

CHARACTERIZATION OF BIODIESEL PRODUCED BY METHANOL-BUTANOLYSIS OF CASTOR OIL

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Abstract

Crude Castor oil was transesterified using methanol, mixtures of methanol and butanol in molar percentages and potassium hydroxide as catalyst. The optimum reaction conditions, based on the percentage yield of biodiesel, were 45 mins reaction time at 65°C and 1.5w/w% catalyst. The alcohol/oil ratio and agitation rate were both held constant at 12:1 and 450rpm respectively throughout the process. The yield of biodiesel from castor oil at such optimum reaction conditions were 87.1%, 85.7 % and 81.7 for 100%, 95% and 90% methanol-butanol molar blends respectively. . The specific gravities at 15°C were 0.898 and 0.902ml/g, kinematic viscosities at 40°C varied from 6.4 to 7.8 cSt. The calorific values were between 10690 and 10708 cal/g and the flash points were found to be within the range 144 to 150°C. The standard specifications for biodiesel (ASTM D67651) show that the specific gravity, flash point and calorific value requirements were satisfied. The higher viscosity (above 6.0 cSt.) can be controlled by the use of additives. Alternatively, blending with petroleum diesel will lead to improvement of the flow properties of the biodiesel fuel.

Keywords: Transesterification, Castor oil, methanol/butanol molar blend, Biodiesel yield.

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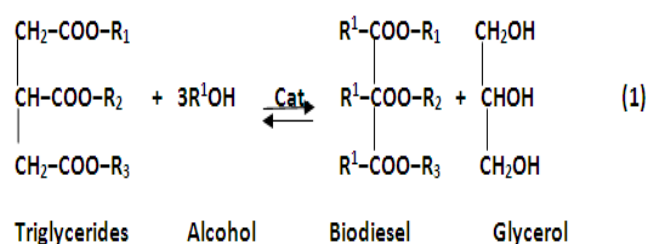
1. INTRODUCTION

Currently, fossil fuel is a major source of energy all over the world. In recent times, however, emphasis has been placed on environmental pollution created when fossil fuel is burnt. It has been reported that carbon dioxide and methane are two green house gases that are increasing in concentration in the atmosphere and are directly linked to global warming. The world is facing threats of uncertainty surrounding the current cost and the future availability of fossil fuels. It is evident that the demand for energy is likely to increase in the nearest future. Against this increasing demand, the government and the industry are searching and placing high premium on alternative sources of energy to address this current and future energy scenario. Therefore, producing alternative fuel, such as biodiesel from castor oil without environmental degradation is a research well worth considering. Biodiesel is an alternative fuel derived from the conversion of agricultural lipids and a simple alcohol into fatty acid alkyl esters and glycerol and is defined as “mono alkyl ester of fatty acid derived from vegetable oil or animal fats”[2].

Conversion of vegetable oils including castor oil into biodiesel involves application of various chemical engineering processing techniques such as: pyrolysis (thermal cracking), microemulsification, direct use and blending (dilution) and transesterification. Of these processing techniques, transesterification is the most preferred method[15,12,1].Transesterification is an ester conversion process that splits up the triglycerides, that is, takes the glycerol of the triglycerides and replaces with alkyl

radical of the alcohol used. It is the reaction of a fat or oil with an alcohol to form fatty acid alkyl esters and glycerol. Through transesterification, high viscosity oil is reduced to a value closer to that of diesel fuel while Cetane number and heating value are saved. The reaction

(equation 1) is reversible and therefore excess alcohol is used to shift the equilibrium to the product side.



The objective of this research work is to produce biodiesel from castor oil via transesterification using potassium hydroxide pellets as catalyst and investigate the properties of biodiesel produced at the optimum conditions. The alcohols that were used in this study are methanol and butanol. Methanol was preferred because it is the least expensive, lightest alcohol and reacts faster than ethanol. Butanol is preferred because of its non-hygroscopic, does not cause corrosion and has a high calorific value. The reaction was catalyzed by a base catalyst because alkaline-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially [7]. The process of transesterification brings

about drastic change in the viscosity of the vegetable oil. The high viscosity component, glycerol, is removed and hence the product has low viscosity like the fossil fuels and is totally miscible with fossil diesel in any proportion[3]. Flash point of the biodiesel is lowered after transesterification and Cetane number is improved.

The seed of Castor, *Rucinus comunis*, is found to contain high amount of oil which was used as the feedstock for the production of biodiesel because it is non-edible and would not compete with food stocks. Castor belongs to the family of Euphorbiaceae, originated from Africa and spread to the Mediterranean, Middle-East and India. It is a hardy plant and thrives well under the same conditions as *Jatropha*. Its seeds have been found to contain oil content between 35-55% by weight[9,4]. Castor is a fast growing ever green shrub and is probably the most highly promoted oil seed crop at present. It is cultivated around the world because of the commercial importance of its oil.

2. METHODOLOGY

2.1 Raw Material

The crude castor oil was purchased from Holyland Nigeria Limited (Ojota, Lagos). Certified methanol 99.8% purity, Phenolphthalein, Butanol of 99% purity, Isopropyl of 99.5% and the potassium hydroxide catalyst (analytical grade) were purchased from Labio Scientific Centre, Surulere, Lagos Nigeria. Distilled water was made available in the laboratory.

2.2 Equipment

The reactor plus mechanical stirrer placed in a water bath equipped with thermometers, Pensky-Martens Closed Cup flash point tester; viscometer tube, separating funnels, retort stands, burettes, pipettes, measuring cylinders, flat bottom flasks, beakers and conical flasks.

2.3 Procedures

Reactions were carried out in a batch reactor. The reactor was equipped with a mechanical stirrer, thermometer and placed on a water bath and the reaction temperatures were maintained as required for the reaction. Castor oil was first degummed by heating the oil to a temperature of 70°C and adding distilled water (5% of the volume of the oil). The mixture was stirred vigorously and the temperature was maintained at 70°C for about 45 minutes. The mixture was allowed to settle down until the oil layer becomes clear. Then, the castor oil was filtered. The filtered oil was heated to a temperature of 100°C to remove any trace of water that could slow down the reaction or cause unwanted reactions. This degummed and filtered oil was used throughout the transesterification process. Then, 300g of crude castor oil was preheated in a glass vessel and divided into three (100g each) in three different batch reactors. 1.0w/w% potassium hydroxide catalyst were dissolved in three separate holding vessels containing 100 % (absolute methanol), 95 % and 90% methanol-butanol molar blends respectively; thus forming potassium methoxide/ meth-butoxide (alkoxide).

The mixtures of alkoxide were added to the pre-heated castor oil in the batch reactors respectively and agitated in a water bath equipped with mechanical stirrer and a thermometer. A constant molar ratio of 12:1 and agitation rate of 450rpm were maintained throughout the reaction period. The reaction was subjected to heating at different temperatures of 50 to 70°C and reaction times of 30 to 90 minutes respectively. At the end of each reaction time, the reaction mixture was poured into separating funnel and allowed to stand for about 12hours. During these times, the solutions of the biodiesel and glycerol separated out in liquid phases; the upper layer was biodiesel and the lower layer glycerol. The phases were separated to recover the biodiesel for washing. The biodiesel was washed a number of times (until the PH of wash water was 7.0) and then dried in order to ensure compliance with fuel quality standards. The yield of biodiesel was recorded. The procedure above was repeated for catalyst concentrations of 1.5 and 2.0w/w%.

2.4 Characterization

The ASTM-08 methods were used for the determination of all the properties of biodiesel produced. The properties such as kinematic viscosity at 40°C, specific gravity at 15°C, calorific value and flash point were determined to know the technical competence of the biodiesel produced for diesel engines. All the investigations were carried out at the Petroleum Research Laboratory in the Department of Chemical Engineering, University of Lagos, Lagos, Nigeria.

2.5 Characteristics of the Biodiesel

The properties of the biodiesel produced at optimum conditions are shown in Table 1. The specific gravities at 15°C were between 0.898, and 0.902ml/g, kinematic viscosities at 40°C varied from 6.4 to 7.8 cSt. The calorific values were between 10690 and 10708 cal/g and the flash points were found to be within the range 144 to 150°C. The standard requirements for biodiesel (ASTM D67651) are shown in Table 6. Tables 2-5 show the variations of the transesterification variables with time. The biodiesels produced from castor oil have higher viscosities. The specific gravity, flash point and calorific value requirements are satisfied. Viscosity can be controlled by the use of additives. Alternatively, blending with petroleum diesel will lead to improvement of the flow properties of the biodiesel fuel.

Table 1: Properties of Biodiesel

Methanol-Butanol Molar Blend	Catalyst conc. %	Reaction Time (min)	Reaction Temp. °C	Specific Gravity at 15°C	Kinematic Viscosity at (mm ² /s)	Calorific value (Cal/g)	Flash Point °C
100	1.5	45	65	0.898	6.4	10708	144
95	1.5	45	65	0.902	7.8	10690	150
90	1.5	45	65	0.898	7.0	10706	146

Table 2: Effect of Reaction Time on Specific Gravity of the Biodiesel

Reaction Time, min	30	45	60
Methanol-Buthanol Molar Blend,%	Specific Gravity at 15°C		
100	0.897	0.898	0.900
95	0.903	0.902	0.899
90	0.902	0.898	0.900

Table 3: Effect of Reaction Time on Kinematic Viscosity of the Biodiesel

Reaction Time, min	30	45	60
Methanol-Buthanol Molar Blend,%	Kinematic Viscosity at 40°C, mm ² /s		
100	7.6	6.4	7.3
95	6.6	7.8	5.4
90	7.4	7.0	6.7

Table 4: Effect of Reaction Time on Calorific Value of the Biodiesel

Reaction Time, min	30	45	60
Methanol-Buthanol Molar Blend,%	Calorific Value, Cal/g		
100	10711	10709	10699
95	10688	10690	10705
90	10692	10706	10713

Table 5: Effect of Reaction Time on Flash Point of the Biodiesel

Reaction Time, min	30	45	60
Methanol-Buthanol Molar Blend,%	Flash Point, °C		
100	150	144	150
95	144	150	166
90	140	146	150

Table 6: The Standard Specification of Biodiesel (Folaranmi,2012 and Sreenivas,2011)

Standard	Specific Gravity at 15°C	Kinematic Viscosity at 40°C, mm ² /s	Calorific Value, Cal/g	Flash Point, °C
ASTMD67651	0.88	1.9-6.0	10600 (minimum)	130 mini.
EN14214	0.86-0.9	3.5-5.0	40MJ/Kg	120 mini.
BIS:15607	0.86-0.9	2.5-6.0	40MJ/Kg	120 mini.

3. RESULTS AND DISCUSSION

3.1 The Biodiesel Yield

Figure 1 shows the effect of time on the yield of biodiesel. It was revealed that the yield of biodiesel was the highest with 100 % (absolute methanol) and then decreased with increase in the quantity of butanol in the molar blends. This agrees with the findings of Ogbu and Ajiwe[10] that alcohol reactivity is in the order of methanol > ethanol > Isopropanol > butanol. This could also be explained from the molecular size of butanol. The higher the molecular size the less reactive the alcohol becomes. From figure 1, at reaction time of 30min, the alcohol molecules were still in bulk surface of the reaction mixture and hence the biodiesel yield was not much. However, the optimum yield of the biodiesel was obtained at reaction time of about 45 minutes for all the blends. This is because the alcohol molecules were fully energized. At reaction time of 60min, the biodiesel yield declined as most alcohol molecules had escaped from reaction mixture because methanol dominated the alcohol proportion and more also the reaction temperature was maintained at 65°C which is the boiling point of methanol.

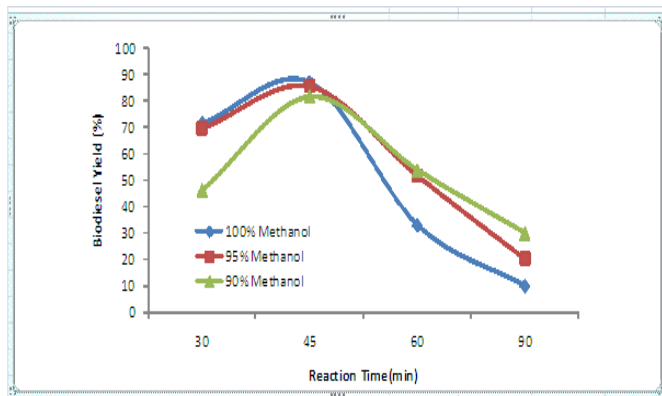


Figure1: The Relationship Between Reaction Time and the Biodiesel Yield

3.3 The Effect Of Reaction Temperature On Biodiesel Yield

The transesterification process can occur at different temperatures depending on the oil used. Temperature increases the energy of the reacting molecules and also improves the miscibility of the alcoholic polar media into a non-polar oily phase, resulting in much faster reaction. The effect of temperature on the yield of biodiesel was also studied at a constant alcohol /oil ratio of 12:1, agitation rate of 450rpm and reaction time of 45min. It was found that temperature has a profound effect on the yield of biodiesel. Figure 2 shows that the yield of biodiesel increased gradually with temperature and an optimum yield was reached at 65°C for the three samples with the 100% methanol having the highest yield of 87% while the 90 % methanol blend has the least yield of 81% biodiesel. This is in agreement with the literature that the temperature near the boiling point of the alcohol gives the fastest reaction yield [14,11,6].

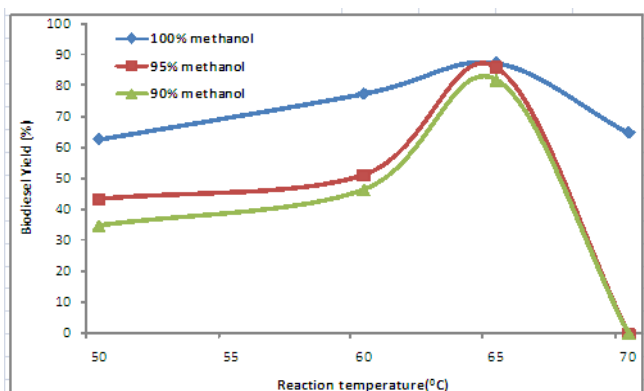


Figure 2: The Relationship Between Reaction Temperature and the Biodiesel Yield

3.4 The Effect of Catalyst Concentration

The presence of catalyst makes transesterification possible. It has been reported from literature that alkali-catalyst transesterification is much faster than acid catalyzed transesterification and less corrosive to industrial equipment [7,12,1,8]. The effect of catalyst at 55° to 70°C and reaction time of 30 to 90min at a constant alcohol molar ratio of

12:1; agitation ratio of 450rpm was investigated. Figure 3 revealed that optimum yields of about 82 to 87% were obtained for the three samples. The optimum yield of the biodiesel occurred at catalyst concentration of about 1.5w/w%

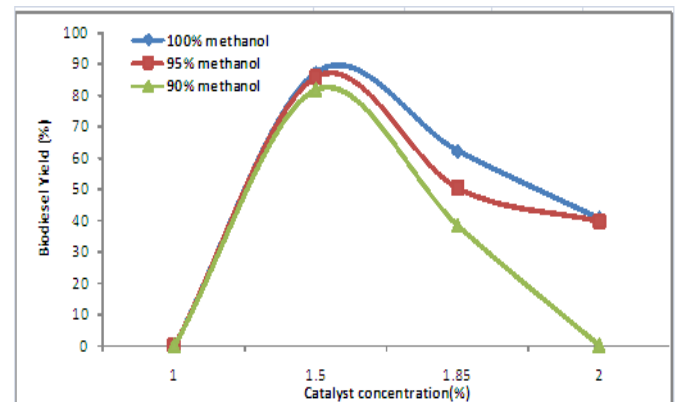


Figure 3: The Relationship Between catalyst concentration and the Biodiesel Yield

4. CONCLUSION

Methanolysis and meth-butanolysis of castor oil have been investigated. The result obtained revealed that the optimum yield at constant alcohol molar ratio of 12:1 and agitation rate of 450rpm was achieved at catalyst concentration of about 1.5w/w%, reaction time of about 45mins and reaction temperature of about 65°C. The specific gravity, kinematic viscosity, calorific value and flash point of the biodiesel produced at optimum reaction conditions in this study were within the ASTM acceptable limits.

Deviation of the transesterification variables from these optimum values tend to a decline in the biodiesel yield. These results show the possibility of economic and sustainable production of biodiesel from castor oil which can be used in diesel engines. Therefore, inexpensive feasibility and environmental impact of production of biodiesel from castor oil can be critically assessed through a high-input mechanised growing of castor as a biodiesel feedstock. This is because, castor is a non-edible crop and will not in anyway compete with food crops.

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