

Application of Synthesized CaO/MgO Catalyst on Transesterification of *Jatropha Curcas* Seed Oil

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ABSTRACT— *In looking for solution to the problems associated with the use of homogeneous catalysts, locally produced hydrated lime was mixed 50:50 with magnesium oxide to incipient, dried and calcined at 760°C for 30 minutes. Five runs of transesterification reactions were carried out using this synthesized catalyst (CaO/MgO) with jatropha curcas seed oil and methanol at 60°C for five different times; 50, 60, 70, 80 and 90 minutes. The yields of 98.4, 99.0, 98.3, 98.1 and 100.0% respectively were achieved with catalyst loading of 1.5%w/w of oil and 5.5:1 methanol to oil ratio. The catalyst was separated out by filtration. With short reaction time and low temperature, clean biodiesel can be produced with relatively little equipment.*

Keywords— clean product, high yield, low temperature, short reaction time

1. INTRODUCTION

Conventional technology to produce biodiesel employs a homogeneous catalyst such as sodium or potassium hydroxide but the downstream separation requires a lot of processes which raises the cost of production. Homogenous catalytic biodiesel production uses a lot of equipment and processes that make the end products (biodiesel and Glycerol) very expensive. The problems of homogenous catalysts include their hygroscopic nature, high pH and harmful to environment [3]. A lot of water is required for process purification and the waste water require special treatment before discharging into water ways. A lot of heterogeneous catalysts have been employed to alleviate these issues. These are in the form of metal oxides such as alkali earth metal oxides, transition metal oxides, mixed metal oxides and supported metal oxides [8]. The catalysts have the general advantage of easy separation from the reaction medium and reusability. Heterogeneous catalysis is thus considered to be a green process. The process requires neither catalyst neutralization nor aqueous treatment steps: the purification steps of products are then much more simplified and very high yields of methyl esters, close to the theoretical value, are obtained [2].

Experimental results revealed that a 12:1 molar ratio of methanol to oil, addition of 1.5% (w/v) CaO catalyst, 70°C reaction temperature, 2% water content in the jatropha curcas oil produced more than 95% biodiesel yield after 3 hours reaction time [5]. The Glycerin produced is of high purity levels (at least 98 %) and is exempt from any salt contaminants [1, 6]. Some of the heterogeneous catalysts are however, expensive and require series of processes for their production.

This research took interest in picking materials that reduce multiple processes; cost and yet produce high yield and quality biodiesel. Calcium oxide was obtained locally from the pilot plant of National Research Institute for Chemical Technology, Zaria combined with magnesium oxide purchased by the Institute to synthesize relatively cheap catalyst for producing biodiesel.

2. MATERIALS AND METHOD

Hydrated lime was collected from Pilot Plant Division of National Research Institute for Chemical Technology, Zaria and magnesium oxide was collected from the chemical store of the Institute. 10.00 g of each hydrated lime and magnesium oxides were measured and mixed in a beaker. Some quantity of distilled water was added to incipient wetness. After thorough mixing the mixture was dried in an oven for 24 hours. The dried sample was fired in a Gallen Kamp muffle furnace at 760^oC for 30 minutes [9]. The calcined catalyst weighed 14.0 g.

2.1 Pretreatment of Oil for Transesterification

1.0 g of *Jatropha curcas* oil was added to 25.0 g of propan-2-ol. This mixture was titrated against 0.1 M potassium hydroxide. A blank titration was performed by titrating 25.0 g of propan-2-ol against 0.1 M potassium hydroxide. The acid value of the oil was evaluated as;

$$FFA = \frac{(v-b) \times 0.1 \times 56.1}{1.0g}$$

Where, v is the oil/propan-2-ol titre value, b it blank titre value.

The FFA of the oil was found to 34.78 and its %FFA was 17.39. It was esterified by heating 200.0 g of the oil with 2.25 x %FFA and 0.05 x %FFA [4] on a hot plate at 60^oC for 60 minutes. The FFA of the esterified oil was determined and was found to be 0.1869; hence its %FFA was 0.093. This value is acceptable for transesterification with base solid catalyst.

2.2 Transesterification

100 g of the esterified oil was transesterified with 20 g (20% m/m of oil) of methanol, 1.5 g (1.5% m/m of oil) of CaO/MgO catalyst for 50 minutes at 60^oC. Four more transesterifications were carried out for 60, 70, 80 and 90 minutes.

2.3 Biodiesel Analysis

The product was first filtered to obtain the catalyst. The filtrate was separated into biodiesel and glycerol with separating funnel. A crude test was performed to ascertain the reaction completion by dissolving 10 ml of the biodiesel in 40 ml of methanol. The result was satisfactory. After shaking, there was a complete dissolution confirming the complete transesterification.

2.3.1 Density Determination

The density of the biodiesel samples collected was determined with relative density bottle. Table 1 below shows the densities of the samples for different products.

3. RESULTS AND DISCUSSION

Table 1: The products yields and densities

Reaction Time (minutes)	Yield (%)	Density (g/cm ³)	EN Standard (g/cm ³)
50	98.416	0.907	0.86-0.90
60	98.995	0.898	
70	98.312	0.928	
80	98.134	0.911	
90	100.000	0.897	

The densities were estimated with relative density bottle, out of the five samples two of them that were produced at 60 and 90 minutes reaction time fall within the accepted standard of ASTM and EN; 0.86-0.90 g/cm³ [7, 11]. Fortunately, the two samples have the highest yield; 98.995% and 100.00% as shown in Table 1 and 2. As shown in table 2, the products at 60 and 90 minutes do not have ethyl esters as do others produced at 50, 70 and 80 minutes. Probably, the

presences of ethyl esters in them contribute to their high densities. The products at 60 and 90 minutes have higher lighter methyl esters. Their methyl esters fall within C12 to C19 while others have including C20 to C26 in addition to ethyl esters of C18 to C20.

All the productions contained methyl 10-undecenoate except that of 90 minutes. The following methyl esters are found in all productions methyl palmitolate 0.72% average, methyl hexadecanoate 12.4% average, methyl-14-methylpentadecanoate 8.3% average, methyl 9-octadecanoate 8.83% average, methyl-16-methylpentadecanoate 2.21% average and methyl oleate 17.84% average. The following methyl esters are found only in 90 minutes production; methyl laurate, methyl tridecanoate and methyl myristate. The 50 minutes production had 12%, 70 minutes production had 13.88% and 80 minutes production had 0.9% ethyl esters respectively. The methyl esters of 90 minutes production fall within C13 to C19.

Earlier works show longer production time and higher reaction temperature; three hours and 100°C [10] but less yield when compared to the results shown here where we had 99% yield for just 60 minutes and 100% for 90 minutes reaction times.

Table 2: Biodiesel compositions in the products

Methyl ester composition	Molecular Formula	Time (minutes)/ yield (%)				
		50	60	70	80	90
Methyl 10-undecenoate	C ₁₂ H ₂₂ O ₂	0.228	0.300	0.422	0.403	
Methyl laurate	C ₁₃ H ₂₆ O ₂					1.296
Methyl tridecanoate	C ₁₄ H ₂₈ O ₂					0.324
Methyl myristate	C ₁₅ H ₃₀ O ₂					0.864
Methyl palmitoleate	C ₁₇ H ₃₂ O ₂	0.588	0.682	0.880	0.884	0.548
Methyl-11-hexadecenoate	C ₁₇ H ₃₂ O ₂	0.294		0.440		0.548
Methyl hexadecanoate	C ₁₇ H ₃₄ O ₂	12.003	12.480	12.822	12.960	11.904
Methyl 14-methylpentadecanoate	C ₁₇ H ₃₄ O ₂	8.002	8.320	8.548	8.640	7.936
Methyl -7-hexadecenoate	C ₁₇ H ₃₂ O ₂	0.228	0.341	0.440	0.403	
Methyl 15-methylhexadecanoate	C ₁₈ H ₃₆ O ₂				0.132	
Methyl heptadecanoate	C ₁₈ H ₃₆ O ₂				0.264	
Methyl 8-(2-hexylcyclopropyl) octanoate	C ₁₈ H ₃₄ O ₂		0.300		0.442	
Methyl 9-octadecenoate	C ₁₉ H ₃₆ O ₂	14.97	13.040	12.050	11.778	12.948
Methyl 7-octadecenoate	C ₁₉ H ₃₆ O ₂		13.040		12.220	12.948
Methyl trans-8-octadecenoate	C ₁₉ H ₃₆ O ₂				11.778	
Methyl 8-octadecenoate	C ₁₉ H ₃₆ O ₂		13.040			12.948
Methyl trans-9-octadecenoate	C ₁₉ H ₃₆ O ₂			12.050		
Methyl cis-9-octadecenoate	C ₁₉ H ₃₆ O ₂		26.080			
Methyl cis-octadec-11-enoate	C ₁₉ H ₃₆ O ₂			12.050		
Methyl-12-octadecenoate	C ₁₉ H ₃₆ O ₂	12.97		12.050		
Methyl n-octadecanoate	C ₁₉ H ₃₈ O ₂	8.312	8.552	9.192	9.048	9.072
Methyl 16-methylheptadecanoate	C ₁₉ H ₃₈ O ₂	2.078	2.138	2.298	2.262	2.268
Methyl oleate	C ₁₉ H ₃₆ O ₂	26.238	0.341	12.490	23.998	26.180
Methyl dihydrostercolate	C ₂₀ H ₃₈ O ₂		0.341			
Methyl-10-nonadecenoate	C ₂₀ H ₃₈ O ₂	0.298				
Methyl eicosanoate	C ₂₁ H ₄₂ O ₂				0.264	
Methyl tricosanoate	C ₂₄ H ₄₈ O ₂				0.112	
Methyl pentacosanoate	C ₂₆ H ₅₂ O ₂				0.112	
ethyl-9-hexadecenoate	C ₁₈ H ₃₄ O ₂	0.240		0.296	0.300	
Ethyl-9-octadecenoate	C ₂₀ H ₃₈ O ₂	0.480		0.596		
Ethyl Oleate	C ₂₀ H ₃₈ O ₂	0.480		0.596	0.600	
Total		98.416	98.995	98.312	98.134	100.00

4. CONCLUSION

One can control the reaction conditions in order to produce the standard biodiesel using this catalyst (CaO/MgO) by keeping other input conditions and maintain the reaction time at 60 minutes to produce 99% biodiesel or 90 minutes to produce 100% biodiesel. CaO/MgO catalyst is a good catalyst for biodiesel production. It is safe to handle, cleaner and

cheaper than NaOH and KOH. Little quantity of methanol is required (5.5:1 methanol to oil ratio) as against 12:1 or even higher ratios as reported by many literatures. The use of CaO/MgO catalyst will reduce the cost of biodiesel in the market because, the catalyst can be easily separated and reused, does not require water washings and drying of the product as in the case of homogenous process. A lot of energy is saved using CaO/MgO catalyst as compared to homogenous ones.

5. ACKNOWLEDGEMENT

This work was supported by National Research Institute for Chemical Technology, (NARICT) Zaria. All the equipment and chemicals used in this work belonged to NARICT.

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