

An Experimental Study of Biodiesel Synthesis from Groundnut Oil. Part I: Synthesis of Biodiesel from Groundnut Oil under Varying Operating Conditions.

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Abstract: Biodiesel is gaining more and more importance as an alternative fuel due to the depleting fossil fuel resources. Chemically biodiesel is monoalkyl esters of long chain fatty acids derived from renewable feedstock like vegetable oils and animal fats. It is produced by transesterification in which oil or fat is reacted with a monohydric alcohol in the presence of a catalyst. In this research, biodiesel was produced from groundnut oil under varying operating conditions (considering only temperature, catalyst concentration and reaction time being more prominent factors affecting the reaction). The optimum temperature, catalyst concentration and reaction time were found to be 70° C, 1% (wt of oil) and 1 hr respectively. Also properties there should be comma in between viscosity, specific gravity and flash point of the biodiesel produced were investigated and the results obtained shows agreement with international standards. Part II of this paper will discuss the kinetics of the reaction.

Key words: Biodiesel; Transesterification; Reaction conditions; Kinetics and Petrodiesel

INTRODUCTION

The world population is continuously increasing with an average annual growth rate of 1.17% and as such the demand for petroleum is increasing with each passing day (CIA, 2007). This may also be attributed to the limited resources of petroleum crude. In that case it becomes an utmost necessity to search for alternative fuels which are renewable. It is in line with this that the developed and now the developing world want future transport fuels and technologies that deliver lower toxic emissions, lower green house gases, greater efficiency of energy use, less dependence on foreign oil imports and affordable.

Biofuel is now a major contributor to the economic growth of any nation that intends to be self reliant. According to petroleum economists, global diesel demand is likely to continue to grow at around 3% per year while demand for certain other refined production is likely to flatten and even decline (Tony, 2003). This brings about biodiesel to complement the extra need.

Biodiesel is a cleaner burning fuel than diesel and a suitable replacement. It is made from non-toxic, biodegradable, renewable sources (vegetable oils and fats). Biodiesel can be produced in many ways (Chandrashekhar, 2007). The method used in laboratory is transesterification which is actually a replacement of alcohol group from an ester by another alcohol.

This research work is aimed at optimising the production of biodiesel from groundnut oil through transesterification reaction and study some of the factors affecting its production in order to establish the kinetics of the reaction.

Groundnut Production:

Groundnut is the 13th most important food crop of the world. It is the world's 4th most important source of edible oil and 3rd most important source of vegetable protein. Groundnut seeds contain high quality edible oil (50% approx.), easily digestible protein (25%) and carbohydrates (20%). It is grown on 26.4 million ha worldwide with a total production of 36.1 million metric tons, and an average productivity of 1.4 metric tons/ha (Fukuda, 2001).

Vegetable oils are mainly composed of fatty acids in the form of triglycerides. Triglycerides are fatty acid esters having three alkyl groups attached to a parent alkane (Propane in particular). The following table gives the fatty acid composition of groundnut oil on a percentage basis.

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Table 1: Analytical Properties of Groundnut Oil

% of oil in seed or kernel	45-55
Specific Gravity at 25°C	0.910-0.915
Saponification Value	188-195
Iodine Value	84-100
Melting Point °C	26-32

(Source: Chinyere, 2005)

Table 2: Fatty Acid Composition of Groundnut Oil

Fatty acid	% Composition
Palmitic acid (Hexadecanoic)	6.0-9.0
Stearic acid (n-Octadecanoic)	3.0 - 6.0
Oleic (C18:1)	52.0-60.0
Linoleic acid (C18:2)	13.0-27.0
Arachidic acid C20 (Eicosanoic)	2.0-4.0
Lignoceric acid	1.0 - 3.0
Behenic acid	1.0 -3.0

(Source: Chempro.in)

Biodiesel Properties and Description:

Biodiesel is a light to dark yellow liquid, it is practically immiscible with water, has a high boiling point and low vapour pressure. Typical methyl ester biodiesel has a flash point of 150 °C (300 °F), making it rather non-flammable. Biodiesel has a density of 0.88 g/cm³. Biodiesel uncontaminated with starting material can be regarded as non-toxic (Ma, 1998).

Advantages of Biodiesel over Conventional Diesel:

Biodiesel possesses several distinct advantages over petro-diesel regarding exhaust emissions (Kegl, 2008). Its primary advantages are that it is one of the most renewable fuels currently available and it is also non-toxic and biodegradable. It can also be used directly in most diesel engines without requiring extensive engine modifications (Van, 2004a). Combustion efficiency remained constant using either biodiesel or diesel fuel (Dorado, 2003b). Compared to mineral diesel, biodiesel generally causes a decrease of unburned HC, CO and an increase of NO_x emission (Tat, 2007). Biodiesel can reduce by as much as 20% the direct (tailpipe) emission of particulates, on vehicles with particulate filters compared with low-sulfur (less than 50 ppm) diesel. Particulate emissions as the result of production are reduced by around 50%, compared with fossil-sourced diesel (Van, 2004b).

Table 3: ASTM Standards for Biodiesel

Property	Method	Limits	Units
Flash point, closed cup	D 93	130 min	°C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40°C	D 445	1.9 - 6.0	mm ² /s
Sulfated ash	D 874	0.020 max	wt. %
Copper strip corrosion	D 130	No. 3 max	-
Cetane number	D 613	47 min	-
Acid number	D 664	0.80 max	mg KOH/g

MATERIALS AND METHODS

Three different sets of experiments were conducted in which different parameters were varied to optimize biodiesel production reaction conditions. The parameters are temperature, time of reaction and catalyst concentration. This section will explain the procedural steps in the bio-diesel synthesis.

Varying Temperature:

40ml of oil was measured using a measuring cylinder and poured into a conical flask. The oil was then pre-heated to 70°C (using oil bath with temperature regulator).

0.3595g of sodium hydroxide pellets (1 weight % of oil) was weighed and added to 10.0ml of methanol (6:1 methanol to oil ratio). The mixture was stirred until all the pellets dissolve into solution of sodium methoxide. The sodium methoxide solution was then added to the pre-heated methanol. Mixing/stirring was maintained until homogeneity is achieved. The reaction mixture was maintained at a temperature of 70°C for 40 minutes. The product of the reaction was left for 16 hours for proper settling of the glycerine produced. Bio-diesel was separated from the glycerine using a separating funnel. The same experimental procedure was repeated for other values of temperature (70°C, 55°C, 40°C and 32°C) keeping all other parameters constant.

Varying Catalyst Concentration:

In these sets of experiments, temperature and time of reaction were kept constant. The alcohol to oil ratio was also maintained at a constant value of 6:1. The same experimental procedure above was repeated, but with varying concentration of catalyst (0.17976g, 0.071904g, 0.53928g and 0.71904g of sodium hydroxide pellets) keeping all other parameters constant (temperature at 70°C and time at 40 minutes).

Varying Time of Reaction:

The time of reaction was varied keeping the other parameters constant. The catalyst concentration was maintained at 1% (oil weight) and temperature was maintained at 70°C, because in the previous experiments these reaction conditions were the best in terms of yield (volume of product). Only the reaction time was varied from 15, 20, 60 and 80 minutes. All other experimental variables were kept constant.

Washing of biodiesel product:

The products of the transesterification reaction Fatty Acid Methyl Esters (FAME) contain some impurities like unreacted methanol, sodium methoxide and possibly sodium alkylate (soap), and therefore it needs some forms of purification before it can be used in diesel engines. Since all the impurities are polar groups, water is a suitable solvent for dissolving them. The following procedure was used in washing the biodiesel:

20ml of water was measured using a measuring cylinder and poured gently on the product sample. The mixture was gently stirred to avoid foam formation. Shaking rigorously is not advised (Van, 2004b). The mixture of water and biodiesel was left for 16 hrs to settle into two phases viz; water-impurities phase and biodiesel phase. The two phase mixture was then separated using a separating funnel. The biodiesel layer was then heated to about 100°C for 1hr to evaporate the remaining water molecules in it.

Determination of Specific Gravity (IP 59/72):

A clean dry empty 50ml density bottle was weighed and the mass was recorded as M_g , it was then filled up with distilled water and subsequently with the samples. The mass of the bottle and water were recorded as M_{1g} and M_{2g} respectively Hence, the specific gravity was evaluated¹⁴. This procedure was used to determine the specific gravity of all the samples.

Viscosity Measurement:

Brookfield viscometer measures viscosity in the speed range of 0.1rpm to 100rpm (1rpm = 1.703s⁻¹) with spindle size numbered from 1 to 7. The smaller the quantity of the sample the larger the spindle number to be used. For this study, since the quantity was small (except for the raw sample), spindle number 7 was used throughout and the angular speed selected was 50rpm. The following procedure was used to determine the viscosities of the samples. The viscometer spindle No 7 was inserted into the shaft of the instrument. The oil sample at room temperature of 25°C was poured into a 10ml beaker and placed on the bench; the viscometer spindle was lowered into the sample up to the marked level so that the spindle head was completely immersed. The spindle rotated clock-wisely inside the oil sample. The pointer of the dial deflected and stabilized on a given dial value. The reading was then taken.

Determination of Flash Point Using ASTM D97-73:

The oil sample was placed in the Pensky-Martin's cup in such quantity as to just touch the prescribed mark on the interior of the cup. The cover was then fitted onto the position on the cup and Bunsen burner used to supply heat to the apparatus at a rate of about 5°C per minute. During heating, the oil was constantly stirred. As the oil approaches its flashing, the injector burner was lighted and injected into the oil container after every 12 second intervals until a distinct flash was observed within the container. The temperature at which the flash occurred was then recorded.

The test was duplicated for each of the oil samples and the average value of the flash point recorded.

Gross Calorific Value (GCV) determination: The calorific value was determined using Perr 6100 bomb calorimeter. The gelatine capsule used in placing the sample in the calorimeter was weighed; 0.1 g of the biodiesel sample was then added into the lower part of the capsule. The bomb calorimeter was closed and connected to an oxygen cylinder for filling. The calorimeter was properly placed in a water bucket that contains about one litre of water. The calorimeter was switched on and it gave automatic readings of the bucket temperature and energy equivalent value. After about 15 minutes, the calorimeter reading of the jacket temperature was then recorded. The experiment was then repeated for the other biodiesel samples, though some of them using different masses. The calorific values are then determined.

RESULTS AND DISCUSSION

Biodiesel was produced under different operating conditions (catalyst concentration, time of reaction and operating temperature), and the product analysed in order to ascertain the best operating conditions and the quality of the biodiesel.

Different fuel properties were determined to achieve the stated objective. The properties tested are specific gravity, flash point, viscosity, calorific value and composition using infrared analyzer. The results are as presented here

Transesterification Results:

The volumes of biodiesel obtained in the transesterification reaction before and after washing are given in Tables 4 to 6

Table 4: Transesterification results when catalyst concentration was varied.

Catalyst conc. (%)	Volume before washing (cm ³)	Volume after washing (cm ³)
0.2	23.5	20.4
0.5	29.2	26.0
1.0	32.4	28.8
1.5	26.4	24.8
2.0	15.0	13.2

Table 5: Transesterification results when temperature was varied.

Temperature (°C)	Volume before washing (cm ³)	Volume after washing, (cm ³)
32.0	22.0	20.0
40.0	23.4	20.8
55.0	28.0	25.4
70.0	32.4	28.8
80.0	31.7	29.0

Table 6: Transesterification results when time of reaction was varied.

Time, mins	Volume before washing, cm ³	Volume after washing, cm ³
15	26.9	24.2
20	27.5	25.4
40	32.4	28.8
60	33.1	30.6
80	33.9	30.8

The results given above were used in the determination of the yield of the reaction based on the volume of groundnut oil consumed. The yield was determined in the following way;

$$\text{Yield} = \frac{\text{Volume of Biodiesel produced}}{\text{Volume of groundnut oil used}} \times 100 \% \dots\dots\dots 1$$

A constant oil volume of 40cm³ was used in the whole experiment; therefore the yields will then be evaluated using the volume of biodiesel after washing, since it is the volume of the pure product. Equation 1 was employed in the computation of the fractional yields and consequently the percentage yield.

These values of biodiesel yield were plotted in order to understand the effect of the variation in catalyst concentration. Catalyst concentrations are given in terms of percentage weight of oil. This graph is as shown in Figure 1 below

Also from Table 5 above the volumetric yields of biodiesel were calculated for the varying temperature condition using Equation 1. The results obtained were used to plot Figure 2 to see the trend of the effect of temperature on biodiesel yield as was done for the effect of catalyst concentration.

The third result for the variation of reaction time follows the same pattern as the other ones above. The result is shown in Figure 3 below.

Varying Catalyst Concentration:

1 % (wt of oil) concentration of catalyst was found to give the highest yield. The yield behaviour under varying catalyst concentration is shown in Figure 1. At a catalyst concentration of 2.0%, soap was produced in an excess amount making the biodiesel more viscous than other samples.

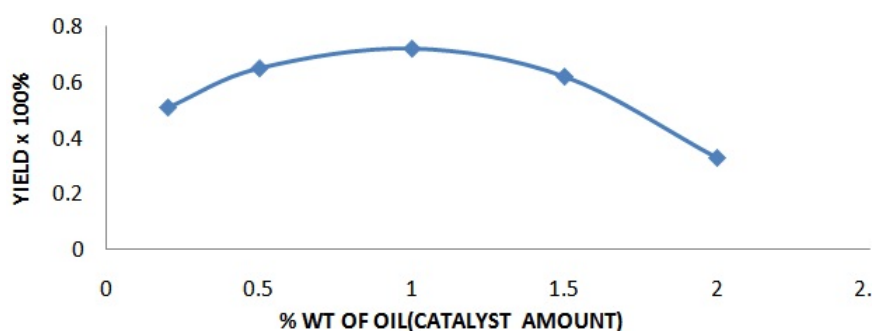


Fig. 1: Catalyst concentration variation based on volume yield.

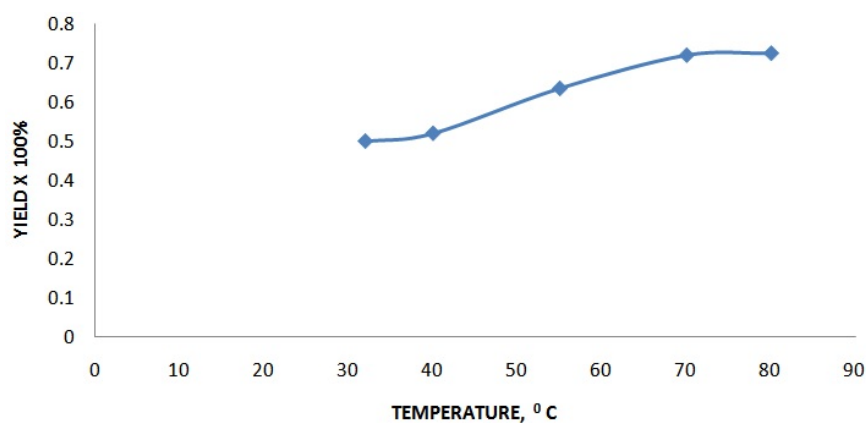


Fig. 2: Temperature variation based on volumetric yield.

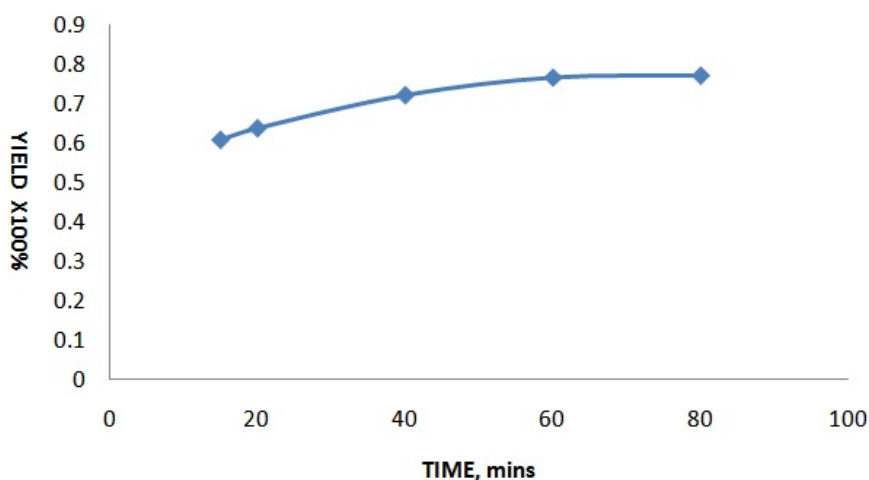


Fig. 3: Time variation based on volumetric yield.

Varying Temperature:

Figure 2 shows the relationship between temperature and yield of biodiesel. From the graph, it can be seen that there was a steady increase in the yield of biodiesel up to 70°C then a gentle increase from 70°C to 80°C. Though the yield obtained at 80°C was slightly more than that at 70°C, but economically, that increase cannot compensate for the energy cost required to give a 10°C rise in temperature. Hence 70°C can be said to be the optimum operating temperature.

Varying Time of Reaction:

Reaction times were varied from 15 minutes to 1 hour 20 minutes. The yields were observed to increase up to 1hr reaction time and then stabilises. As shown in Figure 3, the optimum reaction time is 1 hr.

Results of Calorific Value, Specific Gravity, Viscosity and Flash Point Analysis:

The results obtained for the analysis of specific gravity, calorific value, viscosity and flash point are presented in Table 7 below for all the samples and the raw groundnut oil used for this research.

Table 7: Results of calorific value, specific gravity, viscosity and flash point

Condition/Sample	Spec. gravity sg	Calorific Value (kJ/kg)	Viscosity @ 29 °C (cP)	Flash point (°C)
Temperature (°C)				
32	0.8500	48608.43	6.3	99
40	0.8654	47385.58	4.9	98
55	0.9055	38269.49	4.6	99
70	0.9375	40836.35	4.1	98
80	0.9310	46880.13	4.2	97
Time (min.)				
15	0.8678	41857.26	6.6	100
20	0.9055	30137.23	5.2	99
40	0.9375	46880.13	4.2	98
60	0.9477	46880.13	4.6	98
80	0.9416	40182.97	4.4	98
Concentration (wt%)				
0.2	0.8823	37671.53	4.8	98
0.5	0.8846	40182.97	4.0	96
1.0	0.9375	46880.13	4.2	98
1.5	0.8871	45205.89	4.4	98
2.0	0.8333	36529.97	7.2	101
Raw groundnut oil	0.850	-	26.5	142

The values in the table of results above are summarised in Table 8 below and the values were compared with those of standard biodiesel and Automotive Gas Oil (petrodiesel).

Table 8: Comparison of summarised experimental results with standard biodiesel and AGO results

Property	Biodiesel range of values as obtained in the Lab.	Biodiesel's Standards.	Automotive Gas Oil Standards.
Viscosity, cP	3.0 – 6.8	1.17 – 5.83	1.25 – 4.30
Density, g/cm ³	0.85 – 0.97	0.88	0.81
Flash point, °C	98.0	93 minimum	50 – 58
GCV, kJ/kg	30137.22648 - 48608.42981	-	41830

From the results summary shown above, it can be seen that the properties of the produced biodiesel is in close agreement with those of automotive gas oil (petrodiesel) and also conforms with the Biodiesel's standards.

Conclusions:

In this work biodiesel from groundnut oil has been successfully produced under varying operating conditions in the laboratory. Analytical properties of the produced fuels were tested and an optimum operation condition was ascertained based on the parameters varied. Accordingly, the following conclusions were drawn.

1. At a temperature of 70 °C, reaction time of 1 hour and a catalyst concentration of 1% (weight of oil), the transesterification reaction gave the optimum yield.
2. The rate of the transesterification reaction is decreasing with increasing reaction time.
3. Viscosities, specific gravity, calorific value and flash point were found to meet the international standards.

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