Method for Quantification of Methanol and Sulfuric Acid Required for Esterification of High Free Fatty Acid Oils in Biodiesel Production

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Abstract- Trasesterification of oils and fats using base catalyst is the common method of biodiesel production. However, free fatty acids (FFA) in oils form soap with the base catalyst and hence FFA is converted into esters by acid esterification prior to transesterification. Acid esterification is a reversible reaction and therefore high amount of alcohol (methanol) is required to promote the forward reaction. However, use of large amounts of excess methanol and the catalysts (acid) increases the production cost. Therefore, in this work, a method to quantify feasible amounts of alcohol and acid required for acid esterification of high FFA oils was established. This method is fast, required to estimate only the FFA present in the oil by measuring the acid value and the reactant quantities were estimated based on the weight of FFA. It was shown by using high FFA rubber seed oil that the optimum FFA conversion could be obtained when methanol concentration was 2.5 g/g of FFA, H_2SO_4 concentration was 0.05 g/g of FFA and the reaction time was 30 min. Further, quantification of reactants and reaction parameters were validated with Neem (*Azadirachta indica*) and waste cooking oils at different scales of operation.

Keywords esterification, free fatty acid, biodiesel, pretreatment, rubber seed oil

1. Introduction

Vegetable oils and fats (triglycerides - TG) after transesterification into fatty acid mono alkyl esters (biodiesel) can be used in diesel engines up to 20% biodiesel in blends of petroleum diesel without any modification to the existing engine [1]. The common method for biodiesel production is transesterification of TG using short chain alcohols with an alkaline catalyst. Methanol is widely used among the possible alcohols such as ethanol, methanol and propanol because of its low cost and higher reactivity while potassium hydroxide is the preferred alkyl catalyst. Therefore, the common biodiesel is known as fatty acid methyl esters (FAME). The oils and fats may be edible or non-edible vegetable oil, animal fats or waste cooking oil.

Large-scale production of biodiesel from edible oils has become a controversial issue and therefore attention has been paid on the use of non-edible oils and fats. However, these non-edible oils contain high amounts of free fatty acids (FFA's) which cause alkali-catalysed transesterification difficult. High FFA containing oils create problems due to formation of fatty acid salts (soap) by reacting FFA's in the oil with the base catalysts [2, 3] as shown in Eq. (1). The presence of water in addition to FFA intensifies the formation of soap and even as little as 0.3% water with FFA causes serious problems [4].

$$\text{(1)}$$
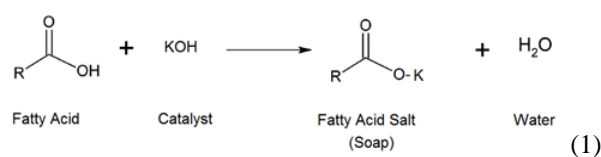
One method use to tackle FFA in TG is caustic stripping where excess quantity of catalyst is added deliberately to form soap and to remove FFA thereby. However, this method reduces the yield of FAME, makes the separation of FAME difficult from the soap-FAME-glycerol emulsion and hence increases the cost of production [3].

Such soap formation is not observed in acid catalysed transesterification of triglycerides and the performance of catalyst is not affected by the presence of FFA. Conversion of both FFA into FAME as well as TG into FAME is possible with acid catalysis. However, the drawbacks of this process are the slow reaction rate, requirement of high reaction temperatures, high molar ratio of alcohol to oil, and the corrosion related issues in acid environment. It is reported that the rate of conversion in acid catalysed transesterification is 4000 times slower than the base catalyzed transesterification [4,5].

Therefore, the current practice is to directly transesterify oils containing FFA less than 2-2.5% (w/w) and to pretreat oils that contain FFA > 2-2.5% prior to transesterification. In the pretreatment process, FFA is converted into FAME by reacting with an alcohol and an acid catalyst (esterification). After acid esterification or pretreatment, FFA reduced (deacidified) oil is transesterified with the alcohol under alkaline catalysis. However, this method requires an extra processing step prolonging the production time and increasing the production cost.

(2)
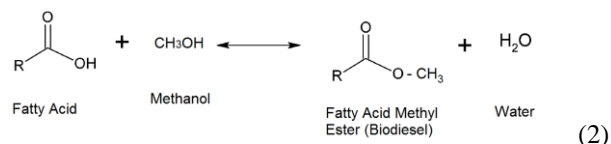
In acid esterfication (Eq. 2), one mole of fatty acid reacts with one mole of methanol to yield one mole of FAME. However, some researchers have used molar ratio of methanol to oil in determining the amount of methanol required for esterification [2, 6] while some others have tried to optimize the reaction based on weight ratio of methanol to oil [7] and another set of researchers have used reactant quantity based on the volume of oil [8]. Further, the quantity of catalyst required for the reaction has also been estimated based on the weight volume or moles of oil. Table 1 summarizes the calculation basis used by some researchers and the dosage of methanol used in their studies. Estimating the methanol quantity according to the weight/ volume or moles of oil does not seem to be reasonable methods since the esterication reaction happens mainly between FFA present in oil and methanol under the operating conditions. Only a very few researchers reported the use of methanol quantity determined based on the moles of FFA present in the oil [9, 10]. The main reason for not to consider the amount of FFA in moles is due to difficulty in estimating the different types of FFA's present in oils and their molar quantities.

Table 1. Methanol dosages and the calculation basis adopted by researchers

Type of Oil	FFA (%)	Methanol		Reference
		basis	ratio	
Crude coconut oil	20.38	methanol:oil volume ratio	various	11
Neem oil	14.94	methanol:oil volume ratio	various	10
Sludge Palm oil	23.2	methanol:oil molar ratio	8:1	6
Sunflower oil +Oleic acid	various	methanol:oil molar ratio	various	12
Crude *Jatropha curcas* oil	15	methanol:oil weight ratio	various	7
Rice bran oil	various	methanol:FFA molar ratio	5:1	13
Waste Cooking oil	100	methanol:FFA molar ratio	various	9
Waste oil	8.7	methanol:oil molar ratio	various	14
Yellow grease	2-32	methanol:FFA molar ratio	various	15
Used cooking oil	5	methanol:FFA molar ratio	various	10
Zanthoxylum bungeanum oil	22.75	methanol:oil molar ratio	various	16
Rubber seed oil	17	methanol:oil molar ratio	6:1	17

The most important variables in the conversion of FFA's to esters are the reaction temperature, alcohol and catalyst dosages and the reaction time. The reaction temperatures maintained by most researchers ranged from 45–65°C in order to maintain the reaction mixture at a temperature below the boiling point of alcohol used in esterification. The maximum reduction of FFA in Sludge Oil Palm is reported at 60°C temperature when methanol was used as the alcohol [6]. It is further reported that the conversion of FFA to FAME decreased when the reaction temperature was greater than 60°C. This may be due to the evaporation of methanol from the mixture which in turn affects the reaction due to

unavailability of reactants. Further, good mixing of reactants is also important for the reaction since TG and methanol are immiscible and hence could results in phase separation [18].

The objective of this work was to develop a method to quantify methanol and catalyst required for the reaction in a less complex manner and to evaluate the chemical dosages and the reaction time required for the esterification of high FFA containing oils

2. Methodology

2.1 Materials

High FFA containing rubber seed oil (RSO) (FFA 27.6%) and neem oil (FFA 14%) purchased from a local supplier in Sri Lanka was used in all the work reported here. Waste cooking oil (FFA 4.9%) was obtained from a restaurant. Methanol (99%) used was from industrial grade whereas sulfuric acid (H_2SO_4 - 98%) was of laboratory grade.

2.2 Acid Esterification

Acid esterification was carried out with RSO which is high FFA containing oil. Initially, methanol and H_2SO_4 dosage and the reaction time were varied to identify the optimized values. In the next stage of work, optimized values of methanol, $_{H2SO4}$ and reaction time were used in the esterification of waste cooking oil and neem oil to validate the parameters optimized with RSO.

2.2.1 Measurement of Reactant Quantity and Parameter Variation

Acid esterification reactions were carried out in 250 ml glass bottles provided with a stopper. A thermometer was placed in the bottle through the stopper and this complete reactor system was heated in a magnetic stirrer hotplate. A magnetic flee was used to agitate the mixture and the same rotational speed was used for all test runs and the temperature was maintained at 55±2°C throughout.

Acid values (AVs) of oil samples were estimated according to ASTM D 1980-67 and the FFA amounts were calculated. 100 g of RSO samples were used in all the tests reported here. The amounts of methanol and H_2SO_4 used were estimated based on the initial amounts of FFA present in oil as shown in equations (3) and (4) respectively. A is g methanol/g FFA in the oil sample while B is the g H_2SO_4/g FFA in the oil and the values used in this work are given in table 2.

$$\text{Methanol amount} = [A \times (\text{weight of oil}) \times \text{FFA\%}] \quad (3)$$

$$H_2SO_4 \text{ amount} = [B \times (\text{weight of oil}) \times \text{FFA\%}] \quad (4)$$

Oil was preheated at 105°C for 10 minutes in order to remove the moisture present in the oil, allowed to cool to 55°C and then subjected to moisture analysis (Moisture Balance Citizen MB200X) to make sure that the residual moisture level was below 0.1%. Then predetermined quantity of H_2SO_4 and methanol were introduced to moisture free oil and the reaction was carried out for the desired time by maintaining the temperature at 55°C while mixing. The reaction time for acid esterification and the amounts of reactants used are given in Table 2.

After the reaction, samples were kept without disturbing for phase separation for 2 hrs and then the top layers consisting of water formed, unreacted methanol, and acid were separated and discarded. Separated bottom layers containing oil, unreacted FFA, and FAME was kept for further phase separation for another 22 hrs. Then the AV of the further settled bottom layers were estimated and the FFA amounts were calculated.

All the experiments were done in duplicates and the AV estimation of each sample was done by averaging 2 titration readings.

2.2.2 Testing with different types of oil for Validation

Further esterification reactions were carried out with different oil quantities (100g – 4000 g) of neem oil and WCO for 30 min at 55⁰C with uniform mixing to validate the scalability of the reactant quantification approach. The amounts of methanol and H_2SO_4 used in these esterification reactions were 2.5 g methanol/ g FFA (g/g) and 0.05 g H_2SO_4/g FFA (g/g).

Esterification of 200- 400g oil samples were carried out in 1 L glass bottles and heated with a heating magnetic stirrer. Samples of 3 & 4 kg were esterified in a 5L scale biodiesel reactor by manual controlling the heater to maintain the temperature at the desired value of 55±2°C. Mixing was achieved with an agitator.

3. Results and Discussions

3.1 Quantification of reactants

Methanol and H_2SO_4 quantities used in the present work were estimated based on the weight of the FFA present in the oil as given in Eq 3 and 4. This method is fast and required to measure only the acid value of oil. Methanol quantity used in this study was in the range 2-3.5 g methanol/g FFA and this corresponds to 19.7 - 30.9 moles methanol per mole of FFA. Even though many researchers have optimized reactant dosages based on the oil weight or oil volume, the most appropriate method of calculating the dosage of reactants is based on the amount of FFA present in TG. However, in order to determine the stoichiometric dosage of reactants, fatty acid profile in the oil should be known. The fatty acid distribution in oils can vary from oil to oil and hence types of FFA's also vary. Further, the type and the quantity of FFA vary with moisture and storage (due to

Table 2. Reaction conditions - quantity of reactants and catalyst used

A (Methanol g/g FFA)	B (H_2SO_4 g/g FFA)	Time (min)
varied	0.05	20
varied	0.05	30
2.5	varied	30
3.0	varied	30
2.5	0.05	varied
3.0	0.05	varied

breakdown of TG) and hence FFA quantification has to be done immediately before esterification. Quantification requires sophisticated analytical methods such as liquid chromatography, gas chromatography or mass spectroscopy, and these analysis are time consuming and costly. This kind of analysis is very much important in understanding the conversions but not feasible in commercial production of biodiesel. Therefore, the method proposed in this work (Eq 3 & 4) for quantification of reactants for acid catalyzed esterification reaction is fast, simple and requires only a small amounts of reactants when compared with previous work [10].

3.2. Effect of water removal

In this study, careful consideration was made to the effect of presence of water in the initial oil as well as in the TG/ FAME layer that is formed after acid esterification. Water in the TG/FAME sample can lead the backward reaction resulting an increase in FFA formed [18]. This could only be possible from the water formed in the esterification reaction (Eq.2) since it was made sure before the experiments that the moisture present in the oil was below 0.1% by heating the oil to 105°C prior to esterification. Further, the effect of water on the backward reaction was minimized by separating the water (after the phase separation) from the TG/FAME layer 2 hrs after the reaction. It has been reported that water has a negative effect on the forward reaction rate and is the primary limiting step for the completion of the reaction [9, 19] no mechanism has been proposed to avoid the effect of water on the reversible esterification reaction. This work shows that the removal of water immediately after phase separation is a practical method that could be adopted in acid esterification of high FFA oils to drive the forward reaction.

3.3 Evaluation of reactant parameters

In this work, main focus was paid on the esterification of FFA with various dosages of alcohol, catalyst and reaction time by keeping the temperature and the rate of agitation constant for all the samples. Several experiment runs were made as given in Table 2 while varying methanol, catalyst concentration and time. Separation of reactants (layer separation) during the reaction was not observed and hence can presume that agitation rate used was adequate. Further, the temperature selected (55°C) does not cause any evaporation of methanol (Boiling point 64.7° C) and hence there was no effect on the reaction due to evaporation of methanol.

FFA conversion efficiencies for 20 and 30 min reaction times with increasing methanol usage are shown Fig. 1. In 20 min reacted samples, there was a significant increase in conversion efficiency (73.5% to 89.3%) with the increase of methanol quantity from 2 to 3 g methanol/ g FFA (17.5 to 26.3 moles methanol: moles FFA). When the reaction time was increased to 30 min with the same catalyst and acid quantities, higher FFA conversion efficiencies were observed. However, the rate of FFA conversion with increased methanol usage is less compared to 20 min reaction time and it was only from 90.4 to 94.4% from 2 to 3 g methanol/g FFA.

According to results obtained for both 20 and 30 min reactions times it can be seen that there is no significant change in FFA when the methanol quantity was increased above 3 g methanol/g FFA indicting that no additional advantage can be expected by increasing the methanol quantity. Similar observation has been reported in acid esterification of high FFA containing Sludge Palm oil (SPO), where minimum of 8:1 and 10:1 molar ratios of methanol to SPO has been used to reduce the FFA content of SPO from 23.2% to below 2% [6] and when the molar ratio increased from 8:1 to 14:1 there has not been a significant change observed in the reduction of FFA. According to another reported work, the maximum conversion efficiency for RSO has been achieved with methanol to oil molar ratio of 6:1 when the reaction time was 30 min and the improvement in the conversion efficiency was not significant when methanol quantity was further increased [17].
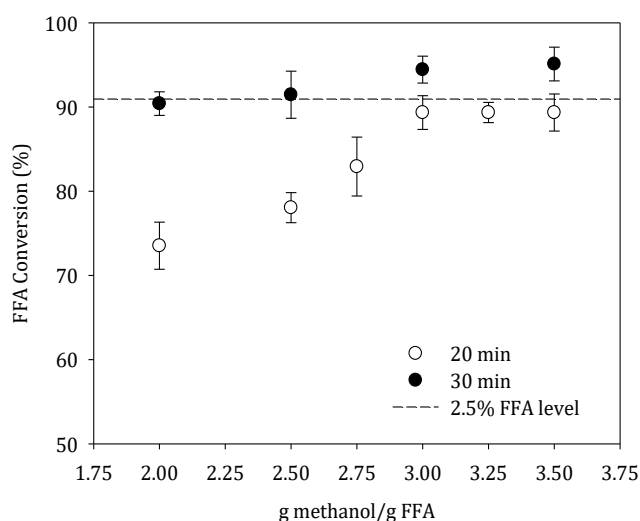

Fig.1. Variation of the percentage conversion of free fatty acids (FFA) present in oils reacted with different methanol quantities for 20 min and 30 min reaction times. Catalyst content in all these samples were kept constant at 0.05 g H_2SO_4 /g of FFA.

Hence these results show that a good conversion of FFA can be obtained with large amount of methanol, however, there is a maximum amount of methanol required to reduce FFA under the given operating conditions.

Sulfuric acid (H_2SO_4), the most common homogeneous acid catalyst for esterification studies was used in this study because of its low cost and availability. The influence of H_2SO_4 quantity on acid esterification was investigated with 2.5 g methanol /g FFA and 3.0 g methanol/g FFA at 30 min for a series of H_2SO_4 quantities and the results obtained are given in Fig. 2.

The conversion efficiency increased for both oil samples with 2.5 and 3.0 g methanol/ g FFA, with increasing amounts of H_2SO_4 up to 0.075 g H_2SO_4/g FFA and there was no further increase in conversion efficiency when H_2SO_4 quantity was further increased. The behaviour is similar to the increase of efficiency with the increase of methanol in the reaction. Further, both curves show that a significant FFA conversion cannot be achieved by increasing H_2SO_4 beyond

0.05 g H_2SO_4/g FFA (5 wt% of FFA). Similar observation has been reported and according to that the increase in catalyst amount has no effect on the final conversion of FFA but on the initial reaction rate [12]. Therefore, 0.05 g H_2SO_4/g FFA was used as the optimum catalyst amount in the rest of the tests carried out.

As in the quantification of methanol, many researchers have considered the quantity of oil used for the estimation of the quantity acid catalyst [7, 12]. However, this study showed that it is much more effective in calculating the quantity of acid catalyst by developing a correlation with the quantity of FFA present in the oil rather than the quantity of oil.
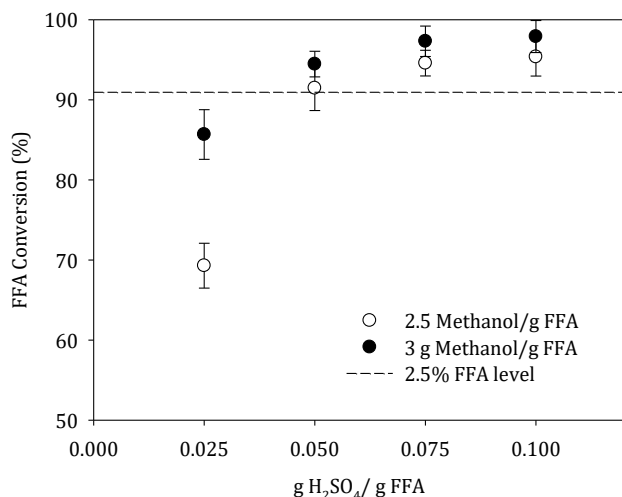

Fig, 2. Variation of the percentage conversion of free fatty acids (FFA) in oils with different amounts of H_2SO_4. The amounts of methanol used were 2.5 and 3.0 g methanol /g of FFA.

The FFA conversion efficiencies calculated for oil samples reacted with 2.50 and 3.0 g methanol/g FFA with 0.05 g H_2SO_4/g FFA and different reaction times are given in Fig. 3. Both curves showed an increase in the conversion efficiency when the reaction time was increased. For samples with 2.50 g of methanol/g of FFA conversion efficiency increased from 78.1% to 95.5% when the reaction time increased from 20 min to 45 min. Further, it can be seen from Fig. 3, that the conversion efficiency is high when

the reaction time is long allowing sufficient time for mass transfer comply with previous work [6,20,21].
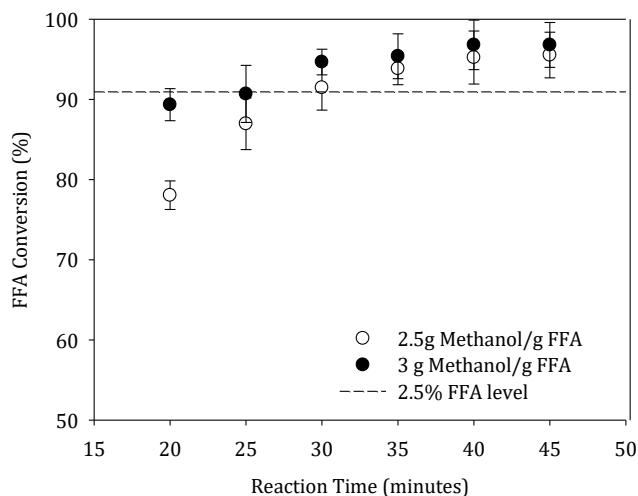

Fig.3. Variation of the percentage conversion of free fatty acids (FFA) present in oils reacted with 2.5 and 3.0 g methanol /g of FFA for different reaction times. Catalyst content in all these samples were kept constant at 0.05 g H_2SO_4 /g of FFA.

Samples reacted for 20 min did not give satisfactory FFA level for transesterification when treated with different methanol quantities (Fig. 1) but resulted acceptable FFA levels with reaction times greater than 30 min with both 2.5 and 3.0 g methanol /g of FFA (Fig. 3). It is clearly seen that the conversion of FFA to FAME increases with an increase in reaction time and with the correct combination of reactants.

According to Fig. 3, there is no significant advantage of using high amounts of methanol when long reaction times are used because 2.50 g of methanol/g FFA curve and the 3.0 g of methanol/g FFA curve are almost overlapping. Therefore, selection of the amount of methanol and the time required for the reaction have to be chosen in consideration of the cost benefit analysis. According to the results obtained in this study 2.50 g of methanol/g FFA and 0.05 g H_2SO_4/g FFA gave satisfactory level of esterification (reduction of FFA) at 55°C and 30 min reaction time.

Table 3. FFA quantity of neem oil and waste cooking oil before and after esterification

Oil type	Sample size (g)	H_2SO_4/FFA (g/g)	Methanol/FFA (g/g)	Initial FFA (%)	Final FFA (%)
Neem oil	300	0.05	2.5	14	1.68
Neem oil	400	0.05	2.5	14	2.24
Neem oil	4000	0.05	2.5	14	2.38
Waste cooking oil	200	0.05	2.5	4.9	2.03
Waste cooking oil	3000	0.05	2.5	4.9	2.25

3.4 Parameter Validation and scale up

Final FFA level after acid esterification of neem and waste cooking oil with different initial FFA levels is given in Table 3. From the data given in Table 3, it can been seen that FFA level of all the oil samples could be reduced to the acceptable level (below 2.5%) by using acid and methanol quantities that have been optimised (2.50 g of methanol/g FFA and 0.05 g H_2SO_4/g FFA) in this work. These data show that the dosage values of acid and methanol calculated according to Eq 3 and 4 were still applicable when the type of oil and the FFA contents were different.

Moreover, scale up studies with neem and waste cooking oil showed acceptable reductions in FFA immaterial of sample size of the oil considered. However, as the size of the oil quantity used in the reaction increased, the reduction in FFA has slightly decreased indicating that the reactants and time combinations for adequate FFA removal may need to be adjusted with scale up.

Conclusion

This work shows that the FFA level in high FFA containing oils can be reduced and make it suitable for transesterification by using a less quantity of reactants as compared to previously reported work. However, the conversion efficiency of high FFA oils during pretreatment (acid esterification), depends on the quantity of reactants and reaction parameters used. In this study, the acid value of the oil was measured and then the reactants required for esterification were quantified based on the weight of FFA. It was proved that this technique is simple to use, reliable and scale-able. Further, investigations proved that optimum reactant concentrations and reaction times would give a reduction of FFA < 2.5 % as required for biodiesel production for three different oils that were considered. The results obtained were validated on different scales of operation.

Acknowledgment

References

[1] Anderson L.G. "Effects of Biodiesel Fuels Use on Vehicle Emissions". Journal of Sustainable Energy & Environment 3 (2012) 35-47

[2] Siti Zullaikah, Yulia T. Rahkadima, Yi-Hsu Ju. A non-catalytic in situ process to produce biodiesel from a rice milling by-product using a subcritical water-methanol mixture. Renewable Energy, 111(2017), 764-770

[3] Agarwala Avinash Kumar, Guptaa Jai Gopal, Dharb Atul. Potential and challenges for large-scale application of biodiesel in automotive sector. Progress in Energy and Combustion Science. 61(2017), 113–149

[4] Lotero, E., Liu, Y., Lopez, D. E., Suwannakarn, K., Bruce, D. A. and Goodwin, J. G. "Synthesis of biodiesel via acid catalysis." Industrial & Engineering Chemistry Research 44(14): (2005). 5353-5363

[5] Andreani L., Rocha J. D. Use of ionic liquids in biodiesel production: A Review. Brazilian Journal of Chemical Engineering. 29(2012), 01, 1 – 13

[6] Hayyan Adeeb, Alam Zahangir, Mirghani Mohamed E.S.,Kabbashi Nassereldeen A., Mohd Hakimi Noor Irma Nazashida, Siran Yosri Mohd, Tahiruddin Shawaluddin. Reduction of high content of free fatty acid in sludge palm oil via acid catalyst for biodiesel production. Fuel Processing Technology 92 (2011) 920–924

[7] Berchmans, H.J., Hirata, S. (2008) Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids Bioresource Technology 99 (2008) 1716–1721

[8] Anya Anya Uzo, Chioma Nwobia Noelle, and Obinna Ofoegbu. Optimised reduction of free fatty acid content from neem seed oil for biodiesel production. *J. Basic. Appl. Chem.*, 2(4) (2012) 21-28.

[9] Uddin M. Rakib, Ferdous Kaniz, Uddin M. Rahim, Khan Maksudur R., Islam M. A. Synthesis of Biodiesel from Waste Cooking Oil. Chemical Engineering and Science, 1(2013), 2, 22-26. DOI:10.12691/ces-1-2-2

[10] Chai, Ming; Tu, Qingshi; Yang, Jeffrey Y.; and Lu, Mingming, Esterification pretreatment of free fatty acid in biodiesel production from laboratory to industry. Fuel Processing Technology 125 (2014) 106–113

[11] Jansri Surachai, Prateepchaikul Gumpon. Comparison of Biodiesel Production from High Free Fatty Acid, Crude Coconut Oil via Saponification followed by Transesterification or a Two-Stage Process. Kasetsart J. (Nat. Sci.) (2011) 45: 110 - 119

[12] Marchetti J.M., Errazu A.F. Esterfication of free fatty acids using sulfuric acid as the catalyst in the presence of triglycerides. Short communication. Biomass and Bioenergy 32 (2008): 892-895.

[13] Zullaikah S, Lai CC, Vali SR, Ju YH.. A two-step acid-catalyzed process for the production of biodiesel from rice bran oil. Bioresource Technology. 96(2005), 17:1889-96.

[14] Prafulla D. Patil, Veera Gnaneswar Gude, Harvind K. Reddy, Tapaswy Muppaneni, Shuguang Deng. Biodiesel Production from Waste Cooking Oil Using Sulfuric Acid and Microwave Irradiation Processes *Journal of Environmental Protection*, 3(2012), 107-113

[15] Diaz-Felix W., Riley M.R., Zimmt W., Kazz M.,. Pretreatment of yellow grease for efficient production of fatty acid methyl esters, Biomass and Bioenergy 33(2009), 558–563.

[16] Junhua Zhang, Lifeng Jiang. Acid-catalyzed esterification of Zanthoxylum bungeanum seed oil with high free fatty acids for biodiesel production. Short Communication. Bioresource Technology 99 (2008) 8995–8998

[17] Ramadhas, A.S., S. Jayaraj and C. Muraleedharan. 2004. Biodiesel production from high FFA rubber seed oil. Fuel 84(4): 335-340.

[18] Anastopoulos George, Zannikou Ypatia, Stournas Stamoulis, Kalligeros Stamatis. Transesterification of

Vegetable Oils with Ethanol and Characterization of the Key Fuel Properties of Ethyl Esters. Energies 2009, 2, 362-376; doi:10.3390/en20200362

[19] Arora R., Toor A.P., Wanchooa R.K., **"**Esterification of High Free Fatty Acid Rice Bran Oil: Parametric and Kinetic Study". *Chem. Biochem. Eng. Q.*, (2015) 29 (4) 617–623

[20] Hancsók, J.; Kovács, F.; Krár, M., Production of vegetable oil fatty acid methyl esters from used frying oil by combined acidic/alkali transesterification. Petrol. Coal. 46(2004) 3, 36-44

[21] Hayyan A., Alam M.Z., Kabbashi N.A., Mirghani M.E.S., Hakimi N.I.N.M., Siran Y.M., Tahiruddin S., Sludge palm oil as a renewable raw material for biodiesel production by two-step processes, Bioresour. Technol. 101(2010), 7804–7811.