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# Biodiesel Production Using Palm Fatty Acid Distillate and Rice Husk Silica Supported NiSO<sub>4</sub> as Catalyst

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**Abstract.** As one of the promising feedstocks for the development of biodiesel, palm fatty acid distillate (PFAD) has weaknesses such as the high free fatty acid (FFA) and water content. In order to overcome the weaknesses, the NiSO<sub>4</sub>-rice husk silica (Ni-RHS) catalyst was used in PFAD esterification. The optimization result at 9 h reaction time and 100 °C showed the MeOH : oil molar ratio is 15:1 and 15 wt.% catalyst amount with 88% of methyl ester. The catalyst could maintain catalytic activity more than 80% in two cycles and it proves that the regeneration and reuse of the catalyst were feasible and handy.

## INTRODUCTION

Fossil fuels have an enormous impact on economic and social levels, as the use of fossil fuels has driven the industry's growth. Fossil fuels are non-renewable fuels, making the price will increase following its availability [1]. Global oil consumption rose by 1.4 million barrels per day in 2018, while the reserves are rapidly declining [2]. In turn, the fossil fuels consumption will increase CO<sub>2</sub> and greenhouse gas emissions [3], CO<sub>2</sub> gas causes critical environmental problems such as climate change and global warming. This research focused on the use of alternative renewable fuels. Alternative energy derived from biological sources such as biodiesel becomes important to the global community [4, 5].

The feedstock for biodiesel is usually the vegetable oils such as coconut oil, palm oil, corn oil, sunflower oil, etc. Using edible oils as biodiesel feedstock could compete with the food demand. In addition, feedstock operating costs (around 80 percent from total cost) have a significant impact on the overall cost of biodiesel production [6]. One alternate feedstock to overcome this problem is the use of by-products and waste oil, such as Palm fatty acid distillate (PFAD). Malaysia annually generated PFAD, almost 752,000 tonnes [7]. PFAD (72.7–92.6% FFA) is a potential and low-cost feedstock for biodiesel production, but the problem is this kind of feedstock easily undergoes a saponification reaction leading to the formation of soap. There are two steps process required to get feedstock containing high FFA. The esterification process using a homogeneous catalyst has few drawbacks, like high operating conditions [8]. Moreover, the isolating of homogeneous catalysts from the reaction mixture is difficult [9, 10]. The exploration of solid catalysts in the esterification reaction has been an interesting focus for researchers and has been extended to the industrial level. The advantages have a positive impact on the cost and environment. There are many types of heterogeneous catalysts, such as organophosphonic acid-functionalized silica, SO<sub>4</sub><sup>2-</sup>/SiO<sub>2</sub> TiO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-SiO<sub>2</sub> [8, 11-13].

In addition, the exploitation of biomass as support material in heterogeneous catalysts synthesis for esterification reaction is very attractive. On the other hand, according to the Department of Statistics Indonesia [14], the paddy production had rise as many as 32.42 million tonnes in 2018. Land utilization in Indonesia for paddy production was at 10.90 million hectares in 2018. It is stated that approximately 0.2 tons of rice husk were produced for each ton of rice harvested (533,000 tonnes rice husk ash (RHA) in 2011) [15]. As a biomass, RHA is abundant and containing much silica (87-99%), making it as a low-cost waste source of amorphous silica precursors [16]. Therefore, with the abundant of rice husk ash in Indonesia, this study utilizes RHA as support material for  $\text{NiSO}_4$  as a solid acid catalyst in PFAD esterification with one-step reaction to produce methyl ester. In deeply, this study investigated the variation of MeOH towards the oil molar ratio, catalyst amount and reusability.

## EXPERIMENTAL

The palm fatty acid distillate (PFAD) was collected from Refinery Palm Oil in Kuantan, Pahang. The Rice husk ash was taken from a rice mill in Samarinda. Methanol, petroleum ether (PE), ethanol, n-hexane, isopropanol, chloroform, sodium hydroxide (NaOH), potassium hydroxide (KOH), glacial acetic acid, potassium iodide, starch solution, sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) were bought from Merck KGaA (Darmstadt, Germany) and R&M Chemicals (Essex UK). Methylheptadecanoate and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  were obtained from Sigma-Aldrich (Switzerland). Thin Layer Chromatography (TLC) (20 x 20 cm, silica gel 60 F254) of HPTLC was purchased from MERCK (Germany). Hammett indicator (crystal violet, bromophenol blue, and methyl red) was obtained from Bendosen. All solvents used are analytical reagent grades.

### Preparation of Feedstock and Catalyst

#### *Rice Husk Silica (RHS)*

RHA was macerated and sieved using a 200 mesh. Then 50 g of powdered ash was washed using 200 mL of 0.1 mol/L HCl for 30 min, continued assisted by ultrasonic for 15 min, and neutralized using deionized water. At last, the clean ash was dried in an oven at 115 °C for 2 h. The resultant RHA was ready to be used as catalyst support and was labeled as rice husk silica (RHS).

#### *$\text{NiSO}_4/\text{RHS}$*

$\text{NiSO}_4$  was impregnated on rice husk silica. An appropriate amount of 0.2 N of  $\text{H}_2\text{SO}_4$  was added into solution until  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  was completely dissolved. It was continuously proceeded by refluxing the ash for about 3 h at 90 °C, separating the solution using the slurry, drying it at 110 °C for 24 h, and it was calcined at 500 °C for 2 h.

#### *Hammett Indicator Analysis*

About 20 mg of catalyst was diluted in 25 mL of methanol, three drops of indicators solution were dropped in solution of catalyst. The solution is left for 2 hours and the color changes of the solution were recorded. If the indicator exhibits a color change, then the catalyst is labeled as stronger than the indicator. Hammett indicators: methyl red ( $H_{\text{ind}} = 4.4-6.2$ ), bromophenol blue ( $H_{\text{ind}} = 3.0-4.6$ ) and crystal violet ( $H_{\text{ind}} = 0-1.8$ ).

#### *Esterification Reaction*

Esterification was conducted in a 250 mL double necks boiling flask. The PFAD following by methanol and  $\text{NiSO}_4/\text{RHA}$  were poured into the flask. The mixture was heated and stirred. Optimizations on the process involved were the MeOH to PFAD molar ratio and the catalyst amount. The product mixture was then poured into separation funnel. The obtained methyl ester was further to be analyzed with water washing and qualitative analysis using thin layer chromatography (TLC). Reusability of catalyst was conducted to examine the potential reusability of the catalyst. The used  $\text{Ni}/\text{SiO}_4$  that recovered by centrifugation was reused by washing with hexane followed by methanol. For the repeated reactions, the dried used catalyst is directly used as a catalyst.

### Methyl Ester Analysis

Following European regulation procedure EN 14103, the researcher used a polar capillary column (DB Wax, 30 m x 0.25 mm i.d x 0.25  $\mu$ m) and methyl heptadecanoate as an internal standard to assess fatty acid methyl ester estimated by equation (1). The instrument was the GC-FID (Perkin-Elmer, Clarus 500).

$$\text{Methyl ester content (\%)} = \frac{A_{\text{total}} - A_{\text{ISTD}}}{A_{\text{ISTD}}} \times \frac{C_{\text{ISTD}} \times V_{\text{ISTD}}}{W_{\text{sample}}} \times 100\% \quad (1)$$

where  $A_{\text{total}}$  is the total peak area of methyl esters;  $A_{\text{ISTD}}$  is the area of methyl heptadecanoate;  $V_{\text{ISTD}}$  is the volume of methyl heptadecanoate;  $C_{\text{ISTD}}$  is the concentration of methyl heptadecanoate; and  $W_{\text{sample}}$  is the weight of sample.

### Acid Value, FFA Content and Iodine Value of PFAD and ME

PFAD and ME has been characterized by several analyses, such as acid value, FFA content, and iodine value. The FFA content was related with an acid. The percentage of FFA conversion of acid is divided by the conversion factor to Palmitic acid. The Palmitic acid was said to be predominant fatty acid in PFAD. After the esterification process, the number of FFA remaining will be shown by the calculation of acid value. The PFAD weighed 0.5 g was first dissolved in 10 mL neutralized isopropanol and few drops of phenolphthalein were added to the solution. The solution was then titrated with standard potassium hydroxide solution at 40 °C and shaken gently until the first permanent pink solution was observed. The acid value is calculated as expressed in equation (2).

$$\text{Acid value (mg KOH/g sample)} = (56.1 \times V \times N) / W \quad (2)$$

where V is the volume of KOH solution used in mL; N is the normality of KOH solution in N; W is the weight of sample in gram.

The iodine value is a measure of the unsaturation of fats and oils. It is expressed as the number of grams of iodine absorbed by 100 g of the fat under the test condition used. The iodine value of PFAD and methyl are determined according to PORIM test method. Approximately 0.15 g of PFAD is dissolved in 15 mL carbon tetrachloride and 25 mL of Wijs solution is added, the solution is left in dark for 1 hour. After that, 20 mL of potassium iodide solution and 150 mL of water is added into the solution. 2 mL of starch indicator is added to the solution and titrated with sodium thiosulphate until blue colour disappears. The experiment is preceded with methyl ester. The iodine value is calculated with equation (3).

$$\text{Iodine value} = 12.69 \times N \times (V_2 - V_1) / W \quad (3)$$

where N is the normality of  $\text{Na}_2\text{S}_2\text{O}_3$  in N;  $V_1$  is the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  for blank in mL;  $V_2$  is the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution of sample in mL; and W is the weight of sample in gram.

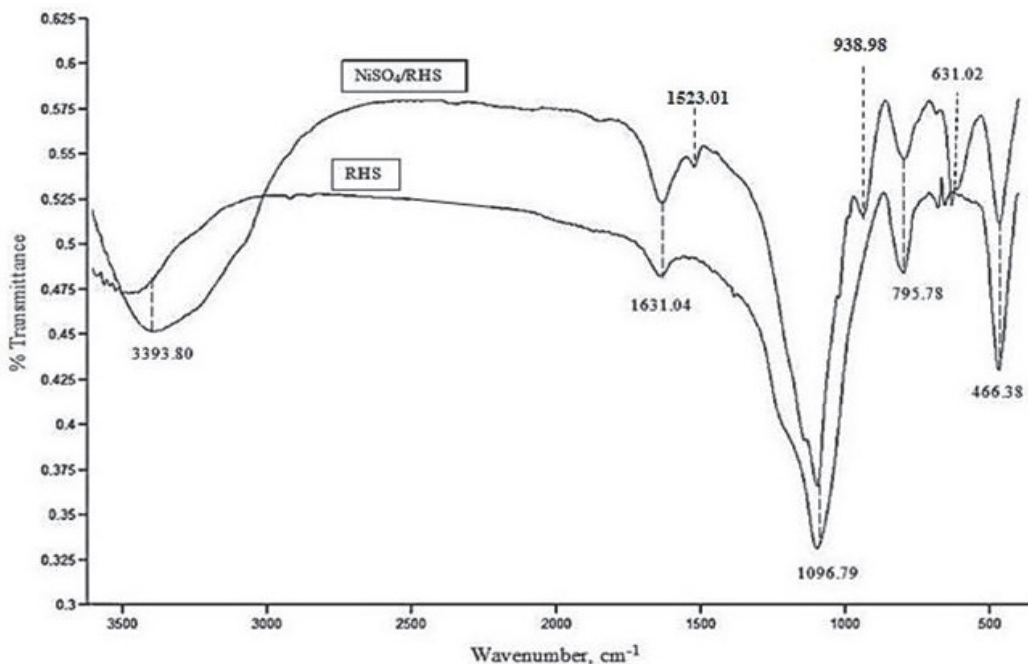
## RESULTS AND DISCUSSION

### Catalyst Characterization

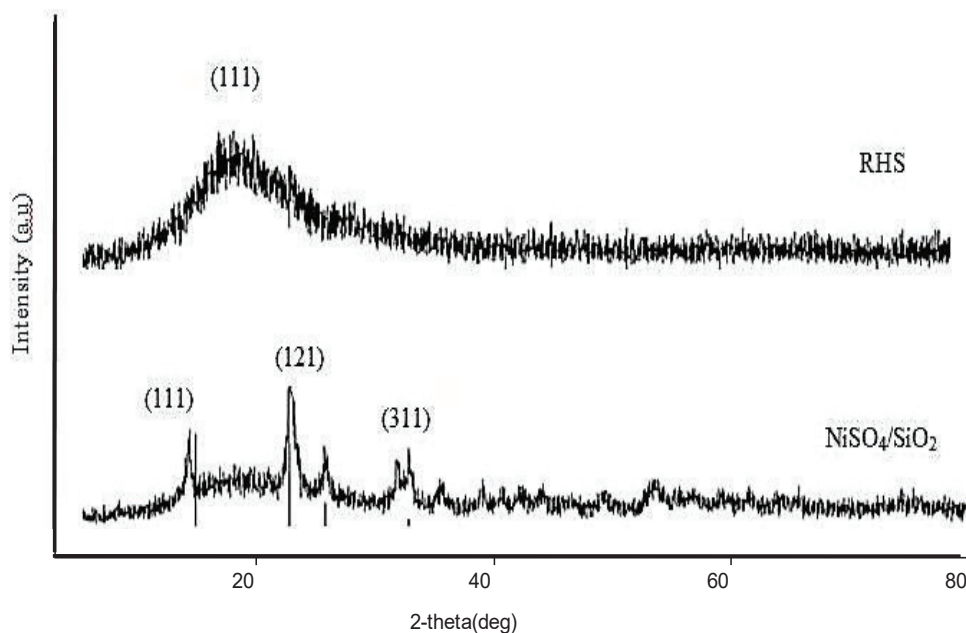
The major functional groups in RHA and  $\text{NiSO}_4/\text{RHS}$  were identified using the FTIR spectra as shown in Fig. 1. The characteristic absorption peaks of RHS at 466.38  $\text{cm}^{-1}$  indicated the Si-O-Si vibration stretching. The peak at 795.78  $\text{cm}^{-1}$  indicated the Si-O vibration bending from Si-O-Si. The Si-O-Si vibration stretching appeared at 1101  $\text{cm}^{-1}$ . The peak at 1631.04  $\text{cm}^{-1}$  was attributed to O-H bending and O-H stretching. All these functional groups were matching the silica network. The wideband around 3393.80  $\text{cm}^{-1}$  was assigned to the O-H vibration of Si-OH and H-OH groups of the associated water molecules [17]. The  $\text{NiSO}_4/\text{RHS}$  catalyst peak appeared at 631.02  $\text{cm}^{-1}$  and indicated the presence of metal  $\text{Ni}^+$ . The frequency at 939.98  $\text{cm}^{-1}$  was attributed to S-O bending. The peak around 1096  $\text{cm}^{-1}$  indicated the presence of Si-O-Ni bonds. The S-O stretching frequency was found at 1523  $\text{cm}^{-1}$ .

The XRD patterns of rice husk silica are shown in Fig. 2. The diffractogram shows a hump peak at  $2\theta$  ranging from 16° to 40° and appeared a large reflection at 21.66°, indicating the amorphous state of silica particles (JCPDS PDF: 01-071-6241). The  $\text{NiSO}_4/\text{RHS}$  pattern diffraction peaks were found at  $2\theta$ : 19.35°, 29.6° and 36.1°.

Furthermore, from the ICDD shows the modification material has Miller indices shows as nickel silicate [111] (ICDD 10701852), alpha Ni<sub>2</sub>SiO<sub>4</sub> [121] (ICDD 10761502) and Ni<sub>2</sub>SiO<sub>4</sub> [311] (ICDD 10740786 ).



**Figure 1.** The Rice Husk Silica and NiSO<sub>4</sub>/RHS FTIR Spectra



**Figure 2.** The calcined RHS and NiSO<sub>4</sub>/RHS XRD pattern

The catalyst acidity was analyzed using Hammett indicator. They were methyl red ( $H_- = 4.4-6.2$ ), bromophenol blue ( $H_- = 3.0-4.6$ ) and crystal violet ( $H_- = 0-1.8$ ). The NiSO<sub>4</sub>/RHS acidity was in the range of  $1.8 < H_- < 4.4$  and confirmed strong.

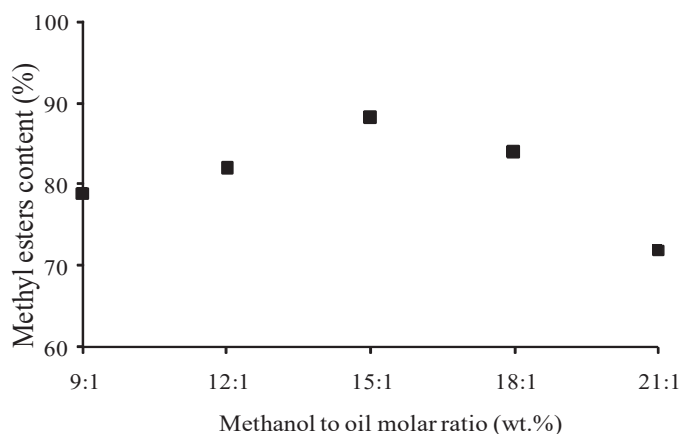
## Methyl Ester Characterization

The PFAD and methyl esters (ME) characteristics were identified by determining the acid value, FFA value, and iodine value. The PFAD and ME acid values were 189.98 and 5.59 mg KOH/g. The ME acid value still high divided supposed value, due to the FFA content. The PFAD and ME FFA values were 86.69% and 2.55%. The PFAD iodine value was 77 mg I<sub>2</sub>/g and the ME was 49 mg I<sub>2</sub>/g, showing the decreasing iodine value after converted into methyl ester. The GC analysis showed that the fatty acid methyl ester contents in ME were methyl palmitate (C16:0), methyl palmitoleate (C16:1), methyl oleate (C18:1), and methyl linoleate (C18:2).

## Methanol-PFAD Molar Ratio Effect on Methyl Ester Content

The methanol molar ratio is one of the important points in the esterification reaction. The amount of methanol increases, the reaction will drive the product, but the higher methanol will lack the recovery of the methanol in the product. State by Leung et al. [18], Methanol recovery costs should be high if the volume of alcohol is always higher than the optimum ratio. Furthermore, the process was economically worse.

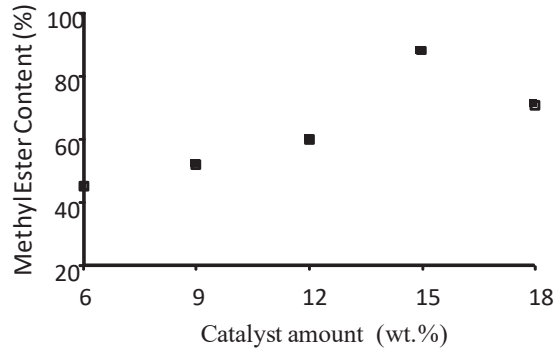
In this study, the MeOH : PDAF was tested in 9:1; 12:1, 15:1, 18:1, and 21:1 ratios. As shown in Fig. 3, the MeOH : PFAD ratio was achieved in the 15:1 molar ratio. Furthermore, increasing the MeOH ratio was not increasing the ME content. Due to the active catalyst sites already filled by methanol molecules instead of PFAD molecules, decreasing the amount of ME content and causing difficulty in separating methyl esters and a by-product as well as complicating the methanol removal process [19]. The remaining by-product would react with excess MeOH in the solution causing esterification or probably driving back the equilibrium reaction and resulting in the lower result of biodiesel [20]. However, using the excess methanol during product purification may result in higher biodiesel production costs as well as methanol separation costs.



**Figure 3.** Methanol to PFAD molar ratio effect on methyl ester content. The reaction condition was in 9 h reaction time, at 120 °C reaction temperature, with 15 wt.% catalyst.

## Catalyst Amount Effect on Methyl Ester Content

The catalyst amount affected the methyl ester production in the reaction. The catalyst amounts in this research were 6, 9, 12, 15, and 18 (wt.%). From the esterification process, the methyl ester content was 48.08, 51.42, 59.45, 84.11 and 61.59 (wt.%). From Fig 4, the increase in the content of methyl ester was when the catalyst amount increased from 6 to 15 wt.% and decreased at 18 wt.%. The use of more catalysts (18 %) will affect the esterification reaction thus decreasing the conversion. With the agreement of Olutoye et al. [8], the contact between methanol and oil will increase on the active site of the catalyst when adding more catalysts. However, adding excessive catalyst will lower the methyl ester content.

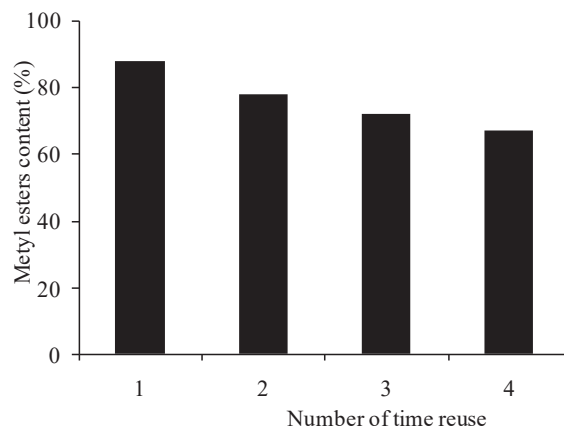


**Figure 4.** Catalyst amount effect on methyl ester content using NiSO<sub>4</sub>/RHS catalyst

The other factor was the higher power consumption to increase the stirring speed as the solution becomes more viscous that resists the mass transfer in the liquid-liquid-solid system and thus decreases the methyl ester content [19, 21] or due to the RHS surface vacancies were filled with metals from the catalysts, as researched by Ma et al. [22]. This finding was similar to the previous reports. The researchers found that increasing catalyst amount caused the stirring problem, increased viscosity and ultimately limited mass transfer [23].

### Catalyst Reusability

A study on heterogeneous catalyst reusability was conducted to minimize the cost in the chemical reaction process. In order to test the reusability of catalysts, the reaction was conducted under optimum condition (Fig. 3.5). The catalyst was recovered from the reaction mixture after reaction completion, then washed using hexane, methanol, and then calcined at 500 °C for 1 h. The catalyst was reused under the same experimental and regeneration methods. From Fig. 5 the methyl ester decreased due to the loss of the active component during the washing and the recovery of the catalyst for subsequent runs.



**Figure 5.** Reusability of catalyst

### CONCLUSIONS

Producing methyl ester by PFAD esterification was conducted by using NiSO<sub>4</sub>/RHS catalyst. The reaction time was 9 h, the methanol to oil molar ratio was 15:1, and the catalyst amount was 15 wt.% resulted in 88 wt.% of methyl ester content. The catalyst could also be reused up to 2 cycles with ME content approximately as many as 80 wt.%. Using a heterogeneous acid catalyst in PFAD's esterification showed a simple process where the catalyst can be easily separated from products.

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