

## OPTIMIZATION OF BIODIESEL PRODUCTION FROM COTTON SEED OIL USING KOH AND NaOH AS CATALYSTS

**S. N. Mirie<sup>1</sup>, G. T. Thiongo<sup>2</sup>, P. N. Kioni<sup>3</sup>, P. N. Kariuki<sup>3</sup> and W. S. Namaru<sup>4</sup>**

<sup>1,2</sup>Department of Chemistry, Jomo Kenyatta University of Agriculture and Technology, Nairobi, Kenya

<sup>3</sup>Kimathi University College of Technology, Nyeri, Kenya

<sup>4</sup>Kenya Bureau of Standards, Nairobi, Kenya

### **Abstract**

Biodiesel is commonly produced by the transesterification of plant oil or animal fat with short chain alcohols. This biomass fuel has received much attention, since it is a kind of alternative, biodegradable, nontoxic, and renewable energy source. It can be used as an alternative fuel in diesel engines with little or no modification in blended or neat form depending on the source of biodiesel. In this study transesterification reactions using cotton seed oil and methanol were performed using NaOH and KOH as catalysts so as to compare the two catalysts and also obtain the optimum reaction parameters which include temperature, and amount of alcohol. The reactions were optimized by varying the amount of methanol and the temperature. The optimum conditions when using KOH as a catalyst were obtained when using 150 % excess methanol at room temperature. Biodiesel of viscosity 4.27 mm<sup>2</sup>/s, acid value 0.26 mgKOH/g and a yield of 83.94 % was obtained. The optimum conditions when using NaOH as a catalyst were obtained when using 150% excess methanol and at temperature of 60°C. The Biodiesel had a viscosity of 4.14 mm<sup>2</sup>/s, acid value of 0.26 mgKOH/g and a yield of 68.60%. The best catalyst was found to be KOH as it gave higher yields under optimum conditions compared to NaOH. At optimum conditions for both catalysts, the fuel parameters measured were within range according to the American Society for Testing and Materials (ASTM) and International Standards Organization (ISO) test methods.

**Key words:** Biodiesel, transesterification, cottonseed oil, catalyst

## 1.0 Introduction

The predicted shortage of fossil fuel coupled with the increase in fuel prices has encouraged the research for other substitutes such as biodiesel. Biodiesel can be defined as the alkyl ester of fatty acids, made by the transesterification of oils or fats, from plants or animals, with short chain alcohols such as methanol and ethanol (Pinto *et al.*, 2005). Biodiesel has advantages over conventional diesel in that it is safe, renewable, non toxic and biodegradable. It contains less sulphur compounds and a higher flash point ( $>130^{\circ}\text{C}$ ). It has reduced  $\text{CO}_2$  emissions and emits 80% fewer hydrocarbons and 50% less particles (Kiss *et al.*). Biodiesel besides lowering the dependence on crude oil foreign exports, it has a positive social impact by enhancing rural revitalization as farmers can grow vegetable oil crops and earn an income. The source for biodiesel production is chosen according to the availability in each region or country. With increasing prices of virgin, edible oils for fuel production there is a growing interest in alternative feedstocks including high-yielding non-edible tropical crops such as *Jatropha curcas*. On a longer term, oil from marine microalgae has been proposed. Algae have oil productivities (L/ha/year) that far exceed that of any land-based crops, which is needed for biofuels to fully meet global demand for transport fuels. Oils from different sources have different fatty acid compositions. The fatty acids are different in relation to the chain length, degree of unsaturation or presence of other chemical functions (Pinto *et al.*, 2005). Catalysts that are used in the biodiesel making process may either be base, acid, or enzyme materials. Sodium hydroxide, potassium hydroxide and sodium methoxide are the most commonly used catalysts. Base catalyzed reactions are relatively fast, with residence times from about 5 minutes to about 1 hour, depending on temperature, concentration, mixing and alcohol: triglyceride ratio (Van Gerpen *et al.*, (2004). Acid catalysts include sulfuric and phosphoric acids. Compared to base catalysts, acid catalysts reactions have been found to be too slow for industrial processing. Acid catalysts are however used to reduce the free fatty acids (FFA 'S) in crude vegetable oils having a high value and then the base catalyst is added in the second stage to convert the remaining triglycerides into biodiesel. In a study by Vincente *et al.*, (2004) transesterification of sunflower oil with methanol gave higher yields when using KOH as compared to when NaOH was used as catalyst. However their methoxide counterparts gave even higher yields because the yield losses due to triglyceride saponification and methyl ester dissolution in glycerol were negligible. The aim of this study was to produce biodiesel from cotton seed oil using KOH and NaOH and also make a comparison between the two catalysts. The optimum reaction parameters which include temperature, and amount of alcohol were also determined.

## 2.0 Materials and Methods

The reagents used were of analytical grade. Methanol, acetone and 2-propanol were purchased from Sigma (Seelze, Germany). The catalysts sodium hydroxide and potassium hydroxide were obtained from Rankem (New Delhi India). Toluene was obtained from Merck (Barcelona, Spain). Cotton seeds were obtained from farmers in Mwea, Kenya and their identity confirmed at the herbarium in botany department, Jomo Kenyatta University of Agriculture and Technology. A screw press (Ruian grain and oil machinery factory Zhejiang China) was used to obtain the oil from the seeds by pressing. The oil obtained from the screw press was first filtered slowly using filter bags then refiltered again using a vacuum pump to remove any scum and particles. Various crude oil properties were measured for the filtered vegetable oil. They included viscosity, acid value specific gravity and fatty acid profiling to establish the fatty acid compositions of the oils.

### 2.1 Fatty Acid Profiling

Fatty acid profiling was done to establish the fatty acid composition of the oil. For the chromatographic analysis cotton seed oil was converted to its corresponding methyl esters according to the method described by Stoffel *et al.*, 1959. A Shimadzu gas chromatograph (GC-9A) equipped with a flame ionization detector and fitted with a glass column (3mm x 1mm) packed with DEGS (Diethylene glycol succinate) was used for the analysis. The injection and detector temperatures were set at  $220^{\circ}\text{C}$  while the column temperature was set at  $170^{\circ}\text{C}$ . The fatty acid methyl esters were identified with the help of standards purchased from Supelco (U.S.A).

### 2.2 Determination of Acid Value

The acid value for the vegetable oil was determined by the method described by Van Gerpen *et al.*, 2004. Two 250ml beakers were prepared by adding 62.5ml of solvent. The solvent consisted of 50% isopropyl alcohol and 50% toluene. 2.5g of the crude vegetable oil was added to one of the beakers (sample beaker) and the other beaker left without a sample (blank beaker). Both beakers were titrated with 0.1N KOH to the first permanent pink color using 2ml of phenolphthalein as an indicator in each. The procedure was done in triplicate and the average obtained. The acid value was calculated using the equation,

$A.V = (A-B) \times N \times 56.1 / W$  where,

A= Number of ml of KOH needed to neutralize sample beaker, B=Number of ml of KOH needed to neutralize blank beaker, N=Normality of KOH solution, W =Weight in gram of sample used and % F.F.A =1/2 Acid value.

### 2.3 Determination of Viscosity

The kinematic viscosity was measured using a capillary viscometer (viscometer no. 38, Kusano Scientific Instrument) immersed in a water bath maintained at 40°C and 10ml of the sample placed in the viscometer. The flow of the sample between two marked points on the viscometer under gravity was recorded. Three readings were taken and the average obtained. The timings of 10ml of water were also recorded. The viscosity was measured according to the equation;

$$\text{Viscosity (Centipoises)} = \frac{\text{Time taken for vegetable oil to flow (seconds)}}{\text{Time taken for water to flow (seconds)}} \times 0.65$$

Where 0.65 =Dynamic viscosity of water at 40°C and

Viscosity in centistokes = Viscosity in centipoises at 40°C / Specific gravity at 40°C

### 2.4 Determination of Specific Gravity

The specific gravity of the oil was measured using a pycnometer. A clean and dry pycnometer of 25ml capacity was weighed ( $W_0$ ) with the help of an analytical balance and then filled with the sample. The stoppers were then inserted and the pycnometer reweighed to give ( $W_1$ ). The sample was substituted with water after washing and drying the bottle and reweighed to give ( $W_2$ ). The expression for specific gravity (Sp.gr) is:

$\text{Sp.gr} = (W_1 - W_0) / (W_2 - W_0) = \text{Mass of the substance} / \text{Mass of an equal volume of water.}$

To get the specific gravity at 40°C the pycnometer was placed in a water bath to attain the required temperature

### 2.5 Transesterification Reactions with KOH and NaOH

Transesterification reactions of cotton seed oil with KOH and NaOH were done with the help of a hot plate magnetic stirrer (Autoscience AM-5250B, Tianjin Instrument Co. Ltd.) capable of maintaining the required temperature. The reactions were done by varying the amount of methanol and reaction temperature while keeping the catalyst amount at a constant. The amounts of KOH and NaOH to use for the experiments were calculated according to Van Gerpen *et al.*, 2004. 91.35g (100ml) of cotton seed oil with a % FFA of 5.67 required 1.66g of NaOH while 1.93g of KOH was required for the reactions. The amount of methanol was varied by using between 0-150 % excess methanol of the stoichiometric amount required for a complete transesterification reaction. The reactions were first done at room temperature (25°C) and some of the reactions repeated at 40°C and 60°C with the various amounts of methanol. The catalysts (KOH and NaOH) were first dissolved in the appropriate amount of methanol and then added to the vegetable oil contained in a separate conical flask having a magnetic rod placed inside. The flask was then placed in the hot plate and the mixture was stirred at a rate of 700rpm for 2hrs. For the reactions at room temperature the flask was stoppered while for the reactions at 40°C and 60°C the flask was fitted with a condenser then, stirred and refluxed continuously for 2hrs. The mixture was then left overnight to settle in a separating funnel. After settling, the mixture separated into two phases, the lower part being glycerin and the upper part the ester layer. The glycerin was then allowed to come out by opening the tap on the separating funnel in order to remain with the ester layer. A vacuum rotary evaporator set at 65°C was then used to remove any excess methanol left. The ester layer was washed by placing it in a separating funnel and spraying warm water (40°C) representing a quarter amount of the biodiesel being washed using a spraying can and removing the water at the bottom of the funnel. This was done until the wash water did not turn pink on addition of phenolphthalein indicator, indicating that the catalyst was washed out. The ester layer was dried after washing by heating the layer at 60°C in a beaker until the layer changed from being cloudy to clear indicating that the water had been evaporated. For the reactions at 40°C and 60°C the magnetic stirrer was set at those temperatures and the same process repeated. The % yield from the reactions was obtained by dividing the weight of biodiesel obtained with the initial weight of the vegetable oil started with. Other parameters measured after obtaining the biodiesel are viscosity, specific gravity and acid value. All the reactions were done in triplicate and average values recorded.

## 2.5 Other Fuel Properties Measurement

The determination of other fuel properties was done at Kenya Bureau of Standards (KEBS), Nairobi using ISO, and ASTM test methods.

## 3.0 Results

### 3.1 Crude Vegetable Oil Properties

The fatty acid composition for cotton seed oil is shown in Table 1 and is compared with literature values (Pinto *et al.*, 2005), while Figure 1 shows the fatty acid methyl ester profile of cotton seed oil obtained from the GC. Linoleic acid (50.3%) was found to be the major fatty acid in cotton seed oil followed by palmitic acid (26.2%). This is supported by Gunstone, (2004), who states that "cotton seed is unique among the commodity vegetable oils in that it contains a relatively high level of palmitic acid while linolenic acid is virtually absent."

Table 1: Fatty acid composition of cotton seed oil

Fatty acid	Composition (%)	Literature values (%) (Pinto <i>et al.</i> , 2005)
Myristic acid (C14:0)	0.8	-
Palmitic acid (C16:0)	26.2	28.6
Stearic acid (C18:0)	2.1	0.9
Oleic acid (C18:1)	19.7	13.0
Linoleic acid (C18:2)	50.3	57.2
Others	0.9	0.3

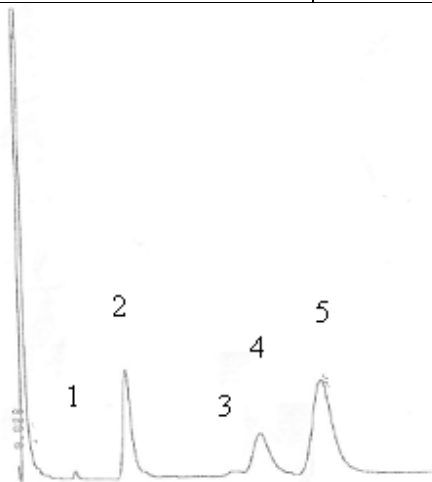


Figure 1: Fatty acid methyl ester profile of cotton seed oil

Peak assignment: 1= C14:0, 2= C16:0, 3 = C18:0, 4 = C18:1, and 5 = (C18:3) methylesters.

The acid value of the oil was found to be 11.3 and % FFA 5.6 (Acid value/2). The viscosity of the oil was found to be 32.57 centistokes and had a specific gravity of 0.9210.

### 3.2 Reactions with KOH

Experiments with cotton seed oil and KOH were first performed at room temperature and the reactions at 100% and 150% excess methanol were then repeated at 40<sup>o</sup> C and 60<sup>o</sup> C as there were the most promising considering the yield and viscosity. Table 2 shows the reactions at room temperature, table 3 reactions at 40<sup>o</sup> C while table 4 shows reactions at 60<sup>o</sup> C.

Table 2: Reactions with KOH at room temperature

Property	ASTM D 6751 – 02 Requirements	0% excess methanol	25% excess methanol	50 % excess methanol	75 % excess methanol	100% excess methanol	150% excess methanol
% Yield	-	78.03 ± 0.72	81.54 ± 1.50	83.75± 1.05	83.82 ± 0.81	83.92 ± 0.33	83.94 ± 1.34
Specific gravity (40°C)	0.88 (25°C)	0.8879± 0.0020	0.8776± 0.0032	0.8803± 0.0024	0.8788± 0.0002	0.8755± 0.0024	0.8760± 0.0017
Viscosity (mm <sup>2</sup> /s) (40°C)	1-6	7.16 ± 0.15	5.80 ± 0.08	5.07 ± 0.10	4.83 ± 0.13	4.35 ± 0.06	4.27± 0.09
Acid value (mg KOH/g)	Max 0.8	0.36± 0.04	0.26± 0.07	0.26 ± 0.07	0.26 ± 0.07	0.26 ± 0.07	0.26 ± 0.03

Table 3: Reactions with KOH at 40 °C

Property	ASTM D 6751 – 02 Requirements	100% excess methanol	150% excess methanol
% Yield	-	83.27 ± 0.4	83.70 ± 0.39
Specific gravity (40°C)	0.88 (25°C)	0.8771 ± 0.0004	0.8790 ± 0.0009
Viscosity (mm <sup>2</sup> /s) (40°C)	1-6	4.63 ± 0.06	4.39 ± 0.01
Acid value (mg KOH/g)	Max 0.8	0.26 ± 0.05	0.26 ± 0.03

Table 4: Reactions with KOH at 60 °C

Property	ASTM D 6751 – 02 Requirements	100% excess methanol	150% excess methanol
% Yield	-	83.03±0.55	83.12 ± 0.91
Specific gravity (40°C)	0.88 (25°C)	0.8753±0.0024	0.8753±0.0022
Viscosity (mm <sup>2</sup> /s) (40°C)	1-6	4.18 ± 0.09	4.08 ± 0.01
Acid value (mg KOH/g)	Max 0.8	0.26±0.03	0.26 ± 0.04

### 3.2.1 Discussion

The highest yield obtained from the reactions of cotton seed oil and KOH as a catalyst was 83.94% and it was obtained when using 150% excess methanol and room temperature (Table 2). The lowest yield was 78.03% and it was obtained when using 0% excess methanol (Table 2). The yield (78.0355%) however is misleading as the biodiesel has a high viscosity (7.1561mm<sup>2</sup>/s) which was out of the required range according to ASTM standards, indicating that the mixture probably contains some amount of triglycerides, monoglycerides and triglycerides in addition to methyl esters. 100% yields were not obtained in the experiments and this can be attributed to the free

fatty acids in the initial vegetable oil which were 5.67% of the total weight of the vegetable oil. The maximum yield possible from the experiments is 94.33% for 100% yield for the reaction as 5.67% are free fatty acids. The reactions using more than 0% excess methanol gave biodiesel with viscosities within range according to ASTM standards. The repeated reactions at 40<sup>o</sup> C and 60<sup>o</sup> C did not show any significant increase in the biodiesel obtained and they recorded a slight decrease in the yields. The acid values for all the experiments were within range according to ASTM standards.

### 3.3 Reactions with NaOH

Experiments with cotton seed oil and NaOH were first performed at room temperature and then the reactions at 100% and 150% excess methanol repeated at 40<sup>o</sup> C and 60<sup>o</sup> C as there were the most promising considering the yield and viscosity. Table 5 shows the reactions at room temperature, table 6 reactions at 40<sup>o</sup> C while table 7 shows reactions at 60<sup>o</sup> C.

Table 5: Reactions with NaOH at room temperature

Property	ASTM D 6751 – 02 Requirements	75% excess methanol	100% excess methanol	150% excess methanol
% Yield	-	43.65 ± 0.27	49.18 ± 0.91	60.56 ± 0.77
Specific gravity (40 <sup>o</sup> C)	0.88 (25 <sup>o</sup> C)	0.8795±0.0042	0.8761±0.0029	0.8760± 0.0040
Viscosity (mm <sup>2</sup> /s) (40 <sup>o</sup> C)	1-6	4.61 ± 0.06	4.16 ± 0.09	4.08± 0.19
Acid value (mg KOH/g)	Max 0.8	0.26±0.07	0.26 ± 0.03	0.26±0.07

Table 6: Reactions with NaOH at 40<sup>o</sup> C

Property	ASTM D 6751 – 02 Requirements	100% excess methanol	150% excess methanol
% Yield	-	65.31± 0.7	65.47± 0.99
Specific gravity (40 <sup>o</sup> C)	0.88 (25 <sup>o</sup> C)	0.8733± 0.0010	0.8741± 0.0018
Viscosity (mm <sup>2</sup> /s) (40 <sup>o</sup> C)	1-6	4.41±0.01	4.33± 0.09
Acid value (mg KOH/g)	Max 0.8	0.36±0.07	0.30 ± 0.07

Table 7: Reactions with NaOH at 60 °C

Property	ASTM D 6751 – 02 Requirements	100% excess methanol	150% excess methanol
% Yield	-	68.32 ± 1.01	68.60 ± 1.67
Specific gravity (40°C)	0.88 (25°C)	0.8739± 0.0017	0.8748± 0.0010
Viscosity (mm <sup>2</sup> /s) (40°C)	1-6	4.14 ± 0.03	4.14± 0.06
Acid value (mg KOH/g)	Max 0.8	0.26 ± 0.26	0.26 ± 0.03

### 3.3.1 Discussion

The highest yield obtained with transesterification of cotton seed oil with NaOH as catalyst was 68.60 % and was obtained when using 150% excess methanol and a temperature of 60 °C (Table 7). An increase in temperature of the reaction resulted to some significant increase in the biodiesel yield. The viscosity and acid values for the experiments were within range according to ASTM standards. Generally the yields when using NaOH as catalyst were lower than when KOH was used as catalyst.

### 3.4 Results for other Fuel Properties Measurements

More biodiesel properties were measured for the best catalyst and the best condition, namely, the biodiesel from transesterification of cotton seed oil with KOH, 150% excess methanol and room temperature. The results are shown in Table 8.

Table 8: Other fuel properties measurement

Property	Method	Apparatus	limits	CSEK
Density @ 20°C (kg/m <sup>3</sup> )	ISO 12937	S.G density meter (DMA 4500)	860-900	881
Kinematic viscosity at 40°C (mm <sup>2</sup> /s)	ISO 3104	Automatic viscometer (HMV 472 HERZOG)	3.5-5.0	4.32
Astm colour	ASTMD 1500	Tintometer (Lovibond PFX880)	Max 3.5	3.3
Copper strip corrosion (3h at 50°C rating, Max)	ISO 2160	Air oven, (Mettler)	Class 1	No tarnish
Density @15°C (kg/ m <sup>3</sup> )	ISO 12185	Density meter (DMA4500)	860-900	885
Flash point °C, min	ASTMD 93	Pensky Martens closed cup tester	130 min	>150

**CSEK**= Biodiesel from transesterification of cotton seed oil with KOH, 150% excess methanol and room temperature.

The results show that the process of transesterification greatly reduces the viscosity as the initial viscosity of the oil was 32.57 centistokes but after transesterification with KOH and 150% excess methanol at room temperature the

viscosity fell to 4.32 centistokes. This leads to improved fuel properties of the cotton seed oil. The flash point for the biodiesel is above 150°C hence it safe to use as there is no risk of explosion .The high flash point also shows that there is no residual alcohol remaining in the fuel. It can be seen from the results that the biodiesel is not corrosive to copper indicating very little effect on corrosion of the engine. All the other properties measured which include kinematic viscosity, density and Astm colour meet the given standard.

#### **4.0 Conclusion and Future Perspective**

Experiments with KOH and NaOH with cotton seed oil were successful as the biodiesel obtained at optimum conditions meet the standards .The biodiesel obtained from the above process can therefore be used successfully as fuel. Experiments with KOH generally gave higher yields than experiments with NaOH. This is well in agreement with Vincente *et al* 2004, where experiments with KOH gave higher yields than those with NaOH when using sunflower oil as the vegetable oil. Near 100% yields were not obtained and this can be attributed to saponification as the cotton seed oil had % FFA of 5.8.

#### **Acknowledgements**

This study was supported by Jomo Kenyatta University of Agriculture through the Research Production and Extension Department (RPE).Some fuel properties were measured at Kenya Bureau of Standards (KEBS). All are greatly acknowledged.



## References

- Bligh, E. G. and Dyer, W. J. A. (1959). A rapid method for total lipid extraction and purification. *An.J.Biochem and Physiol.*, **37**, pp 911-917.
- Deere, J. (1985). Fundamentals of service manual: Fuels, lubricants, and coolants. Deere and company, Illinois, USA .pp 1-25.
- Kiss, A., Dimian, A., and Rothenberg, G. (2005). Solid Acid Catalysts for Biodiesel Production Towards Sustainable Energy. *Adv. Synth. Catal.*, **348**, pp 75–81.
- Gunstone, F. D. (2004). The Chemistry of Oils and Fats: sources, composition, properties and uses. Blackwell Publishing Ltd, 9600 Garsington Road, Oxford OX4 2DQ, UK. pp1-35.
- Knothe, G. (1999). Rapid monitoring of transesterification assessing biodiesel quality by NIR spectroscopy using a fiber-optic probe. *J. Am. oil Chem .Soc.*, **76(7)**, pp 795-800.
- Lee, D. H., Kim, J. M., Shin, H. Y., Kang, S. W. and Kim, S. W. (2006). Biodiesel production using a mixture of immobilized *Rhizopus oryzae* and *Candida rugosa* lipases. *Biotechnol Bioprocess Eng.*, **11**, pp 522–525.
- Pinto, A. C., Guarieiro , L., Rezende, M. J., Ribeiro, N. M., Ednildo A.Torres, E. A., Lopes, A. W., Pereira, A. W. and Andrade J. B. (2005). Biodiesel: An Overview. *J. Braz. Chem. Soc.*, **16(6B)**, pp 1313-1330.
- Vincente,G., Martinez, M. and Aracil, J. (2004). Intergrated biodiesel production: A comparison of different homogenous catalysts systems. *Bioresource Technology*, **92**, pp 297-305.
- Stoffel, W, Chu,F. and Ahrens, E. H. (1959). Analysis of long chain fatty acids by gas-liquid chromatography :Micromethod for preparation of methyl esters. *Anal.Chem.*, **31**, pp 307-
- Van Gerpen, J., Shanks, B., Pruszko, R., Clements, D. and Knothe, G. (2004). Subcontractor Report .August 2002–January 2004.Biodiesel Production Technology. National Renewable Energy Laboratory. pp 1-52.