

Product Qualities of Biodiesel Produced from a Process Intensify Pilot Plant

ABSTRACT:

An investigation on process intensification on biodiesel production was carried with *Jatropha curcas* seed oil, methanol and five solid base catalysts in a process intensified pilot plant. This Process Intensify Pilot Plant does not have the following unit operations as in conventional plants; Neutralizer, Washer, Dryer, Heat exchanger and Condenser to reduce production cost. Five samples of biodiesel were produced with 3 moles of methanol to 1 mole of oil and 1.5 % catalyst loading (w/w of oil). Methyl ester yields of 97.4, 96.94, 95.76, 99.99 and 98.25 % catalyzed by bulk (CaO), super base calcium oxide (CaO/(NH₄)₂CO₃), bulk magnesium oxide (MgO), calcium oxide/magnesium oxide (CaO/MgO) and 10 % impregnated potassium on calcium oxide/magnesium oxide (K-CaO/MgO) were obtained respectively. The products were analyzed in accordance with ASTM standard for biodiesel and were found satisfactory for use in compression ignition engines. All the biodiesel samples were found not to be easily oxidized as they did not have poly-unsaturated esters such as: linolelaidate (18:2) and linoleneate (18:3). It was found that this process produced clean biodiesel devoid of glycerol.

Keywords: Biodiesel, process intensify, pilot plant, quality

1.0 INTRODUCTION

Since fossil fuels sources are finite and the use of their products has been found to have increased the emission of greenhouse gas, CO₂ in our environment therefore, the development of alternative fuels (biofuels) has become important. Biodiesel produced from plant and animal origins is the environmental friendly fuel suitable for replacing fossil diesel due to its numerous advantages. Some of these advantages include; no aromatic compounds [1] low sulphur, higher lubricating action, low carbon emissions [2], higher cetane value and biodegradability. Biodiesel has similar properties to that of fossil diesel this makes it possible for replacing and blending with fossil diesel.

A lot of works have been done on biodiesel production but the cost of production is still very high for commercial application. Biodiesel was prepared by super critical method at reaction temperature of 330-350°C, pressure of 19 – 35 MPa using methanol to oil ratio of 42:1 yield obtained was less than 96.5% [3]. This method consumes a lot of energy and the materials that can withstand these reaction conditions are expensive. Also it wastes a lot of methanol. Fadhi et al., [4] produced biodiesel from spent fry fish oil and methanol in the mole ratio of 1:6 (oil to methanol) using hydrochloric acid. The methanol is in excess which requires energy and materials for recovery and also, the acid has to be neutralized and washed out of the products. The cost of methanol recovery, neutralization of acid, washing and drying of the products (biodiesel and glycerol) is additional costs to the production. This also applies to the use of homogeneous base catalysts. Tang et al., [5] produced biodiesel from rapeseed oil and methanol in the molar ratio of 1:30 (oil to methanol) at 65°C for 3 hours with a yield of 96.1%. High mole ratio in the end raises the cost of recovery which greatly affects the product price. The long reaction time reduces the quantity of production. This duration would have been used for three productions. Also high temperature raises the production cost.

In this investigation, biodiesel was produced in a process intensify pilot plant operated in a continuous process in order to cut down the production cost. Transesterification was carried with *Jatropha curcas* seed oil and methanol in the stoichiometric ratio of 3:1 (methanol to oil) using five different solid base catalysts of 1.5 % (w/w of oil) catalyst loading. These catalysts were; bulk calcium oxide (CaO), super base calcium oxide (CaO/[(NH₄)₂CO₃], bulk magnesium oxide (MgO), calcium oxide/magnesium oxide (CaO/MgO) and 10% potassium impregnated calcium oxide/magnesium oxide (K-CaO/MgO). The plant was operated at 60°C and 1 atmosphere. Figure 1 depicted the process flow diagram of the process intensity biodiesel pilot plant

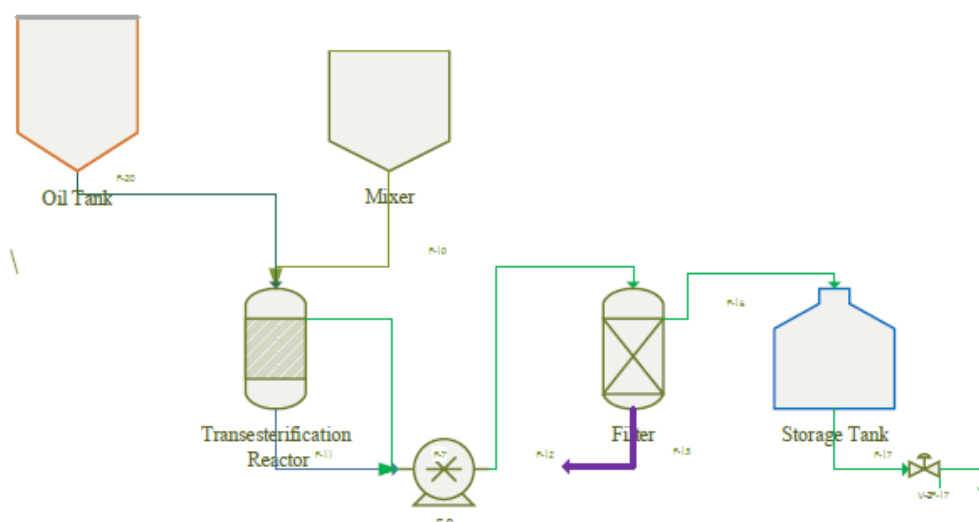


Figure I: Process Flow Diagram of Process Intensify Biodiesel Pilot Plant

2.0 MATERIALS AND METHODS

2.1 MATERIALS

Materials used in the work include; Gallenkamp magnetic stirrer, cheese cloth, funnel, biodiesel pilot plant in Renewable Energy Division of NARICT, GC-MS (QP2010 PLUS SHIMADZU/JAPAN), viscometer, bomb calorimeter, flash point tester, density bottle, sulphur analyzer, cloud and pour point analyzer, *Jatropha curcas* oil, propan-2-ol and methanol. The catalysts used were calcium oxide, super base calcium oxide, magnesium oxide, calcium oxide/magnesium oxide and potassium impregnated calcium oxide/magnesium oxide.

2.2 METHODS

2.2.1 Esterification

Jatropha curcas oil (1 g) was dissolved in 25 ml of propan-2-ol. 2 drops of phenolphthalein indicator was added to the solution and was titrated against 0.1 M potassium hydroxide to pink colour. The value of the free fatty acid was calculated from the titre value. The oil was then refined by esterification process. 1200 ml of the raw *Jatropha* oil was heated to 60 °C in a 2000 ml conical flask. A mixture of methanol and sulphuric acid was prepared as in accordance with ASTM standard reported by Gerpen et al., [6] as in Equations 1 and 2.

$$M_{MeOH} = 2.25 \times \%FFA \times M_o \quad (1)$$

$$M_s = 0.05 \times \%FFA \times M_o \quad (2)$$

where, M_{MeOH} is mass of methanol, FFA is free fatty acid, M_o is mass of oil and M_s is mass of sulphuric acid. 2.25 and 0.05 are constants.

The acid/methanol mixture was added to the oil at 60 °C and the temperature was maintained at 60 °C for 60 minutes. The content was transferred into separating funnel which separated out into oil and aqueous layer. The oil was collected for transesterification after tested and certified.

2.2.2 Transesterification

First, all the valves were checked to ensure they were closed and all the pipes were also connected appropriately. Raw materials; *Jatropha curcas* seed oil, methanol and catalyst were measured based on requirement and were charged into triolein (oil) tank and mixer (mixture of methanol and catalyst) respectively. The stirrer of mixer was switched on. The valves of the two tanks were opened and adjusted to the required flow rates; 80.8 ml/min and 10.8 ml/min for oil and methanol/catalyst flows respectively. These flows were in accordance to molar ratio of 1:3 (oil to methanol).

Following the flows of the reactants into the reactor, the reactor stirrer was switched on. The heater was also switched on and set to 60 °C to heat the reactor content through the water in the jacket. The reactor was placed in water inside the jacket. When the reaction temperature reached 60 °C, it was

maintained for about 70 minutes with the aid of thermostat. A peristaltic pump connected to the reactor was switched on to pump the product to the separators. The products passed through the funnel containing cheese cloths into the separating funnels. The catalysts were collected on the cheese cloths (which act as filters) while the liquid product; biodiesel was collected in to storage tanks.

2.2.3 Biodiesel Quality Test

Methyl ester test

A Biodiesel sample (10 ml) was dissolved in 40 ml of methanol and the mixture was well shaken to determine the completion of transesterification reaction. The samples were later analyzed by GC-MS to determine the methyl esters content.

2.3.4 Methyl Esters Content Analysis with GC-MS

Biodiesel sample was diluted with n-hexane. 2 ml of the solution was collected into a sample bottle and injected into the GC-MS machine. The methyl esters content was calculated from area% of the GC-MS analysis. This analysis was performed on in the Quality Control Unit of NARICT, Zaria.

2.3.5 Viscosity

A beaker of 200 ml was filled to three-quarter of its capacity with biodiesel sample and heated to 40°C. A spindle of a viscometer was adjusted until it submerged into the sample. The viscometer was switched on after spinning; reading was taken from the scale. This analysis was carried out with BrookField SYNCHRO ELECTRIC VISCOMETER in the Department of Chemical Engineering, Ahmadu Bello University, Zaria.

2.3.6 Density

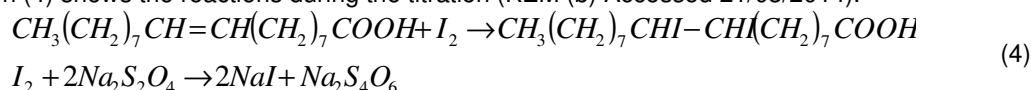
A beaker of 250 ml was filled to 2/3 of its capacity with biodiesel sample and inserted in a 500 ml beaker containing a mixture of ice blocks and water. The temperature was monitored with thermometer. When its temperature fell to 15°C, it was transferred into a relative density bottle, filled and wiped after the stopper was replaced. It was weighed and the density calculated.

2.3.7 Iodine Value

Iodine value analysis was carried out in accordance to ASTM D1959-97 as presented by KEM (a) [7]. 0.3 g sample of biodiesel was taken into a 250ml conical flask with stopper. 10ml cyclohexane (in place of carbon tetrachloride) was added, and dissolved. 20 ml Wijs reagent was added, and stirred. The flask was plugged with stopper, and left for 30 minutes in a dark room at room temperature. Then, 20ml of 100g/l potassium iodine solution was added followed by 100ml distilled water. The solution was titrated with 0.1mol/l sodium thiosulfate solution, to obtain iodine value. A blank level beforehand was performed test likewise. Equation 3 expresses the iodine value.

$$\text{Iodine value (g/100g)} = \frac{(\text{BLI} - \text{EPI}) \times \text{TF} \times \text{CI}}{s} \quad (3)$$

Equation (4) shows the reactions during the titration (KEM (b) Accessed 21/03/2014).



where, BLI is blank titration (17.00 ml), EPI is the titration volume, TF is factor of titration (1.003), CI is Concentration conversion coefficient (1.269) and s is the sample weight (g).

2.3.8 Saponification Value

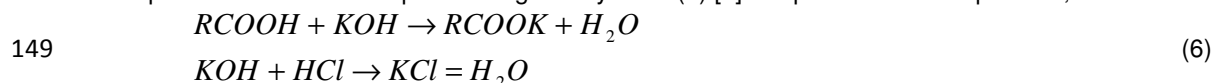
Saponification value analysis was carried out in accordance to ASTM D5558 as presented by KEM (b) [8]. 2.0 g biodiesel sample was delivered into a 250 ml conical flask. 25.0ml of 0.5mol/l potassium hydroxide Ethanol solution was added, and fixed a cooling pipe to the flask. The mixture was heated under reflux for 30 minutes to saponify the biodiesel sample. Two drops of phenolphthalein was added to the saponified sample and was titrated against 0.5 N HCl.

A blank test was performed by titrating 25 ml of 0.5 KOH ethanol solution without biodiesel sample and also not heated under reflux against 0.5 N HCl with two drops of phenolphthalein indicator. Equation 5 expresses saponification value.

$$\text{saponification value} = \frac{\text{blank titre} - \text{sample titre}}{\text{mass of sample}} \times \text{normality} \times 56.1 \quad (5)$$

where, the blank titre value was 38.6 ml.

A saponification reaction equation as given by KEM (b) [8] is expressed as in Equation 6;



150

151 2.3.9 Cetane Number Analysis

152 The cetane numbers of the biodiesel samples were determined from the values of their saponification
153 values and iodine numbers by calculation using Krisnagkura correlation equation [9]. The Krisnagkura
154 equation is expressed as in Equation 7;

$$CI = 46.3 + (5458 / SV) - (0.225 \times IN) \quad (7)$$

156 where, CI is cetane index, SV is saponification value and IN is iodine number.

157

158 The cetane number, CN is expressed as in Equation 8;

$$CN = CI \times 0.72 + 10 \quad (8)$$

160

161 2.3.10 Acid number

162 The volumetric standard sample, potassium hydroxide, the titration solvent and indicator solution were
163 prepared as detailed in ASTM D974 [10]. Using a 10ml glass syringe, biodiesel samples were
164 withdrawn from the sample containers, placed in 250ml conical flasks, and accurately weighed with
165 analytical balance prior to analysis. Samples were then dissolved in 10 ml of the titration solvent (500
166 ml of toluene, 495 ml of isopropyl alcohol and 5 ml of water) [11] and then titrated with 0.02N
167 potassium hydroxide as per ASTM D664. The titration was deemed complete when a colour change
168 from orange to green (or orange to pink) that held for at least 15s was observed in the titration
169 mixture [10].

170 The acid number was calculated from Equation 9 [10];

$$\text{Acid value} \left[\frac{\text{mg KOH}}{\text{g sample}} \right] = \frac{\text{volume KOH (ml)} \times N \text{ KOH (mmol / ml)} \times 56.1 \text{ mg / mmol}}{\text{Sample weight g}}$$

172

(9)

173

174

175 2.3.11 Flash point

176 The flash points of the samples were determined in temperature range from 120-215°C by a digital
177 Pensky-Martens closed-cup apparatus. The cup was filled with the sample fuel, inserted into the
178 apparatus and closed in accordance with ASTM standard D93 [12]. This analysis was performed on
179 Multiple Flash Point Tester Pensky-Martens STANHOPE-SETA 34100-2 in the Department of
180 Chemical Engineering, Ahmadu Bello University, Zaria.

181

182 2.3.12 Energy Content

183 The energy content of the samples were determined in a bomb calorimeter in accordance to ASTM
184 51900 standard (Moser, 2009). The bomb calorimeter was inserted into a metal tank that can be
185 assumed to be adiabatic. The tank was filled with water brought to a suitable temperature. The fuel
186 sample to be investigated was input into the bomb calorimeter, ignited by arcing, and combusted. The
187 calorific value was read from the screen. This test was performed on Parr 6100 Calorimeter in the
188 Department of Chemical Engineering, Ahmadu Bello University, Zaria.

189

190 2.3.13 Pour Point

191 The sample tube was filled to the mark with the biodiesel fuel sample, corked with thermometer. The
192 tubes were inserted into STANHOPE-SETA Cloud and Pour point tester. The samples were checked
193 from time to time until the fluid could no longer flow, this temperature was read and recorded as pour

point. This test was carried out in the Quality Control Department of Kaduna Refining and Petrochemical Company (KRPC), Kaduna.

2.3.14 Dissolved Group I&II Metals

The biodiesel samples were analyzed for dissolved group I and II metals with AAS machine in accordance with EN 14108, EN 14109 and EN 14538[12:13] in the Quality Control Unit of NARICT, Zaria.

2.3.15 Sulphur Content

The sulphur content analyses of the samples were performed on Horiba (sulphur in oil analyzer SLFA-2800) in accordance with ASTM standard D5453[12:13] in the Quality Control Department of Kaduna Refining and Petrochemical Company, Kaduna.

3.0 RESULTS AND DISCUSSION

3.1 Extent of Reaction

The quick ester tests carried out confirmed the reaction was complete as the biodiesel samples dissolved completely in methanol. There was no oil droplet in any of the mixture of methanol/biodiesel samples. It was also observed that there was no separation of the products into biodiesel and co-product, glycerol. The absence of glycerol in the products was further confirmed by GC-MS analysis presented in Table 3. Only two products out of the five had glycerol but very small in quantity; 0.412% and 0.612% in the products catalyzed by bulk CaO and super base CaO respectively.

3.2 methyl esters Yield

The methyl esters content of the products were 97.95, 96.94, 95.76, 99.99 and 98.25 % catalyzed by bulk calcium oxide, super base calcium oxide, bulk magnesium oxide, calcium oxide/magnesium oxide and 10% potassium impregnated calcium oxide/magnesium oxide respectively. Four products except that catalyzed by magnesium oxide met European standard of minimum methyl esters content of 96.5% [1]. The feedstocks of the first three products in Table I had acid value greater than 0.56. The fourth and the fifth that were catalyzed by CaO/MgO and K-CaO/MgO had their feedstocks less than 0.56 FFA. This could have responsible for their higher yields.

Table 1 Biodiesel yields from the continuous process plant

Methyl ester composition	MF	Bulk CaO	Super base CaO	MgO	CaO/MgO	K-CaO /MgO
Methyl decanoate	C ₁₁ H ₂₂ O ₂					3.222
Methyl 10-undecenoate	C ₁₂ H ₂₂ O ₂	0.552				
Methyl 11-dodecenoate	C ₁₃ H ₂₄ O ₂	0.276				
Methyl tridecanoate	C ₁₄ H ₂₈ O ₂					3.222
Methyl palmitoleate	C ₁₇ H ₃₂ O ₂			0.416		
Methyl hexadecanoate	C ₁₇ H ₃₄ O ₂	12.456	12.786	4.844	5.272	3.222
Methyl-7-hexadecanoate	C ₁₇ H ₃₄ O ₂					0.26
Methyl 14-methylpentadecanoate	C ₁₇ H ₃₄ O ₂	8.304	8.524	4.844	7.01	5.064
Methyl 15-methylhexadecanoate	C ₁₈ H ₃₆ O ₂			4.072	4.374	5.064
Methyl 8-(2-hexylcyclopropyl) octanoate	C ₁₈ H ₃₄ O ₂			0.208		0.26
Methyl -3-octadecenoate	C ₁₉ H ₃₆ O ₂				15.624	
Methyl 9-octadecenoate	C ₁₉ H ₃₆ O ₂		12.742	14.872	15.624	
Methyl-6-octadecenoate	C ₁₉ H ₃₆ O ₂	13.218	25.484	14.872		0.26
Methyl cis-octadec-11-enoate	C ₁₉ H ₃₆ O ₂					0.26
Methyl 7-octadecenoate	C ₁₉ H ₃₆ O ₂	13.218	12.742	14.872		
Methyl 8-octadecenoate	C ₁₉ H ₃₆ O ₂	26.436	12.742	14.872	15.624	
Methyl elaidate	C ₁₉ H ₃₆ O ₂	13.218		0.208	31.248	14.586
Methyl oleate	C ₁₉ H ₃₆ O ₂			14.872		
Methyl-14-octadecenoate	C ₁₉ H ₃₆ O ₂					14.326
Methyl-15-octadecenoate	C ₁₉ H ₃₆ O ₂					14.326
Methyl-16-octadecenoate	C ₁₉ H ₃₆ O ₂					14.326
Ricinoleic acid methyl ester	C ₁₉ H ₃₆ O ₃	0.552				

Methyl n-octadecanoate	$C_{19}H_{38}O_2$	7.776	9.536	4.95	5.214	1.842
Methyl-10 -octadecenoate	$C_{19}H_{36}O_2$			0.208		14.326
Methyl 16-methylheptadecanoate	$C_{19}H_{38}O_2$	1.944	2.384	1.65		
Methyl heneicosanoate	$C_{22}H_{44}O_2$					1.842
Methyl docosanoate	$C_{23}H_{46}O_2$					1.842
Total		97.952±0.02	96.94±0.02	95.76±0.02	99.99±0.01	98.25±0.02

The Table 2 provides the summary of the esters content in the five productions. The highest ester was oleate(octadecenoate) followed by palmitate(hexadecanoate) for all the five productions. As can be seen in Table 3, none of the products had linolelaidate and linoleneateestershence;they could be more stable as the stability of biodiesel depends on the quantity of these poly-unsaturated esters and the likes[14]. The products catalyzedby MgO, CaO/MgO and K-CaO/MgO had high oleate esters which make them to be less stable compared to the other two catalyzed by bulk CaO and super base CaO.

Table 2: Summary of esters content in the products

MF	Name	CaO	SB CaO	MgO	CaO/MgO	K-CaO/MgO	% Average esters
8:00	Octanoate	0	0	0.22	0	0.26	0.10
10:00	Decanoate	0	0	0	0	3.28	0.66
11:01	Undecenoate	0.56	0	0	0	0	0.11
12:01	Docenoate	0.28	0	0	0	0	0.06
13:00	Tridecanoate	0	0	0	0	3.28	0.66
16:00	Hexadecanote	21.19	21.98	14.34	16.66	13.85	17.61
16:01	Hexadecenoate	0	0	0.43	0	0	0.09
17:00	Heptadecanoate	1.98	2.46	1.72	0	0	1.23
18:00	Octadecanoate	7.94	9.84	5.16	5.21	1.87	6.00
18:01	Octadecenoate	67.47	65.72	78.13	78.13	73.67	72.63
18:01OH	Rinoleate	0.56	0	0	0	0	0.11
21:00	Ecosanoate	0	0	0	0	1.87	0.37
22:00	Docosanoate	0	0	0	0	1.87	0.37

The relative oxidative rate of the biodiesel samples can be estimated from the expression provided by Zuleta et al.[14]in Equation 10.

$$OX = [0.02(\%O) + (\%L) + 2(\%Ln)] / 100 \quad (10)$$

where, OX is oxidisability, O is oleate, L is linolelaidate and Ln is linoleneate esters present in the biodiesel samples. The relative oxidative rates (oxidisability) of the five samples are presented in Figure 2. The product catalyzed by super base CaO had the least oxidisability because it had the least oleatequantity and that catalyzed by MgO and CaO/MgO had the highest oxidisability as both had highest oleate esters. However, the absence of linolelaidate(18:02) and linoleneate(18:03) esters in the biodiesel samples makethem much more stable to oxidation.

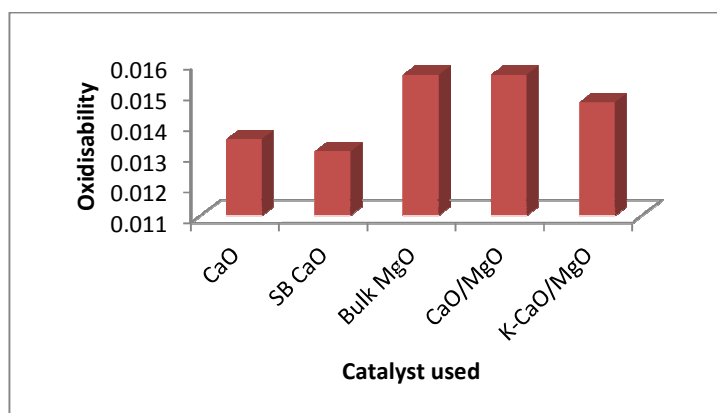


Figure 2: Relative oxidative rate of the products

Transesterification of triglycerides is more of non-reversible reaction as supported by Aspen HYSYS simulation [15] and reactions that have been carried out. By inserting only the forward reaction kinetic parameters such as activation energy and frequency factor, the simulation converged. The reactions carried out at 60°C in the stoichiometric quantity yielded 99.99% methyl esters which would have not if the reaction is actually reversible. The yield 99.99% was one of the results obtained from the constructed pilot plant that was simulated and designed in accordance to the stoichiometric ratio 3:1 (methanol: oil) [15]. A record of 94.27% methyl ester yield had been achieved with stoichiometric ratio from canola oil, methanol and potassium methoxide catalyst at 50°C [16]. This achievement also supports irreversibility of the transesterification reaction. It has also been reported by Endalew et al., [17] that one stage esterification and transesterification of *Jatropha curcas* oil with a combination of CaO and $\text{Fe}_2(\text{SO}_4)_3$ and Li-CaO and $\text{Fe}_2(\text{SO}_4)_3$ yielded 100% methyl esters each but with mole ratio of 9:1 methanol to oil. The results of our investigation were supported by Romero et al., [18], that transesterification is an equilibrium reaction but the reverse reaction does not take place or negligible because, the glycerol does not dissolve in the product. But not only that the glycerol does not dissolve in methyl esters, it was not produced at all in some reactions as shown in Figure 3 and in Table 3. This method produced biodiesel at cost effective by way of reducing the quantity of methanol, quantity of heat, number of unit operations and at shorter time and also separation protocol. This was achieved with a simulated, design and constructed processes intensify pilot plant by Ibrahim et al. [15].

It can be deduced that CaO/MgO had the highest catalytic activity among the five tested catalysts used in this study. Bulk MgO catalyst could not convert free fatty acids contained in its feedstock as solid base catalyst do not react with free fatty acids. It is the only product that does not meet the minimum ester standard. Its product had the highest quantity of fatty acids compared to others as presented in Table 3.

Despite application of low quantity of methanol it was discovered that the products still contained methanol due to repeated esterification before transesterification. This was possible because, the triglycerides that were oxidized to free fatty acid and were esterified to methyl esters after esterification were no longer available for transesterification. This confirms that high acid feedstock after esterification would require methanol less than the stoichiometric quantity provided the reaction temperature is not higher than 65°C, the boiling point of methanol.

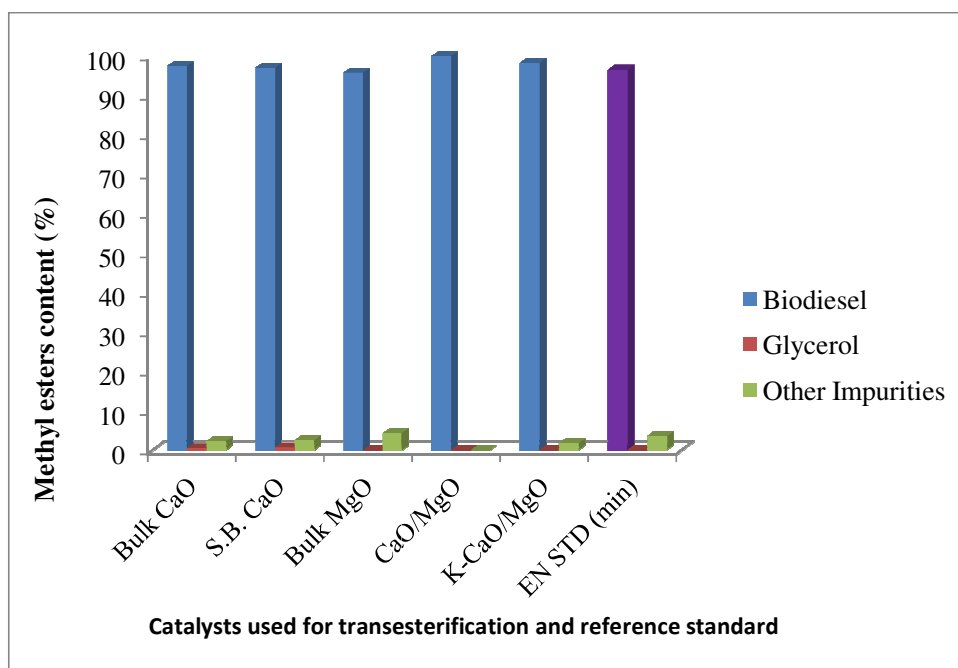


Figure 3: Samples methyl esters content compare with EN Standard

Table 3: Non-Methyl esters content in the products

Non-methyl esters		Bulk CaO	Super Base CaO	MgO	CaO/Mg O	K- CaO/MgO
	MF					
Glycerol-2-monooleate	C ₂₁ H ₄₀ O ₄	0.412	0.612			
9-Octadecenoate	C ₅₇ H ₁₀₄ O ₆	0.412	0.612			
9-Hexadecenal	C ₁₆ H ₃₀ O	0.824	0.612	1.26		0.35
9-Octadecenal	C ₁₈ H ₃₄ O		0.612	0.63		
n-Undecylenic aldehyde	C ₁₁ H ₂₀ O					0.35
Cyclododecane epoxide	C ₁₂ H ₂₂ O					0.35
13-Tetradecenal	C ₁₄ H ₂₆ O	0.412	0.612			
7-Tetradecenal	C ₁₄ H ₂₆ O					0.35
9-Octadecenoic acid	C ₁₈ H ₃₄ O ₂			0.63		
9-Hexadecenoic acid	C ₁₆ H ₃₀ O ₂			1.066		
Myristic acid	C ₁₄ H ₂₈ O ₂			0.218		
Eicosanoic acid	C ₂₀ H ₄₀ O ₂			0.218		
Linoleoyl chloride	C ₁₈ H ₃₁ ClO					0.35
n-Octadecenoic acid	C ₁₈ H ₃₄ O ₂			0.218		
Total non-methyl esters		2.056 ±0.02	3.06 ±0.02	4.24 ±0.02	0±0.01	1.75±0.02

The samples kinematic viscosities were within the range of ASTM D445 1.9-6.0 mm²/s and IS standard IS 15607:2005, 2.5-6.0 mm²/s [14] but two products catalyzed by bulk CaO and super base CaO had their viscosities higher than EN standard of 5.0[3:12] as shown in Figure4a. The two products that were catalyzed by MgO and CaO/MgO had densities slightly higher than ISO 3675 /P 32 ISO standard 0.86-0.90 g/cm³[13] as shown Figure4b.

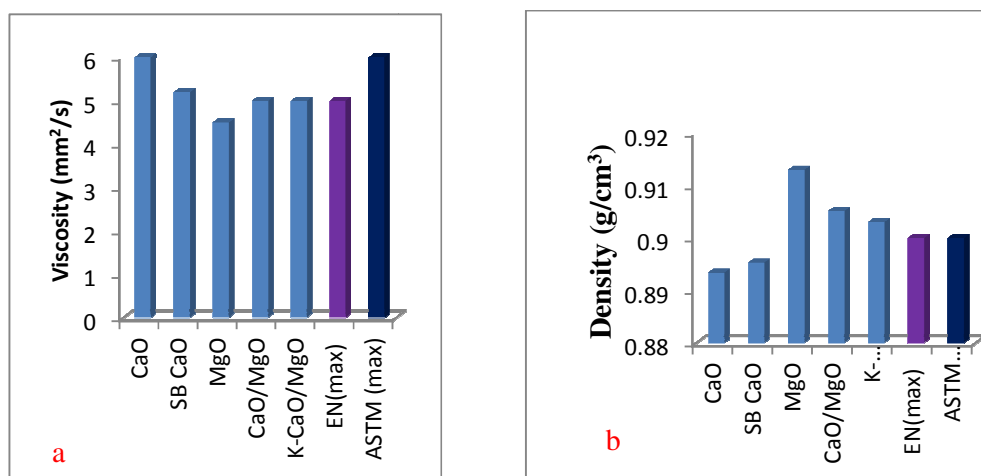


Figure 4: Comparison of samples viscosities and densities with standards

The iodine values of the samples were generally low with that catalyzed by bulk magnesium oxide the highest approximately 70 and that catalyzed by 10% potassium impregnated CaO/MgO the lowest with a value of 42. All have iodine value less than EN minimum standard of 120 [13]. Figure 5a shows the comparison of the samples iodine value with that of European (EN) standard. Iodine value is a measure of unsaturation. Low iodine values indicate low level of unsaturation of the biodiesel. This could be due to absence of linolelaidate and linoleate esters.

All the samples had high saponification values as shown in Figure 5b; though no standard value available to compare with. There was no ASTM and EN standard for biodiesel saponification value to compare with our samples' values. The saponification values were determined for the purpose of calculating cetane numbers.

There are many methods of estimating cetane value of biodiesel but the one the authors found most suitable was the Krisnagkuracorrelation equation relating saponification value and iodine value with cetane index [4]. The super base calcium oxide and 10% potassium impregnated CaO/MgO catalyzed products had approximate 55 cetane number followed by that of bulk CaO, CaO/MgO and bulk MgO the least with a value of 48. They all have cetane number higher than ASTM standard of 47 for biodiesel [15] as shown Figure 6a. Compared to EN standard; those catalyzed by bulk MgO and CaO/MgO were below. The EN standard for biodiesel cetane values is 51 [2:13].

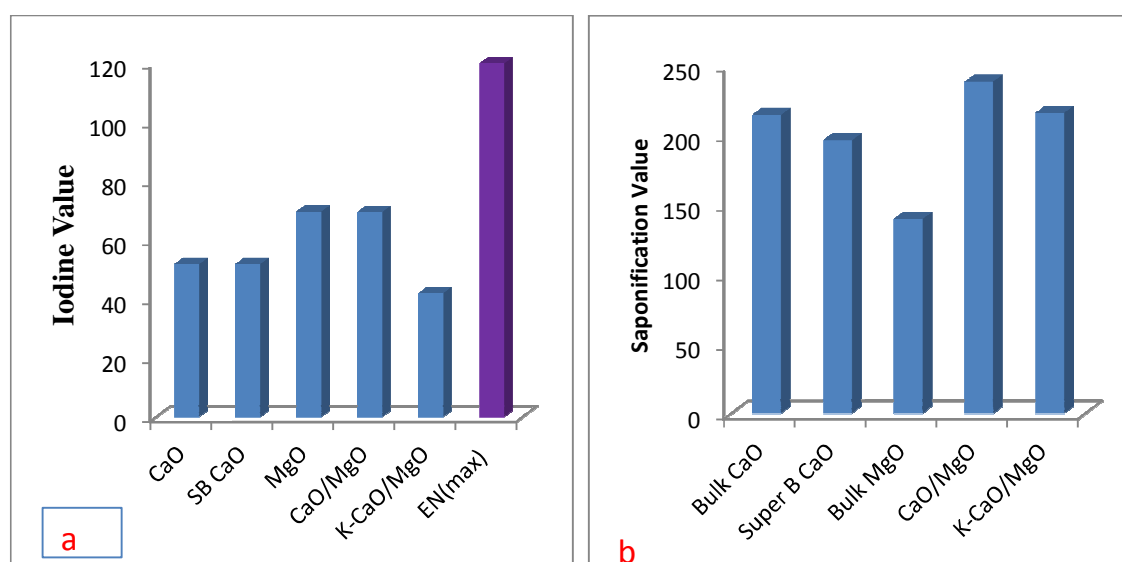


Figure5: Comparison of samples Iodine value with EN standard and saponification value

The first three products have acid value greater than EN standard EN 14104 of 0.5 mg KOH/g but less than the ASTM D664 maximum standard of 0.8 mg KOH/g [12:13]. Hence, the entire products met ASTM standard for biodiesel for use in compression ignition engines as presented in Figure6b. The acid value of biodiesel depends on the source feedstock. *Jatropha curcas* oil is highly acidic compared to the edible oils used in Europe (rapeseed oil) and U.S. (soybean oil) for biodiesel production.

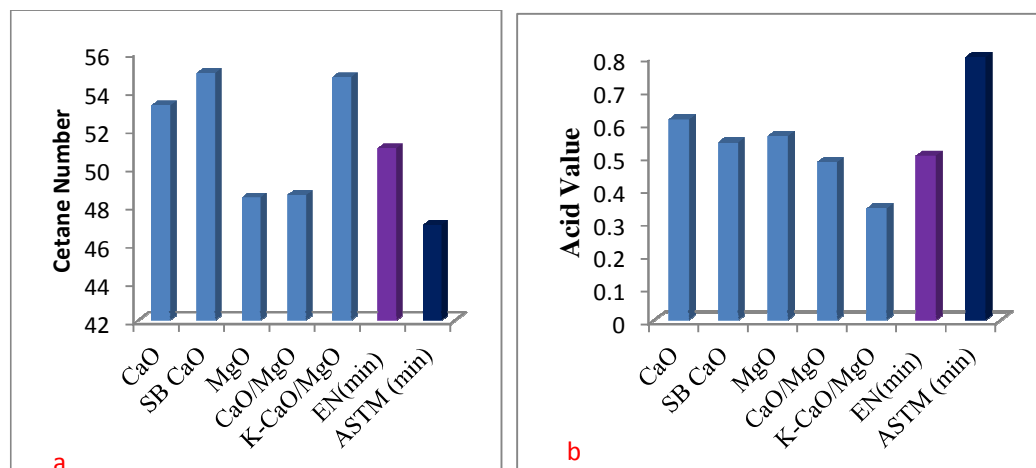


Figure 6: Comparison of samples cetane numbers and acid values with standards

The flash points of the samples produced were above the minimum ASTM standard D93 which is 120°C for biodiesel [12:13] as shown in Figure7a. Hence, the products are safe for transportation, piping and storage. The minimum energy content for biodiesel as reported by Flach et al., [19] is 37.50 MJ/kg; hence all these products had energy content above minimum standard for biodiesel as shown in Figure7b.

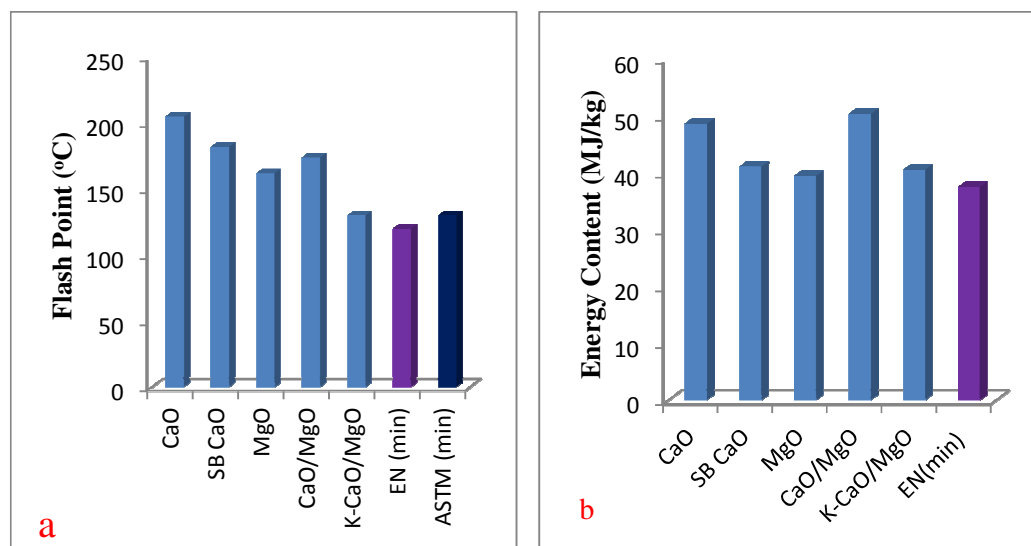


Figure 7: Comparison of samples flash points and energy contents with EN standards

The sulphur contents were low in negative values indicating their values were negligible. Figure8a shows the sulphur content of the biodiesel samples in comparison with EN and ASTM standards. This low sulphur makes biodiesel more suitable for use than fossil diesel. Use of biodiesel in transport vehicles and other power generating sources saves the environment from sulphur oxides emission.

The pour points of the sample were low, though there was no standard value either from ASTM or EN to compare with. Figure8b shows the pour point of the biodiesel samples.

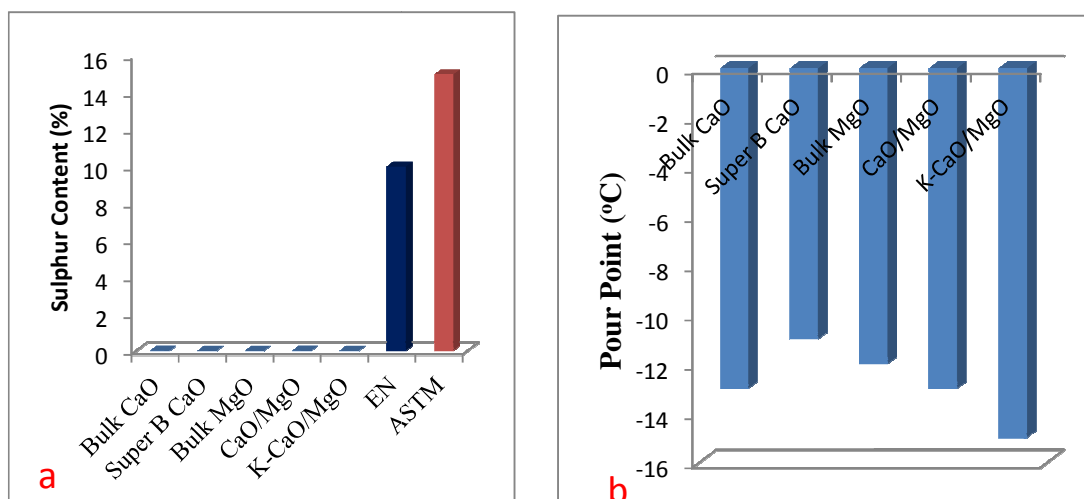


Figure 8: Comparison of sulphur content of samples with standards and pour points

The samples had very low dissolved metals. Their dissolved group I&II metals were lower than maximum EN standard of 5 mg/kg[13] as shown in Figure9.

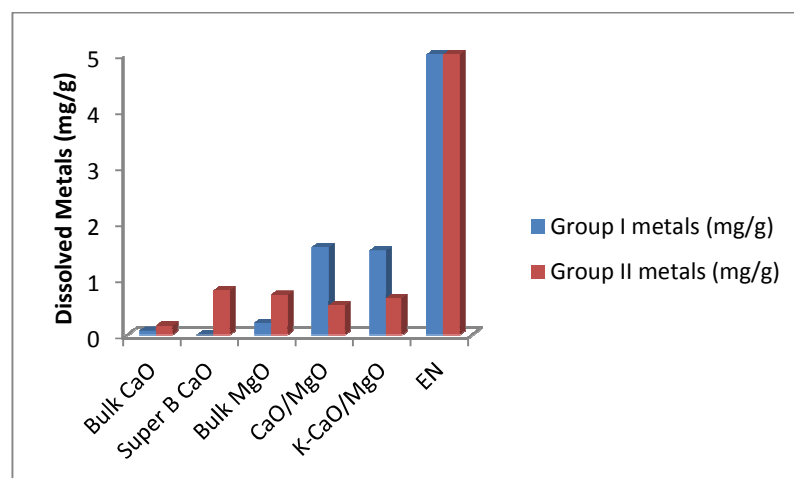


Figure 9: Dissolved group I & II metals in biodiesel samples in comparison with standard values

These results indicate that transesterification is more of an irreversible reaction. The reaction is supported by only forward reaction kinetics. Many researchers used higher mole ratio of methanol to oil (6:1 and above) in order to achieve complete reaction but it is established by the results in this investigation that, it is not cost effective using mole ratio higher than 3:1 methanol to oil provided the reaction temperature is not higher than 65°C. If production of biodiesel using higher mole ratio is a condition for reversible reaction hence, transesterification is not a reversible reaction since it can be carried out at stoichiometric quantity. The reaction is first order [19:20]with respect to triglyceride but not reversible as claimed by Moser, [12] and Urréjola et al.,[20].

4. Conclusion

Biodiesel samples were produced in a **process intensify pilot plant** from *Jatropha curcas* seed oil and methanol in the ratio of 3:1 (methanol to oil) using solid base catalysts. With this quantity of methanol, excess methanol was still found in the products, because much of the oxidized triglycerides

after esterifications were no longer available for transesterification again. With this method no glycerol was produced along with biodiesel. The samples were characterized in accordance with ASTM standard methods and were found satisfactory for use in compression ignition engines. The products had no linolelaidate and linoleate esters hence; they could be very stable in terms of oxidation. The method adopted is cost effective and therefore can bring down the cost of biodiesel production which is the great problem facing the contemporary biodiesel producers. The five solid base catalysts used in this study exhibited good catalytic activity for biodiesel production. The reactions did not support the reversible conditions claimed by some researchers. High quality biodiesel were produced with continuous stirred tank reactor in stoichiometric quantity (3:1) without glycerol.

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