Comparative Analysis of Production of Biodiesel via Homogeneous and Heterogeneous Transesterification

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Abstract: This work studies the synthesis of biodiesel from heterogeneous solid base transesterification. The solid base catalyst consists of 98.5% of calcium oxide and 1.5% of lithium. Catalyst concentration ranging between 1-2 wt % Li-CaO in relation to oil was first mixed as a catalyst in methanol in the mixing tank for 30 minutes at a temperature of 60℃. Oil preheated at a temperature of 100℃ was thereafter transferred into the reactor where methanol and catalyst mixture from mixing tank were added to it. The biodiesel produced was characterized and its properties compared in respect of the American Society for Testing and Materials (ASTM D6751) and EN 14214 limits for biodiesel. The effects of five process parameters namely; reaction time, temperature, stir speed, catalyst concentration and methanol-oil ratio on the biodiesel yield were also investigated. The analysis of results obtained indicated that heterogeneous catalysts exhibit a less corrosive character and can be used in a fixed reactor, leading to safer, cheaper and more environment-friendly operations requiring fewer number of separation steps when compared with homogeneous catalysts. The fuel properties of biodiesel produced are within the limits of ASTM D6751 and EN 14214 standards for biodiesel and are similar to the fuel properties of fossil diesel which confirms the successful synthesis of biodiesel using heterogeneous solid base catalyst.

Keywords: Base Catalyst, Biodiesel, Reactor, Transesterification, Yield

1. INTRODUCTION

Biodiesel can be synthesized by the transesterification reaction of triglycerides of vegetable oil or animal fat with a short chain primary alcohol in the presence of catalysts. The choice of catalyst employed for the transesterification reaction however depends on the amount of free fatty acid in the vegetable oil (Le *et al.,* 2012) Biodiesel synthesis using solid catalysts could potentially lead to cheaper production costs because of re-use of the catalyst and the possibility of carrying out both transesterification and esterification simultaneously (Lopez *et al.,* 2005). Singh *et al.* (2010) carried out the transesterification of soybean oil with methanol to fatty acid ester over the solid super acid catalysts of tungstated zirconia-alumina (WZA), sulphated zirconia-alumina (SZA) and sulphated tin oxide (STO) at $200^oC\text{-}300^oC$ in a fixed bed reactor under atmospheric pressure and reported tungstated zirconia-alumina as promising solid catalyst for the production of biodiesel from soybean oil resulting in over 90% conversion (Singh *et al.,* 2010). However, a high molar ratio of alcohol to oil, large amount of catalyst and high temperature and pressure are required when utilizing heterogeneous catalyst to produce biodiesel. Examples of heterogeneous catalysts used in biodiesel production are: $Kl/Al_2O_3,$ Li/CaO, $KNO_3/Al_2O_3,$ CaO, KOH/NaX zeolite, ZrS/Si, or ZnS/Si, $Eu_2O_3/Al_2O_3,$ KF/ Eu_2O_3, Ca $(OCH_2CH_3)_2$, and S-$ZrO_2.$ According to Romero *et al.* (2011), different studies, however, have been carried out using acid catalysts (Di Serio *et al.,* 2008; Lotero *et al.,* 2005; MacLeod *et al.,* 2008; Marchetti *et al.,* 2007; Zhu *et al.,* 2006). The benefit with solid catalysts, acid or basic, is the lesser consumption of catalyst in the reaction. Besides, heterogeneous catalysts exhibit a less corrosive character and

can be used in a fixed-bed reactor, leading to safer, cheaper and more environment-friendly operations and the number of separation steps is less than when using homogeneous catalysts (Romero *et al.,* 2011). The heterogeneous catalysts do not leave neutralization salts in the glycerol, and are plausible to be retained in the reactor by filtration (Di Serio *et al.,* 2008; Kaita *et al.,* 2002; Kawashima *et al.,* 2009; Kovacheva *et al.,* 2001; MacLeod *et al.,* 2008; Madje *et al.,* 2004; Park *et al.,* 2010; Suppes *et al.,* 2004; Waghoo *et al.,* 1999; Xie and Liu, 2010; Yan *et al.,* 2008; Romero *et al.,* 2011). The most commonly studied heterogeneous basic catalysts are alkaline metals carbonates (Na_2CO_3, K_2CO_3), alkaline earth metal carbonates ($CaCO_3$), alkaline earth metal oxides (CaO, MgO, SrO, BaO) and other oxides as ZnO (Dossin *et al.,* 2006; Encinar *et al.,* 2005; Fukuda *et al.,* 2001; Liu *et al.,* 2007; López *et al.,* 2005; Ma & Hanna, 1999; MacLeod *et al.,* 2008;Verziu *et al.,* 2008; Romero *et al.,* 2011). The aim of this work is to produce biodiesel at a cost effective rate, hence heterogeneous transesterification is an attractive option because of the disadvantages of homogeneous base-catalyst transesterification of high energy-consumption, costly separation of the catalyst from the reaction mixture and the purification of crude biodiesel.

2. METHODOLOGY

In order to reduce the cost of the production, heterogeneous solid catalysts such as metal oxides was employed for the conversion of palm olein virgin oil to biodiesel with 99.8% pure methanol and Lithium doped calcium oxide (Li-CaO) as catalyst, methanol being in excess to oil (ratio 9:1). This is because the catalysts can be easily separated from the reaction mixture, and can be reused. The choice of solid base

catalyst was informed by the fact that solid base catalyst are most active than solid acid catalyst (Lee *at al.,* 2012; Arzamendi *et al.,* 2007; Perego and Bosetti, 2001). Beside this, CaO is also abundant in nature and widely used among the alkaline earth metals (Dermibas 2007; Couchan and Sarma 2011; Antunes *et al.,* 2008; Verziu *et al.,* 2008; Sharma *et al.,* 2011). The catalyst consists of 98.5% of calcium oxide and 1.5% of lithium. Catalyst concentration ranging between 1-2 wt % Li-CaO in relation to oil was first mixed as a catalyst in methanol in the mixing tank for 30 minutes at a temperature of 60℃. Oil preheated at a temperature of 100℃ was transferred into the reactor where methanol and catalyst mixture from mixing tank were added to it. Alcohol is made to react with fatty acids of the oil to form mono-alkyl ester and crude glycerol. The reaction between the fat or oil and the alcohol is a reversible energy reaction and so the alcohol must be added in excess to drive the reaction towards the right complete conversion. Continuous mixing of the mixture was done in the reactor at temperatures ranging between 40-90℃ and stir speed between 200-400 rpm for 1-7 hours. This ensures the reaction is driven to completion with phase separation into two layers: the top biodiesel and the bottom glycerol. The catalyst; CaO and excess methanol were recovered from the reaction product by calcination. Since the solubility of methyl ester (biodiesel) is low, the heavier, co-product, glycerol settles out. With excess alcohol, the unconverted triglycerides was essentially zero. However, some monoglycerides and diglycerides were present. Due to their polarity, partially reacted glycerides were preferentially attracted to the glycerol phase and then removed when the phase is separated. Both the dried biodiesel and glycerol was then transferred to the respective storage tanks for storage. The production flow chart for biodiesel production is shown in Figure 1.
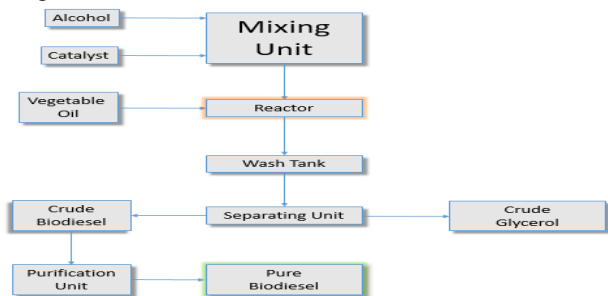

Figure 1: Production Flow chart for Biodiesel

Table 1 compares the process of homogeneous and heterogeneous alkali catalyzed transesterification.

Table 1: Comparison of Heterogeneous and Homogeneous Catalysed Transesterification

S/N	Factors	Homogeneous	Heterogeneous
1	Reaction time	Fast	Moderate
2.	Biodiesel Yield	High (91.6%)	Moderate (78%)
3.	Cost	Costly	Cheaper
4.	Catalyst recovery	Not possible	Recovered and re used
5.	Product purification	Complex and technical as stages of washing are required	Simpler. Washing process not required
6.	Side reactions	Small amount of soaps and gels are observed to be formed	Formation of soaps and gel are not observed
7.	Corrosiveness	Corrosive	Less corrosive

3. RESULTS AND DISCUSSION

Results obtained gave an optimum yield of biodiesel as 78% at a reaction time of 4 hours, reation temperature 70°C, stir speed 350 rpm, catalyst concentration 1.4 wt.% and methanol to oil ratio 9:1 with methanol in excess. This was similar to the results obtained by Huaping *et al.* (2006) during the transesterification of *Jatropha curcas* oil with methanol catalyzed by calcium oxide. The yield of FAME was higher than 93% under the conditions namely the catalyst amount of 1.5 wt.%; temperature of 70 °C; molar ratio of 9:1; and reaction time 3.5 hours. The characterization of the properties of the biodiesel produced was carried out at the Central Research Laboratory, Department of Chemical and Petroleum Engineering, Afe Babalola University, Ado Ekiti, Nigeria and Redeemers' University, Ede, Nigeria. The results obtained is presented in Table 2 and was found to be within the ASTM and EN limits for biodiesel.

Table 2: Characterization of Biodiesel from Palm Olein Oil

S/N	Property	Test Result
1.	Colour	Golden brown
2.	Density (kg/m^3)	905
3.	Specific Gravity	0.902
4.	Kinematic Viscosity (mm^2/sec)	4.20
5.	Flash Point (^{o}C)	171
6.	Pour Point (^{o}C)	-19
7.	Cloud Point (^{o}C)	-14
8.	Saponification value (% mass)	123
9.	Acid value (mg NaOH/g)	0.1721
10.	Free fatty acid (% mass)	0.482
11.	Iodine Value (% mass)	664
12.	Peroxide Value (Meq peroxide/kg oil)	18

4.1 Effect of Process Parameters on Biodiesel Yield for Heterogeneous Alkali Tranesterification

The effect of reaction time at different time interval was examined on biodiesel yield for homogeneous acid transesterification. The dependency of reaction time studied at different time intervals ranging from 1-5 hours revealed that about 4 hours of reaction was sufficient for the completion of the heterogeneous alkali transterification process and optimum conversion of oil to biodiesel (78%). From Figure 2, increase in reaction time increases the biodiesel yield from 1-4 hrs after which there is decrease in biodiesel yield after 4-5 hrs hence the optimum yield of biodiesel was obtained at reaction time of 4 hrs.
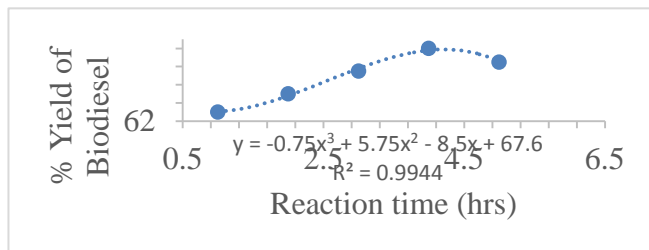

y = -0.75x^3 + 5.75x^2 - 8.5x + 67.6
R^2 = 0.9944

Figure 2: Effect of Time Variation on Biodiesel Yield

Figure 3 studies the effect of temperature on biodiesel yield. Increase in temperature increases the biodiesel yield from 40-60°C after which there was decrease in biodiesel yield after 60°C with continuous increase in temperature. This is because the yield of biodiesel decreases when reaction temperature is close or above to the evaporating temperature of methanol (67°C) as methanol which is supposed to drive transesterification reaction to completion will be evaporated. Hence the optimum yield of biodiesel was obtained at reaction temperature of 60°C.
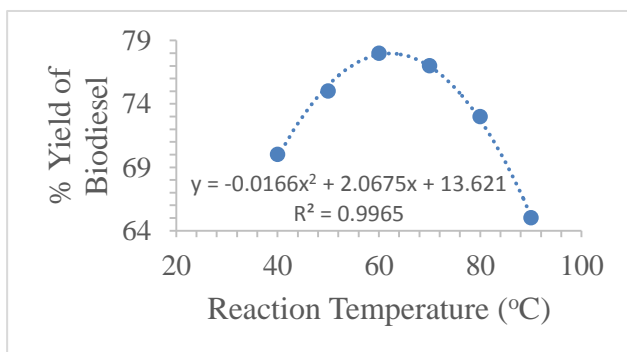

y = -0.0166x^2 + 2.0675x + 13.621
R^2 = 0.9965

Figure 3: Effect of Temperature Variation on Biodiesel Yield

Increase in stir speed increases the collision rate at the catalyst interphase. From Figure 4, stir speed of 350 rpm produces an optimum yield of biodiesel (78%). Below this

speed the speed may not be enough to break the chains of fatty acid and drive the reaction to completion and above this speed the agitation is observed to be too high resulting in splashing of the reaction mixture thereby bringing about decrease biodiesel yield.
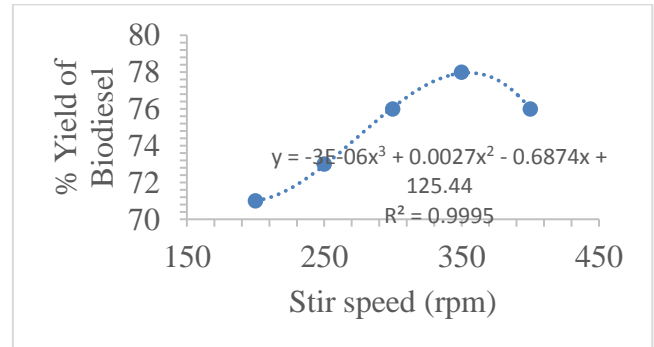

y = -3E-06x^3 + 0.0027x^2 - 0.6874x + 125.44
R^2 = 0.9995

Figure 4: Effect of Stir speed Variation on Biodiesel Yield

The effect of catalyst concentration on biodiesel yield is shown in Figure 5. The catalyst consists of 98.5% of calcium oxide and 1.5% of lithium. Catalyst concentration ranging between 1-2 wt % Li-CaO in relation to oil The optimum catalyst concentration that produces the highest yield of biodiesel was 1.4 wt% which produces a 78% yield of transparent methyl ester. Concentration of catalyst below this may not adequately speed up the conversion reaction resulting in low yield and for catalyst concentrations above 1.4 wt%, it is no longer desirable as there is observed transition from transesterification reaction to saponification reaction.
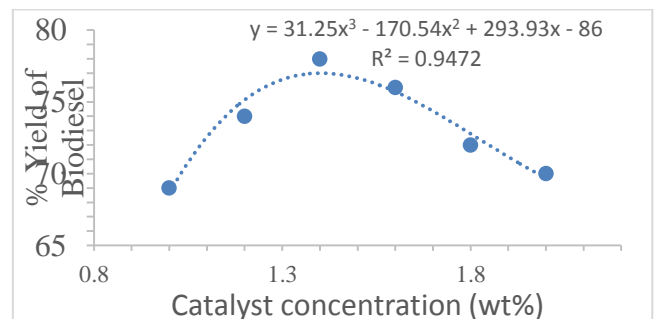

y = 31.25x^3 - 170.54x^2 + 293.93x - 86
R^2 = 0.9472

Figure 5: Effect of Catalyst Concentration on Biodiesel Yield

From Figure 6, a molar ratio of 9:1 (Methanol being in excess of oil) produces an optimum yield of biodiesel (78%), which drives the equilibrium of the reaction forward thus producing more biodiesel. Too much methanol will reduce the flash point thus eroding an important advantage of biodiesel.
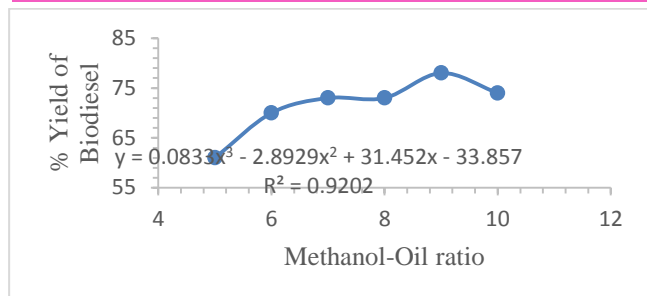
Figure 6: Effect of Methanol-Oil ration on Biodiesel Yield

4. CONCLUSION

Heterogeneous catalysts exhibit a less corrosive character and can be used in a fixed reactor, leading to safer, cheaper and more environment-friendly operations requiring fewer number of separation steps when compared with homogeneous catalysts. The production of biodiesel was cost effective, hence heterogeneous transesterification is an attractive option because of the disadvantages of homogeneous base-catalyst transesterification of high energy-consumption, costly separation of the catalyst from the reaction mixture and the purification of crude biodiesel. Also, the fuel properties of biodiesel produced are within the limits of ASTM D6751 and EN 14214 standards for biodiesel and are similar to the fuel properties of fossil diesel which confirms the successful synthesis of biodiesel using heterogeneous solid base catalyst.

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