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Research Article

# Determination of Flow Properties of Refined Cotton Seed Oil Biodiesel

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**Abstract** In this study, the basic flow properties of cotton seed methyl ester like density, viscosity, cloud and pour points was carried out to determine the changes when fatty acid methyl ester was blended with diesel fuel. Empirical and generalized equations, validated by using measured values, to predict the density, viscosity, cloud and pour points of the blends.

In order to predict these properties, mixing rule was evaluated as a function of the volume fraction of biodiesel in the blend. The effect of biodiesel fraction on each of these properties and to the effects of temperature on the density and viscosity were investigated. The blends (B10 –B100) were prepared on a volume basis. Generalized equations and Arrhenius equation for predicting the density and viscosity of the blends were used. The low values of the absolute average deviations (AAD) and the maximum absolute deviations (MAD) obtained confirmed the solubility of the mixing rule used. For all the blends, it was observed that the results obtained from the measured and estimated values of density and viscosities were in good agreement. From the results, the density and viscosities of the blends decreased with increase in temperature while these properties increased with increase in biodiesel content in the fuel blend. The cloud point and pour point of the blend increased as the biodiesel concentration increased. The values obtained from empirical equations for predicting the relationship between cloud points, pour point and biodiesel content in the blends were in good agreement with the experimental value.

**Keywords** Cotton seed biodiesel, blend, flow properties, kinematic viscosity and Gibbs free energy

## 1. Introduction

The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Vegetable oils have very high viscosity for use in most existing diesel engines as a straight replacement fuel oil. There are a number of ways to reduce the viscosity of vegetable oils. One of the most common methods used to reduce oil viscosity is called transesterification. This process results in the production of a fuel comprised of mono alkyl esters of long chain fatty acids called biodiesel. Biodiesel is the most widely accepted alternative fuel for diesel engines due to its technical, environmental and strategic advantages.

Biodiesel is also the only alternative fuel that has passed the Environmental Protection Agency (EPA)-required Tier I and Tier II Health Effects testing requirements of clean Air Act Amendments of 1990 [1-2]. In addition, biodiesel is a promising alternative to crude oil-derived diesel fuels because it is renewable, significantly reduces particulate matter, hydrocarbon, carbon monoxide and life cycle net carbon dioxide emissions from combustion sources [1, 3-4]. Because of these advantages, biodiesel has gained considerable attention in recent years.

Biodiesel has enhanced biodegradability, toxicity and improved lubricity in comparison with convectional diesel fuels. In addition, it is completely miscible with petroleum diesel, allowing the blending of these two fuels in any proportion [3]. In addition, it has the potential to relieve the non-crude oil producing countries from their dependence in foreign crude oil.

Edible and non-edible vegetable oils remain the major feedstock for biodiesel production. Tallow or animal fats, used cooking oil and algae have also been used [4]. When using biodiesel in unmodified diesel engines, one issue that needs to be addressed is that biodiesel fuels have different properties from petroleum diesel. Biodiesel, produced from vegetable oils or animal fats, generally has higher density, higher viscosity, higher cloud point and higher cetane number, and lower volatility and heating value compared to commercial grades of diesel fuel [5]. Other drawbacks of biodiesel include worse low temperature properties, greater emissions of some oxygenated hydrocarbons, higher specific fuel consumption and decrease in brake thermal efficiency [6-7]. Engine manufacturers have raised concerns about some these properties as they may affect the engines performance and emissions since the engines were originally optimized with petroleum diesel [8]. Although B100 (100 volume % biodiesel) is rarely used, when these limits are met, the biodiesel can be used in most modern engines without modifications while maintaining the engine’s durability and reliability [9-10]. Although biodiesel is miscible with petroleum diesel in any proportion, not all the blend proportions may be used in in diesel engines. The Engine Manufacturers Association (EMA) reported that biodiesel blends up to 5% should not cause engine and fuel systems problems [11]. Blends of up to B20 (20 volume % biodiesel and 80 volume % petroleum diesel) mixed with petroleum diesel can be used in nearly all diesel equipment and are compatible with most storage and distribution equipment [9, 12]. Hence the warranty on most new engines only allows a maximum of B20 to be used [13]. It is asserted that 90% of air toxics can be eliminated by using B100 whereas 20 to 40% are reduced using [14]. However, if the full benefits of biodiesel as a renewable fuel are to be realized, it must be used in a greater proportion. Therefore, to further tap into the benefits of using biodiesel, there is the need to increase ratio of biodiesel in biodiesel- diesel blends.

It is important to know the basic properties of biodiesel-diesel blends as some of these properties are required as input data for predictive and diagnostic engine combustion models. In addition, it is necessary to know if the fuel resulting from the blending process meets the standard specifications for diesel fuels [3]. Density and kinematic viscosity are the parameters required by biodiesel and diesel fuel standards because they are key fuel properties for diesel engines [15]. Density directly affects the engine performance characteristics, and it is used as a precursor for a number of other fuel properties such as heating value and viscosity [1]. On the other hand, diesel fuel injection systems measure the fuel by volume. So the changes in the fuel density will influence engine output power due to a different mass of fuel injected [15]. Even more, density kinematic viscosity is an important property regarding fuel atomization, as well as fuel distribution. High viscosity causes poor atomization during the spray, increases the engine deposits, needs more energy to pump the fuel and wears fuel pump elements and injectors [16].

The density and viscosity of the fuels affect the start of injection, the injection pressure, and the fuels spray characteristics, so that they influence the engine performance, combustion and exhaust emissions [9]. Analysis of these results can easily be carried out when the key properties of biodiesel-diesel fuel blends are known. As the fuel properties differ from those of diesel fuels, the different engine performance and emissions will occur when biodiesel is used in diesel engines. Therefore, more investigations are needed about the fuels before using them in a diesel engine. Various techniques or methods and empirical model have been developed for measuring and predicting the density and viscosity of pure biodiesel and its blends with diesel [8, 17-21].The cloud and pour points of biodiesel cab be reduced by blending it with no 2 diesel fuel as the cloud and pour points of biodiesel are higher than petroleum diesel. Also, the lubricity of petroleum diesel increases on addition to biodiesel [22]. Various techniques and empirical models have been developed for cloud and pour points measurements of pure biodiesel from different feed stocks and its blends with diesel fuels [22-23]. Both cloud and pour points of biodiesel and its blends with diesel fuel decreases with biodiesel concentration and by the addition [24] of pour point depressants [25-26].

However, in spite increasing attention on biodiesel globally, the production and consumption have not been felt in Nigeria [27]. Hence this piece, involves determining some of basic flow properties of cotton seed oil and their blends with diesel fuel as function of biodiesel fraction and temperature, and comparing Andrade and Erying equations in order to evaluate the thermodynamics fuels’ flow.

## 2. Materials and Methods

### 2.1. Materials

Refined cotton seed oil was procured from Shoprite, Enugu, Nigeria and petrodiesel was obtained from Total filling station, Awka, Nigeria.

### 2.1.1. Biodiesel Production and blend preparation

50 ml of oil was measured using measuring cylinder and poured into a conical flask. The oil was pre-heated to 50 °C (using water bath with temperature regulator). 0.6 g of sodium hydroxide pellets was weighed and added to 10ml methanol. The mixture was stirred until the pellets dissolved into solution of sodium methoxide. The sodium methoxide solution was then added to the pre-heated oil in a 250ml three-neck glass flask equipped with flat-blade impeller. The impeller was placed centrically close to the bottom. The flask was immersed in a glass chamber filled with water circulating from a thermostatic bath by means of pump. Mixing was continued were maintained until homogeneity was achieved. The reaction mixture was maintained at a temperature of 65°C for 2 hours. The product of the reaction was kept overnight for proper settling of the biodiesel produced. The product was separated from glycerol using separating funnel.

The product of the transesterification reaction of Fatty Acid Methyl Ester (FAME) contained some impurities like unreacted methanol, sodium methoxide and sodium alkylate (soap). The impurities were removed before biodiesel was used for blending.

50 ml of water was measured using measuring cylinder and poured gently on the product sample. The mixture was gently stirred to avoid foam formation. The mixture of water and biodiesel was left for some hours to settle into two phases namely; water- impurities phase and biodiesel phase. The two phase mixture was then separated using separating funnel. The biodiesel layer was then heated to 100 °C for 1 hour to evaporate the remaining water molecules in it. The biodiesel was characterized according to ASTM standard and Nigeria standards as described [28].

Biodiesel from cotton seed oil and petrodiesel were splash blended in 250 ml conical flask with continuous stirring to ensure uniform mixing. The properties of petrodiesel are listed in Table 1.

### 2.1.2. Viscosity measurement

Dynamic viscosity measurements were made with Brookfield viscometer in a constant temperature water bath. For viscosity as a fraction of biodiesel, the experimental data have been correlated by empirical second-degree polynomial equation and polymath software 5.1 was used to determine the constants.

$$\eta = Ax^2 + Bx + C \tag{1}$$

Where A, B, C are constants

The variation of kinematic viscosity with temperature for different types of fluids is commonly represented with empirical second degree equation [9].

$$\eta = \exp\left(A + {}^{B}\!/_{T} + {}^{C}\!/_{T^2}\right) \tag{2}$$

Where η is the kinematic viscosity (mm$^2$/s) and T is temperature (°C) and A, B and C are fluid constants. This equation can be termed a second order polynomial equation in 1/T and the values of A, B and C was done using polymath 5.1 version software. The values of A, B and C are presented in Table 3 below.

The mixing used was proposed by Arrhenius. This equation makes use of mole fraction and absolute viscosity. Although, volume fraction and kinematic viscosity was used in the study because the estimated values were close to the measured values.

Therefore, Arrhenius- type equation:

$$\ln \eta_B = V_{CSB} . \ln \eta_{CSB} + V_D . \ln \eta_D \tag{3}$$

Where $\eta_B$, $\eta_{CSB}$, $\eta_D$ is the kinematic viscosities of the blend, cotton seed oil biodiesel and diesel respectively (mm$^2$/s), and $v_{csb,}$ $v_D$is the volume fraction of cotton seed oil biodiesel and diesel respectively. The use of Arrhenius-type equation has been found to be useful in predicting the viscosity of biodiesel- diesel fuel blends without needing viscosity measurements. Hence, the viscosity of the blends were calculated from equation (2) and validated by using the measured viscosity values. As in density, the equations obtained from regression analysis by using the measured values, were used to estimate the dependence of viscosity of the biodiesel blends on biodiesel fraction and temperature respectively. Mixing rules were used to estimate the basic properties of blends as a function of pure fuel properties and biodiesel content. The suitability of these rules was evaluated by means of absolute average deviation (AAD) and maximum average deviation (MAD), and calculated as;

$$AAD = \frac{100}{N} \sum \left| \frac{EXP - CAL}{EXP} \right| \tag{4}$$

$$MAD = \max 100 * \left| \frac{EXP - CAL}{EXP} \right| \tag{5}$$

Where N is the number of experimental points, EXP and CAL stand for experimental and calculated values respectively.

### 2.1.3. Density

Density of biodiesel and biodiesel blend was measured using the density bottle to measure the density and specific gravity of the cotton seed biodiesel, diesel fuel and their blends. The biodiesel and the blends were cooled to 29°C before taking the measurements with density bottle. The tests were carried out twice and the average results recorded. The measured density of biodiesel and their blends with petro diesel were correlated as a function of biodiesel fraction and temperature respectively using the linear square method. The linear regression equations formulated are as follows:

$$\rho = a(T) + b \tag{6}$$

Where T is the temperature (°C), $\rho$ is the density in (kg/m$^3$), sg is the specific gravity, a and b are correlation coefficients.

$$\rho = Ax + B \tag{7}$$

Where $\rho$ is the density (kg/m$^3$), A and B are coefficients and x is the biodiesel fraction.

The density of the blends was also evaluated from the densities of each component using the equation [8].

$$\rho_{blends} = \rho_{iX_i} \tag{8}$$

$\rho_{blends}$ and$\rho_i$ and represent the density of the blends and the component i respectively, and $X_i$ is the biodiesel fraction.

The calculated values for the cotton seed biodiesel and its blends were compared with measured values and the results are shown in Table 4. This equation has been employed to calculate the densities of the blends based on the measured densities of the pure biodiesel and the petrodiesel fuel. The results are used to determine the applicability of the blending rule to the tested biodiesel fuel according to [8].

### 2.1.4. Cloud and Pour points measurements

The cloud point (CP) and pour point (PP) were measured according to the method described [29].

## 3. Results and Discussion

### 3.1. Characterization of biodiesel and petrodiesel

The basic properties of biodiesel and petrodiesel are presented in the Table below.

**Table 1:** Basic properties of cotton seed oil biodiesel at 29°C

| Properties | cotton seed biodiesel | Petroelum diesel |
|---|---|---|
| Density (kg/m$^3$) | 860 | 854 |
| Kinematic viscosity (mm²/s) | 6.81 | 3.94 |
| Acid value (mgKOH/g) | 0.24 | 0.3 |
| Flash point (°c) | 173 | 54 |
| Pour point (°c) | 5.0 | -19 |
| Cloud point (°c) | 7.0 | -12 |
| High heating value (MJ/kg) | 39.54 | 45 |
| Cetane number | 56.06 | 48-65 |
| Ester value (mg/g) | 165 | - |

### *3.2 Viscosity and density results*

Many national standards on biodiesel give the density of biodiesel from 860kg/m$^3$*to 900kg/m$^3$ [30]. The density of cotton seed oil biodiesel produced is 860kg/m$^3$. Petroleum diesel has a lower density than biodiesels. The density and viscosity of biodiesel has been known to depend on the fatty acid composition of the mixed esters and their purity [17]. Also, the density of diesel fuel varies depending on the refinery feedstock and the blending streams in the diesel fuel boiling range. The density of the blends will lie between the values of pure biodiesel and diesel fuel. Table 4 shows the measured density values, the calculated density values from regression analysis, the regression coefficient, the absolute error and percentage error in equation (7). The measured and calculated values are in good agreement. The minimum regression coefficient ($R^2$) is 0.9820 for the biodiesel-diesel blends. The maximum absolute error between the measured and calculated density values is 0.048%. According to some standards such as UNI 10635 (Italy) and SS 15543 (Sweden), at 4O°c the viscosity of biodiesel falls between 1.9 and 6.0mm²/s. The viscosities of biodiesel fuels are higher than those of diesel fuels. Hence it is expected that the viscosities of the blends will fall in the range between the pure biodiesel and the diesel fuel. Table 2 shows the measured and calculated viscosity values from regression analysis, the regression coefficient, absolute and percentage error obtained in equations (1) and (3), respectively. The minimum regression coefficient ($R^2$) is 0.9930 for the fuel blends. The maximum percentage error obtained from equation (4) is 1.65 as compared to 0.75% from equation (3).* Table 3 also shows the root mean square deviations (Rmsd) for the correlations and the lowest temperature at which repeatable viscosity data could be collected before the onset of crystallization. From the Table 3, it can be seen that the deviations are smaller for the mixtures with diesel fuel; this is probably due to the viscosity being closer to that of biodiesel. Hence, the model with smaller Rsmd represent the data accurately than the one with larger values and it agrees with the results from previous work done [19].

**Table 2:** Measured and calculated viscosity value of cotton seed biodiesel-diesel blends.

| **Vol. of biodiesel** | **Measured** | **Calculated** | **Error %** | **Absolute error %** | **Ax10$^{-5}$** | **B** | **C** | **R²** |
|---|---|---|---|---|---|---|---|---|
| B0 | 4.200 | 4.200 | 0.0000 | 0.0000 | 5.500 | 0.024 | 3.210 | 0.998 |
| B10 | 4.410 | 4.4207 | 0.0110 | 0.0250 | 6.000 | 0.023 | 3.650 | 0.997 |
| B20 | 4.740 | 4.6029 | 0.0970 | 0.0340 | 6.500 | 0.020 | 3.620 | 0.996 |
| B30 | 4.980 | 4.8203 | 0.1620 | 0.3201 | 7.000 | 0.019 | 3.516 | 0.998 |
| B40 | 5.030 | 4.9943 | 0.1157 | 0.0230 | 7.000 | 0.014 | 2.618 | 0.997 |
| B50 | 5.200 | 5.1671 | 0.0329 | 0.0063 | 7.000 | 0.012 | 2.145 | 0.996 |
| B60 | 5.600 | 5.4014 | 0.1086 | 0.0190 | 7.000 | 0.011 | 2.140 | 0.997 |
| B70 | 6.030 | 5.9410 | 0.0890 | 0.0160 | 6.000 | 0.015 | 1.821 | 0.994 |
| B80 | 6.400 | 6.3885 | 0.1150 | 0.0017 | 3.000 | 0.006 | 1.557 | 0.994 |
| B90 | 6.750 | 6.6407 | 0.1093 | 0.0160 | 2.320 | 0.004 | 1.350 | 0.996 |
| B100 | 6.810 | 6.8100 | 0.0000 | 0.0000 | 1.100 | 0.002 | 1.202 | 0.993 |

**Table 3:** Viscosity correlation coefficients using (Eq.2) and statistics.

| **Vol. of biodiesel** | **A** | **B** | **C** | **R$^2$** | **Rmsd** |
|---|---|---|---|---|---|
| B0 | 11.0935 | -0.0462 | 4.692x 10$^{-5}$ | 0.9865 | 0.0178 |
| B10 | 8.6467 | -0.0315 | 2.542x 10$^{-5}$ | 0.9758 | 0.0182 |
| B20 | 10.5267 | -0.0425 | 4.219x 10$^{-5}$ | 0.9901 | 0.0147 |
| B30 | 12.4867 | -0.0542 | 5.994x 10$^{-5}$ | 0.9893 | 0.0149 |
| B40 | 7.4084 | -0.2393 | 1.542x 19$^{-5}$ | 0.9896 | 0.0145 |
| B50 | 3.5293 | -6.9890 | 1.860x 10$^{-5}$ | 0.9893 | 0.0144 |
| B60 | 8.7051 | -0.0325 | 3.055x 10$^{-5}$ | 0.0964 | 0.0242 |
| B70 | 10.9857 | -0.0453 | 4.903x 10$^{-5}$ | 0.9852 | 0.0157 |
| B80 | 12.6472 | -0.0566 | 6.867x 10$^{-5}$ | 0.9560 | 0.0232 |
| B90 | 10.6628 | -0.0447 | 5.133x 10$^{-5}$ | 0.9424 | 0.0260 |
| B100 | 9.3860 | -0.0375 | 4.189x 10$^{-5}$ | 0.9747 | 0.0155 |

**Table 4:** Measured and Calculated density of cotton seed biodiesel-diesel blends using equation (7).

| Fuel sample | A | B | $R^2$ | Measured | Calculated | Absolute error | error % |
|---|---|---|---|---|---|---|---|
| 0 | 0.701 | 840.4 | 1.000 | 833.4 | 832.9 | 0.0005 | 0.006 |
| B10 | 0.695 | 846.1 | 0.999 | 838.7 | 838.5 | 0.0002 | 0.002 |
| B20 | 0.710 | 850.7 | 1.000 | 843.6 | 843.1 | 0.0005 | 0.006 |
| B30 | 0.705 | 855.9 | 1.000 | 848.9 | 842.2 | 0.0067 | 0.079 |
| B40 | 0.469 | 867.7 | 0.982 | 854.2 | 853.7 | 0.0005 | 0.006 |
| B50 | 0.469 | 873.0 | 0.982 | 859.5 | 859.0 | 0.0005 | 0.006 |
| B60 | 0.469 | 878.3 | 0.982 | 864.8 | 864.3 | 0.0005 | 0.006 |
| B70 | 0.469 | 883.6 | 0.982 | 870.1 | 869.6 | 0.0005 | 0.006 |
| B80 | 0.469 | 888.9 | 0.982 | 875.4 | 874.9 | 0.0005 | 0.006 |
| B90 | 0.469 | 894.2 | 0.982 | 880.7 | 880.1 | 0.0006 | 0.007 |
| B100 | 0.469 | 899.5 | 0.982 | 886.0 | 882.4 | 0.0036 | 0.040 |

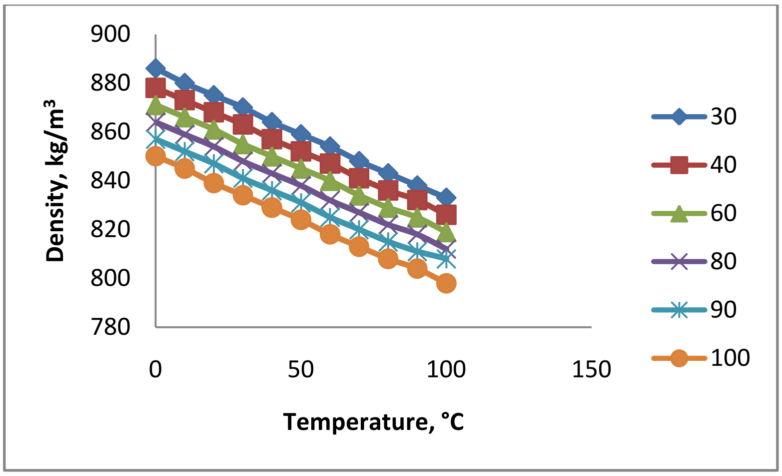


*Figure 1: Variation of density of cotton seed biodiesel-diesel blends with temperature*

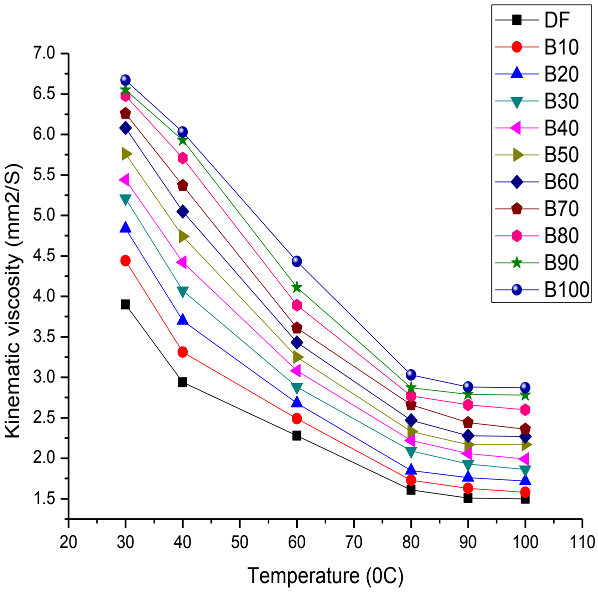


*Figure 2: Variation of kinematic viscosity of cotton seed for biodisesel-diesel blends with temperature*

**Table 5:** Regression constants and Regression coefficient for viscosity as a function of temperature using equation (2).

| **Fuel** | **A** | **B** | **C** | **$R^2$** |
|---|---|---|---|---|
| DF | 0.001 | 0.046 | 5.290 | 0.987 |
| B10 | 0.001 | 0.042 | 4.700 | 0.956 |
| B20 | 0.001 | 0.039 | 5.462 | 0.994 |
| B30 | 0.0002 | 0.021 | 5.106 | 0.986 |
| B40 | 0.0002 | 0.027 | 5.467 | 0.991 |
| B50 | 0.0003 | 0.029 | 5.737 | 0.992 |
| B60 | 0.0002 | 0.028 | 5.868 | 0.996 |
| B70 | 0.0001 | 0.023 | 6.702 | 0.995 |
| B80 | 0.0001 | 0.009 | 5.993 | 0.989 |
| B90 | 0.0003 | 0.019 | 5.907 | 0.993 |
| B100 | 0.0002 | 0.021 | 5.624 | 0.997 |

### 3.3 Cloud and Pour Points measurements

Cloud and pour points are the key flow properties for winter fuel specification. The pou point is always lower than the cloud point. All biodiesel fuels exhibit poor cold flow properties with cloud and pour points higher than those of petroleum diesel fuel and the same,applies to cotton seed biodiesel. The results of measured, calculated values, absolute error and

percentage error of the cloud and pour points of cotton seed biodiesel and its blends are shown in tables 6 and 7 respectively. The experimental measurment was further correlated as a function of blend by a second – order polynomial model and plotted on Figures (3), (4)and (5) respectively. Regerssion analysis of the data using Polymath 5.1 software and shows that the polynomial equation is a better fit for the measured values than a linear equation.

**Table 6:** Measured and calculated cloud point values

| **Blend** | **Measured Cloud point (K)** | **Calculated Cloud point (K)** | **Absolute error %** | **Error %** |
|---|---|---|---|---|
| B0 | 261.0 | 262.0 | 1.0000 | 0.0030 |
| B10 | 263.2 | 262.9 | 0.3000 | 0.0011 |
| B20 | 264.5 | 263.9 | 0.6000 | 0.0023 |
| B30 | 265.9 | 265.2 | 0.7000 | 0.0026 |
| B40 | 267.0 | 266.7 | 0.3000 | 0.0011 |
| B50 | 268.5 | 268.3 | 0.2000 | 0.0074 |
| B60 | 269.8 | 270.2 | 0.4000 | 0.0015 |
| B70 | 271.0 | 272.2 | 1.2000 | 0.0044 |
| B80 | 274.0 | 274.4 | 0.4000 | 0.0015 |
| B90 | 277.0 | 276.8 | 0.2000 | 0.0007 |
| B100 | 280.0 | 279.4 | 0.6000 | 0.0020 |
| AAD = 0.25%, MAD = 0.74% | | | | 0.0276 |

**Table 7:** Measured and calculated pour point values

| **Blend** | **Measured pour point (K)** | **Calculated pour point (K)** | **Absolute error %** | **Error %** |
|---|---|---|---|---|
| B0 | 254.0 | 254.8 | 0.8000 | 0.0031 |
| B10 | 255.8 | 256.0 | 0.2000 | 0.0008 |
| B20 | 258.0 | 257.3 | 0.7000 | 0.0027 |
| B30 | 259.8 | 259.0 | 0.8000 | 0.0031 |

| | | | | |
|---|---|---|---|---|
| B40 | 262.0 | 260.9 | 1.1000 | 0.0042 |
| B50 | 263.0 | 263.0 | 0.0000 | 0.0000 |
| B60 | 264.4 | 265.4 | 1.0000 | 0.0037 |
| B70 | 267.0 | 268.1 | 1.1000 | 0.0041 |
| B80 | 270.0 | 271.0 | 1.0000 | 0.0037 |
| B90 | 275.3 | 274.2 | 1.1000 | 0.0040 |
| B100 | 278.0 | 277.6 | 0.4000 | 0.0014 |
| AAD = 0.28%, MAD = 0.42% | | | | 0.0308 |

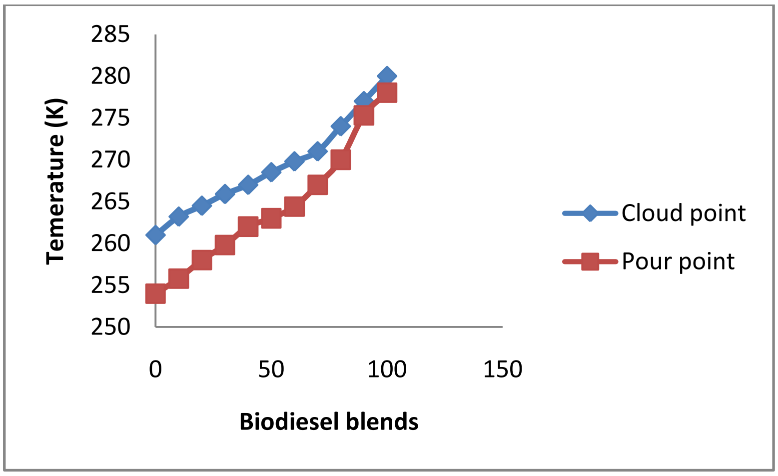


*Figure 3: Variation of Cloud and pour point with biodiesel and biodiesel – petrodiesel blends.*

The proposed equations for the calcualation of cloud point and pour point of cotton seed biodiesel as a function of its blend is:

$$T_{CP} = 261.95 + 0.0809V_B + 0.0009336V_B^2 \quad (9)$$

$$T_{PP} = 254.80 + 0.0995V_B + 0.0012844V_B^2 \quad (10)$$

Where $T_{CP}$ is the cloud point temperature, $T_{PP}$ is the pour point temperature, and $V_B$ is the volume of biodiesel. The cloud and pour points of biodiesel decrease as the biodiesel fraction in the mixture increases. Figure 4 and 5 shows the graph of the predicted value and the measured values. This shows that measured and predicted are in good agreement. This is further indicated by the values of $R^2$, absolute average deviation (AAD) and maximum standard deviation, MAD.

Equation (9) gives AAD = 0.25%, MAD = 0.74% and $R^2$ = 0.9882, While equation (10) AAD = 0.28, MAD =0.42% and $R^2$ = 0.9837.

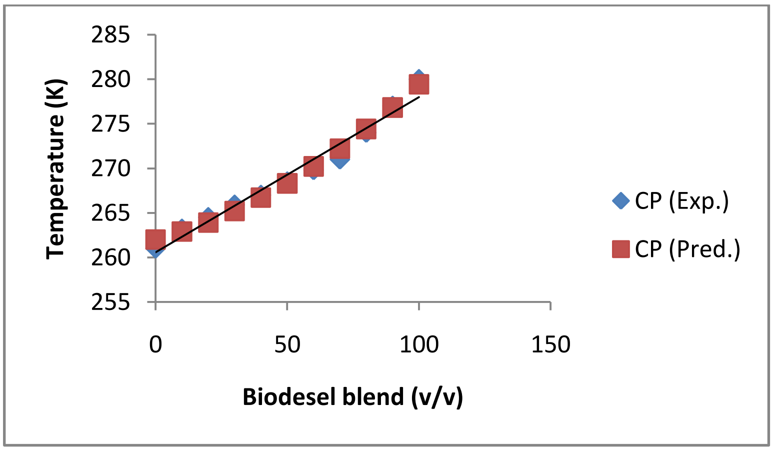


*Figure 4: Measured CP (Exp.) and predicted value CP (Pred.) of cloud point of biodiesel and its blend*

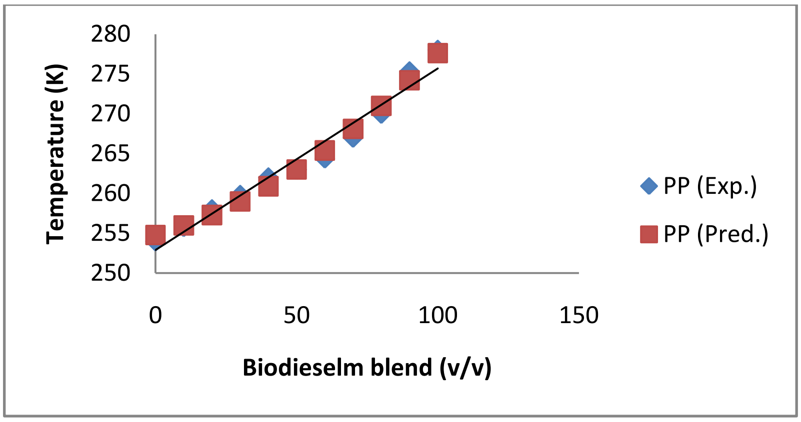


*Figure 5: Measured PP (Exp.) and predicted value PP (Pred.) of pour point of biodiesel and its blend*

### 3.4 Effect of temperature

The density was measured as a function of temperature for the pure biodiesel, diesel and their blends are shown in figure 1. In figure 1, the points indicate the measured values whereas the lines are linear square regression lines. In the temperature range (30-100°C) studied, the biodiesel fuel and its blends with diesel fuel have a similar linear density-temperature relationship. The regression lines closely follow the measured values. Hence there are no qualitative differences in the behaviour of the different blends. Linear regression was used to correlation the experimental values and presented in table 4. From the table, it can be seen that the value of regression coefficient ($R^2$) is higher than 0.98 in all cases showing that the linear regression can represent very closely the density-temperaure relation for the fuels tested.

### 3.5 Effect of biodiesel fraction

Figure 6 shows the variation of density of cotton seed biodiesel-diesel blends with biodiesel fraction. The measured points correspond to the points and calculated data as a line from regression analysis. The figure also shows that the density of the blend gets closer that of that of diesel fuel as the biodiesel content decreases in the blend. Hence the density of the fuel blend increases with increase in the amount of biodiesel in the blend. The predicted errors AAD and MAD for biodiesel-diesel fuel blend for density at various temperatures are presented in Table 5.

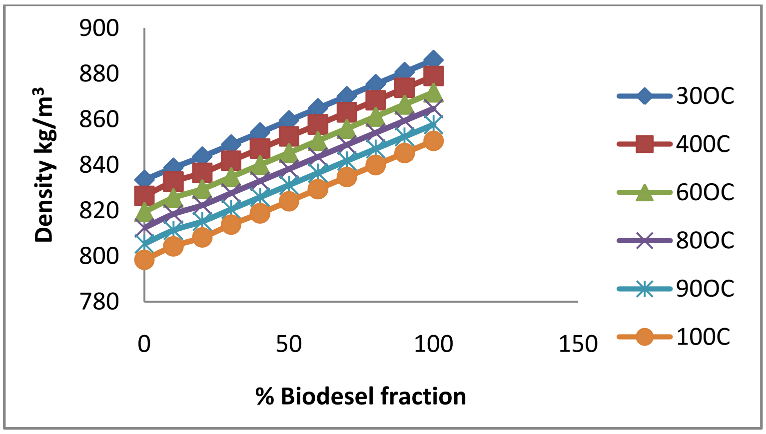


*Figure 6: Variation of density of cotton seed biodiesel-diesel blends with biodiesel fraction.*

The absolute average deviation (AAD) and maximum average deviation (MAD) estimated from the blend density are 0.028% and 0.480% respectively.

Figure 7 shows the variation of viscosity of the blend with biodiesel fraction. The figure indicates that the biodiesel fraction in the mixtures increases as the viscosity of the blend increase. Figures 6 and 7 are identical showing that viscosity does not change for blends up to 20% [2, 9, 31]. The AAD and MAD obtained using the chosen mixing rule for estimating viscosity 0.025% and 0.200% respectively.

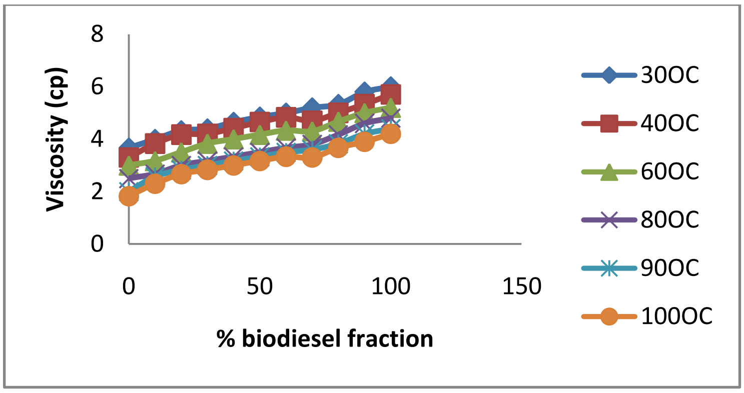


*Figure 7: Variation of viscosity with biodiesel-diesel fuel blends with biodiesel fraction.*

**Table 8:** Prediction errors for cotton seed biodiesel-diesel fuel blend for density at various temperatures

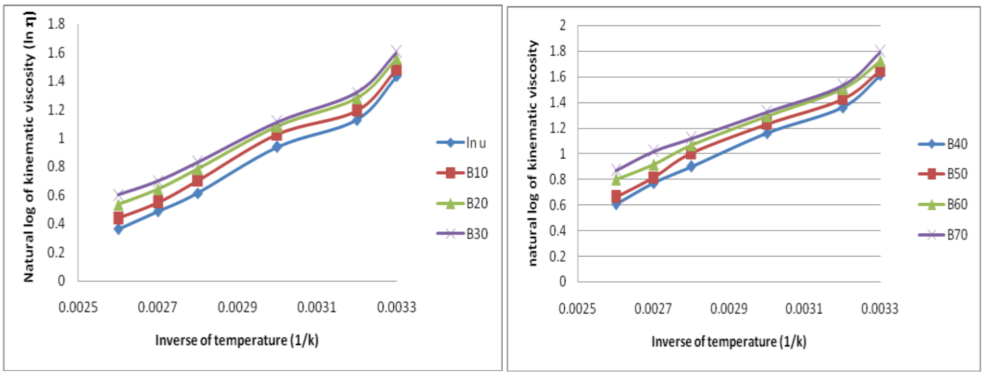
| **Vol. of biodiesel** | **Density at 30°C** | | **Density at 40°C** | | **Density at 60°C** | | **Density at 80°C** | | **Density at 90 °C** | | **Density at 100 °C** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AAD (%) | MAD (%) | AAD (%) | MAD (%) | AAD (%) | MAD (%) | AAD (%) | MAD (%) | AAD (%) | MAD (%) | AAD (%) | MAD (%) |
| B0 | 0.005 | 0.033 | 0.020 | 0.100 | 0.005 | 0.073 | 0.030 | 0.080 | 0.004 | 0.051 | 0.024 | 0.120 |
| B10 | 0.002 | 0.012 | 0.014 | 0.010 | 0.005 | 0.072 | 0.030 | 0.080 | 0.004 | 0.051 | 0.026 | 0.130 |
| B20 | 0.005 | 0.033 | 0.020 | 0.100 | 0.005 | 0.073 | 0.030 | 0.080 | 0.004 | 0.051 | 0.026 | 0.120 |
| B30 | 0.072 | 0.480 | 0.004 | 0.020 | 0.005 | 0.073 | 0.054 | 0.150 | 0.006 | 0.080 | 0.006 | 0.031 |
| B40 | 0.005 | 0.033 | 0.020 | 0.100 | 0.005 | 0.073 | 0.030 | 0.080 | 0.004 | 0.051 | 0.024 | 0.120 |
| B50 | 0.005 | 0.033 | 0.020 | 0.010 | 0.005 | 0.073 | 0.030 | 0.080 | 0.004 | 0.051 | 0.023 | 0.110 |
| B60 | 0.005 | 0.033 | 0.020 | 0.010 | 0.005 | 0.073 | 0.030 | 0.080 | 0.004 | 0.051 | 0.023 | 0.110 |
| B70 | 0.005 | 0.033 | 0.020 | 0.010 | 0.004 | 0.060 | 0.030 | 0.080 | 0.004 | 0.051 | 0.001 | 0.004 |
| B80 | 0.005 | 0.033 | 0.020 | 0.010 | 0.005 | 0.073 | 0.030 | 0.080 | 0.004 | 0.051 | 0.023 | 0.110 |
| B90 | 0.006 | 0.040 | 0.020 | 0.010 | 0.005 | 0.073 | 0.027 | 0.200 | 0.001 | 0.014 | 0.026 | 0.130 |
| B100 | 0.036 | 0.024 | 0.006 | 0.030 | 0.02 | 0.326 | 0.032 | 0.100 | 0.000 | 0.000 | 0.032 | 0.150 |

**Table 9**: Prediction errors for cotton seed biodiesel-diesel blends for viscosity at various temperatures.

| **Vol. of biodiesel** | **Viscosity at 30 °C** | | **Viscosity at 40 °C** | | **Viscosity at 60 °C** | | **Viscosity at 80 °C** | | **Viscosity at 90 °C** | | **Viscosity at 100 °C** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AAD (%) | MAD (%) | AAD (%) | AAD (%) | MAD (%) | AAD (%) | MAD (%) | AAD (%) | MAD (%) | MAD (%) | AAD (%) | MAD (%) |
| B0 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.008 | 0.000 | 0.000 | 0.000 |
| B10 | 0.002 | 0.200 | 0.000 | 0.000 | 0.018 | 0.007 | 0.003 | 0.005 | 0.030 | 0.016 | 0.006 | 0.003 |
| B20 | 0.003 | 0.002 | 0.000 | 0.003 | 0.033 | 0.003 | 0.021 | 0.002 | 0.110 | 0.067 | 0.002 | 0.011 |
| B30 | 0.003 | 0.023 | 0.012 | 0.001 | 0.014 | 0.005 | 0.035 | 0.012 | 0.060 | 0.080 | 0.002 | 0.001 |
| B40 | 0.002 | 0.020 | 0.000 | 0.000 | 0.006 | 0.001 | 0.010 | 0.001 | 0.070 | 0.013 | 0.005 | 0.027 |
| B50 | 0.061 | 0.130 | 0.000 | 0.001 | 0.018 | 0.001 | 0.084 | 0.003 | 0.016 | 0.020 | 0.002 | 0.011 |
| B60 | 0.021 | 0.200 | 0.015 | 0.008 | 0.001 | 0.033 | 0.023 | 0.023 | 0.012 | 0.010 | 0.005 | 0.027 |
| B70 | 0.001 | 0.012 | 0.020 | 0.009 | 0.011 | 0.007 | 0.005 | 0.003 | 0.015 | 0.013 | 0.002 | 0.043 |
| B80 | 0.016 | 0.140 | 0.003 | 0.002 | 0.025 | 0.016 | 0.011 | 0.005 | 0.025 | 0.020 | 0.008 | 0.016 |
| B90 | 0.001 | 0.012 | 0.004 | 0.002 | 0.002 | 0.002 | 0.014 | 0.002 | 0.001 | 0.030 | 0.003 | 0.034 |
| B100 | 0.000 | 0.000 | 0.004 | 0.002 | 0.002 | 0.002 | 0.014 | 0.007 | 0.000 | 0.003 | 0.000 | 0.000 |

### 3.6 Thermodynamics studies

The thermodynamics process was studied by investigating the the relation between Andrade equation and viscosity for the biodiesel-diesel blend. Figure 2 was used to investigate the relationship between viscosity and Andrade equation for the eleven samples. The rheological tests carried out showed that the viscosities of the biodiesel-diesel blends decreased with increase in temperature. Variation of the viscosity with temperature was exponential. This variation was analyzed using Andrade Equation (μ = AexpB/T). The Andrade parameters in Table 10 were obtained from the analysis of the linear regression lines of Figures 8 (a and b).



(a) (b)

*Figure 8: Log of kinematic viscosity of cotton seed biodiesel-diesel blends versus inverse of temperature.*

**Table10:** Andrade parameters for seed biodiesel-diesel samples.

| Sample | A x $10^{-2}$ | B | Linear Andrade Equation |
|---|---|---|---|
| DF | 1.7569 | 1645.43 | lnµ=1645.43/T-4.0416 |
| 10 | 2.0482 | 1617.35 | lnµ=1617.35/T-3.8882 |
| 20 | 2.4473 | 1584.69 | lnµ=1584.69/T– 3.7102 |
| 30 | 2.824 | 1552.83 | Lnµ=1552.83/T- 3.5669 |
| 40 | 3.1844 | 1525.56 | lnµ=1525.56/T– 3.446 |
| 50 | 3.7208 | 1494.28 | ln µ=1494.28/T–3.2912 |
| 60 | 6.2039 | 1344.46 | lnµ=1344.46/T– 2.780 |
| 70 | 6.000 | 1381.90 | ln µ=1381.90/T–2.8134 |
| 80 | 12.6363 | 1163.55 | lnµ=1163.55/T– 2.0686 |
| 90 | 14.7785 | 1133.64 | lnµ=1133.64/T– 1.9120 |
| 100 | 21.3568 | 1036.91 | lnµ=1036.91/T– 1.5438 |

**Table 11:** Gibbs free energy of cottonseed biodiesel biodiesel-diesel samples.

| Sample | DF | B10 | B20 | B30 | B40 | B50 | B60 | B70 | B80 | B90 | B100 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Delta G_{vis}$(KJ/mol) | 13.68 | 13.45 | 13.18 | 12.90 | 12.68 | 12.42 | 11.18 | 11.49 | 9.67 | 9.43 | 8.62 |

The Andrade equations for the cotton seed biodiesel-diesel samples could be compared with Eyring equation, to have a glimpse on the thermodynamics of the fuels flow. Eyring and Andrade equations are given in equations (10) and (11) respectively.

$$\mu = A\exp\left(\Delta G_{VIS}/T\right) \tag{11}$$

$$\mu = A\exp\left(B/RT\right) \tag{12}$$

Where A and B are Andrade constants; $\Delta G_{vis}$= free energy of activation of flow; µ = dynamic viscosity; T = absolute temperature; R = universal gas constant (8.314Jmol$^{-}$1). By comparison, the parameter $\Delta G_{vis,}$ for each sample can be estimated from the expression:

$$\left(\Delta G_{VIS}/RT\right) = B/T \qquad (13)$$

Therefore,

$$\Delta G_{VIS} = BR \qquad (14)$$

The value of the $\Delta G_{vis}$calculated for the samples are presented in Table 11 for cotton seed oil (CSO) and petro diesel, respectively. These values of free energies of activation for the flow ($\Delta G_{vis}$) gives an insight on the nature of packing of the molecules in each fuel sample, and the extent of the forces of interaction among the molecules [11]. From the values of $\Delta G_{vis,}$ it can be seenthat the molecules of methyl cotton seed are closely packed, due to the highvalues of $\Delta G_{vis.}$ The effect of this, are the high density, viscosity and crystallization temperature.

## 4. Conclusion

The statistical regressions fitted properly the variation of density and kinematic viscosity obtained from experimental values. The biodiesel fuel and its blend had a linear density-temperature relationship which is almost the same with diesel fuel. The temperature increases as the kinematic viscosity decrease.

The mixing rule was found suitable for predicting the basic flow properties of cotton seed biodiesel-diesel blends as a function of biodiesel fraction. Hence biodiesel fraction increased as the density and viscosity increased.

Empirical relation was developed to predict cloud and pour points. It was observed that increase in biodiesel fraction lead to a decrease in cloud point and pour point.

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