

The Influence of Molar Ratio of Methanol to PFAD and Esterification Reaction Time towards Biodiesel Characteristics Palm Fatty Acids Distillate Produced

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Abstract— PFAD is potential enough to be developed as a biodiesel feedstock because it is cheap and always available. But the FFA in PFAD is so high, so esterification process is necessary to lower levels of the FFA. High levels of FFA PFAD and a solid form at room temperature need necessary studies to determine the needs of methanol as a reactant and reaction time esterification for high yield and characteristics of biodiesel. Esterification of PFAD were carried out to study the effect of : molar ratios of methanol to PFAD of 6 : 1 – 10 : 1 and reaction time of 60 – 120 min. The optimum condition for esterification process was molar ratio of methanol to PFAD at 10 : 1 with 2 wt% of H₂SO₄ at 60°C and 60 min. The amount of FFA was reduced from 97,17 wt% to less than 10 wt %, at the end of esterification process. The characteristic of biodiesel produced were 9.36 mg KOH/gr acid value, 5.01% FFA, 244 mg KOH/g saponification, 47.94 mg I/gr iodine value, 890 kg/m³ density, and negative result for determination water and sediment content.

Keywords— Biodiesel; Palm Fatty Acid Distillate (PFAD); esterification.

I. INTRODUCTION

Utilization of vegetable oil as a raw material source of energy is seen as one of the solutions to energy crisis. Besides, it can be obtained from renewable sources which are also more environmentally friendly. In the development, the debate emerges between the positive and negative exploration of resources as a source of energy. The use of raw materials is also the food seen treathening food security. A new issue that arises is the occurrence of competition use of resources resulting in the rising price of food itself. The solution is good enough to utilize oil instead of non-food oil sources and industrial waste containing oil [1],[2].

PFAD (Palm Fatty Acid Distillates) is a product of cooking oil which has a free fatty acid content of about 93%. As in [3] PFAD contains free fatty acids is very high around 75-95%. Bright yellow PFAD intangible is solid at room temperature [4].

As in [4] the process of making biodiesel from PFAD consists of two stages, i.e., esterification and continued with the process of purification. This process is done because PFAD is free of fatty acids. Esterification process uses acid catalyst to convert fatty acids into biodiesel and continued with the process of purification to neutralize the acids that may still be present on the esterification reaction and for

reacting fatty acids which have not been converted to be ester.

Esterification reactions are influenced by several factors, including the amount of reactant (molar ratio of methanol and oil), free fatty acid, the reaction temperature, reaction time, and the type and concentration of catalyst [5]. In esterification reactions, alcohol need to be added, so that the conversion process reaction can run perfectly. The type of alcohol can be used as solvents are methanol, ethanol, propanol and butanol. The methanol solvent is often used because the price is cheaper than other types of alcohol and can react quickly with triglycerides and can dissolve the acid and base catalysts. In addition, methanol is polar and has a short chain.

As in [6] The production of biodiesel was carried out in 250 cm³ screw capped bottle. Preheated palm fatty acid distillate (PFAD) was first measured into the bottle, followed by methanol and H₂SO₄ as catalyst. Operating parameters for efficient esterification include reaction temperatures in the range of 70-100 °C, molar ratios of methanol to PFAD in the range of 0.4:1- 8:1, quantity of H₂SO₄ catalyst in the range of 0-0.502 weight percent of PFAD, and reaction times in the range of 15-240 minutes were investigated. The production mixture was poured in a separating funnel and then allowed to settle into two phases. The bottom fatty acid methyl ester (FAME) layer was

separated and purified by washing with water before being analyzed.

While [7] produced biodiesel by esterifying PFAD and maintaining it at the reaction temperature in a refluxed batch reactor. The mixture of the methanol and concentrated sulfuric acid were added to the molten PFAD with continuous stirring for 120 minutes. The variables investigated in the esterification step were the molar ratio of methanol to PFAD (varied from 16:1 to 24:1) and reaction temperatures (60 and 70 °C) by using concentrated sulfuric acid catalyst (1 % v/w of PFAD). From their experimental results, the esterification processes reduce the acid value of the raw material down from 183 mg/g KOH to less than 0.50 mg/g KOH.

Based on the description above, the writer is interested in conducting research entitled “The Influence of Molar Ratio of Methanol to PFAD and Esterification Reaction Time towards Biodiesel Characteristics Palm Fatty Acids Distillate Produced”.

II. MATERIALS AND METHODS

A. Chemical

PFAD was obtain from Palm Oil Industry in Padang. All chemicals including methanol, sulfuric acid and chemical for analyze are commercial grade.

B. Analysis of PFAD Physicochemical

Characterization of PFAD in this research is done by analyzing the phycochemical of PFAD include analysis of acid value, iod value, FFA, and the saponification number. Characterization is intended to find out the early physicochemical of PFAD before further processing into biodiesel.

C. Esterification of PFAD

Esterification process is intended to lower the levels of free fatty acids (FFA). The esterification step was carried out by melting PFAD and maintaining it at the reaction temperature below the boiling point of methanol (60 °C), in a refluxed batch reactor. The mixture of methanol and concentrated sulfuric acid were added to the molten PFAD with continuous stirring for 60 and 120 minutes. The reactor was kept at the desired temperature . In order to prevent alcohol loss by volatility, the water that circulated inside the reflux condenser was cooled. The starting time of the reaction was the addition of the acid catalyst in the form of H₂SO₄ (2% of the weight of PFAD) and molar ratio of methanol with PFAD (6: 1, 8: 1 and 10: 1).

After esterification process is finished, next is the process of separation between the rest of the catalyst, water and methanol methyl ester by way of deposition of biodiesel for 12 hours. Next do the washing biodiesel and the process for removing the warming water on biodiesel.

D. Experiment Framework

Variables used in esterification reaction is molar ratio of methanol to PFAD (A) in 3 levels, namely 6: 1 (A1), 8: 1 (A2) and 10:1(A3). Reaction time (B) in two levels, i.e. 60 minutes (B1) and (B2) 120 minutes. Each combination

treatment is done 3 times. Research design used was Complete Random Design (RAL) with factorial pattern.

Prints a range of analysis results continued with the real difference distance test (Duncan) to figure out the combination treatment resulted in a significant difference of yield, acid value, FFA, iodine value, saponification value, density, water and sediment content.

III. RESULT AND DISCUSSION

A. Analysis of PFAD

Research on the production of biodiesel is using Palm Fatty acids Distillate (PFAD). PFAD is a by-product from the processing of palm oil containing high FFA. Analysis of PFAD include: acid value, iodine value and saponification nvalue. Analysis Physicochemical properties of PFAD results are presented in Table 1.

Acid value is used to determine the quality of the oil/fat. The higher number of the acid contained in the oil, the higher the level of the oil damage anyway [8]. Acid value that is owned by PFAD in this research is 202,40 mg KOH/g sample. The results showed that the value of percent free fatty acids (FFA) PFAD of 97%.

TABLE I
ANALYSIS PHYCOCHEMICAL PROPERTIES OF PFAD

Physicochemical Properties	PFAD
Acid value (mg KOH/ g)	202,40
FFA (%)	97,17
Iodine value (mg I/g)	71,90
Saponification value (mg KOH/g)	202,41

Data : Result of the Study

Iodine value is the important oil quality parameters, because it is used to express the degree of unsaturation of an oil or fat. The research shows that the number of the iod about 71.40 mg I/g.

The saponification is the amount of milligrams KOH needed to saponification one gram of oil or fat. The results showed that the number of PFAD saponification obtained of 202,40 mg KOH/g of sample.

B. Biodiesel Yield

Biodiesel yield is calculated to find out the amount of biodiesel produced after splitting and launder. The yield of biodiesel produced in this study ranged from 91,27% - 98,24%

Analysis of variance ($\alpha= 0.05$) for molar ratio of methanol to PFAD and esterification reaction time pointed out that the ratio of molar methanol: PFAD and esterification reaction have a significant effect towards yield of biodiesel produced, whereas the interaction between the molar ratio of methanol: PFAD and esterification reaction time does not influence the real yield of biodiesel.

Duncan Test about the effects of molar ratio of methanol: PFAD towards yield shows that the yield of biodiesel in the molar ratio of methanol PFAD 6: 1 (92,32%) and molar ratio of methanol PFAD 8:1 (93,26%) is different with molar ratio of methanol PFAD 10: 1 (97,32%).

The yield of biodiesel produced has a tendency of increasing in line with the increase in the molar ratio of methanol: esterification reaction PFAD time. Graph of the

relationship between the molar ratio of methanol:PFAD and esterification reactions time presented in Figure 1.

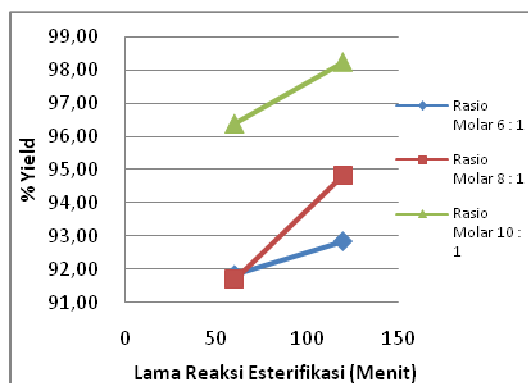


Fig 1. Graph of the relationship between the molar ratio of methanol: PFAD and esterification reactions time toward yield of biodiesel produced

Based on Figure 1 noted that the more amount of methanol is added and the longer reaction time esterification occurs due to yield. This increasement due to the use of excess amounts of methanol can shift the equilibrium towards products. The more ratio of methanol used then the higher yield of biodiesel was produced.

C. Pshycochemical properties of Biodiesel

1) Acid Value

The number of acid is one of the default parameters important for biodiesel. Acid value is defined as the number of milligrams of KOH/NaOH used to neutralize the free fatty acids contained in one gram of oil/fat [8]. Acid value shows the number of free fatty acids remaining after esterification processes. The number of maximum acid in biodiesel is 0.5 mg KOH/g.

In this study the resulting acid value is ranging between 24.6- 4.71 mg KOH/gr. Analysis of variance ($\alpha = 0.05$) for the molar ratio of methanol: PFAD and esterification reaction time pointed out that the ratio of molar methanol: PFAD had a significant effect towards acid number of biodiesel produced, while esterification reactions time and interactions between the molar ratio of methanol: PFAD and esterification reaction time do not influence the number of real biodiesel acid.

Duncan Test results about the effects of molar ratio of methanol: PFAD towards acid number indicates that the number of molar ratio on biodiesel acid methanol PFAD 6: 1 (17.88 mg KOH/g) and the molar ratio of methanol PFAD 8: 1 (19,88 mg KOH/gr) different molar ratio of methanol with PFAD 10: 1 (7,26 mg KOH/gr)

Acid number of biodiesel produced has a tendency of decreases with an increase in the molar ratio of methanol: PFAD and esterification reaction time. Graph of the relationship between the molar ratio of methanol: PFAD and esterification reactions time towards acid value is presented in Figure 2.

Esterification reactions are proven can decrease the number of acid. It can be seen from the number of acidic materials PFAD high amounting to about 202,40 mg KOH/g can be reduced to 24.6 - 4.71 mg KOH/gr. However the number of acid that results from this research are still higher

than the level This is because biodiesel produced is rough that still contains free fatty acids and acidic catalyst residues. As in [6] explained that the residue of free fatty acids and the rest of the catalyst can be lowered by the addition of neutralization process 3 M NaOH (NaOH is dissolved in aquades), done warming up for 15 minutes at a temperature of 80°C.

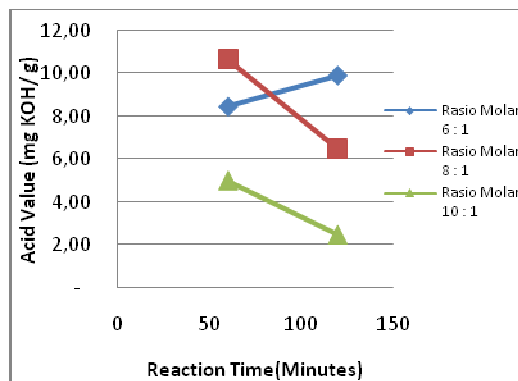


Fig 2. Graph of the relationship between the molar ratio of methanol: PFAD and esterification reactions time toward acid value of biodiesel produced

2) FFA (Free Fatty Acid)

The content of free fatty acids (FFA) is associated with an acid. Percentage of FFA number conversion of acid divided by the conversion factor to Palmitic acid. This is because the Palmitic acid is the predominant fatty acid in the PFAD. The results showed that the value of FFA biodiesel produced around 2.26% - 11,81.

Analysis of variance ($\alpha = 0.05$) for the molar ratio of methanol: PFAD and esterification reaction time pointed out that the ratio of molar methanol: PFAD has the real impact toward FFA biodiesel produced, while esterification reaction time and interaction between the molar ratio of methanol: PFAD and esterification reaction time did not affect FFA biodiesel.

Duncan Test about the effects of molar ratio of methanol: PFAD towards FFA value indicates that the value FFA on biodiesel of the molar ratio of methanol : PFAD 6: 1 (9,21%) and molar ratio of methanol: PFAD 8: 1 (8,59%) differed markedly with molar ratio of methanol : PFAD 10: 1 (3,75%).

The value of the resulting biodiesel FFA has a tendency of decreases with an increase in the molar ratio of methanol: PFAD and esterification reaction time. Graph of the relationship between the molar ratio of methanol: PFAD and reaction esterification time of FFA value presented in Fig.3.

Esterification reactions are shown to lower the value of the FFA. It can be seen from the FFA PFAD high raw material which is about 97,7% can be lowered to 2.26% - 11,81%. However the number of FFA that results from this research are still higher than the level This is because biodiesel produced is rough and need to purifying. As in [7] explained that the Transesterification post-treatment after esterification process was also studied. In the transesterification step, the reactions were carried out with 0.6 % of KOH catalysts, methanol to PFAD ratio of 8:1 and reaction time of 40 minutes. After transesterification post-treatment, the acid value of the biodiesel was found to

reduce below 0.80 % with the purity of biodiesel higher than 98 % .

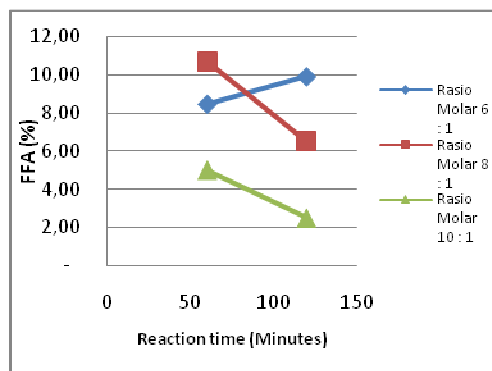


Fig 3. Graph of the relationship between the molar ratio of methanol: PFAD and reaction esterification time of FFA value

3) Saponification Value

The Saponification value is the number mg KOH needed to soap 1 g of oil or fat. The number of saponification shows a large number of free fatty acids and esters in biodiesel. The saponification value is influenced by the molecular weight and degree of saturation of fatty acids constituting [8]. Oil or fat with low molecular weight will have a number higher than soaping oil or fat with high molecular weight.

The results showed that the saponification number the resulting biodiesel revolves around the 228,58% - 364,33 mg KOH/gr.

Analysis of variance ($\alpha = 0.05$) for the molar ratio of methanol:PFAD and esterification reaction time pointed out that the ratio of molar methanol:PFAD and esterification reaction time as well as the interaction between the molar ratio of methanol:PFAD and esterification reaction time have no effect toward real numbers of biodiesel saponification value.

High value of saponification indicate that the number of compounds tri, di and monoglycerides have been reduced due to methyl ester converted. This is due to the molecular weights of the methyl ester has low molecular weight so that the number of saponification is high.

Biodiesel that is produced from different raw materials would have a number of different saponification. For example, the number biodiesel saponification number from sunflower seed oil is 179-186 mgKOH/gr [9].

4) Iodine value

Iodine value is the number of grams of iodine that is absorbed by the 100 grams of oil. The number of double bonds, which more and more is shown by the number of the iod. Iodine number determination is based on titration. Unsaturated glyseride of fats or oils have an ability to absorb a number of iod forming a compound which is saturated. To know the number of the iodine that absorbed by oil, the excess is titrated with sodium tiosulfate [10].

The result of the study indicated that biodiesel iod number produced is around 37,45 – 50,28 g I_2 /100gr. Analysis of variance ($\alpha = 0.05$) for the molar ratio of methanol: PFAD and esterification reaction time pointed out that the ratio of molar methanol: PFAD, esterification reaction time and interaction between the molar ratio of methanol: PFAD and

esterification reaction time did not give a significant affect to iodine value.

5) Density

Density shows the comparison of weight and volume, this characteristics related to the heat and energy resulted by diesel machine. In this study, the density test was done in temperature 40°C. The result shows that the biodiesel density resulted is around 0,9025 – 0,8705 gr/cm³.

Analysis of variance ($\alpha = 0.05$) for the molar ratio of methanol: PFAD and esterification reaction time pointed out that the esterification reaction time gave the significant effect to biodiesel produced, while esterification reaction time and interaction between the molar ratio of methanol:PFAD and esterification reaction time do not gave the significant effect to density of biodiesel.

Biodiesel density produced has a tendency of an increase in the esterification reaction time. Graph of the relationship between the molar ratio of methanol: PFAD and reaction esterification time of density presented in Figure 4.

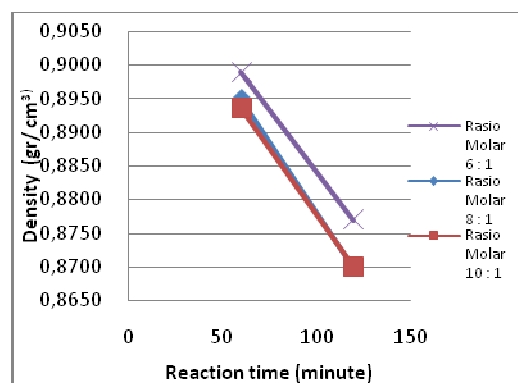


Fig 4. Graph of the relationship between the molar ratio of methanol: PFAD and reaction esterification time towards density of biodiesel produced

Biodiesel density resulted by this study is already fulfill the SNI standard around 0,85-0,89 gr/cm³. Biodiesel density is influenced by molecule weight, moistures, and free fatty acid in biodiesel. Besides, the density is also influenced by carbon chain and not fat degree of biodiesel. Biodiesel density will reduce as well as the increase of carbon chain and non fat degree

6) Water and Sediment

Water is one of the polluter in biodiesel. There is still water in the biodiesel will cause the onset of corrosion if applied on a machine. The high water content in biodiesel will also trigger the growth of microorganisms that will form deposits in biodiesel. Moisture relates also to the storage of biodiesel. High water content in biodiesel in process storage in a long period of time will increase free fatty acids biodiesel and lowering the quality of biodiesel.

Sediments contained after the process of leaching is the glycerol that react with water. The presence of sediment in biodiesel being applied on the machine will result in the onset of carbon deposit so that the combustion process runs is not perfect. Deposits of carbon will inhibit fuel channel, hinder the operation of the machine and cause rapid injection pipe is broken. These deposits can cause bad effect on the machine.

Analysis of water and sediemen of biodiesel results negative. Water and sediemen contained in a very small amount or may be considered non-existent. Water and sediment is derived from methyl-washing process that has been separated from the rest of methanol and a catalyst.

D. Fuel properties of PFAD biodiesel

The fuel properties of biodiesel obtain in this study are summarized in Table 2. The It can be seen that several of its properties are out range of fuel properties prescribed in the latest Indonesian standards for biodiesel. Acid value and FFA content are still high. According to [6] the FAME still had residual FFA and requiring further purification.

TABLE III
FUEL PROPERTIES OF PFAD BIODIESEL

Properties	Biodiesel in this study	Indonesian Standar (SNI)[11]
Acid value (mg KOH/ g)	9,36	0,8
FFA (%)	5,01	< 1
Iodine value (mg I/g)	47,9	Max 115
Saponification value (mg KOH/g)	244	
Density at 40°C kg/m ³	890	850-890
Water and sediment content (% -V)	Negative	Max 0,05

IV. CONCLUSIONS

A process for the production of biodiesel from PFAD has been evaluated. The final product is light brown material and several properties are not meeting the requirement of Indonesian biodiesel standards due to the biodiesel still has a high content of FFA and its need to purifying.

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