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Biodiesel Viscosity and Flash Point Determination

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ABSTRACT
In this research, biodiesel samples of different percentages of blend biodiesel (Palestinian biodiesel prepared from waste oil) and petro-diesel were studied. The density, refractive index, flash point and viscosity of the samples were measured. The flash points were measured as a function of percentage of biodiesel, the results emphasized that the flash point increases as the percentage of biodiesel increases in the sample. Two equations were proposed to obtain more suitable prediction of the flash point. The values of flash points of biodiesel were compared with the standard value of flash point of biodiesel. The comparison shows that samples contain more than 40% biodiesel which coincide with standard values. The values of kinematic viscosity of biodiesel were compared with the Palestinian standard value 10147of biodiesel. The comparison shows that samples contain less than 72% biodiesel which coincide with the standard value. Taking into consideration results of kinematic viscosity and flash point, one can suggest percentage 71% of biodiesel and 29% petro-diesel as the best percentage of the two mixed materials, according to the Palestinian standards.

Key words: *Biodiesel, viscosity, flash point, refractive index, density*

1. INTRODUCTION

Biodiesel is defined as the mono-alkyl esters of long chain fatty acids, derived from renewable vegetable oils or animal fats for use in the ignition of engines. Vegetable oils which are used in preparing biodiesel are: soybean oil, sunflower oil, ground nut oil, canola oil, corn oil, and waste oil which constitute a mixture of all previous kinds of oil after being utilized [1,5].

Biodiesel possesses technical and environmental advantages, low toxicity, derivation from renewable sources, superior flash point more than petro diesel and biodegradability, and lower overall exhaust emissions [8, 11, 18]. Biodiesel's characteristics strongly depend on various plant feed stocks, growing climate conditions, soil type, plant health and plant maturity upon harvest. These parameters affect the physical and chemical properties, which also have direct relationship with performance and emission of the engine [19].

Nita and Geacai measured the density and the kinematic viscosity and presented data for a vegetable oil, diesel fuel and biodiesel in the temperature range of 20 ºC to 60 ºC. Empirical models were proposed to predict these properties at different temperatures [14].

Rao and his group made a study to estimate the mathematical relationships between the kinematic viscosity, density, and flash point among various biodiesel samples [16].

Thiago and his group studied the kinematic viscosity and presented an experiment to canola, sunflower, corn, and soybean. They compared the curves obtained for the kinematic viscosity versus temperature with the curves obtained by modeling the kinematic viscosity dependency on temperature [17].

Moradi and his group studied the effects of temperature and volume fraction of biodiesel and diesel on the density and kinematic viscosity of blends, they used five biodiesels: sunflower, canola, and soybean waste cooking oil edible tallow. Density and kinematic viscosity of mixtures were measured at several temperatures. Results showed that by reducing temperature and increasing the volume fraction of biodiesel, density and kinematic viscosity increased [10].

Bahti evaluated the viscosity of vegetable oils, and fitted the viscosity with well - known rheological equations [2]. The dynamic viscosity of olive oil samples of different storage ages on yearly and weekly basis from different locations was measured as a function of temperature by Nierat [13].

In this work, the kinematic viscosity of biodiesel is measured and compared with the standard values. In addition the dependence of dynamic viscosity of blends of biodiesel on temperature is studied. The flash point of the biodiesel is determined and compared with the standard values. The density and refractive index of biodiesel in different temperatures are measured and compared with the standard values.

2. THEORY

Viscosity

Viscosity is a fundamental characteristic property of all liquids. It is a measure of internal resistance present in each real fluid causing the fluid to oppose the dynamic variation of its motion thus restricting its tendency to flow [9]. Viscosity is expressed in two distinct forms:

a. Absolute or dynamic viscosity

b. Kinematic viscosity

Dynamic viscosity is defined as the ratio of shear stress (force over cross section area) to the rate of deformation. It is presented by:

$$\eta = \frac{\tau}{\frac{\partial u}{\partial x}} \quad (1)$$

Where, η is dynamic viscosity (Pa.s), τ is shear stress (N/m^2) and $\frac{\partial u}{\partial x} = \gamma$ is rate of deformation or velocity gradient or better known as shear rate (1/s) [7].

Kinematic viscosity requires knowledge of mass density of the liquid (ρ) at that temperature and pressure and is defined as

$$\upsilon = \frac{\eta}{\rho} \quad (2)$$

Where, υ is the kinematic viscosity, ρ is the mass density of the liquid [4].

Flash Point

Flash point is a minimum temperature at which a fuel gives sufficient vapors which can be mixed with air will ignite momentarily [1]. Determination of flash point is needed for every type of biodiesel to classify it as nonhazardous under the National Fire Protection Association (NFPA) code (NREI) [12].

Mass Density

Fuel mass density (ρ) is the unit of mass per unit of volume. Fuel mass density directly affects fuel performance, such as cetane number, heating value, and viscosity which are strongly connected to mass density [3].

$$\rho = \frac{M}{V} \quad (3)$$

Refractive Index

The index of refraction (n) for a substance is the ratio of the speed of light in empty space c to the speed of light in the substance υ and mathematically it is written as

$$n = \frac{c}{v} \quad (4)$$

3. EXPERIMENTAL

The dynamic viscosity and density of the biodiesel are measured over range of temperature and different percentages of biodiesel and diesel, to reach the standard values of biodiesel kinematic viscosity which are in the range of [3.5-5 mm^2/s] at 40 ºC, and standard values of density at 15 ºC which are in the range [0.86-0.90 g/cm^3]. Flash point also is measured and compared with the minimal standard value which is 101 ºC. Finally, refractive index is measured at different temperatures (Palestine Standards Institution, 2014).

Samples Preparation

Every sample contains 80 ml with different percentages of biodiesel and diesel. Biodiesel is prepared from waste and manufactured in Palestine. Diesel is obtained from gas station licensed from Palestinian General Petroleum. The percentage of samples is given in Table 1.

Table -1 Percentages of biodiesel and diesel fuel used in preparing Samples

Biodiesel Blend	Biodiesel		Diesel	
	Percentage	Amount (ml)	Percentage	Amount(ml)
B100	100%	80	0%	0
B90	90%	72	10%	8
B80	80%	64	20%	16
B76	76%	60.8	24%	19.2
B72	72%	57.6	28%	22.4
B71	71%	56.8	29%	23.2
B70	70%	56	30%	24
B69	69%	55.2	31%	24.8
B68	68%	54.4	32%	25.6
B65	65%	52	35%	28
B60	60%	48	40%	32
B50	50%	40	50%	40
B40	40%	32	60%	48
B30	30%	24	70%	56
B20	20%	16	80%	64
B10	10%	8	90%	72
B0	0%	0	100%	80

Apparatus and Measurements

HX-Z Electronic Balance was used to measure the mass

Pycnometer: 10 ml glass bottle with stopper was used to keep the volume constant.

Refractive Index

The refractive index of the biodiesel samples was measured by using Boaco digital refractometer.

Flash Point

The flash point of biodiesel was measured by flash point tester which consists of 80 ml closed copper cup.

4. STATISTICAL ANALYSIS

The obtained results were tabulated and statistically analyzed. The statistical analysis of the data was done by using Microsoft Office Excel. The equations were fitted using three parameters:

1-The coefficient of determination R2 gives the proportion of the variance of one variable that is predictable from the other variable.

2- Percentage of average absolute deviation (AAD %) of the data. The AAD% indicates how the calculated values are closed to experimental values. The AAD% is given by the following equation:

$$AAD\% = \frac{1}{N}\sum \frac{\eta_{experimental} - \eta_{calculated}}{\eta_{experimental}} \quad (5)$$

Where N is the number of experimental points, $\eta_{experimental}$ the experimental viscosity and $\eta_{calculated}$ the calculated viscosity [6].

3- Standard deviation (SD): A measure of the dispersion of a set of data from its mean.

$$SD = \sqrt{\frac{1}{N}\sum(\eta_{experimental} - \eta_{calculated})^2} \quad (6)$$

Where N is the number of experimental points, $\eta_{experimental}$ the experimental viscosity and $\eta_{calculated}$ the calculated viscosity [4].

5. DATA AND ANALYSIS

Density Results

The density is measured for all samples at 15 ºC, 27 ºC, and 40 ºC the relationship between density and biodiesel percentage at 15 ºC is given in Fig. (1).

The density shows a linear proportional relationship with percentage of biodiesel with coefficient of determination R^2 equals 0.9779. The linear relation is described by Eq. (7).

ρ = 0.0596 X + 0.7938 (7)

The linear relation at 27 ºC is described by Eq. (8) with coefficient of determination R^2 equals 0.9925.

ρ = 0.0608 X + 0.7821 (8)

The linear relation at 40 ºC is described by Eq. (9) with coefficient of determination R^2 equals 0.9811.

ρ = 0.0561 X + 0.7777 (9)

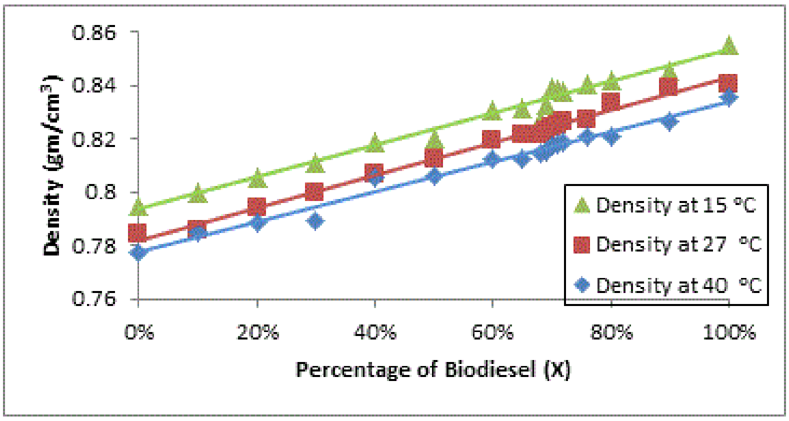

Fig. 1 Density versus percentage of biodiesel at 15 ºC, 27 ºC, and 40 ºC

Refractive Index Results

The refractive indices of biodiesel for all samples were measured at three different temperature degrees. The relations between refractive indices and temperature of biodiesel samples B100, B71, B50, and B10 are shown in Fig. (2).

The relations of the three samples show that the refractive indices values decrease when temperature increases.

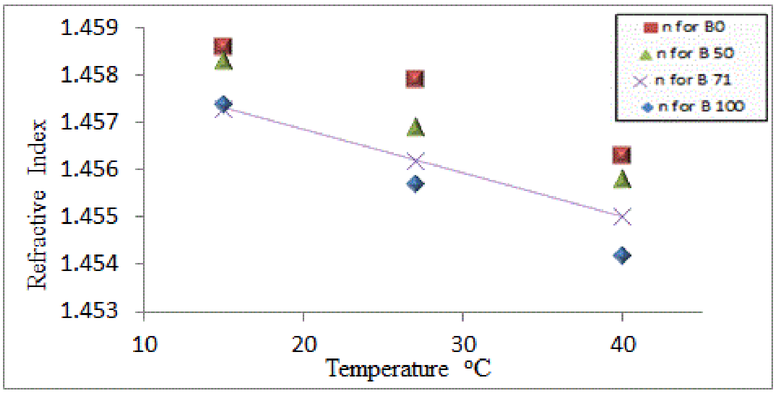

Fig. 2 Measured Density refractive indices versus temperature for B100, B71, B50, and B10

Flash Point Results

The flash and boiling points for all samples were measured. The relationship between flash points and percentages of biodiesel in the samples is shown in Fig. (3).

The flash point values increase as the percentage of biodiesel increases in the sample.

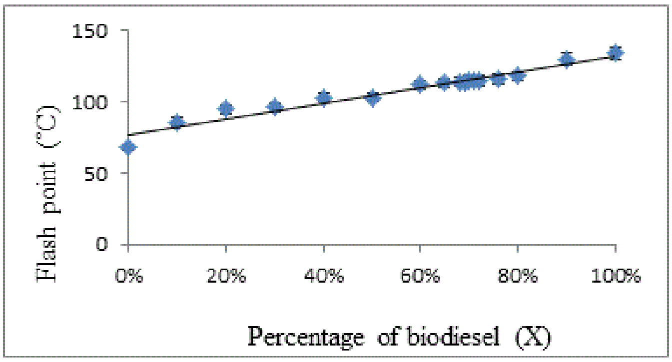

Fig. 3 Measured flash points versus percentage of biodiesel

Flash Point and Theoretical Prediction

Proposed Equations

a. Exponential Formula

The measured flash point is fitted using the proposed formula (10)

$$FP = 23.189\, e^{0.009 T_b} \quad (10)$$

Where *FP* the flash point in ° C is, T_b is the boiling point in ºC. The value of AAD% is 1.2% the results of this fitting in addition to experimental values, are shown Fig. (4)

Fig. (4) shows that the measured values of the flash point decrease in exponential curve, and shows that the measured values of flash point agrees with the calculated flash point from exponential formula Eq. (10).

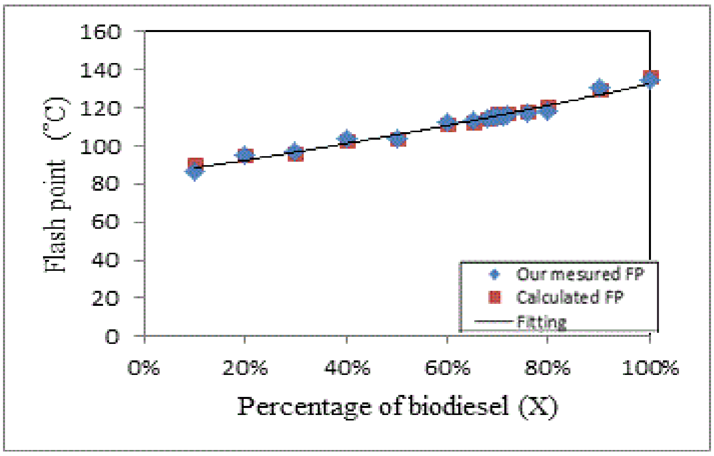

Fig. 4 Measured and calculated values of flash points using exponential formula Eq. (10)

b. Linear Formula

$$FP = 1.1248\, T_b - 103.9907\, \rho \quad (11)$$

Where *FP* is the flash point in ºC, T_b is the boiling point in ºC, and ρ is the mass density in gm/cm3. The value of AAD% between the experimental values and calculated values is 1.2% and the value of SD is 1.5. Fig. (5) shows the experimental and calculated values of the flash point from linear formula.

Fig (5) shows the measured and calculated value of the flash point from equation (11). They are close to each other which indicate good prediction of flash point.

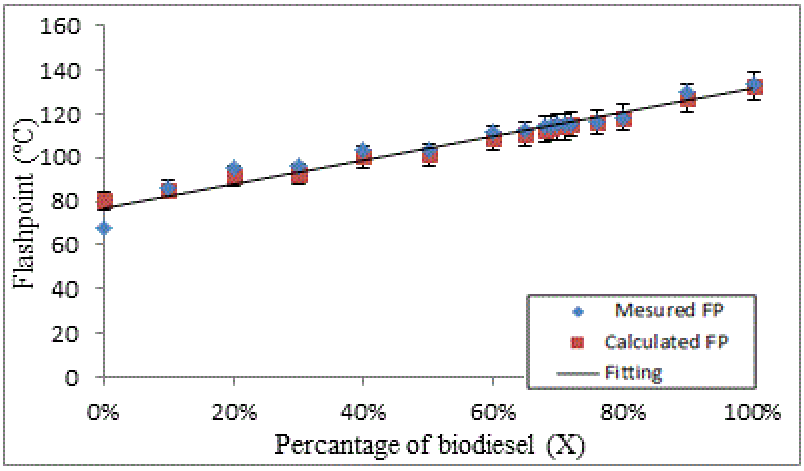

Fig. 5 Measured and calculated values of flash points using linear formula Eq. (11)

Viscosity Results

The dynamic viscosity was measured for all samples at five different temperature degrees. The relationship between dynamic viscosity and temperature of B71, sample is shown in Fig. (6).

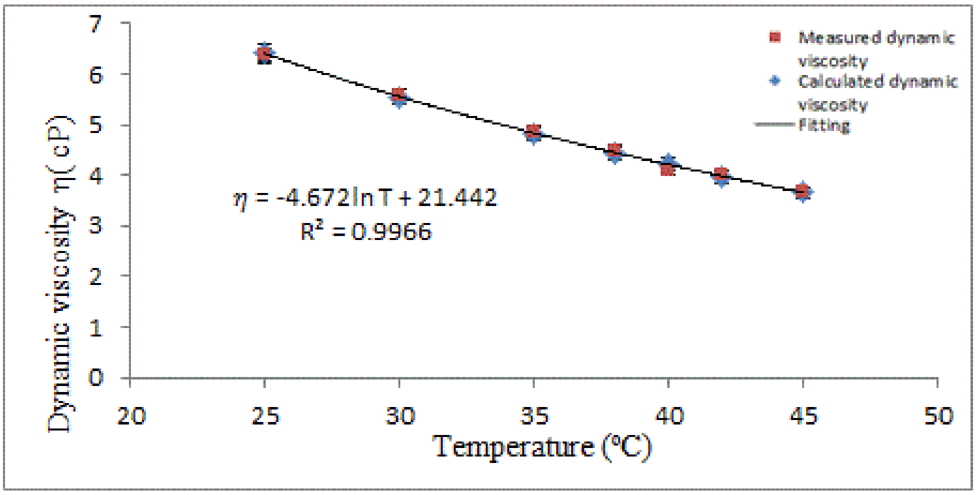

Fig. 6 Measured and calculated values of dynamic viscosity as a function of temperature of B71 sample from Eq. (12)

Theoretical Predictions of Viscosity Results

In this section, a new equation is proposed to describe the dynamic viscosity relationship of biodiesel versus temperature.

Logarithmic Formula

Two - constant logarithmic equation is proposed to describe the dynamic viscosity as function of temperature

$$\eta = A\,Ln\,T + B \qquad (12)$$

Where is the dynamic viscosity in cP, T is the temperature in ºC, and, *A* and *B* are two specific constants for every percentage of blend biodiesel and diesel in cP. The values of A and B are given in Table (2).

Table -2 The values of A and B constants which are given in Eq. (12)

Biodiesel Blend	A (cP)	B (cP)	R2
B100	-6.045	27.929	0.9978
B90	-5.463	24.948	0.9976
B80	-4.719	21.703	0.9979
B76	-4.828	22.109	0.9915
B72	-4.705	21.586	0.9962
B71	-4.672	21.442	0.9966
B70	-4.563	21.046	0.9907
B69	-4.334	19.691	0.9747
B68	-3.910	18.265	0.9712
B65	-4.331	19.869	0.9884
B60	-4.117	19.004	0.9865
B50	-3.683	17.197	0.9988
B40	-3.179	14.924	0.9548
B30	-3.072	14.334	0.9763
B20	-3.558	16.002	0.9921
B10	-2.627	12.528	0.9908
B0	-1.920	9.854	0.9703

The experimental results of dynamic viscosity were compared with results obtained by logarithmic Eq. (12). Fig.(7) shows the experimental and calculated values of the dynamic viscosity for B100 sample.

The measured and calculated values of the dynamic viscosity for B100 sample shown in Fig. (7) decrease in a logarithmic shape as temperature increases

The value of AAD% is 0.75%, it is small value. R^2 value is 0.9978 which means that 99.78 % of viscosity values can be expressed by Eq. (12).

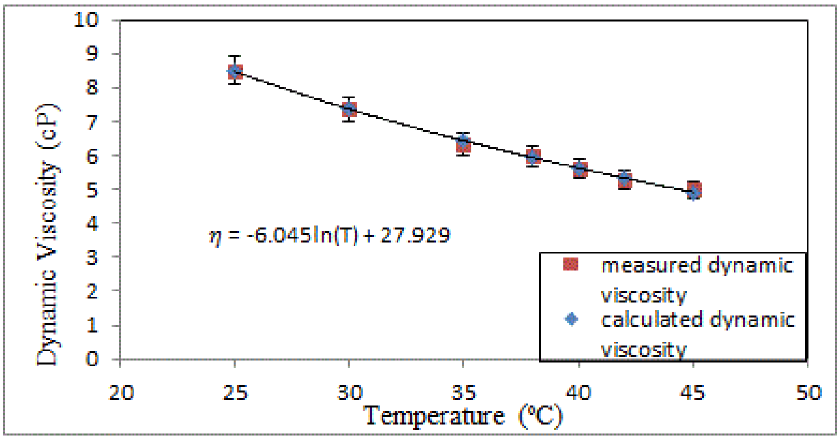

Fig. 7 Measured and calculated values of dynamic viscosity as a function of temperature of B100 sample from Eq. (12)

6. DISCUSSION AND CONCLUSION

Density

The biodiesel-diesel blend density increases as the percentage of biodiesel increases in the sample. The biodiesel is denser than diesel because the former has a higher degree of instauration. The degree of instauration of the molecule is an indicator of the number of double bonds present in its fatty acid chain, a higher number of double bonds representing a higher degree of instauration. Density increases as the degree of instauration increases. The Biodiesel density decreases linearly as function of temperature. As temperature of biodiesel increases, biodiesel particles speed up and spread out. This causes the biodiesel to expand, its volume increases. This causes the density to decrease with temperature.

Refractive Index

The measured values of refractive indices decrease as temperature increases. High temperature makes the biodiesel less dense and viscous; this cause light to travel faster in the biodiesel which make the refractive index decreases. Lowering temperature makes the biodiesel more dense and viscous, which causes light to travel slower in the medium so the medium has larger value for the refractive index.

10

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Flash Point

The measured values of flash points increase as the percentage of biodiesel in the sample increases. The value of flash point depends on the boiling point which increases as the molecular weight increases; so the flash point of biodiesel higher than diesel as result of increases the molecular weight of the biodiesel.

The relation between kinematic viscosity and the percentage of biodiesel in the sample shows increase the kinematic viscosity as the percentage of biodiesel increases in the sample, this because biodiesel is more viscous than diesel. The higher viscosity of biodiesel refer to a main reason which is the higher molecular weight of the biodiesel than diesel.

Standard Values

The standard values of biodiesel are compared with the measure values in order to find the best percentage that can be used to produce biodiesel which can be described as a renewable fuel. Table 3 gives comparison between measured values and standard values of biodiesel.

Table -3 Comparison between the measured values and standard values of biodiesel

Property	**European/Palestinian Standards**	**Measured Values**	**Samples has Standard Properties**
Mass Density at 15 ºC	0.860-0.900 g/cm^3	0.856 - 0.800	No sample
Kinematic Viscosity at 40 ºC	3.50-5.00 mm^2/s	3.54-6.74	B0-B71
Flash Point	101.0 ºC at minimum	86.5-134.1	B40-B100

Table 3 gives that the samples contain (40% - 71%) biodiesel agree with flash point and Kinematic viscosity standard values of biodiesel. The sample contains 71% biodiesel and 29% petro diesel is the best percentage agrees with the standard values of biodiesel.

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