Production of Biodiesel through Transesterification of Avocado (*Persea gratissima*) Seed Oil Using Base Catalyst

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ABSTRACT

Biodiesel is produced through a chemical process called transesterification, which refers to a catalysed chemical reaction involving vegetable oil and alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol as a by product. Biodiesel is petroleum substitution in which its quantity continually decreases due to increasing of demand. Plenty of plants could be used as raw material for biodiesel, for example is avocado (Persea gratissima) seed. This is a waste that being thrown out after the flesh is taken. Therefore, avocado has a higher economic value to be used for consumption. Avocado is not only as an edible commodity but also as feedstock for production of biodiesel. The purposes of this research are producing biodiesel from avocado seed oil (Persea gratissima) so it can be used for alternative fuel, studying the effect of molar ratio avocado seed oil to methanol and reaction temperature to yield the highest methyl ester content, and also studying the effect of washing method and comparing between the conventional method (using water) and dry washing method to reach the highest methyl ester content. Variables that are used in this research are molar ratio of methanol to avocado seed oil, reaction temperature, and washing method. Transesterification process runs for 60 minutes, with NaOH as base catalyst concentration is 1% by weight. Avocado seed oil contains free fatty acid less than 2%, so that transesterification process can be carried out with no addition step to convert free fatty acid content become esters. Crude biodiesel which is yielded from transesterification process still contains of impurities, such as traces of glycerine, unreacted methanol, rest of base catalyst, and soap stock. So it needs to be washed out. There are two washing methods, which are water washing and dry washing. The use of dry washing method is expected to be technically feasible with less complexity than the water washing method, thereby making it a competitive alternative to commercial biodiesel production. From this research, it can be concluded that the characteristic of biodiesel from avocado seed oil is acceptable for alternative fuel. The optimum condition is obtained at molar ratio of 1:6 (alcohol to oil) and temperature 60°C. Washing method with water is resulting methyl ester content of 82.7119%, while for dry washing method resulting methyl ester content of 84.5678%. Therefore, the best washing method is dry washing in difference of 1.8559%.

***Keywords**: Biodiesel, transesterification, avocado seed oil, dry washing.*

INTRODUCTION

Increase in human population plays an important role to the existence of energy supply, especially for unrenewable energy. In a long term, import of petroleum fuel will dominate national energy supply. So that government has to make a policy about alternative renewable fuel.

The alternative fuel must be technically acceptable, economically competitive, environmentally acceptable, and easily available. Increasing environmental concern, diminishing petroleum reserves, and agriculture based economy of our country are the driving forces to promote biodiesel as an alternative fuel. In USA and Europe, biodiesel derived from vegetable oil and animal fats is being used to reduce air pollution and dependence on fossils fuel.

Biodiesel is known as fuel derived from renewable resources for use in diesel engines. Biodiesel is environmentally friendly liquid fuel similar to petroleum diesel in combustion properties [1].

As an alternative fuel, it has many advantages. It is derived from a renewable, domestic resource, thereby relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum fuel, biodiesel has a more favorable combustion emission profile, such as low emission of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the greenhouse effect [1].

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical

reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol.

Catalysts may either be base, acid, or enzyme materials. For base catalysts, the most commonly used materials are sodium hydroxide, potassium hydroxide, and sodium methoxide. Most base catalysts systems use vegetable oil as feedstock. One limitation to the alkali-catalyzed process is its sensitivity to both, water and free fatty acid. The presence of water may cause ester saponification under alkaline conditions. Also, free fatty acids can react with an alkali catalyst to produce soaps and water. Thus, dehydrated vegetable oil with less than 2 wt. % free fatty acids, an anhydrous alkali catalyst and anhydrous alcohol are necessary for commercially viable alkali-catalyzed systems [2].

Table 1. Physical and chemical properties of avocado seed oil [3].

Physical Properties	Quantity
Specific Gravity (25°C)	0.915-0.916
Melting point	10.50°C
Flash point	245°C
Refractive index	1.462
Viscosity	0.357 poise
Chemical Properties	**Quantity**
Free Fatty Acid	0.367%-0.82%
Saponification number (mg KOH/g)	246.840
Iod number (mg *iodine*/g)	42.664
Acid number (mg KOH/g)	5.200
Esther number	241.640
Peroxide number (Milliequivalents peroxide per 1000 gram oil)	3.3
Unsaponifiable matters	15.250 %

Washing biodiesel as a process came about as a method developed to remove the reactants-residues of the transesterification reaction by which biodiesel is produced. The washing techniques divide to water washing and dry washing. Dry washing with magnesium silicate as an adsorbent can decrease cost and production time, because it doesn't need addition process to remove water after washing. Also, it doesn't cause emulsion between fuel and water that make easier to separate.

Avocado seed is useless biomass material that contains triglycerides and has low FFA (free fatty acid) content, which is 0.367% (Table 1), so it can be processed to biodiesel through transesterification. Nevertheless, authors try to examine the potential of avocado seed as alternative energy resources that environmental friendly. Therefore it can meet the domestic energy demand.

RESEARCH METODOLOGY

Operational Condition and Variables

On this research there are 3 stage of processes, which are preliminary stage, main reaction stage, and purification stage.

Preliminary stage is carried out in order to get avocado seed oil content and purify it, so the oil ready to processed by transesterification using base catalysts. This stage contains of extraction, distillation, and degumming.

Main reaction stage is transesterification. The operational condition for this stage are retention time 60 minutes and 1% wt. NaOH toward oil. Whereas the variables are molar ratio oil to methanol (1:4, 1:5, 1:6, 1:7, and 1:8) and temperature reaction (40°C, 50°C, and 60°C).

Purification is the final processing stage before the fuel is ready to use. The purification removes catalysts and reactant residues, glycerol, and other impurities. For the purification stage, biodiesel from transesterification process is washed by two different methods. First method is water washing method using 50% vol. warm water (±50°C) that is stirred together with crude biodiesel. And the second is dry washing method using 0.5% wt. magnesium silicate as adsorbent for the impurities in the crude biodiesel.

Feedstock and Equipments

The feedstocks are avocado seed, n-hexane, H_3PO_4, methanol, NaOH (solid), magnesium silicate, and aquadest. The research is laboratory scale using transesterification reactor as the main equipment.

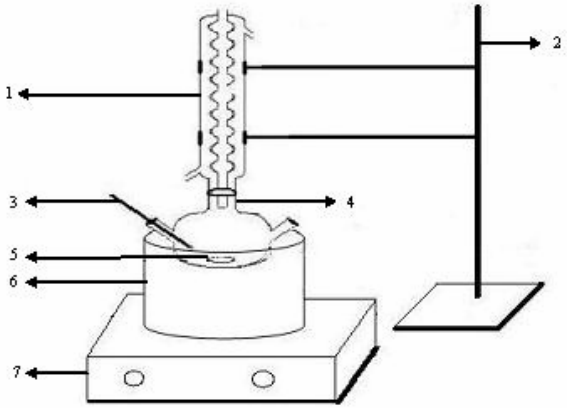

Figure 1. Transesterification Equipment

Explanation:
1. Condenser
2. Statif and Clem holder
3. Thermometer
4. Three neck flash
5. Stirrer
6. Water bath
7. Hot plate stirrer

Research Procedure

The preliminary stage begin with avocado seed's size reducing until 120 mesh, then to be dried at 110°C to remove water content. For the extraction, n-hexane (solvent) uses to extract avocado seed oil and continued with distillation to get more purify oil. Then, degumming is carried out with the addition of H_3PO_4 at 50°C and stirred for 30 minutes. Refined oil

from degumming was continued to transesterification process with operational condition and variables determined in before. Crude biodiesel produced have to purify with washing. For water washing, the mixture of biodiesel and warm water is stirred for 5 minutes. Then the mixture is settled until it form two layers, in which the top layer is biodiesel and the bottom one is water that contain impurities. The wash water is drained off. But it still contains water that has to be removed with drying at 110°C. whereas for dry washing method doesn't involve water, so it doesn't need water removal in the end of process. The mixture of biodiesel and magnesium silicate is stirred at 55°C for 15 minutes. Then biodiesel is separated from adsorbent that contain impurities using filter vacuum pump.

RESULT AND DISCUSSION

Oil extraction from avocado seed use solvent extraction with n-hexane. Solvent extraction was chosen because it can produce oil content in the amount of 15%; compare with mechanical extraction using screw press that result no oil content in the least.

Free fatty acid (FFA) level of avocado seed oil is just 1.55% (less than 2%), so it needs no esterification process to convert FFA into methyl ester. The oil can be processed by transesterification directly.

Next stage react oil with methanol using sodium methoxide as base catalyst, called transesterification. The reaction results crude fatty acid methyl ester (crude biodiesel), containing glycerol and other impurities. So biodiesel must be washed first in order to get higher methyl ester content. As mentioned before, there are two washing method, water washing and dry washing method.

Effect of temperature and molar ratio oil to methanol toward methyl ester content of biodiesel

There are several important factors that influence transesterification reaction, such as temperature and molar ratio of oil to alcohol (methanol) [4].

Ester formation occurs at 45-60°C after 1 hour. That temperature appropriate with the properties of methanol whose boiling point is 64.7°C. Higher temperature refers to methanol loss because of vaporization and also result fewer methyl ester content. Transesterification is an exothermic reaction; rise in temperature will push equilibrium into reactant side [5].

Figure 2 and 3 show that all variables give the same tendencies for methyl ester content, except for 1:8 molar ratio oil to methanol. At 1:8, both method of washing show decrease in methyl ester content at 60°C. These phenomena occur because of excess in methanol that makes glycerol separation be more difficult. Biodiesel from this variable still contain glycerol that impact to decrease in methyl ester content [5].

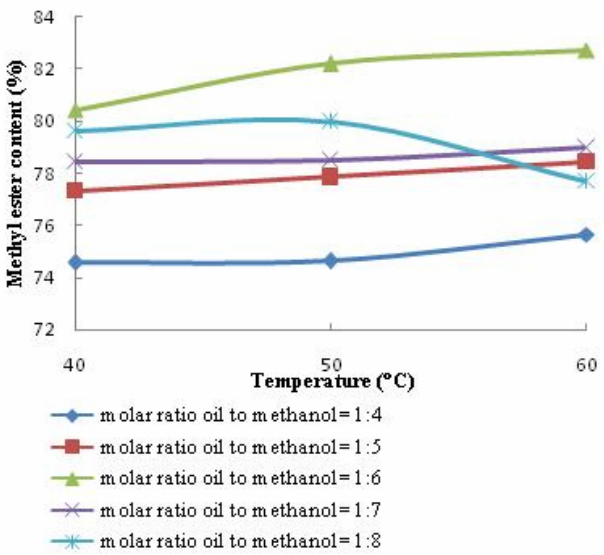

Figure 2. Effect of temperature toward methyl ester content using water washing method

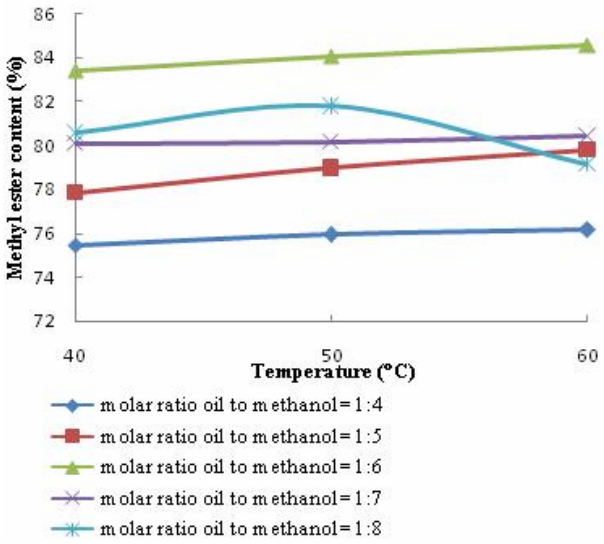

Figure 3. Effect of temperature toward methyl ester content using dry washing method

Based on Figure 2, the highest methyl ester content is given by molar ratio of 1:6 for oil to methanol at 60°C, which is 82%. It also described by Figure 3 (dry washing method), with methyl ester content at 84%.

Effect of washing method can be found out from Figure 2 and 3, in which dry washing method give the highest methyl ester content. Dry washing method is applied to overcome the flaws in water washing method that must be added by water

removal process. Dry washing method needs fewer times than another. Magnesium silicate as adsorbent, can bind the impurities (unreacted methanol, catalyst residue, and glycerol). It has strong affinity to bind polar compound, such as methanol and glycerol [6].

Characteristic of biodiesel from avocado seed oil

Before use for fuel, refined biodiesel with 84% methyl ester content should be analyzed first in order to find out the qualities. The analysis include of methyl ester content, density, viscosity, cetane index, flash point, and pour point.

Methyl ester content is detected by Gas Chromatography-Mass Spectrometry (GC-MS) and continued with Gas Chromatography (GC). GC-MS use to know what kind of compounds present in biodiesel. Figure 4 shows one of the GC result of our research. Range retention time is read, and continued with GC in the same temperature and column condition. Refined biodiesel is analyzed using GC HP 6890 series with HP-5 column 5% phenyl methyl siloxane. Kinds of methyl ester that be analyzed is methyl oleic and methyl palmetic because they are main compound exist in the avocado seed oil (Table 2).

Table 2. Fatty acid composition of avocado seed oil [7].

Fatty Acid	%
Palmetic Acid C16 : 1	11.85
Palmitoleic Acid C16 : 1	3.98
Stearic Acid C18 : 0	0.87
Oleic Acid C18 : 1 7	70.54
Linoleic Acid C18 : 2	9.45
Linolenic Acid C18 : 3	0.87
Arachidic Acid C20 : 0	0.50
Eliosenoic Acid C20 : 1	0.39
Behenic Acid C22 : 0	0.61
Lignoceric Acid C24 : 0	0.34

The characteristic of biodiesel should be known to figure out its quality. Viscosity is one of the most important parameter that influences machine performance. Viscosity is a basic design specification for the fuel injectors used in diesel engines. Too high viscosity make the injectors do not perform properly [8]. Viscosity is measured using viscometer Ostwald.

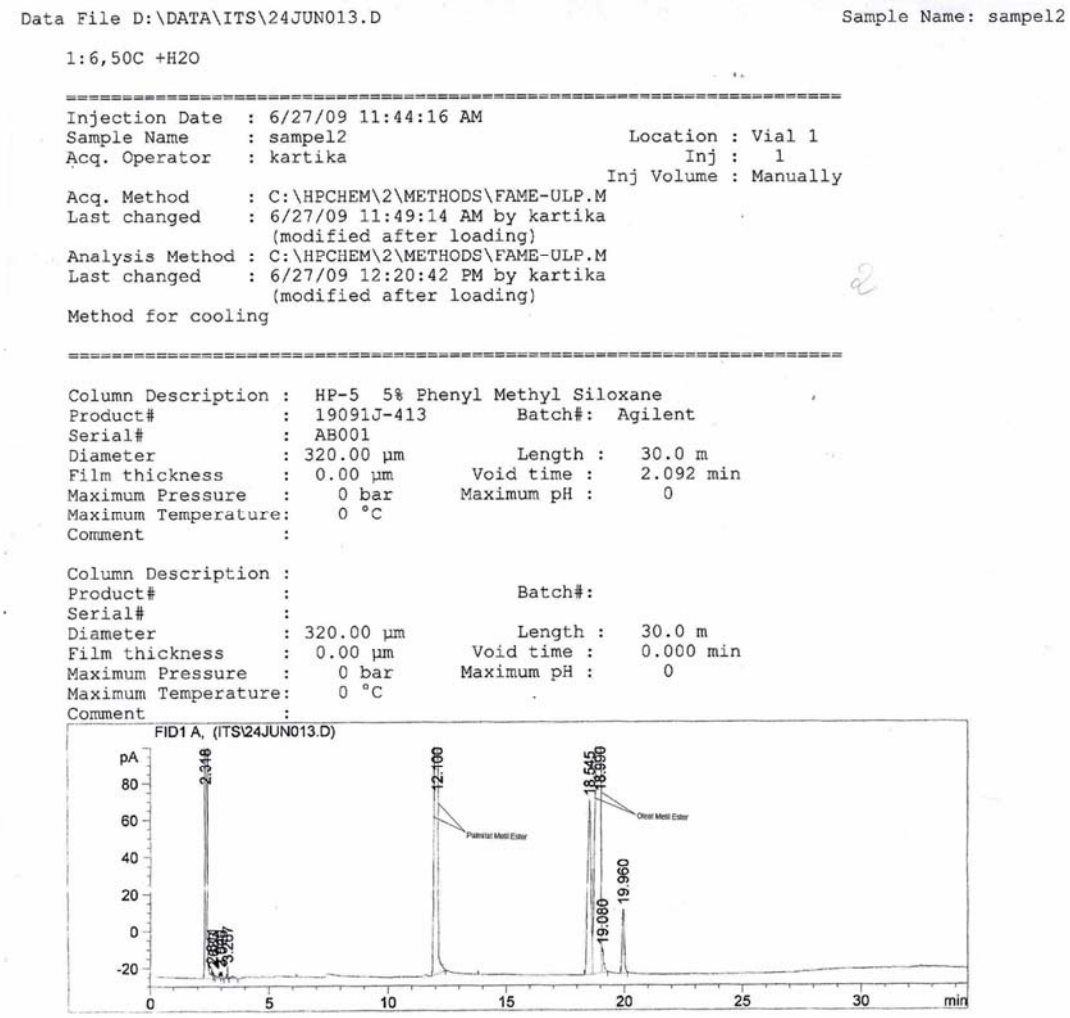

Figure 4. Chromatogram GC

Figure 5. Viscometer Ostwald [10].

For measuring density, densitometer is used at given temperature. Calculated cetane index (CCI) needs the data of density (D) and middle boiling point (B) to be processed by Equation 1:

$$CCI = 454.74 - 1641.416D + 774.74D^2 - 0.554B + 97.803(\log B)^2 \quad (1)$$

Cetane index is a measure of the ignition performance of a diesel fuel obtained by comparing it to reference fuels in a standardized engine test; it is a measure of how easily the fuel will ignite the engine [8].

The flash point is defined as the lowest temperature corrected to a barometric pressure of 1 atm, at which application of an ignition source causes the vapors of specimen to ignite under specified conditions of test [8]. Flash point is measured using Cleveland open-dish test (ASTM D92-90; IP 36/84).

Figure 6. Densitometer

Figure 7. Cleveland open-cup tester [9]

Table 3. Comparison between Biodiesel from avocado seed oil and Standard value of Biodiesel [10].

No	Parameters	Analysis Result	Standard Value
1	Density at 15°C (kg/m^3)	877.68	850-890
2	Viscosity at 40°C (mm^2/s)	4.9581	2.3-6.0
3	Flash point (°C)	184	<100
4	Pour point (°C)	-7	<0
5	Heating value (MJ/kg)	41.33	37-39
6	Cetane index	47.945	>47

Pour point is the lowest temperature at which fuel can still pour. This parameter is measured using ASTM D97-87.

Based on Table 3, biodiesel from avocado seed oil appropriate with standard value for diesel fuel. So this biodiesel can be applied in diesel engine or even blend with petroleum diesel fuel.

CONCLUSION

- Biodiesel from avocado seed oil is obtained by transesterification process using sodium methoxide as catalyst and to be washed by water wash system and dry wash system. This biodiesel meet the requirements for diesel fuel.
- Optimum condition to get the highest methyl ester content for biodiesel from avocado seed oil is obtained at 60°C with molar ratio oil to methanol 1:6.
- The best washing method is dry washing method which result 84.57% for methyl ester content.

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