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Thermodynamic and Viscometric Evaluation of Biodiesel and Blends from Olive Oil and Cashew Nut Oil

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Abstract
Biodiesel is a 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, transesterification process was used to convert olive oil and cashew nut oil into biodiesel (methyl ester). The selected material used in the preparation of this biodiesel was methanol, alkaline catalyst (KOH), constant temperature of 70 ^{o}C at 1.5hrs, to optimize the experimental conditions for maximum biodiesel yield. The thermodynamic properties of the biodiesel produced such as heat content of the pure biodiesel (B100) and the blends were investigated.

Keywords: *Biodiesel, heat content, bomb Calorimeter, blends, viscosity.*

Introduction

Biodiesel: Biodiesel is a fuel made from plant or animal oils which can be used in conventional diesel engines to serve as a substitute for petro diesel or blended with petro diesel to reduce emissions. It is oxygenated, sulphur free, biodegradable, non-toxic, and environmentally friendly alternative automotive fuel. The demand for petroleum is increasing with each passing day due to an average annual growth rate in the world population[1,2]. This increase may lead to a higher demand of crude petroleum and in that case it becomes a necessity to search for alternative fuels which are renewable. The developing world want future transport fuels and technologies that deliver lower toxic emission, Lower greenhouse gases, greater efficiency of energy use, as well as less dependence on foreign oil imports. Bio fuel is 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 products is likely to flatten and even decline[3]. This brings about the desire to develop efficient biodiesel to complement the extra need. Biodiesel is gaining attention worldwide as an alternative automotive fuel due to depletion of petroleum products at a faster rate and strict environment regulations. Unlike raw vegetable oil, full-grade biodiesel is registered with the Environmental Protection Agency (EPA) with specification ASTM D6751 as a legal motor fuel for sale as well as distribution.

The major constraint in wide spread use of biodiesel is the production cost. Considerable research work has been done to reduce the cost of biodiesel by using low cost feed stocks such as animal fats, restaurant waste oil and frying oil[4-6]. These low cost feedstocks are more challenging to process because they contain high amount of free fatty acids (FFA).

The depletion of world petroleum reserves and increased environmental concerns has stimulated the search for alternative renewable fuels that are capable of fulfilling an increasing energy demand[7]. In recent decades, research concerns and knowledge about the external benefits of renewable raw materials have intensified the efforts for sustainable energy sources. Biodiesel plays a major role in this field because of the world-wide research, development, and deployment activities of this sustainable energy source[8]. Due to the recent increased awareness and development in this area, High consumption of conventional energy resources and increasing emission regulations has motivated an intense search for alternative fuels over the decades[9].

Biodiesel Production and cost: The cost of the fat or oil used to produce biodiesel clearly affects the cost of the finished product, constituting up to 60–75% of the overall financial burden; therefore, less expensive raw materials are preferred[10]. In the UK for example, recycled cooking oil is currently the main feedstock of choice for biodiesel production due to its low purchase price. Once the limited quantities of used industrial frying oils have been fully given over to biodiesel, additional raw feedstocks may come from the cultivation of rapeseed crops[11,12]. Among all the proposed methods to convert oils to biodiesel, transesterification of the triglycerides seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel[13]. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation and a by-product (glycerol) that has commercial value[14]. There are different transesterification processes that can be applied to synthesize biodiesel:
(a) base-catalyzed transesterification,
(b) acid-catalyzed transesterification,
(c) enzyme-catalyzed transesterification, and
(d) supercritical alcohol transesterification. Biodiesel is currently synthesized using homogeneous alkaline catalysts because the transesterification reaction by an acid catalyst is much slower than the base-catalyzed reaction[15-18]. Base-catalyzed transesterifiction is used in this research experiment. Biodiesel is not distributed as widely as traditional petroleum diesel, but distribution infrastructure is improving.

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[19]. 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, when uncontaminated with starting material can be regarded as non-toxic.

Blending: Petrodiesel – Biodiesel blends are products most commonly distributed for use in the retail diesel fuel marketplace. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix:
100% biodiesel is referred to as B100
20% biodiesel is labelled B20
5% biodiesel is labelled B5
2% biodiesel is labelled B2

Environmental protection agency EPA research shows that biodiesel reduces most emissions from unmodified diesel engines. The amount of emissions reduced depends on the blend level. For example, B100 produced from olive oil and cashew nut oil reduces life cycle CO_2 emissions by 78% compared to petroleum diesel. This effect is linear with blend level, so a B5 blend reduces life cycle CO_2 emissions by 3.8%. Low-level blends will also cause small reductions in emissions of hydrocarbons, carbon monoxide, particulate matter, and harmful air toxics. Obviously, the higher the percentage of biodiesel, the more ecology-friendly the fuel is. Blends of 20% biodiesel with 80% petrodiesel, (B20) can generally be used in unmodified diesel engines. Biodiesel can also be used in its pure form (B100), but may require certain engine modification to avoid maintenance and performance problems.

Heat Content: The energy content (also referred to as heating value or calorific value) of diesel fuel is its heat of combustion; the heat released when a known quantity of fuel is burned under specific conditions. Calorific values are measured experimentally with a bomb calorimeter. The procedure which determines the heat of combustion or calorific value of solid and liquid materials which are burned as fuel at constant volume is called bomb calorimetry.

Viscosity: Viscosity is defined as the thickness of oil and is measured by time taken for a fixed amount of fluid to travel through a vent having a known size. Kinematic viscosity is simply a measure of resistive flow of fluids under the influence of gravity. Petrodiesel with high viscosity form larger droplets upon injection and lead to poor combustion, increase exhaust smoke as well as emissions[20]. Fuels with very low viscosity may not provide adequate lubrication in fuel injection pumps leading to leakages and increase wear. Technically, biodiesel has a higher kinematic viscosity than petrodiesel due to factors like chain length, position, number, and nature of double bonds, including the nature of oxygenated atoms[21]. However, biodiesel viscosity depends on the feedstock and blending with petrodiesel can be carried out to adjust viscosity values.

The objective of this study was to produce quality biodiesel from olive oil and cashew nut oil and to characterise the biodiesel and the blends both thermodynamically and viscometrically, using bomb calorimeter and viscometer. In this research we have tried to study the blends characteristics beyond the well studied and characterised B20 biodiesel – diesel blend.

Material and Methods

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. Calorific values were recorded on Eco calorimeter (2K), while Viscometer (Rheotek TCB-7) was used for viscosity determination

Production of Biodiesel from Olive Oil: 50ml (36.0g) of olive oil was measured and poured into a conical flask. The oil was preheated to 70^{o}C. Sodium hydroxide (0.225g) was weighed and added to 20ml of methanol in a conical flask. The sodium hydroxide and methanol were properly mixed by stirring till the entire pellet dissolves to form sodium methoxide solution. The sodium methoxide solution was poured into the preheated olive oil. The solution was mixed and stirred properly until homogeneity was achieved. This same procedure was followed while using potassium hydroxide as catalyst. The reaction mixture was maintained at a temperature of 70^{o}C for 1.5hr. The product was poured into a separating funnel and left overnight for proper settling of the glycerine produced.

Production of Biodiesel from Cashew Nut Oil – the same procedure as above was followed in the cashew nut biodiesel production.

Washing of Biodiesel: The products of the transesterification reaction Fatty Acid Methyl Esters (FAME) contain some impurities like unreacted methanol, potassium methoxide and the by product of biodiesel (glycerol) 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: 30ml 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[22]. The mixture of water and biodiesel was left for 5 hrs to settle into two phases which are; water-impurities phase and biodiesel phase. The two phase mixture was then separated using a separating funnel, drying is recommended. The yield of over 70% was obtained for both biodiesels

The Bomb Calorimeter: A calorimeter is a device used for measuring the heat of reactions, physical changes and heat capacity. A simply laboratory calorimeter like the Eco bomb calorimeter, can be used to measure calorific value (CV) of most liquid oils similar to that of solids like coal. This is done by placing a known mass of sample (not more than 1.5g) in a pressurized vessel, igniting the sample and finally measuring the heat value in a controlled environment. The method involves first calibrating the calorimeter using a pellet of benzoic acid (1.216 g). The pellet is then tied to a 13 cm length of cotton (0.080 g), placed inside the sample boat and attached to 7 cm length of nickel chrome wire (0.011 g) that was stretched between the electrodes. Oxygen is added through the gas inlet valve to give a pressure of 3000KPa and the system is ignited until the system indicates calibration is complete.

The pre weighed sample is placed into a crucible; the firing cotton placed in contact with the sample and the vessel pressured with oxygen gas. The firing cotton is then ignited and the sample gets ignited because of contact with the firing cotton. The burning of the sample leads to a rise in temperature of the vessel and the temperature of the vessel is very accurately measured by the Eco bomb calorimeter and this represents the calorimetric value of the sample. However, if a viscous sample is used, then a syringe can be used to place the oil into the crucible and a spatula should be used to place a non viscous sample into the crucible[23].

Results and Discussion

Table 1 summarises the records of blends and heat content of olive oil biodiesel, which shows that as the percentage of biodiesel is increasing from B2 to B50 in blend with petro diesel, the heat content decreases. The petrodiesel (P100) heat content obtained was 44.65 MJ/Kg

Blending reduces the rate at which petro diesel causes toxic emission and greenhouse gasses that lead to air pollution [24].

Figure 1 depicts the graphical representation of table-1, showing the trend as the petro diesel is blended with biodiesel. Indicating that as the percentage of blends increases the heat content decreases.

The difference in viscosity between the parent oil and the methyl ester derivatives can be used to monitor the biodiesel production. Figure 2 represents plot of the kinematic viscosity values (from table 2) of olive oil, its biodiesel and the petrodiesel. The viscosity values at the same temperature for olive oil biodiesel are greater than that of petrodiesel and below the viscosity of the pure oil samples. This therefore shows that viscosity values for a biodiesel can be adjusted to favour usage in engine system by blending with petrodiesel. The ASTM D975 standard for biodiesel at $40^{O}C$ lies within the range 1.9-6.0 mm^2/s and the value of $6.18 mm^2/s$ was obtained for olive oil biodiesel at $40^{O}C$.

Table 3 also shows similar result but different values compared to that of table 1. It shows that as the percentage of biodiesel is increasing from B2 to B50 in blending with petro diesel the lower the heat content.

The graphical representation is shown in figure 2 which shows the trend as petro diesel is blended with biodiesel and reveals that the heat content decreases as the blend increases.

Conclusion

In this research, biodiesel was produced from olive oil and cashew nut oil by the transesterification process considering the most prominent factors affecting the reaction which are temperature, catalyst concentration and the reaction time. The calorific value of the biodiesel produced was lower than petro-diesel calorific value. The result from the bomb calorimetric measure of the biodiesel – petrodiesel blend reveals that as biodiesel percentage increases, the heat content decreases. Though the lower the heat content of petro-diesel the lower energy it releases to diesel engines, great success is achieved in reducing the toxic emission that lead to environmental pollution. We have also shown that transesterication process of the pure olive oil reduced considerably its high viscosity value to that comparable with the viscosity of petro diesel. These above results will definitely be beneficial to the biodiesel producers, distributors, and end-users (customers), as a blend component help in developing cleaner air and healthy environment. As well, blending biodiesel with petrodiesel can be carried out to adjust viscosity values.

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Table 1: Records of blends and heat content of olive oil biodiesel

Blends of olive oil (B * X)	Heat contents (MJ/Kg)
Olive oil biodiesel (B100)	39.92
B2	44.50
B5	43.92
B20	43.15
B50	41.68

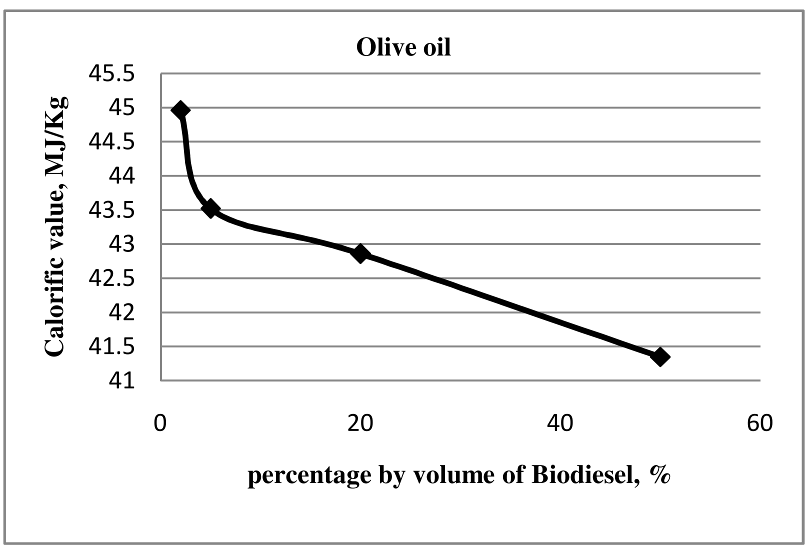


Figure-1: The plot of calorific value versus blends of olive oil biodiesel - diesel.

Table-2: Kinematic Viscosity of Samples Kinematic Viscosity (mm^2/s)

Temp (^{O}C)	Petrodiesel	Pure olive oil	olive oil biodiesel
30	5.7	55.85	6.72
35	4.74	54.39	6.48
40	4.41	44.67	6.18
45	4.29	37.53	5.7
50	4.17	32.13	5.55
55	4.02	27.09	5.28
60	3.87	23.52	5.13
65	3.81	20.61	4.92
70	3.72	18.36	4.77

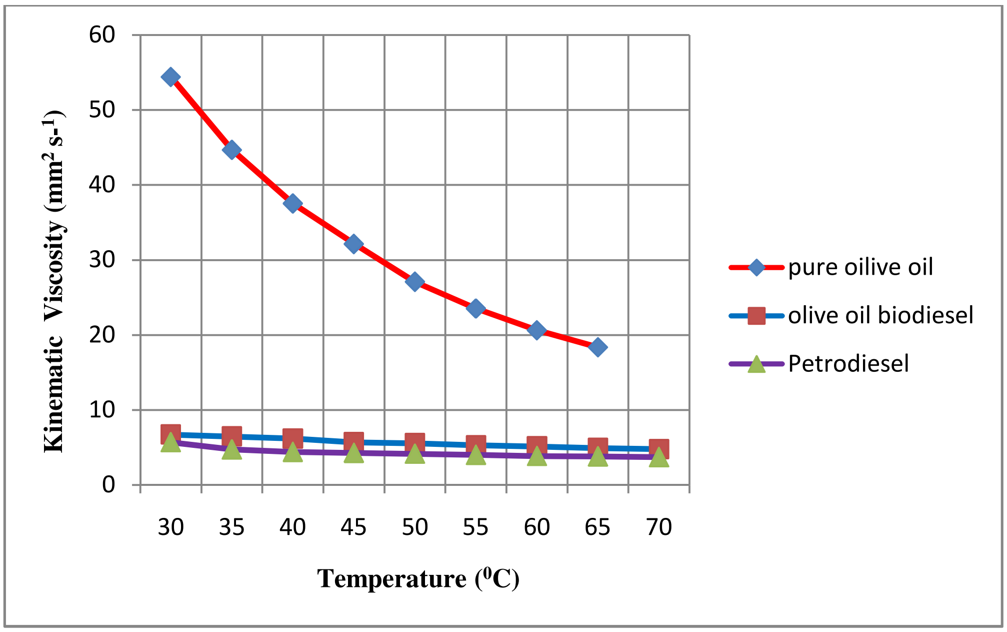
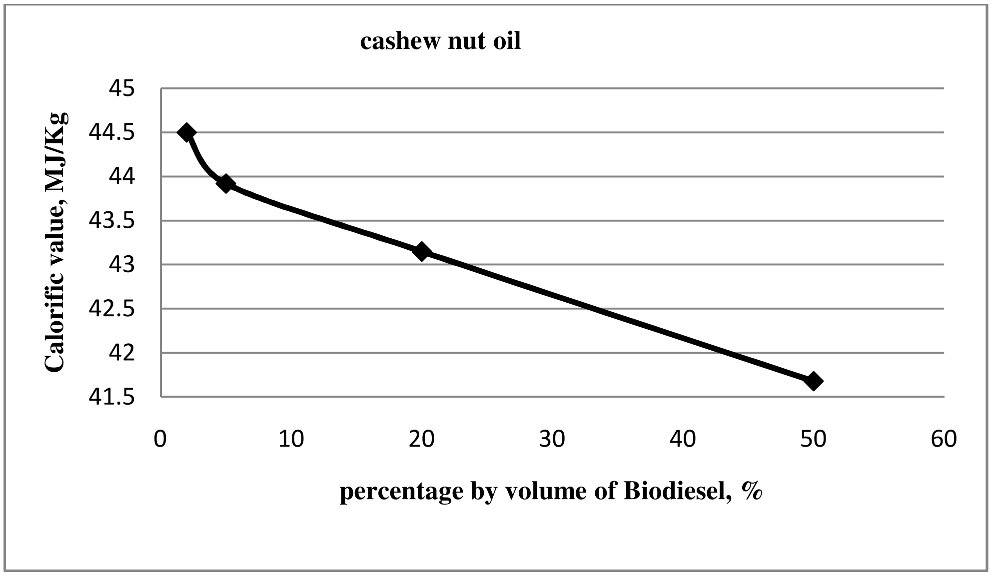


Figure-2: Kinematic viscosity of pure olive oil, olive oil biodiesel and petrodiesel at different temperature.

Table 3: Records of blends and heat content of cashew nut oil biodiesel

Blends of olive oil (B*X)	Heat contents (MJ/Kg)
Olive oil biodiesel (B100)	39.52
B2	44.96
B5	43.52
B20	42.86
B50	41.35

Figure-3: The plot of calorific value versus blend of cashew nut oil.


cashew nut oil
Calorific value, MJ/Kg
45
44.5
44
43.5
43
42.5
42
41.5
0
10
20
30
40
50
60
percentage by volume of Biodiesel, %