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Evaluation of Biodiesel Produced from Blends of Sunflower Oil and Beef Tallow Through Base Catalysis

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Abstract: The inclination towards climate change and environmental pollution mitigation directs this research toward creating an alternative fuel source to fossil fuel for use in developing tropical countries. This study is designed to investigate biodiesel (alkyl esters) obtained by transesterification of blends of refined sunflower oil and beef tallow using NaOH as catalyst. Triglycerides in the oils reacted with alkanols to produce fatty acid alkyl esters (FAAE) and glyerols as by-product. A pretreatment process of esterification was carried out to remove excess free fatty acids (FFA). Some physical properties such as pour point, cloud point, flash point, density and kinematic viscosity were investigated for the sunflower oil/beef tallow (SO/BT) ratios. The examined physical properties of the methyl esters changed significantly as the beef tallow ratio in the mixture increased in the mixtures. The ratios of 40%SO/60%BT and 60%SO/40%BT exhibited values within standard range of biodiesel and petroleum diesel of ASTM D 6751 and EN 1424. The values of the cold-flow properties of the biodiesel ratios obtained are of convenience for use in tropical regions rather than polar regions.

Keywords: Biodiesel, Alkyl Esters, Transesterification, Sunflower Oil, Beef Tallow, Kinematic Viscosity

1. Introduction

The production and use of fossil fuel in engines with internal combustion causes environmental problems such as rising carbon dioxide levels in the atmosphere, increasing the average ambient temperature of the Earth. In consequence, a global movement toward the renewable energy sources is one way to help to meet the increased energy needs of humanity [1]. Therefore, Research and development activities such as Biodiesel Production are carried out. Developing countries such as Nigeria, which relies heavily on imported refined petroleum products at about 30% of total imports, require substantial mitigation processes to reduce their carbon footprints [2]. Having alternative clean energy source is a necessity for the high-energy consumption in these countries. Biodiesel production is a safe and feasible process that can be carried out by individuals in their backyards. It substantially reduces emissions of un-burnt hydrocarbons, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons and particulate matter [3]. Similarly, biodiesel helps to reduce green-house gas emissions because the net level of carbon-dioxide in the atmosphere is not increased by burning biofuels owing to the fact that Green House gases produced during the combustion of biofuels are recycled as carbon-dioxide during photosynthesis and absorption process by plant [4]. Biodiesel is often blended with petroleum diesel to enable complete combustion of fossil fuels due to presence of oxygen in the biodiesel matrix [5]. Inedible Vegetable oils and animal fats are a convenient source for biodiesel in Nigeria. Oils such as beef tallow, sunflower oil and canola are not widely utilized for food in Nigeria. This is generally as a result of lack of refinement to improve the tastes and smells of such oils [6]. Thus, the innovation for using these oils as fuel source is a requirement in order to reduce the countries toxic emissions and provide a convenient energy source to power diesel engines. Recent projections of the cost of biodiesel show that the cost of biodiesel based on animal fats is less by 30-50% than that based on vegetable oils [1, 7, 17]. This is as a result of lack of utilization of animal for consumption through refining. Furthermore, exhaust emissions from beef-tallow-based biodiesel and its blends are lower than that of petroleum-based biodiesel, similar to those obtained from vegetable oils such as sunflower, canola, soya bean oils [8].

Biodiesel is produced simply by the reaction of fatty acids and alcohol to produce fatty acid alkyl esters FAAE (biodiesel) and glycerol as the by-product [9, 6]. Transesterification, also called alcoholysis, is the process of displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is used instead of water. Suitable alcohols include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are utilized most frequently, especially methanol because of its low cost and its physical and chemical advantages [10]. Thus, FAAE obtained by transesterification can be used as an alternative fuel for diesel engines [11]. These reactions are often catalyzed by the addition of an acid or base catalyst. The transesterification reactions are conventionally performed using homogeneous base or acid catalysts. Different groups of heterogeneous catalysts such as: metallic, solid bases, solid acids and natural catalysts can be also applied for efficiently converting oil/fat to ester [12]. This process has been widely used to reduce the viscosity of triglycerides, thereby enhancing the physical properties of renewable fuels to improve engine performance. Recently, biocatalysts like free-suspended or immobilized lipases are used as very promising reaction agents, although they have not yet been commercialized because of high price of operation [28].

This research implored the use of a base homogeneous catalysis whereby reaction conditions usually include alcohol: fat molar ratio around 6:1, catalyst amount of about 1% of the weight of oil used and a reaction temperature and time of 60°C and 1hr. Usually, fats contain high free fatty acids FFA content due to the degree of saturation which is the main factor determining the use of base or acid catalyst in the biodiesel production processes via transesterification reaction. The presence of base catalysts in the reaction mixture influences soap formation, catalyst loss and ester yield reduction. Also, they have a negative effect on process economy by complicating separation of final products (biodiesel and glycerol). Therefore, the use of base catalysts is preferable when the fats have a lower FFA content. However, these problems arise with using animal fats as a feedstock in the biodiesel production, such as poor solubility of tallow in methanol and high free fatty acid content, which cause soap to form with alkali catalysts [13, 5]. Therefore an esterification process is first carried out using an acid catalyst to lower the FFAs to a minimum [14].

2. Experimental

2.1. Materials

The feedstock used in this experiment is beef tallow and refined sunflower oil, incurred from a local retail market in Garki2, Abuja. All other reagents such as the alcohol and catalyst were available in the school biochemistry laboratory.

The methanol used was from Loba Chemie chemicals with 0.790-0.793g wt. per ml at 20°C, min 99.5% purity and NaOH from fine-CHEM Ltd was used as catalyst. For the esterification of beef tallow, H_2SO_4 of 97-98% purity from Kermel Company with about 1.834 wt. per ml at 20°C was used.

2.2. Methods

Sunflower oil (SO) and beef tallow (BT) were mixed at specific ratios of 95%SO/5%BT, 60%SO/40%BT, 40%SO/60%BT and 5%SO/95%BT.

2.2.1. Esterification

Given that animal fats such beef tallow content a higher amount of free fatty acids, a pretreatment process (esterification) was conducted; 1.5g of conc. H_2SO_4 were added to 150g of methanol. It was mixed and added slowly to 50g of melted beef tallow. It was stirred on a hot plate using a magnetic stirrer for an hour at 55-60°C. The mixture was allowed to settle. Methanol, water and sulfuric acid with excess FFA rose at the top. The top layer was decanted. The bottom layer fraction was then used for the transesterification process [13-17].

2.2.2. Transesterification

A mixture of 100g of methanol and a 1wt.% NaOH (1.0g) was stirred until complete dissolution of catalyst. The solution was then added to heated 50g of oil/fat, in a flat bottom flask and was stirred at 400rpm for 1hr30mins at a controlled temperature of 55-60°C [3, 6, 21]. A condenser was connected to avoid loss methanol before completion of reaction. The mixture was then put in a separating funnel and allowed to settle 24hrs [22]. Distinct fractions of biodiesel were decanted. 25% of methanol with corresponding catalyst to the top fraction was added to complete conversion of triglycerides. 3 drops of conc. H_2SO_4 was added to blends containing beef tallow to neutralize the reaction while being stirred [23]. It was allowed to settle in a separating funnel. The reaction formed a cloudy solution due to presence of water as a result of neutralization. 2g of Na_2CO_3 was added to the cloudy solution as drying agent and allowed to settle to 24hrs. Na_2CO_3 was filtered out from the methyl ester after complete absorption of water.

Transesterification of triglyceride with alcohol showing three consecutive and reversible reactions. R, R, R3 and R' represent alkyl groups [2].

Triglyceride		Alcohol		Fatty acid esters		Glycerol
CH_2-OOC-R_1			catalyst	R_1-COO-R'		CH_2-OH
CH-OOC-R_2	+	3R'OH	$\rightleftharpoons$	R_2-COO-R'	+	CH-OH
CH_2-OOC-R_3				R_3-COO-R'		CH_2-OH

$$\text{1. Triglyceride (TG) + R'OH} \xrightleftharpoons{\text{Catalyst}} \text{Diglyceride (DG) + R'COO}\boldsymbol{R_1}$$

$$\text{2. Diglyceride (DG) + R'OH} \xleftrightarrow{\text{Catalyst}} \text{Monoglyceride (MG) +R'COO}\boldsymbol{R_2}$$

$$\text{3. Monoglyceride (MG) + R'OH} \xrightleftharpoons{\text{Catalyst}} \text{Glycerol (GL) + R'COO}\boldsymbol{R_3}$$

2.2.3. Biodiesel Quality Properties

I. Percentage Yield: Arthur Jurj. [21], listed and described some technique that characterizes the quality of biodiesel according to percentage yield which they pointed as the most important analysis for biodiesel. It is a calculation that determines the amount biodiesel produced from an amount of oil used for transesterification. A high percentage yield verifies that an experiment was carried out well. Percentage yield is carried by;

$$\frac{\text{Actual value}}{\text{Theoretical value}} \times 100 = \text{Percentage Yield} \quad (1)$$

It is expected that the percentage yield for used biodiesel should be less than that of an esterified biodiesel, due to the fact that the used biodiesel was produced from a sample that had more amount of fatty acid present [24].

II. Density: is a factor, which influences the efficiency of atomization and depends on alkyl esters content and the remained amount of alcohol. The density values between 860 and 900 kg/m^3 are adopted by the EN14214 standard [25].

III. Kinematic viscosity: is the ratio of dynamic viscosity to the density of the fluid. Most fluids such as petrodiesel and biodiesel increase in viscosity with decreasing temperature. This is influenced primarily by the experimental conditions and the extent of the transesterification reaction [26].

IV. Flash point: The lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test. The flash point is a determinant for flammability classification of materials. The typical flash point of pure methyl esters is greater than 200°C, classifying them as non-flammable. However during production of biodiesel, not all the methanol may be removed, making fuel flammable and more dangerous to handle and store if the flash point falls below 130°C [27].

V. Cloud point and pour point: Initially, cooling temperatures cause the formation of solid wax crystal nuclei that are submicron in scale and invisible to the human eye. Further decreases in temperature cause these crystals to grow. The temperature at which crystals become visible is defined as the cloud point (CP) because the crystals usually form a cloudy or hazy suspension. Due to the orthorhombic crystalline structure, unchecked crystalline growth continues rapidly in two dimensions forming large platelet lamellae. At temperatures below CP, larger crystals fuse together and form large agglomerates that can restrict or cut off flow through fuel lines and filters and cause start-up and performance problems the next morning The temperature at which crystal agglomeration is extensive enough to prevent free pouring of fluid is determined by measurement of its pour point (PP) [29].

3. Results and Discussion

Percentage Yield of Biodiesel ratios

The percentage yield for biodiesel ratios obtained after transesterification were calculated using the formula: $Y=\frac{Actual\ Value}{Theoritical\ Value}\times 100$ the initial volume of used for all ratios was 55g.

***Table 1.** The ratios of SO and BT blends at 40/60% and 60/40% yielded more biodiesel than glycerin at the experimental temperature of 50-60°C.*

Biodiesel ratio SO/BT (%)	Initial volume (ml)	Final volume (ml)	Percentage Yield (%)
95%SO/5%BT	55.0	33.8	61.5
60%SO/40%BT	55.0	36.5	66.3
40%SO/60%BT	55.0	38.2	69.5
5%SO/95%BT	55.0	35.2	64.0

3.1. Effect of Ratio of SO/BT on the Pour Point and Cloud Point of Biodiesel

Poor low-temperature flow properties are one of the most important hurdles for biodiesel.

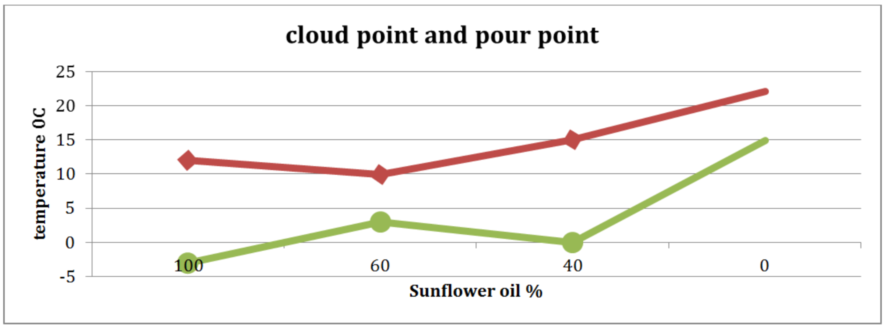

***Figure 1.** Effect of Ratio of SO/BT on cloud point and pour point.*

The cloud points and pour points of biodiesel samples in Figure 1 increased as the percentage of beef tallow in the mixtures increased. The increase in the saturated fatty acid ratio and the decrease in the unsaturated fatty acid were seen responsible for these increases [14]. Cloud points and pour points for the biodiesel are too high as compared to conventional diesel fuels. This set back makes biodiesel a poor or rather unsatisfactory for use in cold regions.

3.2. Effect of Ratio of SO/BT on Flash Point of the Biodiesel

The flash point is a significant safety indicator during the storage, transportation and operation of fuel.

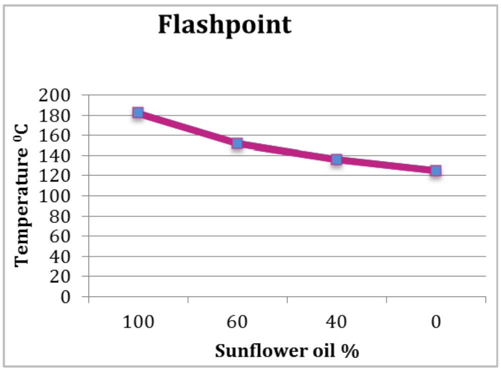

***Figure 2.** Effect of Ratio of SO/BT on Flash Point of the Biodiesel.*

The flash point of biodiesel is generally significantly higher than those of petroleum-derived fuels. Soybean methyl ester (SME), the biodiesel made from soybean oil feedstock, may have a flashpoint as high as 138°C or more [15]. The minimum flash point of biodiesel based on the EN14214 specification is 120°C. The flashpoints of biodiesel samples had favorable flash points, including the mixtures.

3.3. Effect of Ratio of SO/BT on Viscosity of Biodiesel

Viscosity of the biodiesel is important because of a proper operation engine, flowing of fuel through pipelines, injector nozzles, orifices, etc., and finally, effective atomization of the fuel in cylinders [20]. All viscosity measurements in this project were carried out at 40°C

Viscosities of the 95%sunflower oil and beef tallow were considerably higher than those of the blends as shown Figure 3. The kinematic viscosity increases for the fatty compound with an increase in the number of carbon atoms (chain length) and decreases with an increase in the number of double bonds primarily [18]. Other than these factors, position and nature of the double bond are other parameters influencing viscosity subordinately. Sunflower oil appears to have a high viscosity due to more fatty acid content consisting of about 67% linoleic acid. As Sunflower oil ratio drops off to 60% in the mixture, this referred to the simultaneous effect of decreasing linoleic acid and increasing oleic acid from the beef tallow methyl ester ratios in the biodiesel.

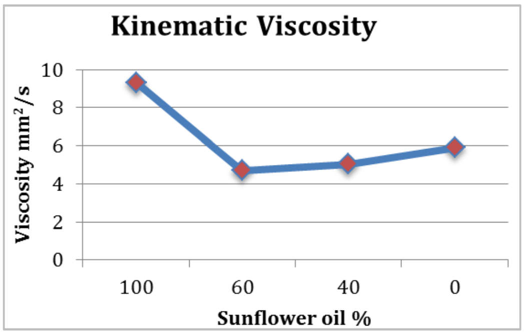

***Figure 3.** Effect of percentage of sunflower on Viscosity of biodiesel.*

3.4. Effect of Ratio of SO/BT on Density of Biodiesel

Density or specific gravity has been described as one of the most basic or important parameters of fuel as certain performance indicators such as heating value and cetane number are correlated with it [19].

The densities of the blends from 60% SO to 5%SO exhibited little variations unlike that of the 95%SO, which has higher than the other biodiesel samples. The density of the 95% SO could due to residual methanol in the sample. The lower the density or specific gravity of an oil, the higher it API [25]. Therefore, the sample with the lowest density is the 40%SO/60%BT.

General values obtained from performance tests on biodiesel blends was compared to standard values for diesel fuels:

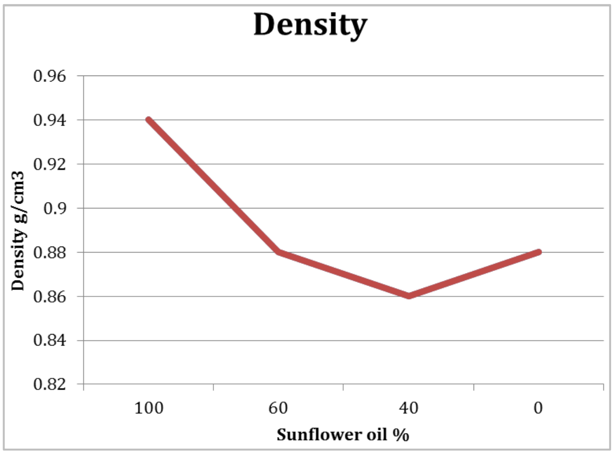

Figure 4. *Effect of percentage of Sunflower oil on Density of biodiesel.*

Table 2. *Biodiesel physical tests values compared to standard diesel values.*

Experimental Values of the Biodiesel					Standard Values of Diesel fuels		
Parameters	SO/BT=95%/5%	SO/BT=60%/40%	SO/BT=40%/60%	SO/BT=5%/95%	Petroleum diesel EN 590-1999	Biodiesel Europe EN 14214	Biodiesel USAASTM D 6751-07b
Density at 25°C g/cm^3	0.940	0.880	0.860	0.880	0.820–0.860	0.86-0.90	
Kinetic viscosity at 40°C mm^2/s	9.32	4.70	5.05	5.91	2.0–4.5	3.5-5.0	1.9–6.0
Flashpoint°C	182	152	136	125	55 min	120 min	130 min
Cloud point°C	12	10	15	22	–18	-	-
Pour point°C	-3	3	0	15	–25	-	-

The blends of biodiesel ratios produced as compared to the standard values biodiesel and petroleum diesel at EN and ASTM standards [29], have shown that the 40%SO/60%BT blend and 60%SO/40%BT blend are within standard values for all parameters. The pour point temperatures as compared to that of conventional petroleum diesel oil are much higher.. It was observed that the physical properties of biodiesel obtained from the 60% sunflower oil / 40% beef tallow and 40% sunflower oil / 60% beef tallow were sufficient in view of present ASTM and EN standards. At these mixture ratios, the levels of parameters were found to be: pour point=3°C, 0°C; cloud point=10°C, 15°C; kinematic viscosity at 40°C=4.7mm^2/s, 5.05mm^2/s. In addition to this, the flash point=152°C, 136°C and the density at 25°C=0.880g/cm3, 0.860g/cm3 for these ratios blend.

4. Conclusion

Beef tallow and sunflower oil have moderate values of physical properties required within biodiesel standards, such as the kinematic viscosity and pour and cloud point. Therefore, it can be put forward that beef tallow and sunflower oil can be used in high percentage as well as there mixtures or blends as biodiesel raw materials, without lowering biodiesel quality significantly as a feedstock in biodiesel production. It is necessary to take advantage of these fuel sources to reduce the raw material cost, which consists of up to 70% of the total cost of biodiesel. The optimization of biodiesel yields is using novel catalysts to boost production quantities are being researched by several scientists.

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