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Comparative Study of Homogenous and Heterogeneous Catalytic Transesterification of High Free Fatty Acid *Jatropha curcas* Oil: Effects on Products Quality

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***Abstract* – The effects of high free fatty acids in feedstocks on biodiesel qualities was investigated in this study by carrying out homogenous and heterogeneous catalytic transesterification of 3.36 FFA *Jatropha curcas* seed oil with methanol. The catalysts used were NaOH and MgO, same methanol to oil molar ratio catalyst loading and reaction conditions. The reactions were carried out at 60oC for 60 minutes and 3:1 moles of methanol to oil. Methyl esters contents for homogenous products were satisfactory; 95.5%, 98.4%, 97.4% and 85.7% but poor viscosities 0.5 mm2/s, while heterogeneous products had low methyl esters contents;77.9%, 73.7%, 71.1% and 76.2% but had satisfactory viscosities of 3.5 mm2/s. The acid values in the products of the two processes were too high 0 to 12% for homogenous and 7.3% to 9.5% for heterogeneous. The products of two processes did not satisfactorily meet the EN 14214 and ASTM D6751 standards due to effect of the free fatty acids in the feedstock.**

***Keywords* – Comparative Study, Effect of Free Fatty Acid Feedstock, Transesterification.**

I. INTRODUCTION

Biodiesel is continuing gaining acceptance internationally due to its environmental benign nature. Its degradability, no toxicity, low emission of carbon monoxide, particulate matter and unburned hydrocarbons and also renewability [1] have made it to be accepted for use in compression ignition engines. It is free of sulphur and aromatic compounds, has higher energy content and lubricating machines parts better than fossil diesel. Especially biodiesel from plant oils do not have sulphur except that produced from animal fats [2]. Biodiesel has higher cetane number (ranging from 45-70) than fossil diesel (40-52) [3]. Biodiesel is compatible with conventional diesel fuel and already comprises a commercial fuel in Europe and U.S. [4] in the percentage of 10 and 20 called B10 and B20 respectively.

According to Guo and Fang [5] homogeneous alkali catalysts can convert triglycerides to fatty acid alkyl esters (FAAEs) with high yield, less time and low cost, but separating the catalyst from the product mixture is technically difficult. The use of homogeneous catalysts requires neutralization and separation from the reaction mixture, leading to a series of environmental problems related to the use of large amounts of solvents and energy [6]. According to Singh *et al*,.[7] the most commonly used alkaline catalysts in the biodiesel industry are potassium hydroxide (KOH) and sodium hydroxide (NaOH) flakes which are inexpensive, easy to handle in transportation and storage, and are preferred by small producers. The homogenous acids catalysts, apart from catalyzed transesterification very slow are corrosive to the equipment [5].

This study was carried out to determine the effects of high free fatty acid in feedstocks on the transesterification reactions and products. A *Jatropha curcas* oil of 3.36 free fatty acid was used to produce biodiesel with methanol in 1:3 molar ratio (oil/methanol) using NaOH and MgO as catalysts. The catalyst loading were the same for both and also same reaction conditions were maintained.

II. MATERIALS AND METHODS

The materials used in this investigation include; NaOH, MgO as catalyst, 0.1M KOH, methanol, concentrated sulphuric acid, phenolphthalein, propan-2-ol, *Jatropha curcas* seed oil, conical flasks, burette, magnetic stirrer, thermometer, viscometer and GC-MS machine.

2.1 Transesterification

FFA of raw *Jatropha curcas L* oil was determined by dissolving 1.0 g of it in 25 mL of propan-2-ol. The resulting solution with two drops of phenolphthalein was titrated with 0.1 M KOH to pink colour. The raw oil was divided into two. 100 g of one part was transesterified with methanol and 1.2 g of NaOH and same mass of the second part was transesterified with methanol and 1.2 g magnesium oxide (MgO). In both reactions 3 moles of methanol was used with one mole of oil. The catalyst loading in the two cases was 1.2% of the mass of oil. The transesterifications were carried out in conical flasks on magnetic stirrers simultaneously for 60 minutes. The transesterified products were transferred into separating funnels for separation after filtration. The one catalyzed by MgO remained uniform. The one catalyzed by NaOH was separated into biodiesel, glycerol and soap. The biodiesel was collected washed and dried. This process was repeated until it stopped foaming. This experiment was repeated with 4.5, 6 and 7.5 moles of methanol to one mole of oil.

2.2 GC-MS Analysis

2 ml of each sample was diluted with n-hexane. The resulting mixture was filled into a sample bottle and inserted into the GC-MS machine. The machine was run and the chemical components of the sample were analyzed. The methyl esters content was calculated from area% of the GC-MS analysis. This analysis was

performed on GCMS-QP2010 PLUS SHIMADZU/ JAPAN in the Quality Control Unit of NARICT, Zaria.

2.3 Viscosity

100 ml beaker was filled to three-quarter of its capacity with biodiesel sample, heated to 40oC and immediately placed on viscometer and a spindle of a viscometer was adjusted until it submerged into the sample. The viscometer was switched on after spinning; reading was taking from the scale. This analysis was carried with Brookfield SYNCHRO LECTRIC VISCOMETER in the Department of Chemical Engineering, Ahmadu Bello University, Zaria.

2.4 Density

The sample biodiesel was cooled to 15oC using piece of ice blocks. An empty relative density bottle was first weighed, reweigh when filled with water and reweigh when filled with sample biodiesel. The relative density of the sample was calculated and converted to density.

III. Results and Discussion

The free fatty acid of the raw oil was 3.36 which were too high for good biodiesel production. The products of homogenous catalyzed process were separated into three layers with biodiesel at the top, glycerol at the middle and soap at the bottom as shown in plate 1. That catalyzed by MgO remained in one layer. The biodiesel products from NaOH were clearer with light yellow colour but the MgO catalyzed products was amber colour as shown in plate 2. The MgO catalyzed products had higher acid value because; the formation of soap by the reaction of NaOH with fatty acids reduced the acid value in the NaOH catalyzed products.

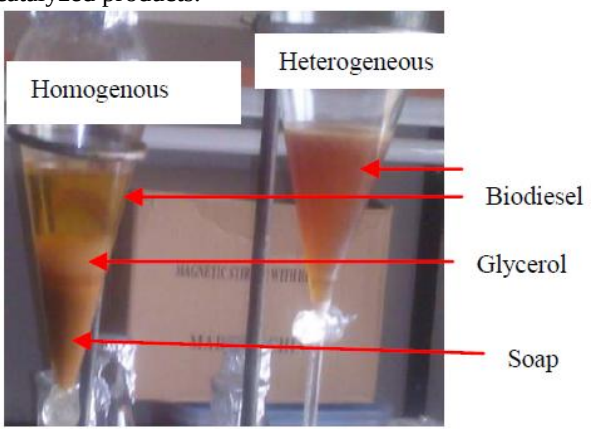

Plate 1: The two products of the transesterifications in separation process

Generally, the methyl esters yield by MgO catalyzed reactions was low compared to that of NaOH catalyzed reactions. The highest obtained from MgO catalyzed reactions was 77.9% whereas NaOH catalyzed reaction had 98.25% methyl esters. Probably, the high free fatty acid content reduced the catalytic strength of MgO resulting in the formation of high quantity of impurities as shown in Figure 3. The quantity of methanol has no significant influence in the methyl ester yield as confirmed in this study. The highest methyl ester by MgO catalyzed reaction was obtained at 3:1 methanol to oil mole ratio whereas that catalyzed by NaOH was at 4.5:1.

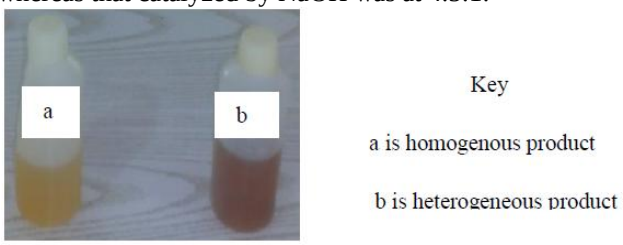

Plate 2: The two products showing different colours appearance

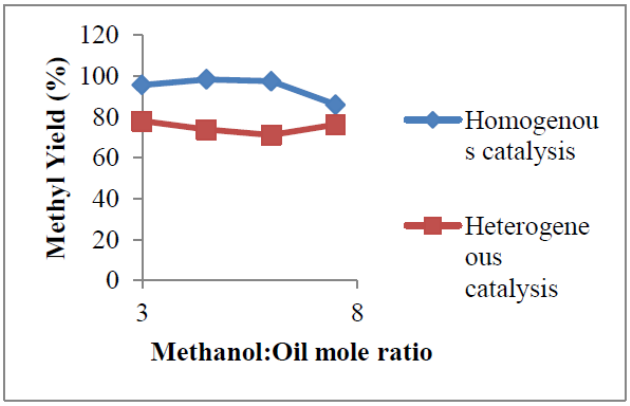

Fig.1. Comparison of methyl esters yield in the products

On the average, the free fatty acid values of the MgO catalyzed products were higher than that of NaOH catalyzed products. The acid values of NaOH catalyzed products were low due to the reaction of NaOH with free fatty acid to yield soap. Soap was formed from all the products of NaOH catalyzed reactions. However, a zero acid value was obtained when the methanol/oil ratio was 4.5 coincidentally, MgO catalyzed reaction had its lowest acid value at the same molar ratio. The acid value of the NaOH catalyzed reaction rises from zero to 12.87% when the molar ratio was 7.5 as shown in Figure 2. A feedstock with free fatty acid value greater than 3 has been confirmed unsuitable for homogenous base catalytic transesterification [8].

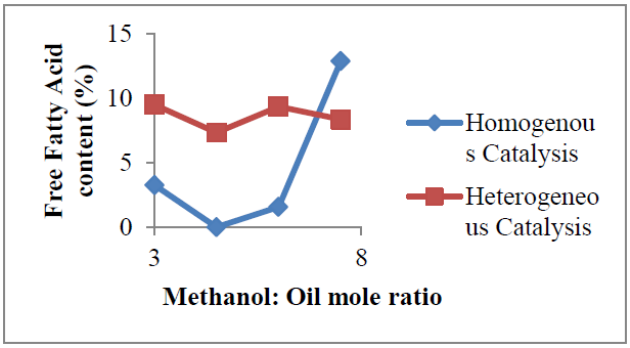

Fig.2. Comparison of free fatty acid content in the products

High free fatty acid in the feedstock had resulted to high impurities in MgO catalyzed products shown in Figure 3

as the catalyst could not react with the fatty acids. Due to some reactions involving free hydrogen liberated from the cleavage of triglycerides, compounds like alkanals and alkanones were formed by reduction of fatty acids. High free fatty acids in feedstocks affect transesterification catalyzed by both homogenous and heterogeneous based catalysts [9].

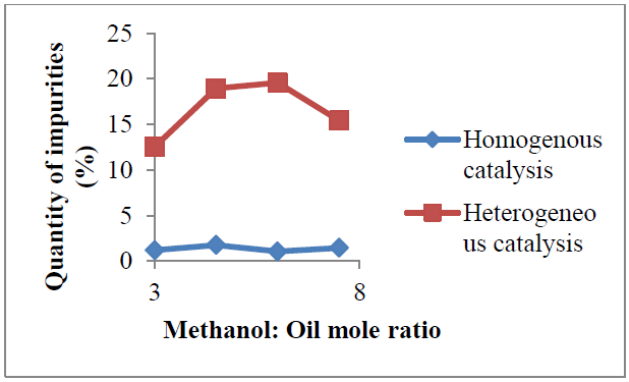

Fig.3. Comparison of other impurities in the products

The viscosities of all the productions catalyzed by MgO met both the ASTM and EN minimum standards but that catalyzed by NaOH did not. The highest viscosity obtained by NaOH catalyzed products was 0.6 mm2/s which was too low for biodiesel. A biodiesel with too low viscosity provides fine spray, low mass and speed which lead to insufficient penetration and formation of black smoke due to absence of oxygen [10]. Despite high methyl esters content in NaOH catalyzed products, they fail to be accepted due to their too low viscosities. Hence, high acid feedstock had affected the products. All the products catalyzed by MgO had viscosity within the standard of both ASTM and EN but their methyl esters content were below EN standard 96.5% [7;8] and acid values too high above 0.5 and 0.8 [8;10]. Figure 4 shows the viscosities of the NaOH and MgO catalyzed products compared with ASTM and EN standards.

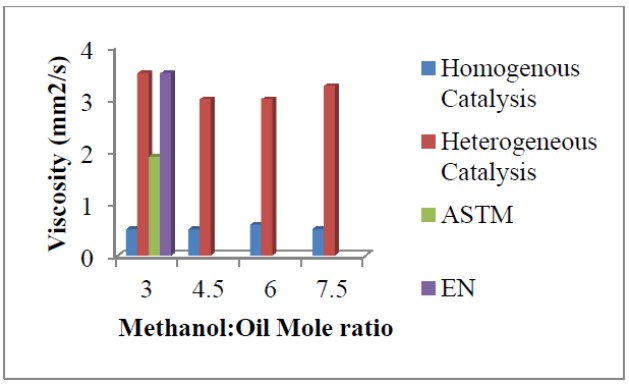

Fig.4. Comparison of viscosities of products with International Standards

Two products catalyzed by MgO had density higher than the two Standards but not too much to affect their acceptability for compression ignition engine if not for their high acid values and low methyl esters content. Figure 5 shows the densities of all the products with NaOH catalyzed products fall within the minimum value of EN and ASTM standards.

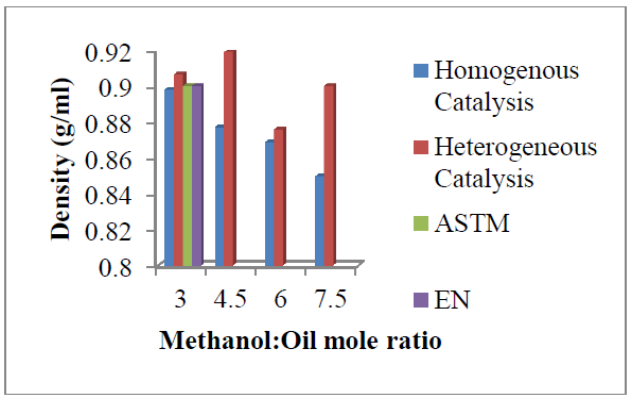

Fig.5. Comparison of densities of products with International Standards

IV. Conclusion

Homogeneous and heterogeneous catalytic transesterification of 3.36 FFA *Jatropha curcas* oil was carried out to determine effect of high free fatty feedstock to biodiesel yield and quality using NaOH and MgO as catalysts. The products of NaOH had high yield of methyl esters but too low viscosities which would lead to incomplete combustion due to fine spray, low mass and speed which lead to insufficient penetration and formation of black smoke due to absence of oxygen [10]. On the other hand, the products of MgO catalyzed process had low methyl esters contents; standard viscosities 3.5 mm2/s, high acid values and high other impurities such as alkanals, alkanones, alcohols and hydrocarbons. The products of the two processes did not satisfactorily meet the ASTM D 6751 and EN 14214 standards for biodiesel [7; 11].

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