiar with the industrial environment so that establishment of a new plant is not the matter and the society can adapt easily and quickly.
7. Waste Disposal: Biodiesel production process will result biodiesel and glycerol by product, the washing water could be retreated and reused.
8. Energy: energy supply is another thing which needs considering in the selection of the manufacturer location. To meet the electricity need, the supply is taken from PLN Bontang, East Kalimantan and Three Cummins Power Generation 823DFJD generator sets powered by KTA38G5 engines, each set prime rated at 823 kW/1029 kVA, and one 1005DFLC genset, powered by a KTA50G3 engine, the set prime rated at 1005 kW/1256 kVA, together with paralleling switchgear (PLN Bontang, East Kalimantan 2004).
9. Taxes: The taxes to be paid may be lower and easier as Bontang is an industrial area.

10. Costs of Construction: a 500-hectare plot of land will cost around 8-9 million US dollar in Bontang, it makes sense as the area is qualified for industrial manufacturer.

## 1.3 Literature review

### 1.3.1 Transesterification

Esterification reaction is mostly used for reducing the FFA level of oil followed by transesterification reaction for converting fatty acid into fatty acid methyl esters. Some people are following esterification process for producing fatty acid methyl esters but the majority will use transesterification process (Hossain and Mazen 2010).

Transesterification of soybean oil, free of synthetic antioxidants, was performed in analytical grade absolute methanol with sodium methoxide (SIGMA-ALDRICH, 95%) as the catalyst at a concentration of 0.8 g 50 mL−1 of methanol. The reaction was heated under reflux at 60 °C and agitated slowly. The biodiesel was separated from glycerol by decantation in a separating funnel.

Transesterification is the most common way to produce biodiesel. It is a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol, as shown in (Fig. 1.5) bellow:

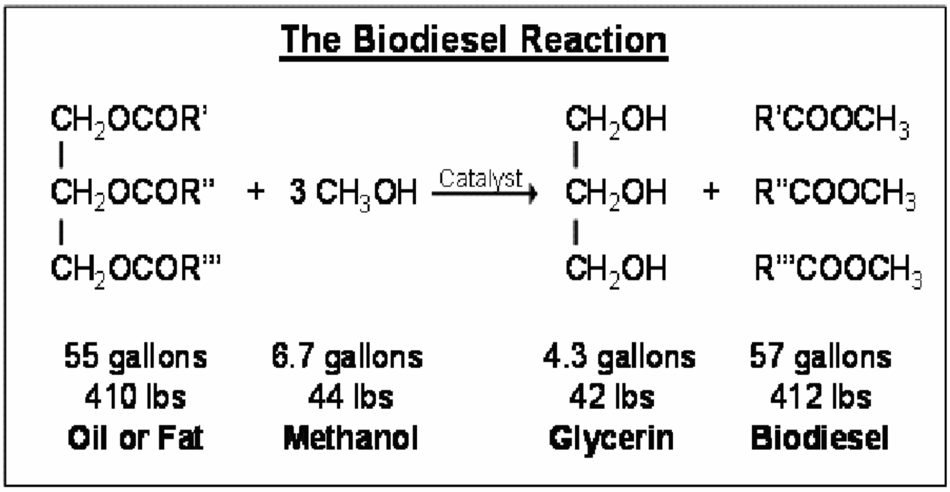


**Figure 1. 5 Schematic representation of the transesterification of triglycerides with methanol to produce fatty acid methyl esters**

This reaction is exothermic, which means it produces heat. Reaction is carried out at a temperature of (50-60)C° (120°F) is optimum temperature) (Wood and Parrott 2013).

### 1.3.2 Ultrasonic processor

Normally, the reaction time of biodiesel production from homogeneous transesterification is around 30 min to 1 h depending on reaction temperature, FFA in oil, and amount of catalyst (A.K Tiwari 2007). To shorten the reaction time, ultrasonic wave is one technique providing excellent mixing between the two phases. It will break down the liquid and form the cavitations bubbles resulting in the rising of mass transfer rate and acoustic streaming mixing (Mason 1999).

The ultrasonic transducer uses cavitations or Nano-sized vacuum bubbles that locally produce high temperatures and extreme pressures when the cavity implodes on itself. This creates jets of liquid that help to overcome the cohesion and adhesion of the WVO and sodium methoxide. This aids in the transesterification and allows for a better and more thorough reaction.

### 1.3.3 Biodiesel Processor

Fig.1.6. illustrates the automated biodiesel processor as before the actual reaction begins, it is important to preheat the WVO to reduce the viscosity and evaporate any water existing in the oil from cooking. The next step is to pre-filter the WVO in order to remove any food particles remaining in the oil so that the oil is clean and ready for the chemical reactions. To achieve this step, the WVO was poured through a series of progressively finer filtering screens. The finest filtering screen should be around 50 to 75 microns. After the pre-filtering stage, the oil is ready to be added to the 60 gallon tank for processing.

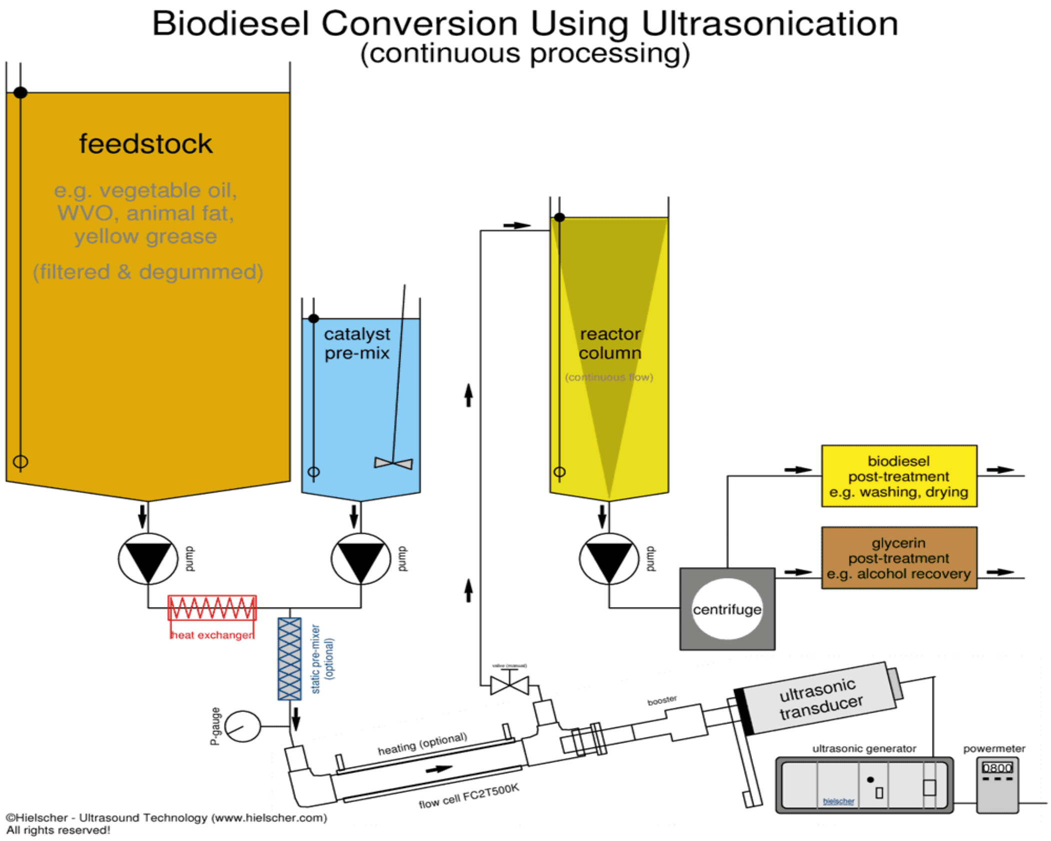


**Figure 1. 6 Illustration of biodiesel processor, reactor and Ultrasonic transducer (continuous process) (Hielscher-Ultrasound Technology 2007)**

A continuous plant leads to better heat economization, better product purity from phase separation by removing only the portion of the layer furthest from the interface, better recovery of excess methanol in order to save on methanol cost and regulatory issues.

Biodiesel has several advantages such as: 1) being biodegradable, 2) being non-toxic, 3) having low emissions of carbon monoxide, 4) having a relatively high flash point (150° C), which makes it less volatile and safer to transport handle than petro-diesel, and 5) it has a good lubricating properties that can reduce engine wear and extend engine life.

The main factors affecting the yield of the resulting ester transesterification reaction are:

1. Molar ratio of WVO/methanol: Different oil to methanol molar ratios like 1:1 and 3:1 have a great affect on reaction yield, reactions in this research were

carried out using 0.5% sodium hydroxide for 2 hours at room temperature. Figure 1.7 showed the yield of biodiesel from waste soybean oil by using different types of molar ratio of oil to methanol. The results showed that increasing of methanol to oil molar ratio increased the yield of biodiesel production. Oil to methanol molar ratio of 1:1 gave the higher yield (71.2%) of biodiesel than 3:1 oil to methanol molar ratio.

2. Catalyst concentration**:** Biodiesel production can be affected by the amount of catalyst used in the reactions. In a research experiment, different concentrations of NaOH like 0.5, 1.0 and 1.5% were used. The reactions were carried out by using methanol with 1:1 oil to alcohol molar ratio for 2 h of reaction time at room temperature. Figure 1.8 shows biodiesel yield using different concentrations of NaOH as a catalyst. From the results, the optimum yield of biodiesel can be obtained at 1.0% of NaOH concentration. It reached 72.7% of the biodiesel yield.

3. Temperature of reaction**:** In research experiment temperature was varied between 25 and 65 °C. For the same final reaction time, the percentage of esters increased with temperature. After 5 min, the esters present in the 65, 45, and 25 °C runs were 84.7, 61.6, and 49.3%, respectively, showing the influence of temperature on ester conversion. At 120 min, the percentages were 94.2, 79.9, and 69.8, respectively (Jose´ M. Encinar 2005)

4. Mixing method**:** Most researchers believe that the effect of Ultrasonic agitation on enhancing transesterification lies mainly in intensifying the mixing of the immiscible methanol and triglyceride phases, especially at the beginning of the reaction. The mixing enhancement is largely due to the collapse of ultrasonic cavitations bubbles and the reduced droplet sizes of low boiling temperature methanol in less-miscible triglycerides (Wu P 2007)

**5. Water content and free fatty acids in WVO:**

Waste vegetables oil contains water from food due to the frying process which also increases the free fatty acids (FFA) in the vegetable oil. However, different vegetable oil will lead to a different FFA composition, acid value, and different kinematic viscosity as seen in Table 1.4 and Table 1.5.

**Table 1. 4 Fatty acid composition (wt %) in WVO and CVO**

| Property | Waste veg.oil | Waste canola oil |
|---|---|---|
| Myristic(C14:0) | 0.9 | 0.1 |
| Palmitic (C16:0) | 20.4 | 5.5 |
| Palmitoleic (C16:1) | 4.6 | 1.1 |
| Stearic (C18:0) | 4.8 | 2.2 |
| Oleic (C18:1) | 52.9 | 55 |
| Linoleic(C18:2) | 13.5 | 24 |
| Linolenic(C18:3) | 0.8 | 8.8 |
| Arachidic (C20:0) | 0.12 | 0.7 |
| Eicosenic (C20:1) | 0.84 | 1.4 |
| Behenic (C22:0) | 0.03 | 0.5 |
| Erucic (C22:1) | 0.07 | 0.4 |
| Tetracosanic (C24:0) | 0.04 | 0.3 |
| Mean molecular wt (g/mol) | 856 | 882 |

**Table 1. 5 Comparison between the properties of WVO and WCO**

| Property | Waste veg.oil | Waste canola oil |
|---|---|---|
| Acid value(mg KOH/g) | 2.1 | <0.5 |
| Kimematic viscosity at 40˚C (cSt) | 35.3 | 30.2 |

The process variables that influence the transesterification of triglycerides, which are catalyst concentration, molar ratio of methanol to raw oil, and kind of catalyst are all affecting products yield. This paper also studies the influence of the Ultrasonic bath on the physical and chemical properties of the feedstock oils on the alkaline-catalyzed transesterification process and determines the optimal transesterification reaction conditions that produce the maximum ester content and yield.

## 1.4 Use of products:

### 1.4. 1 Biodiesel (methyl ester)

1. Producing Hydrogen for Fuel-Cell Vehicles
2. Cleaning Up Oil Spills
3. Generating Electricity
4. Heating Your Home
5. Cooking and Illumination
6. Cleaning Up Tools and Grease
7. Adding Lubricity to Diesel Fuel
8. Removing Paint and Adhesives
9. **Screen Printing Ink Remover**
10. **Auto Wax Remover**
11. **Corrosion Preventative**
12. **Metal Working Lubricant**

### 1.4. 2 Glycerin

1. Drug industry
2. Food Industry
3. Cosmetic Industry
4. Paper Industry
5. Explosives Industry
6. Medical Industry
7. Plastics and textiles industry
8. Coatings and colorants industry
9. Auto Industry

## 1.5 Physical and chemical properties of raw materials and products

### 1.5.1 Raw materials

a. Triglyceride

1) Physical properties:

- molecular form : $C_{57}H_{106}O_6$
- molecular weight : 888.4608 gr/gmol
- form(at 30C˚,1atm : liquid
- appearance : yellow-red
- density : 0.895 g/*cc*
- viscosity : 27 cp
- heat capacity : 0.497 kal/gr C˚

2) Chemical properties:

During frying process, oil is continuously or repeatedly subjected to high temperatures in the presence of air and moisture. Three essential degradation reactions occurs under these conditions are: Hydrolysis causing from the moisture content of fried food. This reaction produces free fatty acids (FFA), mono- and di-glycerides.

- Oxidation: causing from the contact with oxygen. Reaction products are oxidized monomeric, dimeric and oligomeric triglycerides and volatile materials such as aldehydes and ketones.

- Polymerization: causing from these two reactions, and high temperatures. This reaction produces dimeric and polymeric triglycerides with ring structure.

Because of these degradation reactions mentioned above, a number of physical and chemical changes occur in frying oils including increase in viscosity, density, FFA content, total polar material (TPM), polymerized triglycerides, and decrease in smoke point, the number of double bonds, etc. If the frying process is continued, these materials will undergo further degradation and finally the oil will not be appropriate for frying (C 2000).

b. Methanol

1) Physical properties:

- molecular form : $CH_3OH$
- molecular weight : 32.04 gr/gmol
- form(at 30C˚) : liquid
- appearance : colorless
- density : 792 kg/$m^3$
- viscosity : 0.541 cp
- boiling point : 64.5 C˚
- melting point : -97 C˚
- critical temperature : 239 C˚ =(463 F˚)
- heat capacity : 43.829 J/mol.K

2) Chemical properties:

- Chemical reaction of methanol which evaporates in the air producing carbon dioxide and water
  $2CH_3OH + 3O_2 \longrightarrow 2CO_2 + 4H_2O$....(1.1)
- Methanol esterification : methanol reacts with organic acid(formic acid) to form ester
  $CH_3OH + HCOOH \longrightarrow HCOOCH_3 + H_2O$....(1.2)
- Methanol reacts with Sodium at room temperature and releases hydrogen gas
  $2CH_3OH + 2Na \longrightarrow 2CH_3ONa + H_2$ ......(1.3)

In the dominant ICI (now Synetix) process, the syngas mixture of $H_2$, CO, and $CO_2$ is reacted over a copper-zinc-based catalyst at high pressure (50–100 atm) and moderate temperature (200–3000C):

$CO + 2H_2 \leftrightarrow CH_3OH$ .....(1.4) ΔH) 298K = −90.88 kJ/mol

$CO_2 + 3H_2 \leftrightarrow CH_3OH$ .....(1.5) ΔH) 298K = −41.09 kJ/mol

$CO_2 + H_2 \leftrightarrow CO + H_2O$ .....(1.6) ΔH298K = 49.87 kJ/mol

The modern methanol plants have selectivity to methanol of 99%, with energy efficiencies that reach 70% .

### 1.5.2 Supporting materials

Sodium hydroxide

1) Physical properties

- molecular form : NaOH
- molecular weight : 39.9971 g/gmol
- phase : solid
- appearance : white flakes
- purity : 98%
- boiling point 1 atm : 1388 C°
- solubility(water 20 C°) : 1110 g/L
- solubility( methanol 20 C°) : 139 g/L

(PT.Tjiwi Kimia)

2) Chemical properties

NaOH reacts with strong acids to produce salt and water

$NaOH + HCl \longrightarrow NaCl + H_2O$ ...... (1.7)

### 1.5.3 Product / byproduct

a. Methyl ester (biodiesel)

- molecular form : R_COOCH3
- molecular weight : 283.77 g/mmol
- phase : liquid
- appearance : clear yellowish
- density : 810 kg/$m^3$
- viscosity : 7.3 cp
- specific gravity : 0.87-0.89
- cetane number : 46-70
- cloud point : (-11 s/d 16) C°
- boiling point : (182-338) C°
- pour point : (-15 s/d 135) C °
- critical temperature : 239 C° =(463 F°)
- heat capacity : 662.4529 J/kg.K

(German DIN V 51 606).

**Table 1. 6 Biodiesel standards DIN V 51606**

| No | Specification | DIN V 51606 |
|---|---|---|
| 1 | Application | Fatty acid methyl ester |
| 2 | Density | 0.875-0.9 |
| 3 | Viscosity at 40 ˚C , $mm^2/s$ | 3.5-5.0 |
| 4 | Flash point | >110 |
| 5 | Water content | <300 |
| 6 | Cetane number | >49 |
| 7 | Methanol % by weight | <0.3 |
| 8 | Ester % by weight | - |
| 9 | Glycerides % by weight | <1.6 |
| 10 | Glycerol % by weight | <0.25 |
| 11 | Iodine number | <115 |

b. Glycerol

1) Physical properties

- molecular form : $C_3H_8O_3$
- molecular weight : 92.09382 g/mmol
- phase : liquid
- appearance : dark yellowish
- density : 1.261 kg/$m^3$
- viscosity : 2.86 cp
- boiling point : 290 C˚
- melting point : 18 C˚
- flash point : 160 C ˚
- heat capacity : 2.425 J/g

2) Chemical properties

Glycerol reacts with nitric acid to produce propanetriol nitrat and water:

$$C_3H_8O_3 + HNO4 \longleftrightarrow C_3H_7NO_5 + H_2O \quad ...(1.8)$$

## 1.6 General process overview

The chosen process in this plant design of biodiesel is transesterification using waste vegetable oil and methanol, because this process takes place at atmospheric pressure and temperature lower than esterification process, in addition, the raw material used is WVO so transesterification process is more appropriate to give a higher yield, as WVO contain a higher FFA value.

Conversion of biodiesel is up to 95%.

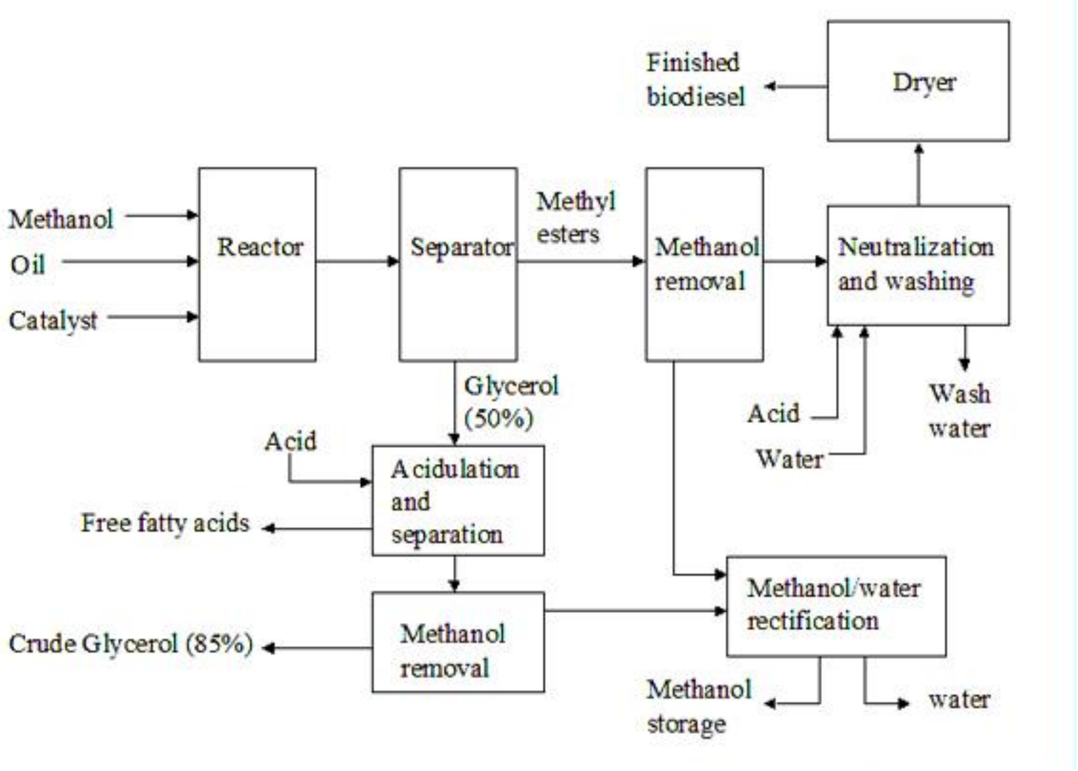


Figure 1. 7 Process flow diagram of biodiesel production