

High Free Fatty Acid (FFA) Feedstock Pre-Treatment Method for Biodiesel Production

Godlisten G. Kombe¹, Abraham K. Temu², Hassan M. Rajabu³, Godwill D. Mrema⁴.

¹ Graduate student, Chemical and Mining Processing Engineering, College of Engineering and Technology, University of Dar es salaam, Tanzania, P.O. Box 35131, Dar es salaam

Corresponding author email: kombe4me@uccmail.co.tz

² Senior Lecturer, Chemical and Mining Processing Engineering, College of Engineering and Technology, University of Dar es salaam, Tanzania, P.O. Box 35131, Dar es salaam

³ Senior Lecturer, Department of Energy Engineering, College of Engineering and Technology, University of Dar es salaam, Tanzania, P.O. Box 35131, Dar es salaam

⁴ Professor, Chemical and Mining Processing Engineering, College of Engineering and Technology, University of Dar es salaam, Tanzania, P.O. Box 35131, Dar es salaam

ABSTRACT

Biodiesel is an alternative fuel for engine and other appliances that is obtained by transesterifying vegetable oils or other materials largely comprised of triacylglycerols with monohydric alcohols to give the corresponding mono-alkyl esters. The quality of feedstocks for the biodiesel production dictates the method of its production and quality. Based on the initial amount of minor components in feedstocks, a process comparison of acid pre-treatment and caustic pretreatment of feedstock for alkali transesterification was done. Acid pre-treatment was carried out with 0.60 w/w methanol-to-oil ratios in the presence of 2% w/w H₂SO₄ as an acid catalyst in 2 h reaction at 60 °C. In caustic pretreatment process, the same amount of oil was neutralized with the required amount of sodium hydroxide based on the initial amount of free fatty acid and gums in the oil. The acid pretreatment process gives a 4% loss in feedstock compared to 20% from the neutralization process. The yields 96% and 94% of biodiesel from acid pretreated and caustic pretreatment feedstock were obtained respectively. The oxidation stabilities of biodiesel from acid pretreatment and neutralized feedstock were 1.12h and 3h respectively. The biodiesel from acid pretreatment oil could not pass the ASTM standard.

Keywords: *Biodiesel; Acid esterification; FFA; Oxidative stability; Jatropha oil*

1.0 INTRODUCTION

The worldwide worry about the protection of environment and the dependence on fossil fuel has given rise to development of alternative energy sources as substitute for traditional fossil fuels. Fossil fuel sources are non-renewable, and will be exhausted in the near future. According to Alekett, (2003) the world's oil reserves are up to 80 percent less than predicted, this calls for alternative sources of energy Biodiesel can be a wonderful replacement to conventional petro-diesel fuel, which can be produced from a renewable domestic resource. It is simply produced by transesterification process whereby the vegetable oil or animal fat (Triglyceride) react in presence of a catalyst with a primary alcohol to give the corresponding alkyl esters of the fatty acid mixture that is found in the parent vegetable oil or animal fat.

Transesterification reactions can be without a catalyst, alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. Alkali-catalyzed transesterification is much faster and most often used commercially (Ma and Hanna, 1999). Alkali-catalyzed transesterification is the most economical process requiring low temperatures and pressures to achieve a 98% conversion yield (Singh et al., 2007). However, one limitation to the alkali-catalyzed process is its sensitivity to the purity of reactants. It is very sensitive to both water and free fatty acids content (Zhang et al., 2003).

The use of edible grade oils as feedstock compete with food supply in the long-term (Chhetri et al., 2008) and accounts for the higher price of biodiesel, since the cost of raw materials accounts for 60 to 75% of the total cost of biodiesel fuel (Krawczyk, 1996). One way of reducing the biodiesel production costs is to use the less expensive feedstock mostly containing fatty acids such as inedible oils, animal fats, waste food oil and byproducts of the refining vegetable oils (Berchmans and Hirata, 2008). However, feedstocks high in free fatty acid ($> 1\%$), are not easily converted by alkali transesterification because of concurrent soap formation of the free fatty acids with the catalyst. Excessive amounts of soap significantly interfere with the washing process by forming emulsions, thus leading to substantial yield losses (Freedman et al., 1984, Canakci and Van Gerpen, 1999). Acid-catalyzed transesterification could have been the best option for high FFA feedstock but the harsh reaction conditions and long reaction times required favor the base-catalyzed reaction (Canakci and Van Gerpen, 1999). Therefore pre-treatments of non edible oils for lowering the FFA in feedstock for alkali transesterification are inevitable.

Neutralization and acid esterification are among the pre-treatment methods to lower FFA for alkali catalyzed transesterification. Neutralization of vegetable oil (caustic refining) is the most commonly used method for lowering the FFA in oils. It lowers the FFA, along with substantial quantities of mucilaginous substances, phospholipids and color pigments (Bhosle and Subramanian, 2005). An alkali is added to the oil and thereby precipitating the FFA as soap stock; the latter is then removed by mechanical separation from the neutral oil. However, for oils with more than 5% of FFA, neutralization causes high losses of neutral oil due to saponification and emulsification (Bhosle and Subramanian, 2005). Acid esterification as pre treatment before alkali transesterification is thought to be the best route which converts the FFA into esters and therefore reduce the losses which could have produced from caustic refining (Van Gerpen, 2005, Kumar et al., 2007).

In Tanzania, *Jatropha* plant (*Jatropha curcas*) has a good potential to be used as feedstock for biodiesel production. It gives a relatively large oil yield; it does not require a lot of water and nutrients. It can grow in very poor soils, thereby reclaiming land (and preventing soil erosion) (Van Eijck and Romijn, 2008). However, *Jatropha* oil is one of such non-edible oils which contains high free fatty acid (FFA), which is far beyond the limit of 1% (Kumar et al., 2007). Hence, lowering FFA for converting *Jatropha* oil, which contains high FFA% into biodiesel, is very much required.

Generally the fuel quality of biodiesel can be influenced by several factors: the quality of the feedstock(minor components i.e. FFA, water, gums, etc), the fatty acid composition of the parent vegetable oil or animal fat (major components i.e. triglycerides), production process and post-production parameters(biodiesel refining and drying) (Van Gerpen, 2003). The information on the quality comparison of biodiesel produced from the neutralized and acid pretreatment processes are hard to find. The present study compares the yield and quality of both feedstock and biodiesel manufactured by the alkali transesterification of neutralized and acid pretreated feedstock.

2.0 METHOD AND MATERIALS

2.1 Materials

Jatropha curcas seeds were purchased on free market in Arusha, Tanzania. The crude oil was extracted mechanically with Chinese oil Expeller model YZS-165. The dark greenish yellow in color oil was carefully decanted and stored in a dark place to prevent oxidation. All chemicals used in the experiments such as methanol (99.5%), sulfuric acid (99% pure) and NaOH in pellet were of analytical grade. The experiments were conducted in a laboratory-scale setup developed at College of Engineering and Technology at the University of Dar es Salaam.

2.2 Methods

2.2.1 Acid Pretreatment

The crude *Jatropha* oil was heated to 60°C while stirred mechanically at 800 rpm under atmospheric conditions to homogenize the oil. The reaction was conducted in a 250 ml four-necked round-bottomed flask attached with a reflux condenser and thermometer and placed in a water bath with a temperature controller. A concentrated sulfuric acid (2% based on oil weight) in 0.60 w/w methanol was heated to 60 °C and added to the reaction flask containing pre heated oil (Zullaikah et al., 2005). This mixture was stirred (800rpm) for 2 hours. The reaction product mixture was then poured into a separating funnel and allowed to settle for 2 hours. The top layer comprised unreacted methanol, whereas the middle layer was oil and fatty acid methylester (FAME) (small amount obtained by conversion of free fatty acids to esters), and water at the bottom layer. The amount of FFA remaining was determined before alkali transesterification. The product was then used for the alkaline transesterification. The acid pretreatment loss was calculated by Equation (1).

$$\text{Acid pretreatment loss} = \frac{\text{weight of crude oil} - \text{weight of pretreated oil}}{\text{weight of crude oil}} \times 100\% \dots\dots\dots(1)$$

2.2.2 Caustic pretreatment (Neutralization)

The amount of sodium hydroxide solution, 20°B concentration (14.33% w/w of NaOH) required was calculated based on the stoichiometric quantity plus 12% excess (Farr, 2000). The alkali was added to 100g of crude *Jatropha* oil at ambient temperature and mixed vigorously (800 rpm) for 3 min. The reaction mixture was then heated while stirring until the temperature reached 65°C to break any emulsion that might have formed during neutralization. The mixture was then centrifuged (8,627 × g for 20min) to remove the soap. The final FFA content was determined and the caustic pretreatment loss was then calculated by using Equation (2).

$$\text{Neutralization loss} = \frac{\text{weight of crude oil} - \text{weight of neutralized oil}}{\text{weight of crude oil}} \times 100\% \dots\dots\dots(2)$$

2.2.3 Alkaline transesterification

The pre treated or neutralized *Jatropha* oil with low percentage free fatty acid was heated to 60°C in a four necked flask and stirred at 800rpm with mechanical stirrer in a water bath. The catalyst sodium hydroxide (NaOH) 0.5% based on oil weight was dissolved in the required amount of methanol (ratio was methanol: oil = 6:1) and added to the pre treated or neutralized oil (Meher et al., 2006). The reaction was conducted for 120min. The resulting product was taken into a separating funnel and stand for 2 hours. Two phases were distinct; biodiesel on top and the glycerol at the bottom. The two phases were separated and the excess methanol in biodiesel was recovered by using a rotarvap. The biodiesel was then washed twice by using de-ionized water (10% by volume), to wash out impurities like soap and other residues. Finally, the biodiesel was heated to 100°C, for 1 hour in rotarvap to remove the moisture. Based on the initial amount of pre treated or neutralized *Jatropha* oil, the Biodiesel yields was then evaluated using Equation 3.

$$\text{Yield} = \frac{\text{Weight of Biodiesel produced}}{\text{weight of oil}} \times 100\% \dots\dots\dots(3)$$

2.3 Analyses

2.3.1 Physico-chemical characteristics of oil.

The acid value of the extracted oil was determined according to AOCS method Cd 3d-63. The percentage of free fatty acids was calculated based on oleic acid(AOCS, 2004). Peroxide value of the oil was determined according to AOCS method Cd 8-53 (AOCS, 2004). The

kinematic viscosity was carried out using Brookfield RV-I. Spindle of S03 was used at 30rpm at the temperature of 40°C. The oxidative stability of the Jatropha oil was determined by Rancimat method using Metrohm 873 Rancimat instrument (Ferrari et al., 2005).

2.3.2 Biodiesel Oil Quality Measurements

2.3.2.1 Viscosity

The kinematic viscosity was carried out using Brookfield RV-I. Spindle of S03 was used at 30rpm at the temperature of 40°C.

2.3.2.2 Oxidation Stability

The oxidative stability is a measure of biodiesel resistance to oxidation. Oxidative stability affects fuel quality of biodiesel. Oxidation can cause acidity in the fuel and form insoluble gums and sediments that can plug fuel filters (Monyem, 2001). Specifications related to oxidative stability are included in the European biodiesel standard EN 14214 and the D6751-07 ASTM biodiesel standard. Both biodiesel standards call for determining oxidative stability at 110 °C with a minimum induction time of 6 h for EN 14214 and 3 h D6751-07 using the Rancimat method (Knothe, 2007).

Determination of oxidative stabilities of biodiesel produced from both neutralized and acid esterified processes were done using accelerated oxidation according to Rancimat method using Metrohm 873 Rancimat instrument. Samples of 6g were analyzed under heating block temperature of 110°C and constant air flow of 10 L/h. The temperature correction factor DT was set to 1.5°C as recommended by Metrohm (Ferrari et al., 2005). All determinations were performed in triplicate and the mean value is reported.

2.3.3 Statistical Analysis

All experiments were performed in triplicate to ensure reproducibility of results. The obtained data was statistically analyzed using Minitab v15 software. The P values less than 0.05 were considered statistically significant.

3.0 Results and discussion

3.1 Physico-chemical characteristics of oil.

The physical and chemical properties are summarized in table 1. The acid value is a measure of the amount of fatty acids, which have been liberated by hydrolysis from the triglycerides due to the action of moisture, temperature and/or lipolytic enzyme lipase. In this study, the acid value was found to be 11.86mgKOH/g. The FFA content was 5.96% which was higher than that of Jatropha oil from Malaysia 2.23% (Akbar et al., 2009). The obtained FFA is far above the 1% limit for satisfactory transesterification reaction using alkaline catalyst.

The peroxide concentration, usually expressed as peroxide value, is a measure of oxidation or rancidity in its early stages (Gunstone, 2004). Peroxide value was found to be 3.07 meq/kg. This peroxide was higher than that of Malaysian Jatropha oil i.e. 0.66meq/kg (Akbar et al., 2009). The kinematic viscosity of Jatropha oil was 41.80mm²/s which was comparable to other sources (Kywe and Oo, 2009). The oxidative stability of Jatropha oil was found to be 18h.

Table 1: Chemical and Physical Properties of Jatropha Oil

Acid Value (mg KOH/g)	% FFA as oleic acid	Peroxide value (meq/kg)	Kinematic viscosity (mm ² /s) @ 40°C	Oxidative Stability (h)
11.86	5.96 ± 0.29	3.07 ± 0.31	41.80	18

3.2 Biodiesel Oil Quality Measurements

3.2.1 Viscosity

Kinematic viscosity limits are present both in ASTM D6751 (1.9 - 6.0 mm²/s @ 40°C) and EN 14214 (3.5-5.0 mm²/s @ 40°C), respectively for biodiesel fuels. Viscosity is a key fuel property because it persuades the atomization of a fuel upon injection into the diesel engine ignition chamber and ultimately, the formation of engine deposits (Knothe and Steidley, 2005). In the current study, The ANOVA t-test shows no significant differences in the kinematic viscosities of Biodiesel from both neutralization and acid pretreatments at the 95% confidence interval. The kinematic viscosity of the biodiesel from neutralized oil was 4.96 mm²/s while that of acid pretreatment was 5 mm²/s. Both biodiesel kinematic viscosity fall within the scope of both the ASTM D 6751 and EN 14214 biodiesel specification ranges.

3.2.2 Acid Pretreatment

The objective of acid pre-treatment was to reduce the FFA contents of crude Jatropha oil before alkali transesterification. The FFA was lowered from 5.96% to 0.3% which is less than the required amount of FFA for alkali transesterification. Berchamans and Hirata (2008) uses similar conditions and lower the high FFA of crude Jatropha oil from 15% to less than 1%. Based on the initial 100g of crude Jatropha oil, the loss on acid pre treatment was 4%. Canakci and Van Gerpen (1999) found out that the water formed in the acid esterification reaction is limited to 0.5w/w% of oil and if it accumulates, it can stop the reaction before completion. The 4% loss can be attributed to the difficult process of separating the excess methanol from the reaction mixture. Methanol-water mixture normally contain some dissolved oil and FFA and therefore the removal of this alcohol also removes the water formed by the esterification reaction (Van Gerpen, 2003).

3.2.3 Caustic pretreatment

Norris (1982) points out that during the caustic pretreatment of the high FFA oils, a loss of oil is normally three times the amount of FFA. This has been observed in soybean and cottonseed oil with high FFA of more than 5%. In this study, the caustic pre treatment reduces the FFA of crude Jatropha oil from 5.96% to 0.14%. Starting with 100g of crude Jatropha oil, the loss during caustic pre treatment was 19%. This is higher than that of acid pretreatment because of high oil losses due to saponification and occlusion of oil in the soapstock (Bhosle and Subramanian, 2005). According to Gingras (2000), the FFA content in the crude oil has a direct bearing on the neutral oil loss and therefore the yield in the case of a high-FFA crude oil is relatively low.

3.2.4 Alkaline transesterification

Caustic pretreated oil gave a biodiesel yield of 96% while the acid pretreated oil gave a yield of 94%. However, based on the crude oil supply, caustic pretreatment gave a yield of 77.8% while the acid pretreatment method gave a yield of 90.2%. The higher yield of 96% from caustic pretreated oil can be explained by the fact that, the lower the FFA in the feedstock for biodiesel the higher the yield (Freedman et al., 1984). Less FFA limit the catalyst depletion, soap formation, and separation difficulties due to the saponification reaction as shown in Figure 1 (Babcock et al., 2008).



Figure 1: Saponification reaction.

3.2.5 Oxidation Stability

Generally, the oxidative stability of Biodiesel depends on the presence of natural antioxidant, degree of unsaturation, and branching of the chain. Knothe, (2005) studied the dependence of

biodiesel fuel properties on the structure of fatty acid alkyl esters and concluded that the properties of the various individual fatty esters that comprise biodiesel determine the overall fuel properties of the biodiesel fuel. Unsaturated fatty acids are significantly more reactive to oxidation than saturated compounds. With respect to long-chain FAMES, polyunsaturated fatty esters are approximately twice as reactive to oxidation as monounsaturated esters (Karavalakis and Stournas, 2010). Kumar et., al (2008) studied the biodiesel production using *Jatropha curcas* oil from India by the alkali transesterification and found out that the oxidative stability was 0.56 h.

In this study, the oxidation stability of biodiesel from acid pretreatment and neutralized feedstock was found to be 1.12h and 3.00h respectively. The ANOVA t-test shows that there is a significant difference between the two values at 95% confidence interval. The biodiesel from neutralized feedstock was more stable than that of pretreated feedstock as it shows high Rancimat induction time. The obtained oxidative stabilities from both pretreatment methods did not meet the required induction time by the EN14214 of 6h. The Biodiesel from neutralized feedstock meets the requirement of the ASTM D6751-07 of 3h induction time (Knothe, 2007). It seems that, during the acid pretreatment step, a modification of the composition of the minor components in the oil particularly the antioxidants, was higher in acid pretreated oil.

4.0 CONCLUSION

Both pretreatment processes have been able to lower the FFA of *Jatropha* oil from 5.96% to the acceptable value for alkali transesterification. The acid pretreatment process shows low losses (4%) in feedstock as compared to 20% loss from the neutralization process. Acid pretreatment process takes much time than neutralization process but gives a high amount of biodiesel due to lower losses in feedstock. However, the oxidation stability of the acid pretreated biodiesel was lower than that of neutralized feedstock biodiesel. The Biodiesel from neutralized feedstock meets the requirement of the ASTM D6751-07 of 3h induction time. The study also shows that, although the oxidative stability of Biodiesel depends on the presence of natural antioxidant, degree of unsaturation, and branching of the chain, it can also depend on the production process of biodiesel.

5.0 REFERENCES

- Akbar, E., Yaakob, Z., Kamarudin, S. K., Ismail, M. and Salimon, J. (2009), *Characteristic and Composition of Jatropha Curcas Oil Seed from Malaysia and its Potential as Biodiesel Feedstock*. European Journal of Scientific Research, 29, 396-403.
- Alekett, K. (2003), *World oil and gas 'running out'*. CNN.
- AOCS (2004), *Official Methods and Recommended Practices of the AOCS*, Illinois, Champaign.
- Babcock, R. E., Clausen, E. C., Popp, M. and Schulte, W. B. (2008), *Yield characteristics of biodiesel produced from chicken fat-tall oil blended feedstocks*.
- Berchmans, H. J. and Hirata, S. (2008), *Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids*. Bioresource Technology, 99, 1716-1721.
- Bhosle, B. M. and Subramanian, R. (2005), *New approaches in deacidification of edible oils--a review*. Journal of Food Engineering, 69, 481-494.
- Canakci, M. and Van Gerpen, J. (1999), *Biodiesel production from oils and fats with high free fatty acids*.
- Chhetri, A. B., Tango, M. S., Budge, S. M., Watts, K. C. and Islam, M. R. (2008), *Non-edible plant oils as new sources for biodiesel production*. International Journal of Molecular Sciences, 9, 169.

- Farr, W. E. (2000), *Refining of fats and oils*. Introduction to Fats and Oils Technology, 136-157.
- Ferrari, R. A., Oliveira, V. S. and Scabio, A. (2005), *Oxidative stability of biodiesel from soybean oil fatty acid ethyl esters*. Scientia Agricola, 62, 291-295.
- Freedman, B., Pryde, E. H. and Mounts, T. L. (1984), *Variables affecting the yields of fatty esters from transesterified vegetable oils*. Journal of the American Oil Chemists' Society, 61, 1638-1643.
- Gingras, L. (2000), *Refining of rice bran oil*. Inform, 11, 1196-1203.
- Gunstone, F. D. (2004), *The chemistry of oils and fats: sources, composition, properties, and uses*, Blackwell.
- Karavalakis, G. and Stournas, S. (2010), *Impact of Antioxidant Additives on the Oxidation Stability of Diesel/Biodiesel Blends*. Energy & Fuels, 24, 3682-3686.
- Knothe, G. (2005), *Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters*. Fuel Processing Technology, 86, 1059-1070.
- Knothe, G. (2007), *Some aspects of biodiesel oxidative stability*. Fuel Processing Technology, 88, 669-677.
- Knothe, G. and Steidley, K. R. (2005), *Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components*. Fuel, 84, 1059-1065.
- Krawczyk, T. (1996), *Biodiesel-alternative fuel makes inroads but hurdles remain*. Inform, 7, 801-815.
- Kumar, A., Kumar Tiwari, A. and Raheman, H. (2007), *Biodiesel production from jatropha oil (Jatropha curcas) with high free fatty acids: an optimized process*. Biomass and bioenergy, 31, 569-575.
- Kumar Naik, M., Charan Meher, L., Kumar Dalai, A. and Narayan Naik, S. (2008), *Biodiesel Production Using Karanja (Pongamia pinnata) and Jatropha (Jatropha curcas) Seed Oil*. Handbook of Plant-Based Biofuels. CRC Press.
- Kywe, T. T. and Oo, M. M. (2009), *Production of Biodiesel from Jatropha Oil (Jatropha curcas) in Pilot Plant*. PWASET, 38, 2070-3740.
- Ma, F. and Hanna, M. A. (1999), *Biodiesel production: a review*. Bioresource Technology, 70, 1-15.
- Meher, L. C., Vidya Sagar, D. and Naik, S. N. (2006), *Technical aspects of biodiesel production by transesterification--a review*. Renewable and Sustainable Energy Reviews, 10, 248-268.
- Monyem, A. (2001), *The effect of biodiesel oxidation on engine performance and emissions*. Biomass and bioenergy, 20, 317-325.
- Norris, F. A. (1982), *Refining and bleaching*. Bailey's Industrial Oil and Fat Products, 2, 253-314.
- Singh, A. K., Fernando, S. D. and Hernandez, R. (2007), *Base-catalyzed fast transesterification of soybean oil using ultrasonication*. Energy Fuels, 21, 1161-1164.
- Van Eijck, J. and Romijn, H. (2008), *Prospects for Jatropha biofuels in Tanzania: an analysis with Strategic Niche Management*. Energy Policy, 36, 311-325.
- Van Gerpen, J. (2003), *Biodiesel production and fuel quality*. University of Idaho, Moscow, ID, 83844.
- Van Gerpen, J. (2005), *Biodiesel processing and production*. Fuel Processing Technology, 86, 1097-1107.
- Zhang, Y., Dube, M. A., McLean, D. D. and Kates, M. (2003), *Biodiesel production from waste cooking oil: 1. Process design and technological assessment*. Bioresource Technology, 89, 1-16.
- Zullaikah, S., Lai, C. C., Vali, S. R. and Ju, Y. H. (2005), *A two-step acid-catalyzed process for the production of biodiesel from rice bran oil*. Bioresource Technology, 96, 1889-1896.