

Ferric Sulphate Catalyzed Esterification of High Free Fatty Acids Content Waste Coconut Oil for Biodiesel Synthesis

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Abstract: Feedstock with high free fatty acids (FFAs) content can be successfully employed for biodiesel synthesis once the high FFA content is reduced to the desired levels. In the present study, the applicability of ferric sulphate as the solid acid catalyst for esterification of FFA in waste coconut oil was evaluated at varying catalyst dosage and methanol:oil molar ratios. 1.25, 2.5, 3.75 and 5.0% w/w $Fe_2(SO_4)_3$ on oil basis was used at methanol:oil ratios of 3.81:1, 5.72:1 and 7.63:1 and at the reaction temperature of 60 °C. The FFA reduced more with the increase in catalyst and methanol:oil molar ratios while the time requirement to reach the esterification equilibrium reduced. Final FFA level of 2.00% w/w on oil can be achieved by esterification at a reaction period of 36.94 minutes in the presence of 3.75% w/w of $Fe_2(SO_4)_3$ catalyst dosage at 7.63:1 methanol:oil molar ratio and 60 °C reaction temperature, which then can be subjected for trans-esterification process. At the end of the considering reaction period the solid $Fe_2(SO_4)_3$ catalyst could be separated from the reaction system.

Keywords: Biodiesel, Esterification, Ferric sulphate, Free fatty acids, Waste coconut oil

1. Introduction

Fatty acid methyl esters (FAME) i.e. biodiesel, is a renewable alternative for petroleum based diesel fuel. It is also environmental friendly as it reduces greenhouse gases emission and hence solution for global warming and climate stabilization. Biodiesel is a fuel derived from renewable biological sources such as plant oils and animal fats through esterification of free fatty acids and trans-esterification of triglycerides. The main method of biodiesel production is the trans-esterification of triglycerides using base catalysts, of which the conversion efficiency is highly affected by the FFA content and the water content in feedstock [1]. Unwanted byproduct formation, severe limitations and inefficiencies occur during trans-esterification of FFA lipid feedstocks via base catalytic trans-esterification [2]. Therefore, high quality, high purity virgin oils are required to avoid the difficulties associated with trans-esterification process of biodiesel production [3], which then results in increased competition with food, cosmetics, industrial and livestock feed demand, and hence much higher production costs of biodiesel fuel [4]. To improve the economics of biodiesel production, lower cost lipid feedstock such as animal tallow and waste oils, and acidulated soapstocks can be used as raw materials for biodiesel production process [5]. The application of low value feedstock for biodiesel production improves the viability of biodiesel production process and also the competitiveness with other types of fuels.

Homogeneous catalysis is the highly preferred catalysis technique used for trans-esterification. But, it possess some technical and environmental disadvantages such as high cost of purification and wastewater generation. Therefore, heterogeneous catalysis has been identified as a possible alternative to overcome the issues relating to homogeneous catalysis [6]. Heterogeneous catalysts enhance the applicability of high acid value oils to be used as feedstock for biodiesel synthesis. The main advantages of

heterogeneous catalysis are the easy separation of catalyst from the product without the necessity of washing, and the reusability.

The catalytic activity and reusability of different Fe-based solid catalysts have been evaluated in several studies. It is revealed that $FeCl_3$, and $Fe_2(SO_4)_3$ have better activity and reusability for esterification of free fatty acid content in waste oils for biodiesel synthesis [7], [8]. Kusakabe and Guana [7] used 4, 8 and 10% w/w of $Fe_2(SO_4)_3$ to esterify the high FFA content of waste oily sludge at the methanol:oil molar ratio of 10:1 and 60 °C. Above 86.0% fatty acid methyl ester (FAME) yield could be obtained for the reuse of two times of the catalyst without rapid decrease in the catalyst activity [7]. Wang et al. [8] used 3% w/w $Fe_2(SO_4)_3$ for esterification of FFA in waste cooking oil, and achieved 97.22% FFA conversion after 4 h reaction at 95 °C at a methanol:oil ratio of 10:1. The catalyst was found to be suitable for reuse at least 10 times with 10% w/w of fresh addition [8].

In the present study, the applicability of $Fe_2(SO_4)_3$ for esterification of high FFA content in waste coconut oil (WCO) is evaluated at varying catalyst dosage and methanol:oil molar ratios.

2. Procedure

2.1 Materials

WCO was collected from restaurants. Methanol, $Fe_2(SO_4)_3$ and all the chemical reagents used for determination of acid value of the oil samples are of analytical reagents grade.

2.2 Determination of FFA

0.5 g of WCO was taken to a titration flask, and thoroughly mixed with 12.5 g of iso propyl alcohol (IPA). Then, it was titrated with 0.1 M NaOH solution at the presence of

phenolphthalein indicator, and the consumed NaOH volume at the end point was recorded (v). The blank titration was repeated for 12.5 g of IPA and the consumed NaOH volume was recorded (b). The acid value (AV) of the WCO was estimated using (1).

$$\text{Acid Value (AV)} = \frac{(v - b) \times N_{\text{NaOH}} \times 56.1 \text{ mg KOH/g}}{W_{\text{WCO}}} \quad (1)$$

The FFA content was then determined using the obtained AV.

2.3 Pretreatment of WCO

The collected WCO from restaurant cooking was filtered through a filter clothe to remove the residual food particles and sludge. Then, the resultant filtrate was heated at 110 °C for 15 minutes to remove the moisture in oil. The pretreated WCO was stored in a container with an air tight cap to avoid contact with atmospheric moisture and used for the research experiments.

2.4 Reactor setup

A laboratory scale batch type experimental setup was employed to evaluate the esterification of FFA in WCO. A flat bottomed two neck flask was used as the reactor vessel which was immersed in a water bath to regulate the reaction temperature at a constant level. An opening of the flask was used to insert a thermometer, and to take the samples out, while the other was used to connect the reactor vessel with a Liebig condenser. The Liebig condenser with a continuous water supply condensed any methanol vapor evaporating from the reaction mixture and fed back to the reactor vessel.

2.5 Experimental design

The present study was conducted to evaluate the applicability of $\text{Fe}_2(\text{SO}_4)_3$ as the catalyst for esterification of high FFA content in WCO. The conversion of FFA in WCO was evaluated with time for batch esterification process for varying catalyst dosage and methanol:oil molar ratios at 60 °C.

1.25% w/w of $\text{Fe}_2(\text{SO}_4)_3$ on oil was added to the flask containing 200 g of WCO. Then, the flask was immersed in the water bath and allowed the system to reach 60 °C. Esterification of FFA was allowed by introducing methanol to the reactor at methanol:oil molar ratio of 3.81:1. Samples of 10 ml were drawn at 30 minutes intervals for 4 hours. The drawn samples were then centrifuged at 2000 rpm for 5 minutes. FFA content of the oil was determined and the percentage reduction of FFA was estimated using (2).

$$\text{FFA Reduction (\%)} = \frac{\text{FFA}_{\text{Initial}} - \text{FFA}_{\text{Final}}}{\text{FFA}_{\text{Initial}}} \times 100\% \quad (2)$$

The procedure was repeated for 1.25%, 2.5%, 3.75% and 5.0% w/w $\text{Fe}_2(\text{SO}_4)_3$ and methanol:oil molar ratios of 3.81:1, 5.72:1 and 7.63:1. The results were analyzed in order to identify the optimum reaction conditions for esterification of FFA in WCO at the presence of $\text{Fe}_2(\text{SO}_4)_3$ for better economical biodiesel synthesis process.

3. Results and Discussion

The FFA level of the WCO was estimated as 12.75% w/w on oil. The samples from the reaction mixture produced three layers at the end of centrifugation. The top layer contained unreacted methanol and produced water during esterification, the middle layer with produced FAME and oil, while the bottom layer contained $\text{Fe}_2(\text{SO}_4)_3$.

At the considering reaction conditions the FFA level of the oil reduced significantly with time.

The time profile of FFA reduction for varying $\text{Fe}_2(\text{SO}_4)_3$ dosage at 3.81:1 methanol:oil molar ratio and 60 °C, was indicated in figure 1. At 1.25% w/w of $\text{Fe}_2(\text{SO}_4)_3$ dosage, FFA level gradually reduced, and the percentage FFA reduction reached a value of 58.1% at the end of 4 hours.

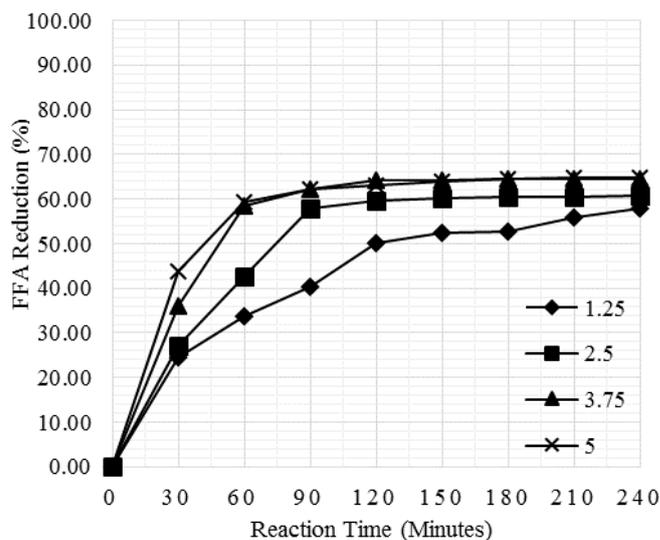


Figure 1: The time profile of FFA reduction for varying $\text{Fe}_2(\text{SO}_4)_3$ dosages at 3.81:1 methanol:oil molar ratio and 60 °C

The FFA reduction rate was higher at the higher catalyst dosage of 2.5% w/w of $\text{Fe}_2(\text{SO}_4)_3$. At these conditions, the system reached an equilibrium state of esterification of FFA by the end of the 4 hours. The catalyst dosages of 3.75 and 5% resulted in similar FFA reduction. At 3.75 and 5% of catalyst dosages, the equilibrium was achieved faster at higher FFA reduction percentage. The maximum possible FFA reduction has been achieved by each system at its equilibrium state. The increase of the catalyst dosage indicated distinguishing increment in FFA reduction at the respective test conditions. Hence, the effect of $\text{Fe}_2(\text{SO}_4)_3$ dosage on FFA reduction was significant at 3.81:1 methanol:oil molar ratio and 60 °C.

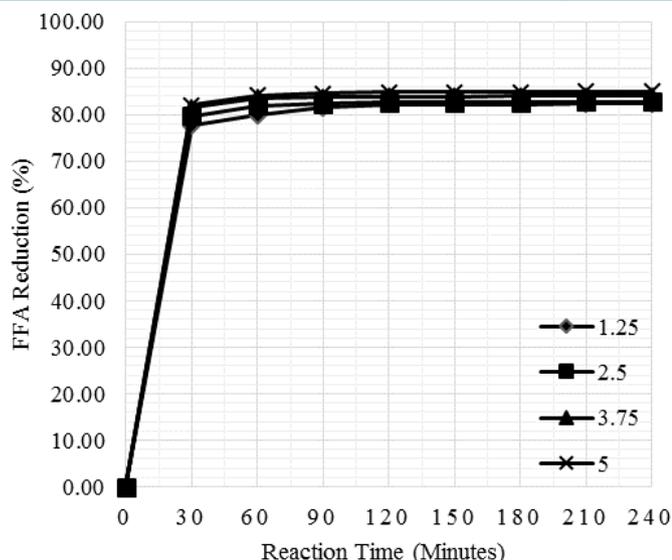


Figure 2: The time profile of FFA reduction for varying $\text{Fe}_2(\text{SO}_4)_3$ dosage at 5.72:1 methanol:oil molar ratio and 60°C

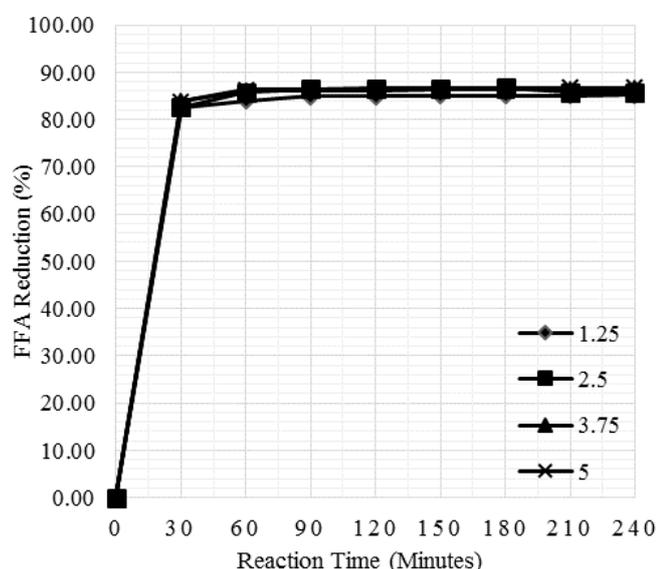
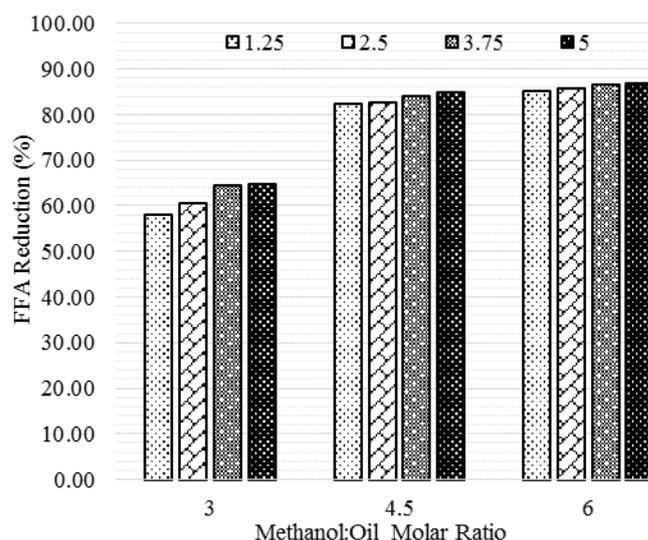


Figure 3: The time profile of FFA reduction for varying $\text{Fe}_2(\text{SO}_4)_3$ dosage at 7.63:1 methanol:oil molar ratio and 60°C

Figures 2 and 3 indicate the percentage FFA reduction for varying $\text{Fe}_2(\text{SO}_4)_3$ dosages at 60°C for methanol:oil molar ratios of 5.72:1 and 7.63:1 respectively. At test conditions of different methanol:oil molar ratios, the FFA reduction was rapid. Considerable FFA reduction occurred within the initial 30 minutes of the reaction. The FFA level reduced further in a very small value for several more minutes, and then the equilibrium state was achieved. The FFA reduction didn't indicate any distinguishing improvement with respect to the increment in catalyst dosage. Hence, the catalyst dosage did not affect significantly on FFA reduction of WCO at the reaction conditions. At 7.63:1 methanol:oil molar ratio the equilibrium reaching was faster than that at 5.72:1. The FFA reduction rate was higher for the methanol:oil molar ratio of 7.63:1 than that of 5.72:1.

The maximum percentage FFA reduction at the test conditions of varying catalyst concentration and methanol:oil

molar ratios at 60°C was indicated in figure 4. The FFA reduction at the methanol:oil molar ratio of 3.81:1 was significantly lower than that at 5.72:1 and 7.63:1. At 3.81:1 methanol:oil molar ratio, the percentage FFA reduction was 58.1, 60.7, 64.5 and 64.8 at catalyst dosages of 1.25, 2.5, 3.75 and 5.0% respectively. The respective results at 5.72:1 methanol:oil molar ratio were 82.4, 82.8, 84.1 and 85.1. At the higher methanol:oil molar ratio of 7.63:1, the percentage FFA reduction was higher. The percentage FFA reduction at this condition was 85.2, 85.8, 86.4 and 86.7% for 1.25, 2.5, 3.75 and 5.0% catalyst dosage.



Figures 4: Maximum FFA reduction for varying $\text{Fe}_2(\text{SO}_4)_3$ dosage and methanol:oil molar ratios at 60°C

The maximum possible percentage FFA reduction increased with the increase of methanol:oil molar ratio from 3.81:1 to 5.72:1. But, there was no considerable increment in FFA reduction for further increment of methanol:oil molar ratio from 5.72:1 to 7.63:1.

The FFA reduction varies only within 82.4 – 86.7 for catalyst dosages of 1.25, 2.5, 3.5 and 5% and methanol:oil molar ratios of 5.72:1 and 7.63:1. Hence, the effect of catalyst dosage was negligible at higher values of methanol:oil molar ratios.

The reaction time required for 84.31% FFA reduction varying catalyst dosages and methanol:oil molar ratios at 60°C was indicated in figure 5. In the present study, FFA reduction of 84.31% was equivalent to a final FFA level of 2.0% w/w on oil. The desirable FFA level for successful alkaline trans-esterification is less than 0.5% - less than 3.0% of FFA on w/w basis of oil [9].

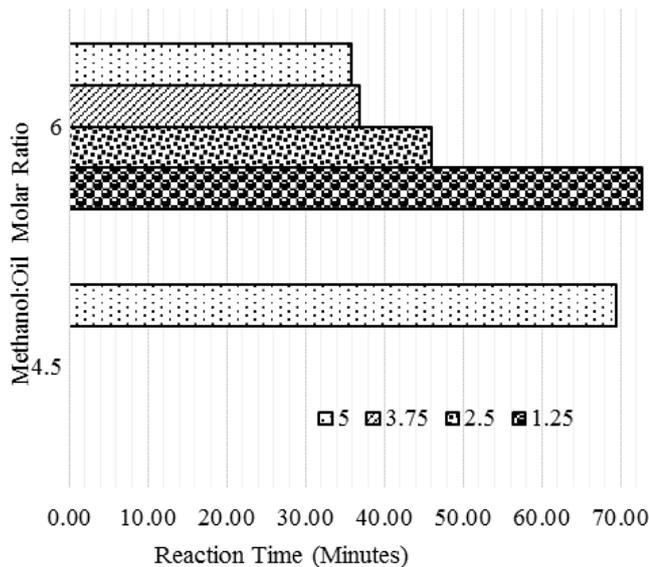


Figure 5: Reaction time requirement for 84.31% FFA reduction at varying $\text{Fe}_2(\text{SO}_4)_3$ dosage and methanol:oil molar ratios at 60 °C

Desirable levels of FFA reduction couldn't be achieved by catalyst dosage of 1.25, 2.5, 3.75 and 5.0% at 3.81:1 methanol:oil molar ratio and 60 °C. At the methanol:oil molar ratio of 5.72:1, the system indicated satisfactory FFA reduction only for 5.0% catalyst dosage at 69.43 minutes of reaction time. For the methanol:oil molar ratio of 7.63:1, the system reached satisfactory levels of FFA for all the considering catalyst dosages. The reaction time requirement to reach satisfactory results was lower at 5.0% catalyst dosage and 5.72:1 methanol:oil molar ratio than that at 1.25% and 7.63:1 of respective reaction conditions.

72.63, 45.96, 36.94 and 35.80 minutes were required at 7.63:1 methanol:oil molar ratio and 60 °C for the catalyst dosages of 1.25, 2.5, 3.75 and 5.0% respectively. Significant reduction of reaction time required to reach the FFA level of 2.0%, can be observed with increasing catalyst dosage.

$\text{Fe}_2(\text{SO}_4)_3$ is soluble in water though insoluble in methanol, FFA and FAME [7]. Hence, water produced during esterification may affect the catalyst performance. It could shift the esterification equilibrium towards the reactants and deactivate the catalyst [10]. The remaining micro scale impurities in the WCO after the pretreatment stage could influence the performance of the $\text{Fe}_2(\text{SO}_4)_3$ catalyst during the esterification of FFA in WCO.

4. Conclusion

The activity of $\text{Fe}_2(\text{SO}_4)_3$ as the solid acid catalyst for esterification of high FFA content WCO was evaluated at varying catalyst and methanol: oil molar ratios at 60 °C. The equilibrium condition was reached faster with increasing catalyst dosage and methanol: oil molar ratios. The effect of increasing catalyst dosage reduced with increasing methanol:oil molar ratios. The maximum possible FFA reduction was not strongly affected by the catalyst dosage or methanol:oil molar ratios above the methanol: oil molar ratio of 5.72:1.

Significant amounts of $\text{Fe}_2(\text{SO}_4)_3$ was required to achieve satisfactory FFA levels at the methanol:oil molar ratios of 5.72:1 and 60 °C to proceed the trans-esterification for biodiesel synthesis. Favorable FFA levels can be achieved at varying catalyst dosages at 7.63:1 methanol:oil molar ratio and 60 °C.

The reaction time for esterification significantly reduced with increasing catalyst dosage and methanol:oil molar ratio. The reaction conditions of 3.75% w/w of $\text{Fe}_2(\text{SO}_4)_3$ dosage at 7.63:1 methanol to oil molar ratio and 60 °C can be identified as the optimum conditions for $\text{Fe}_2(\text{SO}_4)_3$ catalyzed esterification for biodiesel synthesis.

The solid $\text{Fe}_2(\text{SO}_4)_3$ catalyst can be easily separated from the reaction mixture by filtration, and can be reused. Since, the impurities containing in the WCO may affect the quality of the catalyst, the collected $\text{Fe}_2(\text{SO}_4)_3$ by filtration may subject to washing steps for better catalytic performance at repeated use.

5. Future Scope

In this study, the applicability of ferric sulphate as the catalyst for the esterification process of high FFA content WCO was evaluated. The optimum $\text{Fe}_2(\text{SO}_4)_3$ dosage, methanol: oil molar ratio and the reaction time requirement to reach acceptable results at 60 °C can be obtained from the study. The present study can be further improved by reusing the separated $\text{Fe}_2(\text{SO}_4)_3$ and determining the catalytic activity of $\text{Fe}_2(\text{SO}_4)_3$ at the derived optimum reaction conditions. Any required purification stages of used $\text{Fe}_2(\text{SO}_4)_3$, amounts of fresh additions of $\text{Fe}_2(\text{SO}_4)_3$ in order to obtain satisfactory results can be investigated. The esterified WCO can be then subjected to trans-esterification process in order to complete the biodiesel synthesis process, and the properties of the resultant biodiesel can be evaluated for various applications.

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