



Review Article

Effects of Thermal, Physical, and Chemical Properties of Biodiesel and Diesel Blends

Sayyed Siraj^{*}, Renuka Kale, Swapnil Deshmukh

Maharashtra Institute of Technology, Aurangabad, (MS) India

Email address:

lucky.sartaj@gmail.com (S. Siraj)

^{*}Corresponding author

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Abstract: The biodiesels are the fuels composed of mono-alkyl esters of long chain fatty acids derived from the renewable energy sources, such as vegetable oil, animal fat, etc. The thermogravimetric analysis (TGA) from thermal, density and viscosity from physical and iodine value from the chemical properties has been considered for the study, by considering this objective the literature review was done through the research papers of last two decades. The conclusions drawn are as follows, the thermal property TGA is an important property which shows the distillation and decomposition, and it provides behavioural information of a substance are measured as a function of temperature. The density and viscosity from the physical properties for different biodiesel strongly affect the fuel consumptions of engine system and it has been seen that density and viscosity strongly dependent on the temperature. The iodine value from chemical properties, the iodine value for different biodiesel and diesel blends increases as the biodiesel fractions increases in the blends.

Keywords: Thermal Properties, Physical Properties, Chemical Properties, Thermogravimetric Analysis, Density, Viscosity, Iodine VALUE

1. Introduction

Now-a-day energy crises are one of the important issues at global level. Fossil fuels have been utilized everywhere in the world for various applications like industrial, transportation sectors, locomotives and marine etc. The emissions produced by fossil fuels after burning are dangerous for climate in general and human beings in particular; it increases air pollution and global warming. Fossil diesel contributes almost 80% of the world's energy needs [2, 22, 25]. Nevertheless the reservoirs of fossil fuels are depleting rapidly all over the world. So the renewable fuels are the best alternative source available for the same. Variety of crude oil extracted from the various plants is one of the potential sources [6]. Therefore the biodiesel is one of the renewable energy potential sources available for the applications of fossil fuels. The previous data shows the fossil diesel consumption of India in 2008 – 2009 was 51.7 million tons and 159.7 million tons of CO₂ was likely

to be generated by such usage of fossil diesel [10, 11]. So the alternative available for this fossil diesel is biodiesel because it is clean and renewable source of energy. Every country has specific variety of feedstock oil for their biodiesel production; some properties of biodiesel compared with the fossil diesel have given in the Table 1. Biodiesel must be technically feasible, economically competitive, environmentally acceptable and easily available in the world. Biodiesel can offer other benefits, including greenhouse gas emissions, regional development, and social structure, especially to developing countries [10, 11, 38, and 39]. Some of the researchers [7, 22] have put the definition for biodiesel as the biodiesel is oxygenated, sulphur free, biodegradable, non-toxic, and eco-friendly diesel oil. [38, 39] Biodiesel (Greek, Bio, Life + Diesel from Rudolf Diesel) refers to a diesel equivalent, processed fuel from biological sources [19].

Table 1. ASTM standards of biodiesel and fossil diesel [9, 38].

Property	Test Method	ASTM D 975 (Fossil diesel)	ASTM D 6751 (Biodiesel, B100)
Flash point (in °C)	D93	52 min	130 min
Water and sediments	D 2709	0.05 max % vol.	0.05 max % vol.
Kinematic Viscosity @ 40°C	D 445	1.3 – 4.1 mm ² /s	1.9 – 6.0 mm ² /s
Sulfated Ash	D 874	-	0.02 max %wt.
Ash	D 482	0.01 max % wt.	-
Sulfur	D 5453	0.05 max %wt.	-
Sulfur	D 2622/129	-	0.05 max %wt.
Copper Strip Corrosion	D 130	No. 3 max	No. 3 max
Cetane Number	D613	40 min	47 min
Aromaticity	D 1319	35 max %vol.	-
Carbon Residue	D 4530	-	0.05 max %mass
Carbon residue	D 524	0.35 max %mass	-
Distillation Temp. (90% volume recycle)	D 1160	282°C min – 338°C max	-

Biodiesel fuels are attracting increasing attention worldwide as blending component or direct replacement for the diesel fuel in the vehicle engine. Biodiesel comprises alkyl fatty acid (Chain length C₁₄ – C₂₂) esters of short chain alcohols, primarily, methanol or ethanol. [1, 3, 22, and 44] chemically, biodiesel can be defined as a fuel composed of Mono-alkyl esters of long chain fatty acids derived from renewable energy sources, such as vegetable oil, animal fat, etc. Biodiesel is designated as B100 and it must meet to the requirements of (American Society of Testing and Materials) ASTM D 6751 standards and (European Nations) EN 14214 standards. The thermal, physical and chemical properties of biodiesel will influence on combustion flow and storage behaviours [1, 42, and 43].

2. Literature Review

The literature review done through the research papers of last two decades on the basis of thermal, physical and chemical properties. The literature review has given according to the properties:

2.1. Thermogravimetric Analysis (TGA) as Thermal Property

The thermogravimetric analysis (TGA) is helpful technique in characterization of thermal stability and determining conversions of the biodiesel products [5]. TGA analysis is quick and inexpensive technique and can be used in esters boiling point determination and monitoring the transesterification reaction. Thermal analysis also represents a sum of methods of investigations in which physical or chemical properties of a substance, a mixture of substances and / or of reaction products or mixtures of reaction products are measured as a function of temperature or time. In general fossil diesel molecules of different lengths have different properties and different behaviours. Chains of molecules that are longer have higher boiling points [23].

The thermogravimetric analysis (TGA) gives the thermal decomposition of the materials. On ordinate the mass of fluid has been taken as by most of the researchers have and on

abscissa the temperature has been taken. As the temperature increases per minute continuously and constantly in presence of controlled atmosphere (may be nitrogen, oxygen, argon, and air etc.). As temperature increases and simultaneously the substance loose the weight due to decomposition [8]. Generally the temperature increases constantly in TGA analysis by 5, 10, 15°C per minute until it reaches 600°C. Normally two types of calibration required in the TGA analysis first is temperature and second is weight calibration. The temperature calibration is useful for TGA experiments in which precise transition temperatures are essential. In order to perform the weight calibration of TGA, 1 mg, 100 mg, and 200 mg of samples are supplied by the kit of the TGA instrument are used. According to the literature, TGA methodology has used by Rashid et al. for evaluating the transesterification process of Jatropha biodiesel production. Andrade et al. used TGA analysis for evaluation of biodiesel production from buriti oil. The results show that biodiesel and its blends show only one step of mass loss, which was due to the volatilization of various fatty acids present in biodiesel.

Satyanarayana and Muraleedharan implemented TGA methodology for the measurement of onset volatilization temperatures for various oils. The oil was low volatile as compared to biodiesels. It was found that coconut biodiesel was more volatile than rubber and palm biodiesel. Thermogravimetric analysis TGA technique is applied by Patil et al. characterizing the thermal stability of waste cooking biodiesel by measuring the changes in its physiochemical properties expressed as weight change as function of increasing temperature. The temperature range employed was 25 to 600°C. The mass of the waste cooking biodiesel starts to decrease at approximately after 125-130°C, and this step was attributed to vaporization of biodiesel, and second step started to decrease at 232°C, and it may be due to some waste cooking oil that was not transesterified. The literature work shows that the TGA is useful for the assessment of thermal stability of biodiesel [12].

2.2. Density as Physical Property

The density of a material or liquid is defined as its mass per

unit volume. Many researchers prefer the dimensionless term specific gravity, which is defined as the ratio of the density of a substance to the density of a reference substance (usually water) [32, 38, and 44]. Density of the biodiesel, fossil diesel fuel and their blends can be measure by ASTM Standard D 941 or as per European standard of EN ISO 3675 and EN ISO 12185 test methods. Most of the researchers have used Antonpaar density meter, Pycnometer, and Hydrometer in the measurement of density at room temperature or at stated temperature i.e. 15°C [3, 4].

From various research papers the (average) density of the 25 investigated methyl esters, again excluding castor, ranges from 870.8 to 891.5 kg/m³, with the overall average value being 880.2 kg/m³ (i.e. almost 5% higher than the corresponding fossil diesel value). Density increases with the decrease in chain length methyl esters and with unsaturation [14]. Density can impact on fuel consumption as fuel introduced into the combustion chamber is determined volumetrically [1, 21]. Biodiesel fuels are, in general, characterized by higher density than conventional fossil diesel, which means that volumetrically operating fuel pumps will inject greater mass of biodiesel than fossil diesel fuel [1, 38, 39 and 44].

Since the flow is controlled by volume, the expected peak power reduction for engines using B100 is only 5 to 7% less than the fossil diesel because more (g/ml) would flow and vaporize more efficiently given a set throttle (volume) [16, 30]. It should be noted that biodiesel produces more than three times the energy as the same amount of fossil fuel. Biodiesel's higher Specific gravity and density relative to fossil diesel means that on road biodiesel blends are normally made by splash blending the biodiesel fuel on top of the conventional diesel fuel or fossil fuel. The biodiesel has an average density i.e. crude oil density is 12% higher than the fossil diesel [1, 26, and 29].

Actually, it has been argued that there exists a correlation between density and NOx emissions, with lower densities favouring lower NOx, although other researchers have not confirmed such an unequivocal trend [36, 39, and 40]. Tat and Gerpen measured experimentally the specific gravity of 20%, 50%, 75%, and 100% soybean biodiesel as a function of temperature in temperature range of crystallization temperature to 100°C using the standard hydrometer method [28, 35]. The results indicate that the biodiesel and its blends demonstrate temperature dependent behaviour. They developed first degree linear regression equation as given by equation 1.

$$SG = a + bT \quad (1)$$

Where SG is the specific gravity of blended biodiesel, T is the temperature in °C, and a and b are constants that depends on percentage of biodiesel and diesel blends. Tate et al. also reported similar linear equation for three different biodiesels namely canola oil biodiesel, soybean oil biodiesel, and fish oil biodiesel. These equations were developed based on the data obtained which was available in the range of 20-300°C. Tate et al. had also suggested that the equation 2 can be used to

determine the specific gravity of different biodiesel blends at a standard temperature. In this equation the specific gravity of the blend has been considered to be proportional to mass fractions of the constituents.

$$SG_{blend} = \sum SG_i M_i \quad (2)$$

Where SG_{blend} is the specific gravity of the blend, SG_i is the specific gravity of the component i, M_i is mass fraction of the component i. Alptekin and Canakci carried out an experimental tests on different biodiesels made of soybean oil, waste palm oil, sun flower oil, corn oil, canola oil and cottonseed. They suggested first degree empirical equation, which can relate the density of biodiesel blend with the percentage of biodiesel used shown by equation 3.

$$D = Ax + B \quad (3)$$

Where D is the density (g/cm³), A and B are constants which vary with the type of the biodiesel and x is the biodiesel fraction.

2.3. Viscosity as Physical Property

Kinematic viscosity is the primary reason why biodiesel is used as an alternative fuel instead of neat vegetable oils or animal fats [17]. Viscosity is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion. Kinematic Viscosity of the biodiesel, diesel fuel and their blends can be measure by ASTM Standard D 445 or as per European standard of EN ISO 3104 and EN ISO 3105 test methods [15].

The Viscosity ranges have given as per the ASTM D445 standard 3.5 to 5.0 mm²/s and as per the EN ISO 3104, 05 standards 1.9 to 6.0 mm²/s [33]. Most of the researchers have used Redwood Viscometer, Setavis Kinematic Viscometer and Canon-fenske Viscometer tube of size No. 75, 100 used in the viscometer bath for viscosity measurement [38, 42, and 43]. The kinematic viscosity was determined at 40°C by multiplying the constant of viscometer tube and the experimental efflux time, which is the time for a known volume of liquid flowing under gravity to pass through a calibrated glass capillary viscometer tube.

$$\text{Kinematic viscosity} = \text{Calibration constant (mm}^2/\text{s}^2) \times \text{mean time of flow (s) in mm}^2/\text{s} \quad (4)$$

Crude vegetable oils have high viscosity (one order of magnitude higher than the acceptable diesel fuel values), which means that they cannot be used safely as fuels in a compression ignition engine, at least not without prior heating (viscosity decreases exponentially with increasing temperature), and only for relatively small blending ratios [44]. The crude vegetable oils have highest viscosity than biodiesel and biodiesel have higher viscosity than fossil diesel, the crude vegetable oil have viscosity 10 to 17 times higher than that of biodiesel [4, 14].

Several structural features influence the kinematic viscosities of FAME, such as chain length, degree of unsaturation, double bond orientation, and type of ester head

group. Factors such as longer chain length and larger ester head group result in increases in kinematic viscosity [32]. Increasing the degree of unsaturation results in a decrease in kinematic viscosity and as the temperature of oil is increased its viscosity decreases and it is therefore able to flow more readily. Double bond orientation also impacts kinematic viscosity [26, 32].

Viscosity is the most important property of lubricating oil, as it affects the wear rate of engine components. Relatively higher viscosity of biodiesel helps in plugging the clearance between piston rings and cylinder liner effectively, thus reducing blow by losses and fuel dilution of lubricating oil [17-18, 21]. In a diesel engine, higher viscosity leads to less accurate operation of the fuel injectors, and to poorer atomization of the fuel spray, increase in the Sauter mean diameter of the fuel droplets and of the jet break up time; these inefficiencies are exaggerated during cold starting.

Due to the large molecular size of the triglycerides making up about 98% of plant oils, viscosity is higher and volatility is lower than fossil diesel [1, 31]. The brake power of an engine working with plant oils or blends varies in the range of +10% to -18% compared to engines running on fossil diesel under similar operating conditions. However, according to most reports there is power decrease around 2% to 18%. Possible problems are:

- Higher viscosity interferes with the injection process and leads to poor atomization, leading in turn into inefficient mixing of air and fuel which contributes to incomplete combustion.
- It also causes some plant oil to be left unburnt and penetrate the engine crankcase which can cause loss of power [1, 24, 38].

The literature shows, the viscosity of biodiesel can be estimated from well-known mixing laws such as the Grun-Nissan and Katti-Chaudhari laws, which were originally proposed by Arrhenis. The law is given in mathematical form in equation 5.

$$\ln \eta_{max} = x_1 \ln \eta_1 + x_2 \ln \eta_2 \quad (5)$$

Where, η_{max} is the kinematic viscosity (mm^2/s) of the mixture, η_1 and η_2 are the kinematic viscosities of components 1 and 2 and x_1 and x_2 are the mass or volume fractions of component 1 and 2. Alptekin and Canakci investigated the variation of viscosity as a function of different percentages of blends of biodiesel. The test was conducted at 40°C for wide variety of biodiesels such as waste palm oil biodiesel, sunflower oil biodiesel, soybean oil biodiesel, corn oil biodiesel, cottonseed oil biodiesel, and commercial diesel. They developed second degree empirical equation to calculate the viscosity of blended biodiesel taking the fraction of biodiesel in the mixture as the main parameters in equation 6.

$$\eta_{blend} = Ax^2 + Bx + C \quad (6)$$

Where, η is the kinematic viscosity of biodiesel (mm^2/s), A, B, and C are coefficients and x is the biodiesel fraction. In this equation the estimated value can be possible to compare with the actual values for the accuracy of the equation.

Riazi and Al-Qtaibi developed equation 7 for estimation of viscosity of liquid hydrocarbons and petroleum mixtures at various temperatures from their refractive index value (I). However in this model the equation needs the values of molecular weight, specific gravity, boiling point temperature, and refractive index of compounds as input parameters.

$$\frac{1}{\mu} = A + \frac{B}{I} \quad (7)$$

Where, μ is the dynamic viscosity (cp), A and B are constants specific to each component and I is the refractive index.

A modified equation was proposed by Tat and Gerpen to determine the viscosity of the biodiesel at different temperatures in equation 8.

$$\ln(\eta) = A + \frac{B}{T} + \frac{C}{T^2} \quad (8)$$

Where, A, B, and C are constants, T is the temperature in K, η is the kinematic viscosity (mm^2/s).

At last from the above equation 8, Pegg et al. developed the equation 9 to calculate the dynamic viscosity of B100 as a function of temperature in the temperature range of 277 – 573 K.

$$\ln(\eta) = -2.4343 + \frac{216.66}{T} + \frac{293523}{T^2} \quad (9)$$

Where, η is the dynamic viscosity (mPa's) and A (216.66) and B (293523) are constants and T is the temperature (K).

By considering the carbon number, Krisnangkura et al. proposed different equations equation 10 and 11 to determine viscosity of biodiesels with long short carbon structure at different temperatures.

$$\ln(\eta_{c_{12} - c_{18}}) = -2.177 - 0.202z + \frac{403.66}{T} + \frac{109.772}{T}z \quad (10)$$

$$\ln(\eta_{c_6 - c_{12}}) = -2.915 - 0.158z + \frac{492.12}{T} + \frac{103.35}{T}z \quad (11)$$

Where, $\eta_{c_{12} - c_{18}}$ and $\eta_{c_6 - c_{12}}$ are the kinematic viscosities of biodiesels with number of carbon atoms varying from 12 to 18 and 6 to 12 respectively, in mm^2/s , T is the temperature in K, and z is the carbon number. In above equation 10 and 11 the number of carbon atoms is the required a-priori which limits the use of equations [41].

2.4. Iodine Value as Chemical Property

The Iodine Value of the oil is defined as the amount of iodine grams which reacts with 100 grams of the oils. The Iodine is a measure of the unsaturation of fats and oils and hence their potential to become oxidized. The oil is treated with an excess of iodine Monochloride solution in the glacial acetic acid. The amount of iodine absorbed is determined by back titration with standard sodium thiosulfate solution. The iodine value indicates the drying quality of the oil, the drying oils having higher iodine values [20, 40]. The iodine value is of real significance in the examination of fatty oils since most fatty oils have their own characteristic iodine value. Solid fats possess Iodine Value less than 50 whereas drying oils possess

Iodine Values more than 140 while the Iodine Value of non – drying and semidrying oils range from 50 to 140. The iodine value of fatty acids may vary from various ranges and it may vary according to the various mass of oil or fats. Some of the values are given in table from which we have taken in the consideration from the mass of oil or fats [27, 34, and 37].

Table 2. Expected Iodine Value from Mass of Oil [13, 40].

Iodine Value Range	Oil Sample in (g)
< 20	1.0 g
21 to 60	0.25 to 0.50 g
61 to 100	0.15 to 0.25 g
> 100	0.10 to 0.15 g

The Sukumar *et al.* had studied the iodine value and correlated the iodine value to the weights different fatty acid methyl esters (FAMES). At last the results had shown R^2 value 0.978 means different FAMES composition really affects the iodine value. The equation 12 shows the iodine value equation.

$$\text{Iodine Value (IV)} = 35.9 - (0.212 \times P) + (0.660 \times S) + (0.448 \times O) + (1.23 \times L) + (1.73 \times LL) \quad (12)$$

Where, IV is the iodine value, P is Palmitic, S is Stearic, O is Oleic, L is Linoleic, and LL is Lenolenic acid of FAMES

3. Results and Discussion

3.1. Thermogravimetric Analysis as Thermal Property

The fractions which contain fewer carbons that evaporates most quickly. It can be seen that as the percentage of the biodiesel fractions increases in the fossil diesel blends, the blends evaporative temperature increases, normally it has been seen that the fossil diesel evaporates around the temperature of 253°C and huge weight loss takes place of fossil diesel at this point. In TGA analysis the figure 1 which show the information of different blends of biodiesel at different temperatures, as the percentage of biodiesel increases in the blends simultaneously its boiling point increases. The TGA test carried out stepwise as temperature is divided in steps i.e. from room temperature 32°C to 150°C, 151°C to 450°C, and 450°C up to 600°C. In between these temperature ranges the percentage loss of weight has been observed.

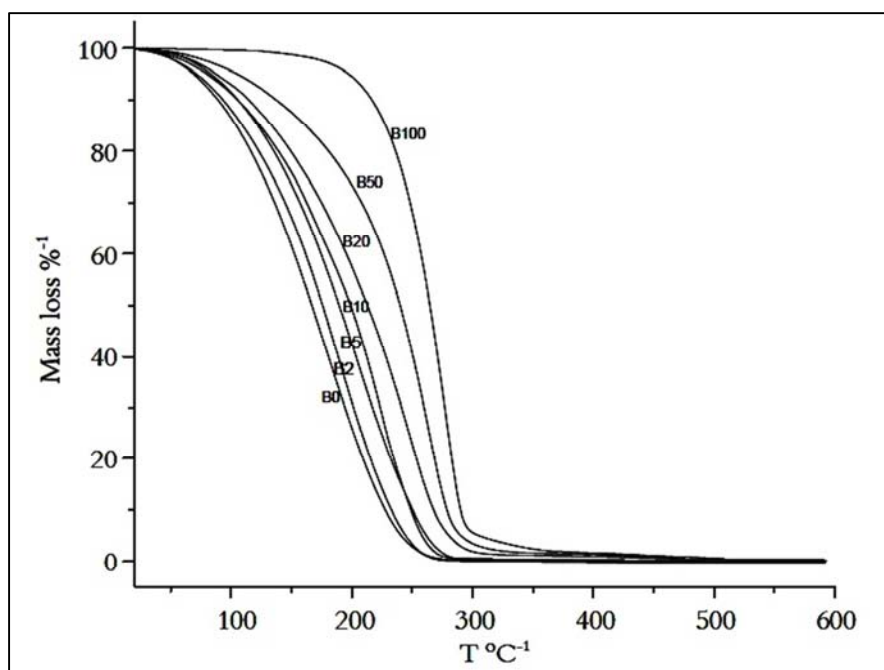


Figure 1. TGA of Biodiesel versus Diesel Blends.

3.2. Density as Physical Property

The density increases as the percentage of biodiesel increases in the blends. As temperature increases the density of biodiesel and diesel blends decreases. So from the literature it has been seen that density is a function of temperature. Figure 2 shows the information about the temperature and density for different biodiesel and their blends.

3.3. Viscosity as a Physical Property

The viscosity of any biodiesel increases as the percentage of

biodiesel increases in the biodiesel and diesel blends. Figure 3 gives the information of the kinematic viscosity for different biodiesels and their blends. Same as that of density the viscosity also increases as the percentage of biodiesel increases in the blends. As the temperature increases the viscosity decreases. Figure 4 shows the information as the temperature increases viscosity decreases, initially at room temperature the viscosity is maximum and at high temperature viscosity is minimum.

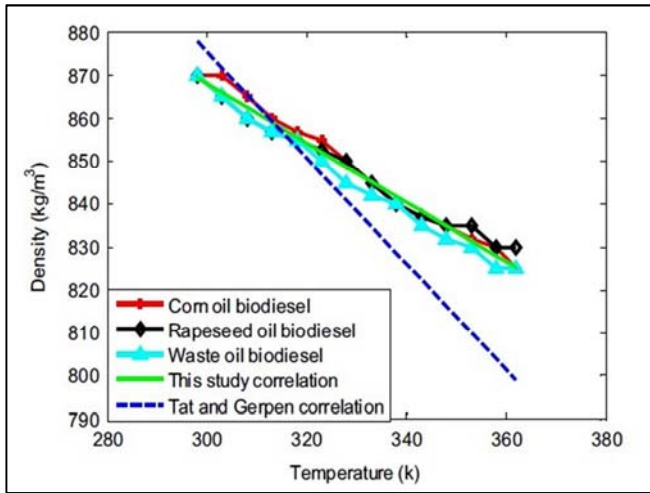


Figure 2. Temperature versus Density.

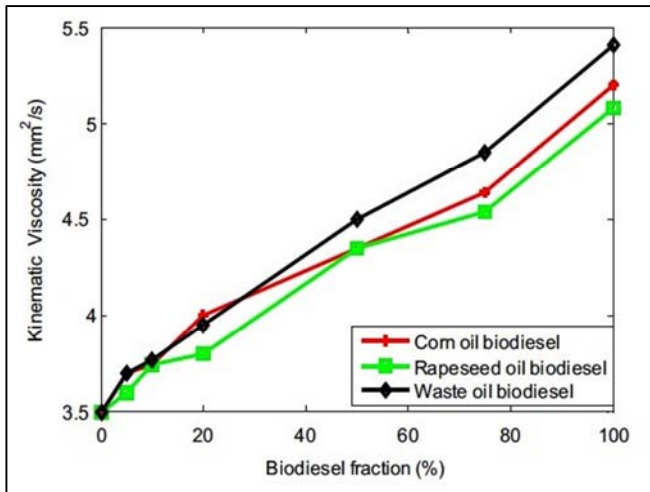


Figure 3. Biodiesel fractions versus kinematic viscosity.

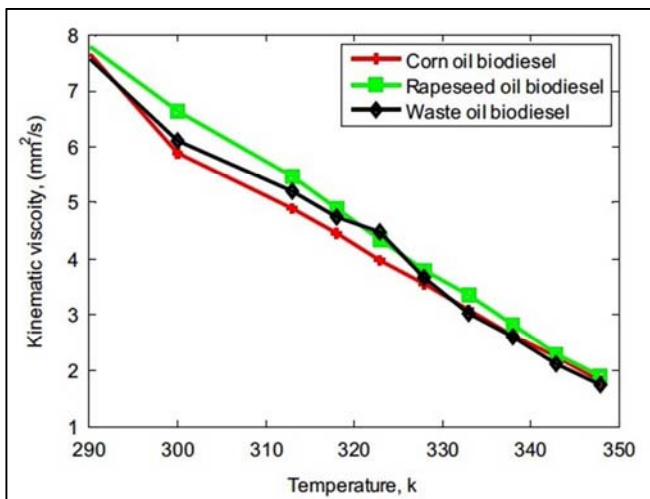


Figure 4. Temperature versus Kinematic Viscosity.

3.4. Iodine Value as Chemical Property

As the iodine value of the oil is defined as the amount of iodine grams which reacts with 100 grams of the oils. The iodine is a measure of the unsaturation of fats and oils and

hence their potential to become oxidized. According the equation 12 which show the FAMES really affect the iodine value. In the figure 5 shows the determined and predicted iodine value which are closer to each other for different biodiesel and their blends.

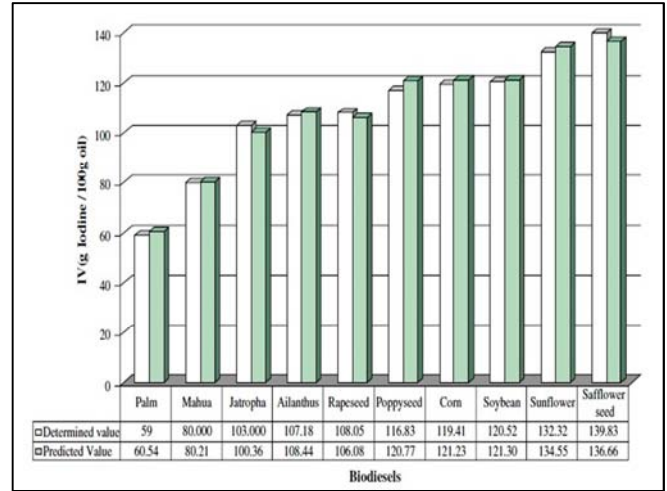


Figure 5. Determined and Predicted IV of different biodiesel.

4. Conclusions

The purpose of this study was to characterize how the thermal, physical, and chemical properties of different biodiesel when blended with fossil diesel.

- The thermogravimetric analysis shown the intervals of distillation of fuel for different biodiesel when it is blended with fossil diesel, biodiesel have higher boiling point as compared to the fossil diesel, as the percentage of any biodiesel increases in the blends its boiling point increases and it may cause the incomplete combustion in the engine with deposit formation. But biodiesel is safer as compared to the fossil diesel because of higher temperature of vaporization.
- It can be clearly seen that there is no equation to the best of authors' knowledge that relates density and viscosity of biodiesel blend, biodiesel fraction, and temperature. Every equation which gives different values of density or specific gravity and viscosity for different biodiesel and diesel blends. As such there is no universal equation available for different biodiesel and diesel blends to estimate these physical properties.
- It has been observed that the chemical property iodine value which is estimated from the weight of the different fatty acid methyl esters for different biodiesel and diesel blends that give strong correlation in between them.

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