Synthesis, Calorimetric and Viscometric Study of Groundnut oil Biodiesel and Blends

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Abstract

Biodiesel has become an important fuel in recent times due to its prospects as an alternative source of energy to petroleum fuels. In this research, biodiesel was synthesized form groundnut oil at 65^oC via base catalyzed transesterification using KOH as the catalyst. The synthesized fatty acid methyl ester after being washed was blended with petroleum diesel in the following percentage by volume of the biodiesel 2%, 5%, 10%, 20% and 30% corresponding to B2, B5, B10, B20 and B30 respectively. The heat content of each blend was measured using a bomb calorimeter. The data obtained was analyzed and was found that the heat content of the blend decreases as the percentage of biodiesel in the blend increases. The research also demonstrates that, the energy output of fuels made from blends of petroleum diesel and groundnut oil biodiesel decreases as the portion of the biodiesel increases.
Keywords: Biodiesel, heat content, bomb calorimetry, blends, groundnut oil.

Introduction

Since the late nineteenth century till now petroleum has been the major source of energy for the world. However, due to the hiking oil prices, depletion of petroleum reserves and more importantly increasing environmental concerns there is need for a cleaner and renewable source of energy[1]. As a result of this, there has been a huge ongoing research in the field of biodiesel.

Unlike fossil fuels, biodiesel is a renewable source of energy, because it comes from biological sources like plants and animals which can be replenished by farming. On the other hand, fossil fuels come from underground deposits of hydrocarbons which cannot be renewed. Biofuels have become a matter of global importance because of the need for an alternative energy at a cheaper price and with less pollution. As a result of soaring prices of petroleum fuel and increased risk of global warming there is an urgent need to find an alternative source of cleaner and less expensive fuel. Consequently, the significance of biofuels as an alternative fuel is largely accounted for by its similar power to petrol diesel (High octane number), increased lubricity over petro diesel, compatibility with engine components and most importantly its environmental (reduced emission of green house gases like CO_2, CO) and health benefits; being sulphur, aromatics free and biodegradable[2,3].

Even though biofuels had been known in the early 1900s more attention has been drawn to it as an alternative source of energy to petroleum in more recent times because of the increasing risk of environmental pollution and ozone layer depletion, high oil prices and depleting world petroleum reserves[4]. Biodiesel is a clean fuel because it only emits a little amount of carbon dioxide into the atmosphere compared to fossil fuels. Also it does not contain any sulfur and as such does not emit any dangerous oxides into the atmosphere when it burns. On the other hand, petroleum diesel emits sulfur oxides, gaseous hydrocarbons and particulate matter in considerable amounts[5,6].

In addition, Biodiesel has a higher flash point of about 130^oC compared to that of petroleum diesel

which is about $64^{o}C$[7]. Hence it is less liable to explode than petroleum diesels, making biodiesel safer to handle than petroleum diesel.

According to the National Biodiesel Board of the United States of America biodiesel is a mono alkyl ester of long fatty acids derived from lipid feedstock such as vegetable oil or animal fat for use in compression diesel ignition engines[7]. Biodiesel is commonly made from a chemical process known as transesterification, which is the conversion of one ester to another via the use of an alcohol in the presence of a catalyst.

Transesterification of Vegetable Oils; Chemistry of the Reaction: Vegetable oils and animal fats contain triglyceride which is composed of three long chains of fatty acid molecules chemically bonded together with a glycerol molecule as shown in the figure below. Where R', R'' and R''' represent the fatty acid chain in the molecule.
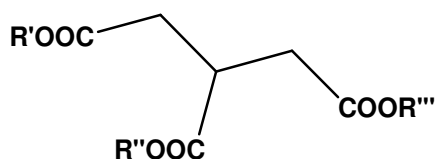
R'OOC

COOR'''

R''OOC

Figure-1: Triglyceride molecule

Biodiesel is commonly formed when methanol is reacted with the vegetable oil or animal fat to form fatty acid methyl ester (FAME—which is the biofuel) and glycerol as the transesterification reaction by product. After the reaction two layers of liquid are formed the glycerol which is denser product settles at the bottom and the FAME forms at the top layer. This reaction is known as transesterification.

A typical flow chart for the production of Biodiesel is shown in fig.1.2.

Both animals and plant fats and oils are typically made of triglycerides which are esters of free fatty acids with the trihydric alcohol, glycerol. In the transesterification process, the alcohol could be deprotonated with a base, usually, (ethanol or methanol) in the presence of KOH or NaOH to make it a stronger nucleophile[9].

Acid Catalyzed Transesterification Reactions: Bronsted acids can be used as catalyst to facilitate the production of fatty acid methyl esters from vegetable oil. Sulfonic and sulfuric acids are the common acids used[10]. Even though acid catalysts give high yields they have longer reaction times of over three hours and they require very high temperatures.

This reaction should only be carried out in the absence of water because the presence of water readily converts the ester to the corresponding carboxylic acids which will reduce the yield of the biodiesel.

Base catalyzed Transesterification Reaction: alkali bases such as sodium hydroxide and potassium hydroxide are the commonly used base catalysts for transesterification reaction. First, of all the base is dissolved in the methanol to form methoxide as shown in the equation 1 below.

ROH + **B** ⟶ **RO⁻** + **BH⁺**

Alcohol   Base catalyst   Alkoxide

Then the alkoxide attacks the carbonyl group of the ester in the oil forming a tetrahedral intermediate. Once this is formed, the new ester is formed and the initial triglyceride molecule becomes a diglyceride. The process starts all over again with the diglyceride leading to the formation of a monoglyceride, which continues until glycerol is formed.

Triglyceride + ROH ⟶ diglyceride + ROOCR'''

Diglyceride + ROH ⟶ monoglyceride+ ROOCR''

Monoglyceride + ROH ⟶ glycerol + ROOCR'
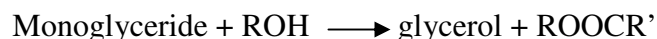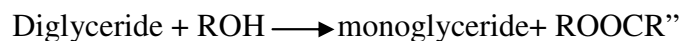
Base catalysts are preferred to acid catalysts because they make the reaction to progress faster [10]. However the reaction can sometimes be hindered due to the formation of soap as a result of hydrolysis of the

ester to free fatty acids (FFA) as shown in the equation 2 and 3 below.

$$RCOOR + H_2O \rightarrow RCOOH + ROH \qquad [2]$$

$$RCOOH + NaOH \rightarrow RCOONa + H_2O \qquad [3]$$

FFA   Base   Soap   Water

Also, the presence of free fatty acids in the oil used might lead to the formation of soap, which reduces the yield of the biodiesel and causes emulsions to form.

Other catalysts besides acids and bases could also be used to speed up transesterification reactions; they include enzymes, non ionic bases and organic polymers.

Groundnut Oil as a Biodiesel Feedstock: Groundnut oil is one of the most consumed vegetable oil. It is the 13th most important food crop in the world. As shown in table 1.2, groundnut oil contains a high percentage of unsaturated fatty acid namely oleic and linoleic acid.

Heat Value of Fuels: The Heat Value of a fuel also known as heat of combustion is amount of energy a fixed quantity of the fuel releases when burnt with oxygen under specific conditions. The energy a fuel releases when it is burnt is used to drive the piston and eventually move the wheels of a vehicle. This means that the heat value of a fuel determines how far a vehicle containing a fixed amount of fuel can go. In order words, a fixed volume of a fuel with a high heat of combustion will travel farther than the same volume of another fuel with a low heat of combustion.

Bomb Calorimeter: A bomb calorimeter is a scientific instrument that measures the heat of combustion of a substance usually at constant volume. Usually, a fixed mass of between 0.4 and 1.5g of the substance to be measured is placed in a metallic crucible. A thread is hung from the instrument into the sample. The sample is placed in a metallic flask called the bomb and oxygen is added to it at a high pressure. The bomb is then placed

within the instrument and the sample is burnt. As the sample is burnt, the hot air is allowed to escape through a thin tube. As it escapes, it raises the temperature of a fixed mass of water. The change in temperature is used by the instrument to calculate the heat of combustion of the substance according to the formula, $q = Cm\Delta T$. Where m is the mass of the sample, C is the specific heat capacity of water, ΔT is the change in temperature and q is the heat of combustion of the sample.

The Viscosity of Biodiesel: Viscosity is the measure of material resistance to flow, the higher viscosity materials flows with great difficulty and a material with less viscosity flow more easily. Most viscometers have two speeds of rotation, 300 and 600 rpm (revolutions per minute), but some are 6 or variable-speed. The name "direct-indicating" reflects the fact that the dial reading at a given speed is a true centipoise viscosity. The viscosity of a fluid can be expressed as a dynamic viscosity or a kinematic viscosity. Dynamic viscosity is measured in units called "centipoise" while Kinematic viscosity takes into account the fluid density and is measured in units called "centistokes" which is equivalent to mm^2s^{-1}. In general the viscosity of a liquid will be reduced as the temperature rises. Relatively viscous oils (as compared to standard diesel fuel) do not fully combust leading to carbon deposition in diesel engines[11]. The viscosity of a biodiesel is approximately an order of magnitude less than the corresponding oil feedstock from which the biodiesel was prepared[12, 13]. Kinematic Viscosity was used in this research. Kinematic viscosity measures the flow resistance of the fuel, e.g., the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. Viscosity is important to diesels and biodiesels because it impacts the operation of components such as the fuel pump. Higher viscosity interferes with injector operation, resulting in poorer atomization of the fuel spray, and has been associated with increased engine deposits. If engines are expected to use higher fractions of biodiesel (instead of the 20% in B-20), they would benefit from redesigned injectors that would accommodate the higher

viscosity to improve spray patterns and atomization. All the biodiesels have viscosities significantly higher than diesel. Because of the high values, biodiesels would be expected to have problems in this area on diesel engines, if measures (such as blending with diesel) are not taken. Viscosity affects fuel atomization by the injectors, engine deposits (increased viscosities associated with increased deposits), and energy use (higher viscosities require more energy by the fuel pump). Because of the potential effect that high viscosities can have on injector spray performance, this property need to be watched in biodiesel production.

Material and Methods

Synthesis of Biodiesel from Groundnut Oil: Groundnut Oil (Obtained from the local Jimeta modern Market manufactured by *Baron*)
KOH (analytical grade manufactured by Acros chemicals)

Methanol (analytical grade manufactured by Fluka chemicals)

Petrodiesel (from ConOil Plc)
Bomb Calorimeter (Cal2k-3)
Viscometer (Rheotek TCB-7)

Experimental Procedure: 40 mL of groundnut oil was heated to 60^oC in a 125 mL Erlenmeyer flask. 0.788 g of KOH was dissolved in 10 mL of methanol to form the methoxide solution. The mass of KOH was about 2% of the weight of the oil. The methoxide solution was then slowly added to the hot oil while stirring with a magnetic stirrer. The mixture was stirred continuously at 60 ^oC for an hour. After one hour the reaction was stopped and the mixture was poured into a 100mL separating funnel, where separation into two clear layers was observed. The upper layer is the biodiesel and the lower layer being the glycerol by product. The lower layer was carefully removed from the separating funnel while the upper layer, the biodiesel was poured into a measuring cylinder, followed by washing and centrifuging.

Measuring the Gross Heat Value
Bomb Calorimeter: The groundnut oil biodiesel was blended with petroleum diesel in the following proportions 2, 5, 10, 20 and 30 percent by volume of biodiesel. These represent B2, B5, B10, B20 and B30 biodiesel-diesel blends respectively. The heat of combustion of each blend was measured using a bomb calorimeter.

Measurement of Viscosity: Kinematic viscosity was determined using a Rheotek TCB-7 Viscometer Bath. 15mL of each fuel oil was measured and transferred into a PSL (Poulten Selfe & Lee Ltd., Essex, England) glass capillary viscometer (3C). The fuel oils were observed over a range of temperatures, from 35 ℃ to 70 ℃, with increments of 5 ℃. The time (in seconds) obtained from the viscometer was converted to kinematic viscosity in mm^2/s by multiplying by the calibration constant (3.0) of the viscometer used.

Results and Discussion

Percentage Yield and Gross Heat Value: The heat content of the blends was found to decrease from B2 to B30 with increasing addition of the biodiesel to the blend mixture as shown in the graph above. Also, the heat value of the groundnut oil biodiesel (fatty acid methyl ester) was found to be higher than that of the groundnut oil feedstock.

The decreasing heat value of the blend as the biodiesel proportion of the blend increases can be accounted for by the presence of oxygen atoms contained in the Fatty Acid Methyl Ester molecules of the biodiesel. Unlike petrol diesel which is composed primarily of hydrocarbon molecules the biodiesel fatty acid molecule contains oxygen bonds. These oxygen atoms are responsible for the tendency of biodiesel to be readily oxidized or burnt. This tendency to be readily oxidized reduces the heat energy released from biodiesel when burnt relative to petroleum diesel. As such, as the proportion of biodiesel increases in the blend the amount of oxygen bonds increases thereby decreasing the heat value of the blend.

Kinematic Viscosity: Fig. 3.2 reveals the temperature dependent kinematic viscosity measurement of the groundnut oil biodiesel; and from the result, as expected the kinematic viscosity value of the biodiesel decreases with increase in temperature

Conclusion

From the results, we have found that the heat content of the blend decreases as the percentage of biodiesel in the blend increases. This can be accounted for by the presence of oxygen atoms in the carbonyl and alkoxy groups of the fatty acid methyl ester which is contained in the biodiesel. On the other hand petro-diesel is primarily made of hydrocarbons. Consequently, increasing the biodiesel components of the blend increases the amount of oxygen carrying groups thereby increasing the combustion properties of the blend but also reducing its heat content. The research demonstrates that, the energy output of fuels made from blends of petroleum diesel and groundnut oil biodiesel decreases as the portion of the biodiesel increases.

The energy of the vegetable oil is improved when it undergoes trans-esterification reaction. Although blends of groundnut oil biodiesel and petroleum diesel produce fuels with lower emissions, it also results in fuels whose energy output is lower than pure. In other words blends of biodiesel and diesel fuels have their combustion properties between those of the parent fuels. The increase in heat content results from a high increase in the number of carbons and hydrogens, as well as an increase in the ratio of these elements relative to oxygen. A decrease in heat content on the other hand is the result of fewer hydrogen atoms (i.e. greater unsaturation) in the fuel molecule
In addition, the temperature dependent measured kinematic viscosity result of the groundnut oil biodiesel is within the standard literature value for a typical biodiesel.

Acknowledgement

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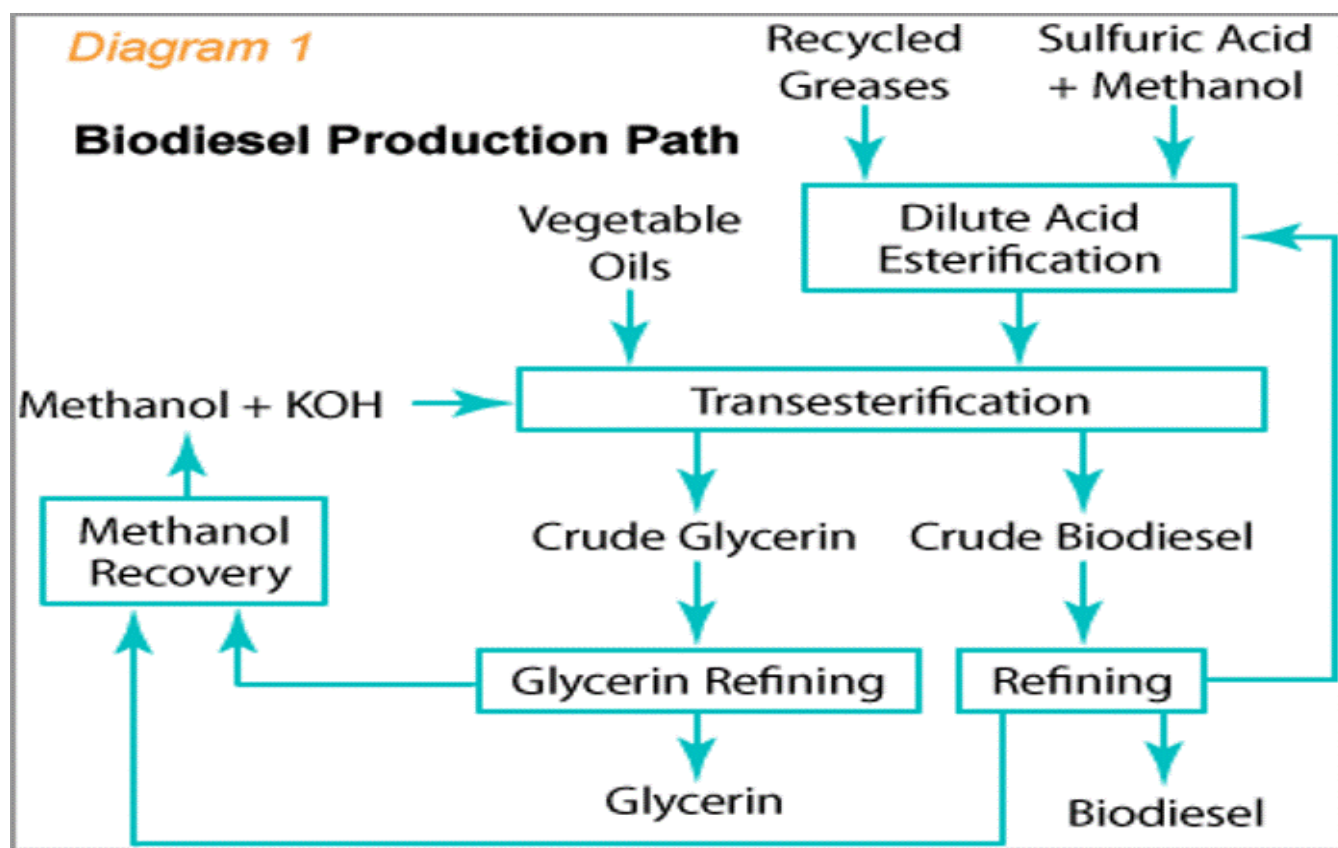
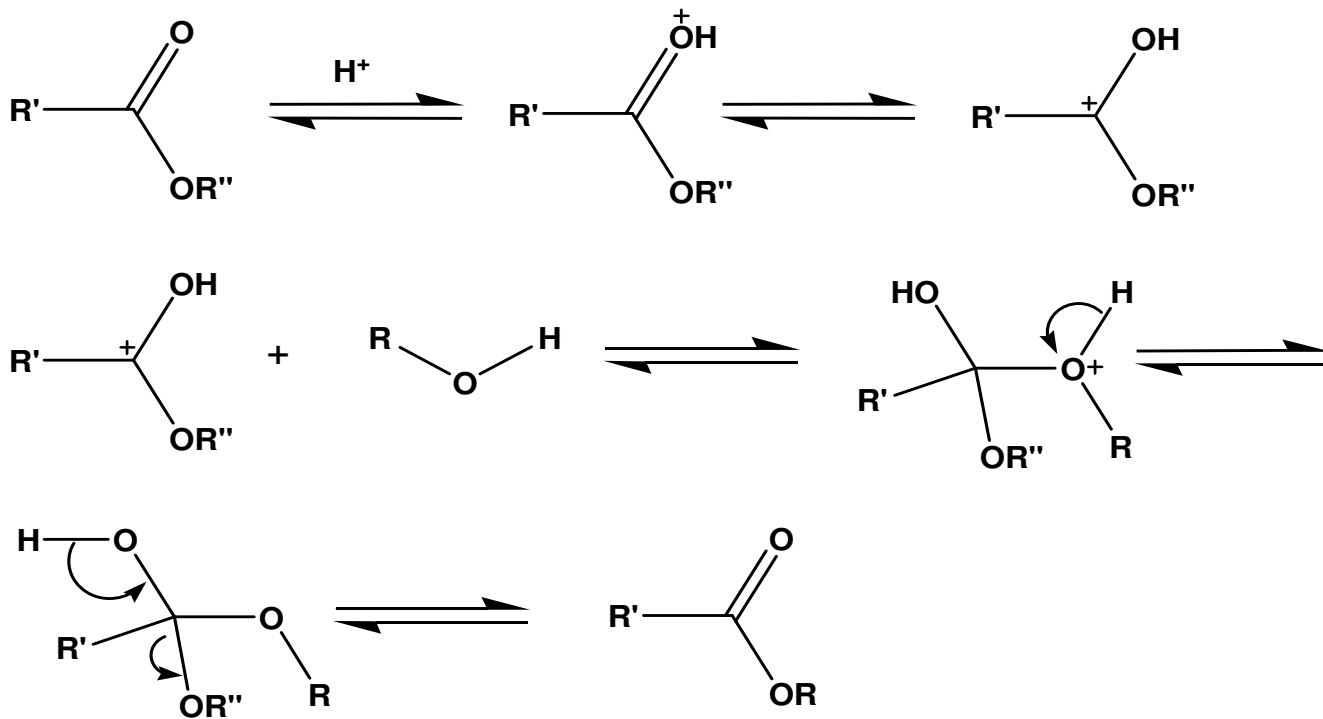**Fig-2: Schematic of biodiesel production. (Source: www.ifl-usa.com)**

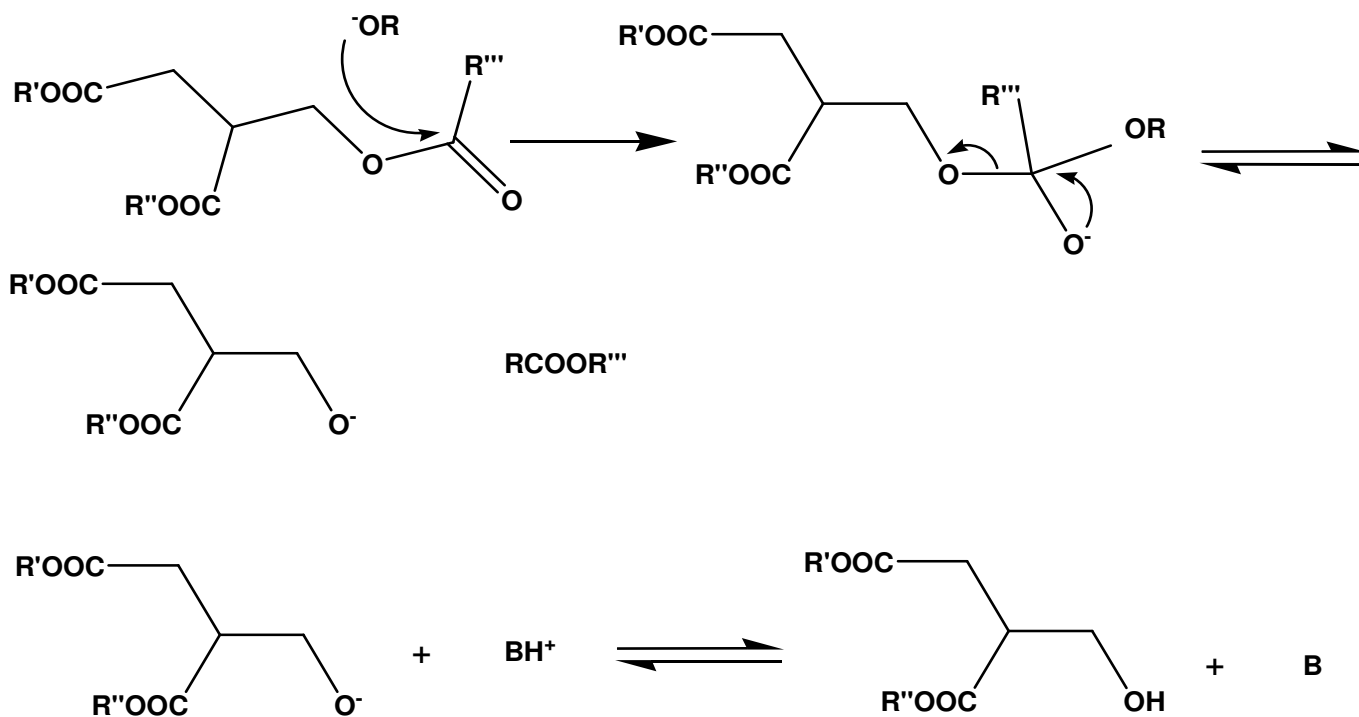**Figure-3: Mechanism for acid catalyzed transesterification reaction**

Figure-4: Mechanism for base catalyzed transesterification

Table-1: Fatty acids in groundnut oil

Fatty acid		% in oil
Oleic acid	C18.1	47.1
Linoleic acid	C18:2	32.9
Palmitic acid	C16:0	10.4
Stearic acid	C18:0	8.9
Alpha linoleic acid	C18:3	0.5
Erucic acid	C22:1	0.2

Table-2: Percentage Yield

	Vol of Oil (mL)	Vol of Biodiesel(%)	Yield (%)
Groundnut Oil	40	33	85

Table-3: Gross Heat Value

	Heat Content (mJ/Kg)
Crude Groundnut Oil	39.30
Crude palm Oil	38.98
G/nut Oil Biodiesel (B100)	39.62
Petrol diesel (P100)	44.65
B2	49.58
B5	45.31
B10	44.41
B30	43.86

Table-4: Kinematic Viscosity for Pure Ground Nut Oil Biodiesel

Temperature (^{o}C)	Kinematic Viscosity (mm^{2}s^{-1})
35	6.78
40	5.94
45	5.46
50	5.19
55	4.83
60	4.56
65	4.32
70	3.96

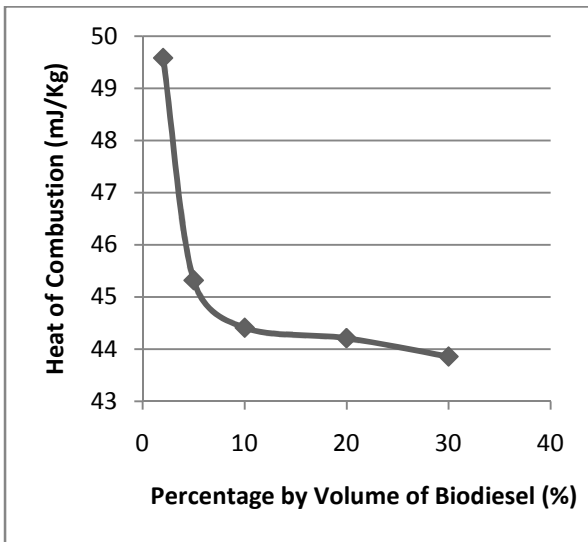The calibration constant K for the Viscometer (Rheotek, ASTM 'Ubbelohde') is: K = 3.0
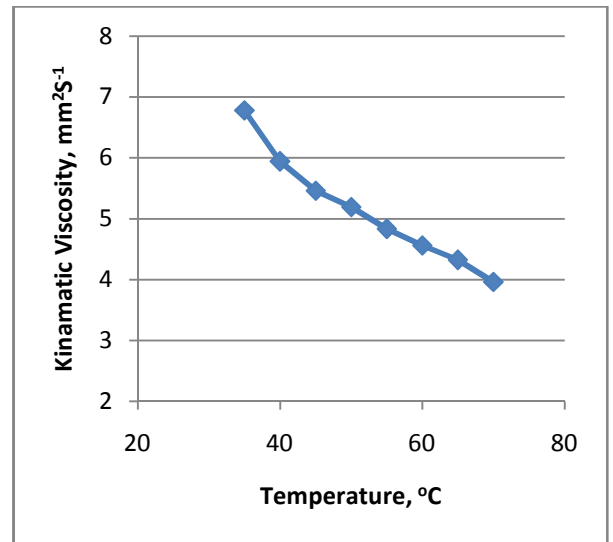

Figure-5: Calorific value of biodiesel-diesel blends

Figure-6: Temperature dependent Kinematic Viscosity