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Synthesis and Calorific Value of Biodiesel by Methanolysis of Castor and Olive Oils in Admixture

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Abstract: Herein we report the methanolysis of castor oil and olive oil admixture to produce biodiesel. Four (4) parameters were investigated namely; temperature (45 ^{o}C-75 ^{o}C), reaction time (30 minutes-150 minutes), methanol-to-oil molar ratio (5:1-15:1and castor oil-to- olive oil ratio (30:70, 45:55, 50:50 and 40:60). All reactions were done at a constant stirring rate of 400 rpm. The optimum values for the investigated parameters were found to be 60^{o}C temperature, 6:1 molar ratio, 120 minute reaction time and 0.5 w/wt % NaOH. The results showed that 92% yield was achieved for 45:55% castor to olive oils composition. This yield was higher than biodiesel yield from either castor oil or olive oil.

Key words: Biodiesel; Methanolysis; Transesterification; Castor oil; Olive oil.

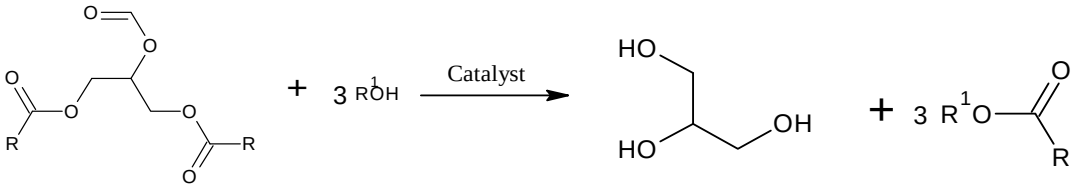
INTRODUCTION

Biodiesel has gained reasonable significance in the recent years as an alternate or extender for fuel oil for the use in diesel engines (Moser, 2009). It can be used individually but mostly blended with petro-diesel because of its relatively limited quantity. Owing to its green source, biodiesel is cleaner and possess better lubricity than petro-diesel (Yusuf N. and Sirajo M., 2009).

Biodiesel has characteristic superior flash point, highly degradability, negligible sulfur content and low toxicity. Its feedstock is readily available and renewable. Thus, making biodiesel production an indispensable venture in our quest to meeting the global energy demand and minimizing environmental hazards associated with the use of non-renewable energy for our diesel engines. It is equally important that growing economies of the world would take this advantage to develop their natural resource utilization and achieve manageable independence from importation.

Biodiesel synthesis had been achieved in different ways, namely: direct use and blending with raw oils, micro-emulsions, thermal cracking and transesterification. This paper explores transesterification method to synthesize the biodiesel. It involves a 1:3 molar ratio reaction of triacylglycerol (TAG) of the oil and a monohydric alcohol to produce glycerol and alkyl-ester (biodiesel). Transesterification takes place in the presence of a catalyst usually an alkali such as NaOH, KOH or an acid (such as H_2SO_4), $ZnCl_2$ or enzymes. Acid catalysis is generally recommended for feedstock with a high level of free fatty acid even though the reaction takes longer than usual to complete (Moser, 2009).

Biodiesel production requires a stating material such as the vegetable oil or fats which could react with the alcohol to transesterify the triacylglycerol into alkylesters. The alcohol forms an alkoxide with an alkali (where alkali is used as a catalyst) to attack the carbonyl carbons of the acyl group in a step-wise reaction to form di- and monoacyl glycerol. A complete reaction has occurred when the alkylester has been formed and glycerol is generated as the by-product (Equation 1).



Equation 1: General equation for biodiesel synthesis from vegetable oil via transesterification.

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The first parameter to consider in deciding what production path to follow is the amount of free fatty acid present in the feedstock (vegetable oil). Free Fatty Acid (FFA) exactly or above 2.5 % is considered very high and therefore a pre-treatment would be recommended.

Pre-treatment is achieved through steam distillation, extraction by alcohol, esterification by acid-catalysis, addition of glycerol into the acidic feedstock using a Lewis acid catalyst such as $ZnCl_2$ and iodine catalyzed esterification of the oil (Leung *et al*., 2009). Since the FFA in castor oil is almost negligible, the pre-treatment step was not done for this work.

A study on biodiesel production by ethanolysis of mixed castor oil and soyaben oils using KOH as catalyst showed no appropriate substrate preference when both oils were transesterified in admixture. However, higher reaction yield and increased purification efficiency were directly correlated with the proportion of soyabean oil present in the reaction mixture (Barbosa *et al*., 2010).

Conceicao *et al* obtained a maximum yield of 92.5 % at 15 minutes of reaction, 6:1 methanol to oil molar ratio and 0.5 % w/w of catalyst by transesterification of pure castor oil from neutralized castor oil with glycerol (Conceicao *et al*., 2010).

This research seeks to determine optimizing parameters of transesterification of pure castor oil and and olive oils in admixture using NaOH as a catalyst, as well as the calorific value determination. Furthermore, the yields would be compared.

MATERIALS AND METHOD

Materials:

Methanol, Sodium hydroxide pellets, Sodium sulphate and Sulphuric acid were used as received from Fluka, Riedel-de Haen, Loba Chemie and BDH respectively. Castor oil and Olive oils were supplied by Philip Harris Limited Shenstone, England and Sun Mark Ltd., England. Viscosities were measured using Uppelhode viscometers and a viscosity bath. Calorific values were recorded on Eco calorimeter (2K).

Experimental Techniques:

In the Trans-esterification of mixture of olive and castor oils, Castor oil and olive oil were mixed at 30:70, 45:55, 50:50 and 40:60 Castor to olive oil percentage compositions while the reaction parameters that gave the best yields for pure castor were made use of except the catalyst concentration. This is because earlier experiment done in the group shows an optimal concentration of 0.5 % The parameters are temperature of 60 ^{0}C, methanol to oil molar ratio (6:1), wt% of the catalyst (0.5), 2 hours reaction time and a stirring rate of 400 rpm.

Varying of Temperature:

Castor and olive oil admixture (50 ml) was measured using a measuring cylinder and poured inside a 400 ml beaker. The oil was pre-heated to 40 ^{0}C. To a stirred methanol, (11 ml, 6:1 methanol to oil molar ratio) was added NaOH (0.49g 1 wt % of the weight of oil) .The mixture was heated gently until all the NaOH has dissolved. The resulting methoxide was then poured in the pre-heated oil for a 2 hour reaction at 400 rpm stirring rate. The products were then poured in to a separatory funnel for phase separation. Two layers were visible after 30 minutes but were left for additional 12 hours for proper settling of the glycerol. The same experimental procedure was repeated for other temperatures (50 ^{0}C, 60 ^{0}C, 70 ^{0}C, 75 ^{0}C) keeping all other parameters constant.

Varying Time:

In these set of experiments, the temperature of 60 ^{0}C, methanol to oil molar ratio (6:1) and wt % of the catalyst (1) were kept constant while varying time from 15, 60, 90, 120 and 135 minutes. A temperature of 60^{0}C was chosen because it gave the highest yield in the previous experiment.

Varying of Methanol to Oil Ratio:

With the reaction time, temperature and fixed at 2 hours and 60 ^{0}C respectively, the methanol to oil molar ratio was also varied from 4:1, 6:1, 8:1 to 10:1 while the concentration of the catalyst was kept at 1 wt %.

Purification of Crude Bio-Diesel:

In order to obtain a pure Bio-diesel, an efficient way of purification was adopted. What appeared to be facile and strategic routes to achieve these protocol were neutralization, distillation and washing

Neutralization:

Soap impurities are broken into soluble salts by neutralizing with acid. 1 ml of 0.1M H_2SO_4 was added to the crude biodiesel. The black suspensions formed are left to settle down and decanted gently into a clean beaker.

Distillation:

Since all the impurities are soluble in water, a wet wash would have achieved the purification but for the fact that castor methyl ester retains much of its methanol. So, distillation was used to recover the unreacted methanol at its boiling point of 65 ^{0}C.

Washing:

The crude biodiesel is thereafter washed with warm distilled water for about three times to remove all soluble salts and suspensions.

Quality Testing:

Viscosity Measurement:

Four Uppelhode viscometers of size 3C were used for the viscosity measurement. About 12ml of each sample to be analyzed was added through the open end. The viscometer was maintained on its stand and then immersed in a viscometer bath that has already been thermostated at 40 ^{0}C. Each viscometer is allowed to stay inside for at least 2 hours. By this time, the oil would have assumed the temperature of its environment. A pipette filler is then placed at on open end and by closing the other one, oil is sucked up above the upper boundary line. Oil is allowed to fall under gravity to the upper mark where the stop watch starts its counting. The watch is stopped when the liquid reaches the lower boundary. The time it takes the liquid to travel from one boundary to the other is multiplied against the calibration constant of the viscometer to obtain the viscosity in mm^2/s.

Calorific Value Determination:

The Bomb calorimeter requires the burning a certain mass of oil sample in the presence of oxygen at a certain temperature and time and determination of the heat involved. This heat value is also called the Gross Calorific Value (GCV). Oil sample (0.34g) was placed in the cup after it had been properly cleaned. A thread was fixed at the suspender just a little above the cup holder making sure the ends of the thread are immersed in the oil. About 3000 kpa of oxygen was pumped inside the tightly fixed vessel and then wait on the calorimeter to display 'insert'. The vessel was inserted, lid was closed and after about 15 minutes, the energy content was seen displayed on the screen in mega joules.

RESULTS AND DISCUSSION

Table 1: Transesterification results for castor and olive oil admixture with varying castor: olive oil percentage composition.

Composition Castor: Olive	Volume before purification (cm^3)	Volume after purification (cm^3)	Calorific Value (MJ/kg)	Viscosity @ 40^{0}C (mm^2/s)
45:55	47.5	46	33.10	5.83
50:50	40.5	39	33.45	6.45
60:40	39	38	35.35	8.70
70:30	39	37	36.03	8.90

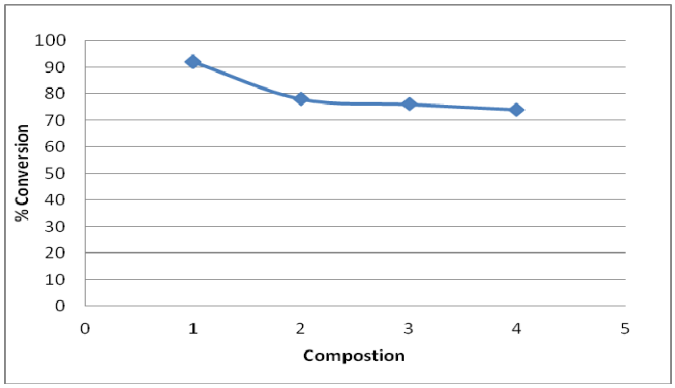

Fig. 1: The Composition Variation Of Castor Oil To Olive Oil Based On Volumetric Yield.

KEY:

Figure	Composition
1	**45:55**
2	**50:50**
3	**60:40**
4	**70:30**

Table 2: Transesterification results for the admixture when temperature was varied.

Temperature (^{0}C)	Volume before purification (cm^3)	Volume after purification (cm^3)	Calorific Value (MJ/kg)	Viscosity @ 40^{0}C (mm^2/s)
45	44	42	33.10	11.02
50	44	42	33.45	11.04
60	45	43	35.35	12.36
70	49	48	36.03	-
75	48.5	47	36.78	-

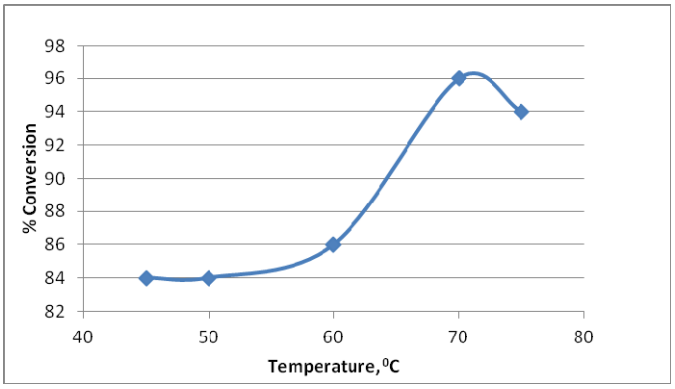

Fig. 2: Temperature Variation Based On Volumetric Yield.

Table 3: Transesterification results for the admixture when time was varied.

Time (mins)	Volume before purification (cm^3)	Volume after purification (cm^3)	Calorific Value (MJ/kg)	Viscosity @ 40^{0}C (mm^2/s)
30	10	8	33.10	28.48
60	30	28	33.45	20.05
90	40.5	39	35.35	21.46
120	45	43	36.03	12.36
150	42	40	36.78	12.40

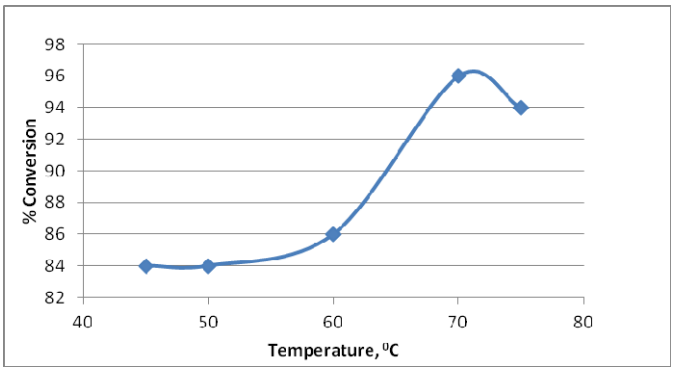

Fig. 3: Time Variation Based On Volumetric Yield.

Table 4: Transesterification results for the admixture when methanol to oil ratio was varied 8.

Methanol:Oil ratio	Volume before purification (cm^3)	Volume after purification (cm^3)	Calorific Value (MJ/kg)	Viscosity @ 40^{0}C (mm^2/s)
5:1	37	40	33.10	14.23
6:1	45	43	33.45	12.36
8:1	45	41	35.35	8.45
10:1	39	38	36.03	8.40
15:1	37.5	35	36.78	9.45

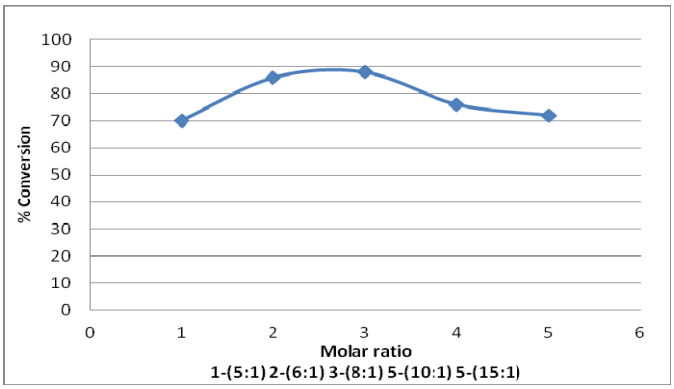

Fig. 4: Molar Ratio Variation Based On Volumetric Yield.

Conclusion:

This experimental work showed that those limiting characteristics associated with castor biodiesel or olive oil biodiesel can be reduced by mixing it in 45:55 rational proportions with olive oil at conditions that optimized biodiesel production from pure castor oil; 6:1 methanol to oil molar ratio, operating temperature of 60 ^{0}C, 0.5wt % catalyst (by weight of oil), 2 hour retention time and stirring rate at 400 rpm. This would not only yield maximum production benefits, but would significantly reduce the risk of probable food shortage as a result of total dependence on edible oils, (olive oil for example) for biodiesel production and the scarcity of raw non-edible oils (castor oil for example) for industrial applications. The result also showed in both calorific value viscosities with increase in castor oil percent composition. Figure 1 displayed the composition variation of castor oil to olive oil based on the volumetric yield. As observed the 45:55 composition gave the highest percent conversion.

Figure 2 shows the temperature dependent on volumetric yield of the admixture. The highest conversion was observed at about 70 ^{o}C. It would be worthy to note Figure 2 and 3 summarised the temperature and temperature dependent volumetric yield of the admixture

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