

CHAPTER III EXPERIMENT

3.1 Materials and Equipment

3.1.1 Materials

- Diesel was donated from Rayong Purifier Public Company Limited.
- Ethanol 99.5% was obtained by the Royal Chitralada Projects.
- Ethanol 99.9% was purchased from J.T.Baker.
- Anhydrous methanol and butanol were purchased from Labscan Co.,Ltd.
- Biodiesel was synthesized through transesterification process.
- Palm oil (Morakot cooking oil)
- Reference standard was purchased from Supelco.

3.1.2 Equipment

- The 3-necked round-bottom flask
- Thermometer
- Reflux condenser
- Hot plate with magnetic stirrer
- Vial tubes
- Glassware
- Water bath
- Evaporator
- Gas chromatograph
- ASTM testing apparatus

3.2 Experimental Procedure

The experiment was divided into 4 sections which are palm oil characterization, biodiesel production, diesohol blending and fuel properties testing.

3.2.1 Palm Oil Characterization

Vegetable oil is normally compounds of the family of triglyceride. Its structure consists of C_3H_6 molecules connected to fatty acids containing 10 to 30 carbon atoms. Vegetable oil is composed of many kinds of fatty acids, accounting for 94-96% of the molecule weight of the triglycerides. In general, most fatty acids in vegetable oil contain 12 to 18 carbon molecules. To determine the fatty acid composition and molecular weight of palm oil, there is an indirect method which analyzes the composition of derived biodiesel product by gas chromatography (GC).

Gas chromatograph equipped with a 30 m capillary coated with a 0.25 μm film of DB-WAX and a flame ionization detector (FID) allows the determination of all fatty acid profile in a single GC run. The conditions of GC are listed as follows:

Injector temperature: 155 °C,

Oven temperature: 230 °C

FID condition:

Temperature: 250 °C,

Carrier gas: He (99.999% purity)

Split ratio: 1:50

One μL of palm oil methyl ester was analyzed by GC. The observed peak was identified by comparison time of the standard. For quantitative analysis, the peak area was then converted to the concentration of each component based on the calibration curves.

3.2.2 Biodiesel Production

Biodiesel were produced through the transesterification of palm oil as raw material with base catalyst by varying types of alcohol. In this study, methyl and ethyl esters were prepared.

- *Palm Oil Methyl ester*

Palm oil methyl esters were synthesized in a batch type reactor using NaOH as a catalyst. The reaction utilized a molar ratio of methanol-to-oil of 9:1 and a catalyst of 0.5% by weight of oil.

In the first step, approximately 34 g of methanol was mixed with 0.5 g of NaOH until all of the catalyst dissolved. 100 g of cooking oil (about 0.12 mol) was placed in a 3-necked round-bottom flask equipped with a thermometer, a reflux condenser and a magnetic stirrer as shown in Figure 3.1. The reactor was controlled by a temperature controller. Dryness is absolutely essential as any water in the system will consume some of the catalyst and cause soap formation which inhibit product separation. The oil was heated to the desired temperature (60 °C) and then the methanol/NaOH solution was added to the oil. This mixture was stirred vigorously for 2 hours at 60 °C, and then was poured into a separatory funnel. After about 8 hours, the separation had occurred and the glycerol was removed from the bottom of the separatory funnel as a dark brown colored liquid. The top ester layer was separated and washed with 200 mL of distilled water for 3 times to remove the catalyst and unreacted methanol until it became completely translucent. Finally, the ester was dried with anhydrous sodium sulfate, approximately 25% wt of raw oil.

- *Palm Oil Ethyl ester*

Palm oil ethyl esters were prepared in much the same way as the methyl esters. The reaction utilized a molar ratio of ethanol-to-oil of 12:1 in order to achieve the maximum conversion. As the ethyl esters tended to form emulsions with glycerol, an amount of water was added to enhance the products separation. The crude ester was separated and washed with distilled water. After washing, the ester was dried with anhydrous sodium sulfate.

- *Palm Oil Butyl ester*

Palm oil butyl esters were prepared using a molar ratio of butanol-to-oil of 12:1 and sodium metal as catalyst. About 170 mg of sodium metal was cut into small pieces and carefully dropped into a flask of anhydrous butanol. After all sodium pieces were dissolved, the solution was poured into the oil of 100 g and the transesterification lasted 3 hours with vigorous stirring at 105 °C. After reaction, the small amount of glycerol was settled at the bottom of flask, and then separated in a separatory funnel. Since butanol cannot be completely extracted from the ester phase by water washing. The esters were further dried in an evaporator at 125 °C to remove any residual butanol and water.

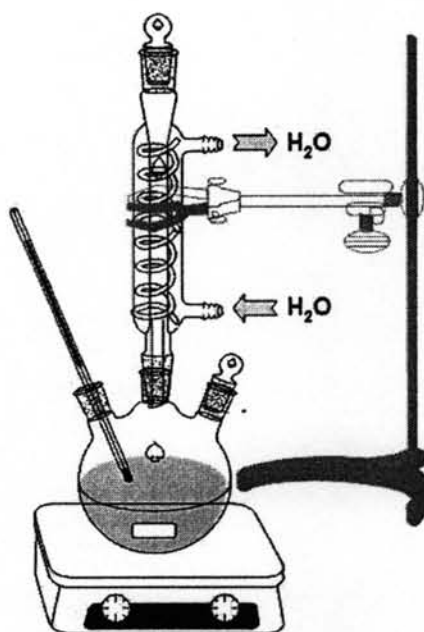


Figure 3.1 Reactor for palm oil alkyl ester production.

3.2.3 Splash-blending

Diesohol was prepared by splash-blending method. Diesel, biodiesel (methyl, ethyl or butyl esters) and alcohol (ethanol or butanol), as shown in Figure 3.2, were mixed together into a homogeneous mixture by a magnetic stirrer. The stirring speed was set at 1,000 rpm for 5 minutes. Then, the final blend was kept in a vial tube for observing the physical appearance. The same procedure was carried out with other ratios of diesel, biodiesel and alcohol. Each component was varied from 0% to 100% by volume in 10% increments. In this study, phase behavior of the three-component systems was investigated by using a physical state diagram. All the blends from the previous step were kept motionless for 7 days at 10, 20, 30 °C to observe the physical stability. After 7 days, the observation data were used to develop the physical state diagrams at different temperatures. However, all the blends were kept motionless at room temperature for 3 months to observe the long term stability.

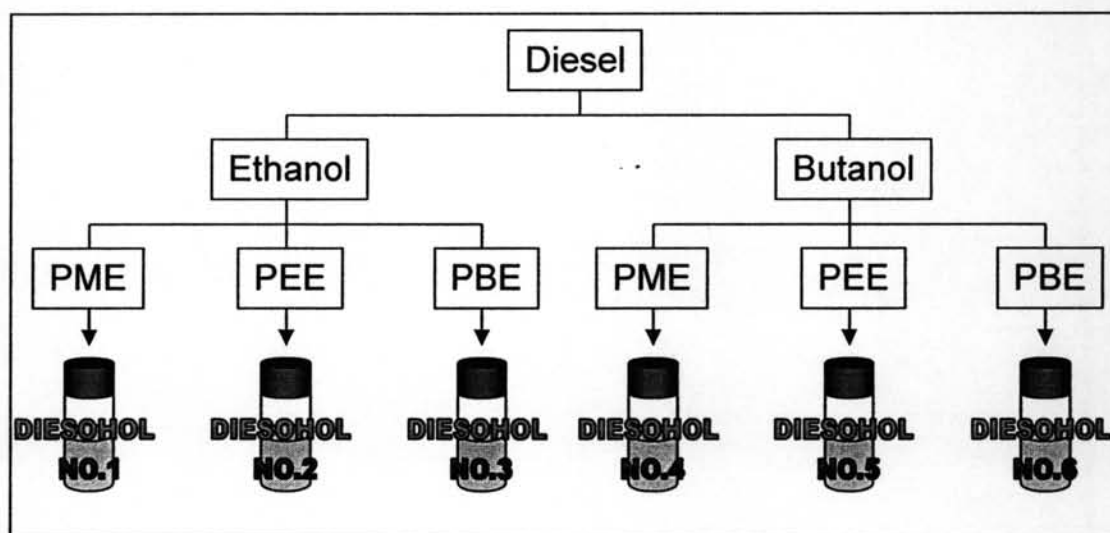


Figure 3.2 Schematic of diesohol blending.

3.2.4 Fuel Properties Testing

Laboratory tests were then carried out using ASTM standards to determine the fuel properties as follows.

- *Density at 15 °C*

Density is defined as the weight of a unit volume of fluid. This property is important mainly in airless combustion systems because it influences the efficiency of atomization of the fuel (Ryan *et al.*, 1984). ASTM D 4052 is the standard test method for density and relative density of liquids by Digital Density Meter. According to the standard, approximately 3 ml of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.

- *Kinematic Viscosity at 40 °C*

Kinematic Viscosity is a measure of the internal friction or resistance of an oil to flow. Even more than density, this is an important property since it affects the operation of fuel injection equipment. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. Kinematic viscosity of the fuel can be measured by viscometer according to ASTM D 445. This test method determines the kinematic viscosity, ν , of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid (approximately 7 ml of sample) to flow under gravity through a calibrated glass capillary viscometer at specific temperature (40°C).

- *Cetane Index*

The Calculated Cetane Index is a supplementary tool to estimate cetane number when used with due regard for its limitations. This test method covers the Calculated Cetane Index formula, which represents a means for directly estimating the ASTM cetane number of distillate fuels from API gravity and mid-boiling point. According to ASTM D 976, the Calculated Cetane Index is determined from the following equations:

$$\begin{aligned} \text{Calculated cetane index} = & -420.34 + 0.016 G^2 + 0.192 G \log M \\ & + 65.01 (\log M)^2 - 0.0001809 M^2 \dots\dots\dots(1) \end{aligned}$$

or

$$\begin{aligned} \text{Calculated cetane index} = & 454.74 - 1641.416 D + 774.74 D^2 \\ & - 0.554 B + 97.803 (\log B)^2 \dots\dots\dots(2) \end{aligned}$$

where:

G = API gravity, determined by Test Method D 287, D 1298, or D 4052,

M = mid-boiling temperature, °F, determined by Test Method D86 and corrected to standard barometric pressure,

D = density at 15°C, g/ml, determined by Test Method D 1298 or D 4052,

B = mid-boiling temperature, °C, determined by Test Method D 86 and corrected to standard barometric pressure.

- *Heat of Combustion*

Heat of combustion is the amount of heat released per unit mass or unit volume of a substance when the substance is completely burned. It is determined by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat transfer corrections. The amount of sample used depends on the heat of combustion of the material. Usually, not more than 1 g is required for one determination.

- *Pour Point*

Pour point is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. It is determined by ASTM D 97, the standard test method for pour point of petroleum products. Firstly, the sample is heated to about 45°C and then cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the pour point. Pour points for most automotive diesel fuels are usually between -15 and 35°C.

- *Flash Point*

Flash point is the lowest temperature at which a fuel will ignite when exposed to an ignition source. ASTM D 56-the standard test method for flash point by Tag Closed Cup Tester-covers the determination of the flash point, by tag manual and automated closed testers, of liquids with a viscosity below 5.5 mm²/s (cSt) at 40°C (104°F), or below 9.5 mm²/s (cSt) at 25°C (77°F), and a flash point below 93°C (200°F). This test method can be used to measure and describe the properties of materials, products, or assemblies in response to heat and flame under controlled laboratory conditions and cannot be used to describe or appraise the fire hazard or fire risk of materials, products, or assemblies under actual fire conditions. However, results of this test method can be used as elements of fire risk assessment that takes into account all of the factors that are pertinent to an assessment of the fire hazard of a particular end use.

- *Oxidation Stability*

Biodiesel consists of long-chain fatty acid esters, derived from renewable sources such as vegetable oils. Depending on the raw material, biodiesel can contain more or less unsaturated fatty acids in its composition, which are susceptible to oxidation reactions accelerated by exposition to oxygen and high temperatures, being able to change into polymerized compounds.

Ten g samples are aged at a constant temperature (110°C) with an airflow passing through at the rate of 10 l/h. The airflow is passed through a measuring cell filled with distilled water. The conductivity is determined continuously and recorded automatically. During the oxidation process volatile acids are formed. These are transported in the stream of air to a second vessel containing distilled water and can be detected by the increase in conductivity. At the end of the ageing period the conductivity increases rapidly. The period up to this point is called "induction period".