

A Laboratory Study of the Effects of Wide Range Temperature on the Properties of Biodiesel Produced from Various Waste Vegetable Oils

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Abstract Biodiesel is an attractive alternative fuel for diesel engines produced from vegetable oils or animal fats by transesterification in the presence of a catalyst. The feedstocks used in this experiment for the production of biodiesel were waste frying oil (WFME) waste canola oil (WCME), and their different percentages are referred to as 25-WFME, 50-WFME and 75-WFME. The samples are sourced from Northern Cyprus. Also, biodiesel was produced at Mechanical Engineering research laboratory. The purpose of this study is to investigate the effect of the temperature on the kinematic, dynamic viscosity and density of the biodiesel samples. Also, this paper examines the cold flow properties as well as the kinematic viscosity, cloud point (CP) and pour point (PP) of the produced biodiesel. The density, kinematic viscosity, CP and PP measurements were made according to ASTM standards. The properties of the produced biodiesel such as viscosity and density were measured within temperature ranges 20–270 °C in steps of 10 °C. The kinematic viscosity, CP and PP were measured within temperature range –10–20 °C. In this study, five general correlations were presented for estimating the density and kinematic viscosity of the blends at several temperatures. The experimental investigation showed that CP and PP of WCME increased with an increase in the concentration of WFME. Furthermore, empirical equations for predicting the viscosity, density, CP and PP for biodiesel samples give values in

good agreement with experiments. The results obtained show that with the increase of the temperature, kinematic viscosity, dynamic viscosity and density decreased.

Keywords Biodiesel · Correlation · Cloud point · Density · Pour point · Viscosity

Introduction

Biodiesel is a clean-burning, renewable fuel, which is defined as the monoalkyl esters of long fatty acids [1–4]. In order to decrease the price of biodiesel, attention has recently been focused on non-edible oils, especially on waste vegetable oils, which are renewable and easily available. Many researchers have investigated the transesterification of waste vegetable oils for the synthesis of biodiesel [5–10]. Transesterification does not change the fatty acid composition of the feedstock. The composition plays an important role to determine some of the main parameters of the biodiesel such as viscosity and cold flow properties. Chain lengths, branching of the chain and degree of saturation generally affect the physical and fuel properties of a fatty acid methyl ester [11, 12]. A change in the nature of the fatty acid profile in the biodiesel leads to overall changes in its fuel properties [13, 14].

One of the most important properties of biodiesel is viscosity, because it affects the fuel injection equipment [15–17], especially in cold weather, since viscosity increases as temperature rises [18]. Biodiesel viscosity is usually higher than that of diesel, and this higher viscosity level result in longer liquid penetration times and worse atomization [17, 19] compared to the case with diesel fuel. Previous studies revealed that the density and viscosity of biodiesel depend on its composition and the temperature

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[20–22]. It was observed that both viscosity and density decrease as the temperature increases.

The effects of main transesterification reaction parameters including the catalyst amount, reaction temperature, reaction time, alcohol/oil molar ratio, on biodiesel properties were investigated by various researchers using different optimization methods such as Response Surface Methodology [23–26]. It has been reported that, an increase in the reaction temperature and alcohol/oil molar ratio lowered the biodiesel yield due to the evaporation of alcohol. Moreover, other researchers have investigated the effect of alcohols on transesterification reaction for the production of biodiesel [27]. It has been concluded that higher alcohols have lesser reactivity so need more catalyst and higher temperature to speed up the reaction.

Several cold flow properties of the diesel and biodiesel fuel are generally used to classify cold weather performance, in terms of the cloud point (CP) and pour point (PP). Researchers have applied various experimental techniques to investigate the cold flow behavior of biodiesel (CP and PP) production from various feedstocks [28–32]. It was revealed that at the temperatures approaching the beginning of crystal formation, the viscosity rapidly increases, and the viscosity of the blend changes of between biodiesel and the diesel.

Some research has been conducted to identify the effect of higher alcohols on biodiesel properties and also to study how cold flow properties can be improved [33]. The most popular higher alcohols are methanol and ethanol, but additional higher alcohols such as 1-propanol, n-butanol butan-2-ol, and iso-propanol are also used. It was obtained that these branched-chain esters reduced the biodiesel crystallization temperature [33].

Several studies have been carried out that focused on replacing diesel fuel with biodiesel, which can be used alone or in blends with diesel fuel [34, 35]. For this reason, in recent years there has been a growing interest on biodiesel production from various vegetable oils in order to widen the available alternatives to diesel fuel.

In this study, biodiesel from waste frying oil and waste canola oil were prepared through transesterification reaction. The effects of temperature (from 20 to 270 °C) on kinematic viscosity, dynamic viscosity, and density of waste oil based biodiesel were examined and compared with those in the standards. Other properties such as Cloud Point, Pour Point as well as kinematic energy were also evaluated from the onset of crystallization to 20 °C. Furthermore, mathematical expressions of temperature dependence of these physical parameters are given to characterize the samples studied. The target of this study is to examine their feasibility for biodiesel production from waste oil in order to promote an economical and environmentally friendly process for biodiesel production. This is

the first study to conduct such an investigation in Northern Cyprus.

Methodology

Biodiesel Samples

Waste frying oil samples were collected from Northern Cyprus and filtered to remove existing inorganic residues. The biodiesel productions from waste oils have been studied in laboratory environment. The similarities in the composition of vegetable oils/animal fats and petroleum derived diesel sustain their conversion to biodiesel [36–38]. Five different biodiesel samples sourced via the transesterification technique were employed, which remains one of the most promising methods [39]. The process transpires in a sequence of three consecutive reversible reactions: triglyceride gets converted stepwise into diglyceride, monoglyceride, and finally, glycerol as a result of which one mole of alkyl ester surfaces in each step [40, 41]. In order to avoid the negative impacts of biofuels on food prices and supplies [42], the transesterification processes in the present study expend waste frying oil and waste canola oil. In this context, waste frying oil refers to a mixture of used frying oil sourced from different restaurants as produced from different feedstock, and waste canola oil refers to used oil from pure canola vegetable oil.

Henceforth, WFME signifies methyl esters of waste frying oil. WCME represents methyl esters of waste canola oil and their different mixing percentages are referred to as 25-WFME, 50-WFME, and 75-WFME, where the number in the prefix indicates the percentage of WFME present in the mixture. Table 1 compares the fatty acid methyl ester composition of WFME and WCME. Also, the composition of each fatty acid present in the mixtures was calculated proportionally according to the required percentages. The fatty acid methyl ester of biodiesel produced from the waste frying oil and canola oil is compared with the available published data in the literature [43–53]. The most common fatty acid components of biodiesel feedstock in the literature were compared with current work, namely, C12:0, C14:0, C16:0, C18:0, C18:1, C18:2, C18:3, C20:0 and C20:1. It is found that the fatty acid composition of the current work was within the range of maximum and minimum of eight fatty acids obtained from the literature and were in good agreement with the published data as shown in Table 1. All samples were sourced from North Cyprus, with the climatic condition tagged as subtropical climate-Mediterranean, according to Koppen climate classification [54]. Calsisol, Leptosol and Vertisol exist as the major soil groups in this area as per Harmonized World Soil Database [55].

Table 1 Fatty acid methyl ester composition (wt%)

	M (g/mol)	Current work						Literature data [43–53]	
		Measured composition (wt%)			Calculated composition (wt%)			Min. value	Max. value
		WFME	WCME		75-WFME	50-WFME	25-WFME		
Methyl caprylate	C8:0	158.2380	0.05	0.00	0.04	0.03	0.01		
Methyl caprate	C10:0	186.2912	0.33	0.00	0.25	0.17	0.08		
Methyl Laurate	C12:0	214.3443	1.18	0.08	0.91	0.63	0.36	0.0	49.2
Methyl myriotate	C14:0	242.3975	0.10	0.00	0.08	0.05	0.03	0.0	25.9
Methyl palmitate	C16:0	270.4507	37.29	5.63	29.38	21.46	13.55	0.9	44.1
Methyl stearate	C18:0	298.5038	4.04	1.57	3.42	2.81	2.19	0.3	23.5
Methyl oleate	C18:1	296.4879	40.42	62.97	46.06	51.70	57.33	1.8	92.5
Methyl linoleate	C18:2	294.4721	17.84	21.34	18.72	19.59	20.47	0.0	77.3
Methyl linolenate	C18:3	292.4562	0.18	6.99	1.88	3.59	5.29	0.0	72.3
Methyl arachidate	C20:0	326.5570	0.00	0.46	0.12	0.23	0.35	0.0	7.5
Methyl erucate	C20:1	324.5411	0.00	1.04	0.26	0.52	0.78	0.0	66.5

Biodiesel Analysis

Biodiesel standards are in place to ensure that only high-quality biodiesel reaches the marketplace. The two most important fuel standards are ASTM D6751 [56] in the United States and EN 14214 (European Committee for Standardization (CEN) [57] in the European Union. Table 2 summarizes the limit values of density and kinematic viscosity for biodiesel and biodiesel petrodiesel blend (B6–B20) fuel, ASTM D7467 [58], ASTM D975 [59], EN 590 [60], ASTM D396 [61] and EN 14213 [62]. In the cases of ASTM D7467, D975, and D396, the

biodiesel component must satisfy the requirements of ASTM D6751 before inclusion in the respective fuels. Correspondingly, in the European Union, biodiesel must satisfy EN 14214 before inclusion into petrodiesel, as mandated by EN 590.

Experimental Setups

The biodiesel samples were analyzed to determine their viscosity, density, and cold flow properties (CP and PP). The effect of temperature on the biodiesel properties including kinematic viscosity, dynamic viscosity, density

Table 2 Generally applicable requirements and test methods

Property	Unit	Standard method	Value according to the standard method
Kinematic viscosity at 40 °C	mm ² /s	ASTM/D.6751	1.9–6.0
<i>ASTM D6751 biodiesel fuel standard</i>			
Kinematic viscosity at 40 °C	mm ² /s	ASTM D445	1.9–6.0
Cloud point	°C	D2500	Report
<i>European committee for standardization EN 14214 biodiesel fuel standard</i>			
Kinematic viscosity at 40 °C	mm ² /s	EN ISO 3104, ISO 3105, EN ISO 310	3.5–5.0
Density at 15 °C	kg/m ³	EN ISO 3675,	
EN ISO 12185	860–900		
Cloud point	°C	EN 23015	Location and season dependant
<i>ASTM D7467 biodiesel-petrodiesel blend (B6–B20) fuel standard</i>			
Kinematic viscosity at 40 °C	mm ² /s	ASTM D445	1.9–4.1
<i>Physicochemical properties of waste frying oils based-biodiesel (ASTM D 6751)</i>			
Kinematic viscosity at 40 °C	mm ² /s	ASTM D445	4.21–6.0
Density at 15 °C	kg/m ³	ASTM D40	867–.....

were tested within the temperature range of 20–270 °C to consider the effect of the injector and fuel supply line temperature. The cold flow properties increased with a higher viscosity values. In addition, high viscosity fuels will take more time to mix with the air inside the engine reducing the quality of the vaporization and atomization of the fuel. To reduce the impact of viscosity, the blending method has a positive effect on diesel engine performance as it improves lubricity [63–67]. Therefore, the temperature effect on cold flow properties and kinematic viscosity were investigated over the temperature range from the onset of crystallization until 20 °C.

Kinematic Viscosity Setup

From 20 to 270 °C Ubbelohde viscometer (ASTM) was used to measure the kinematic viscosity because of its well-known application and accuracy. It enables transparent and high temperature measurement [68]. To ensure precise and stable temperature control during measurements, a digital temperature controller resistance was used to measure the temperature. A uniform temperature inside the silicon oil bath was attained. However, the mixer enabled the regulation of the temperature of a heated oil bath containing the viscometer by means of an electric heater. The temperature of the oil bath was varied from 20 to 270 °C. Each sample was tested four times, and the average viscosity was calculated. Figure 1 shows the experimental setup used to determine the temperature dependence of density and viscosity of the samples analyzed. In order to precisely determine the relationship between the time of flow and the kinematic viscosity for the three viscometers used, calibration of the instrument is necessary. The calibration was done by the manufacturer, SI Analytics GmbH, Mainz according to ASTM D 2525/D 446 and ISO/DIS 3105. The instrument constant, K , [(mm²/s)/s] was determined and given as in Table 3. The calibration constant can be used

up to the temperature of 270 °C, and the influence of the temperature on the capillary constant due to thermal expansion of the Duran glass is negligible [69]. For absolute measurement, the corrected flow time multiplied by the viscometer constant K directly gives the kinematic viscosity (mm²/s) as given in Eq. (1).

$$v = K(t - y) \quad (1)$$

where v , K , t , and y represent the kinematic viscosity, the calibration constant, measured time of flow and kinetic energy correction [70] (HC, as given by the manufacturer) respectively.

From -10 to 20 °C Figure 2 shows the experimental setup used to measure the kinematic viscosity of vegetable oils in the temperature range -10 to 20 °C. The experimental setup consists of a cooling bath (glass aquarium), a compressor, a mixer, and a thermostat. Alcohol (ethanol) is the simplest and cheapest cooling bath. To obtain a uniform temperature distribution within cooling bath, the cooling bath is equipped with a mixer to circulate the alcohol. The bath temperature was controlled using a thermostat, by automatically starting up and shutting down the compressor. A coil connected to a compressor cools down the liquid bath, and the compressor is cooled down by a radiator as shown in Fig. 2. The cooling bath was thermally isolated from the rest of its surroundings by a 3 cm thick Styrofoam layer.

Density Setup

The density measurement was made according to ASTM standard D854. The density of the biodiesel was measured using a pycnometer with a bulb capacity of 25 ml. However, all density measurements were performed in triplicate with the pycnometer. The weighting was done by using a high precision AND an electronic balance (model HR 300,

Fig. 1 Schematic of the experimental setup used to measure the viscosity of biodiesel in the temperature range 20–270 °C

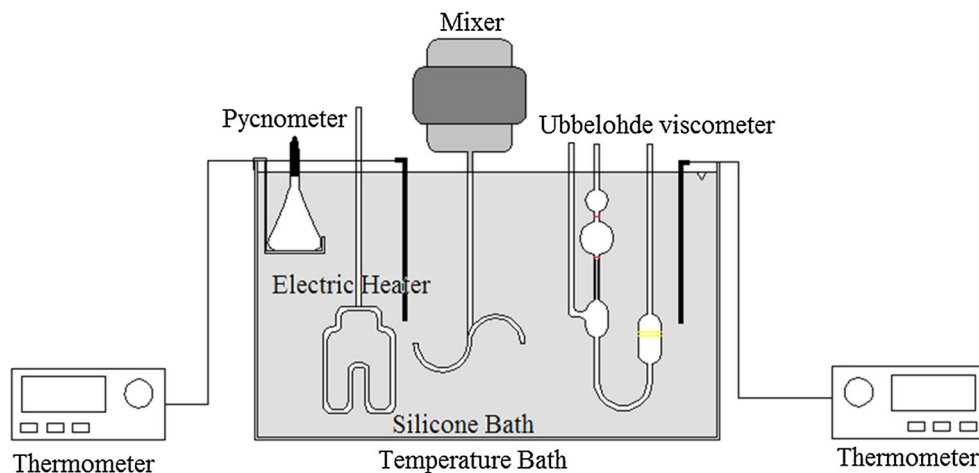


Table 3 Ubbelohde Viscometer technical specifications

Capillary no.	Capillary dia. $I \pm 0.01(\text{mm})$	Constant K, $(\text{mm}^2/\text{s})/\text{s}$	Measuring range (mm^2/s)
0c	0.36	0.002856	0.6–3
I	0.58	0.009132	2–10
IC	0.78	0.02799	6–10

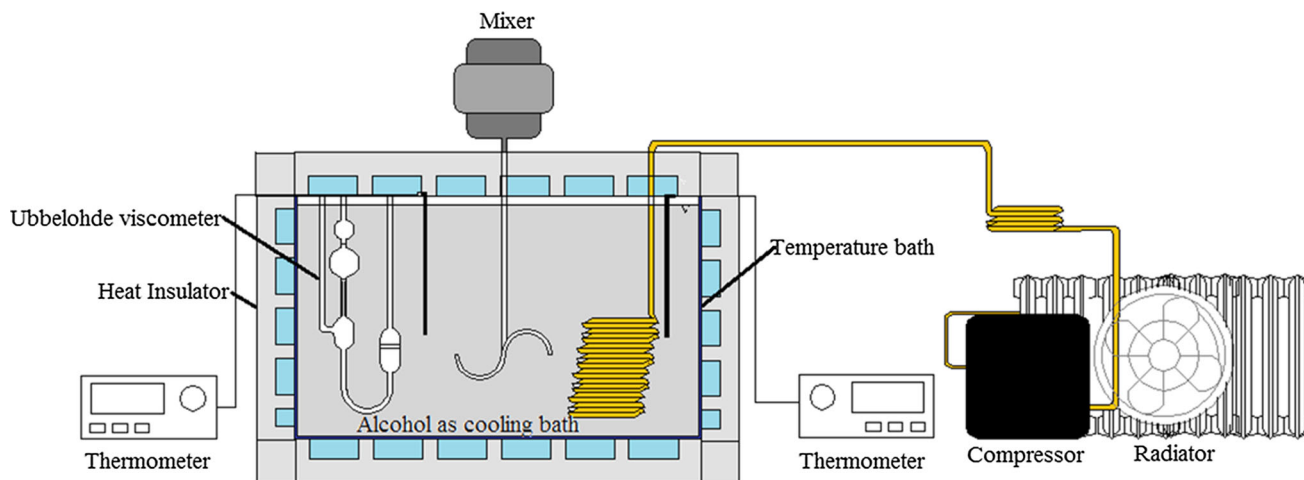


Fig. 2 Schematic of the Cooling bath system for measuring kinematic viscosity in temperature range $-10-20\text{ }^\circ\text{C}$

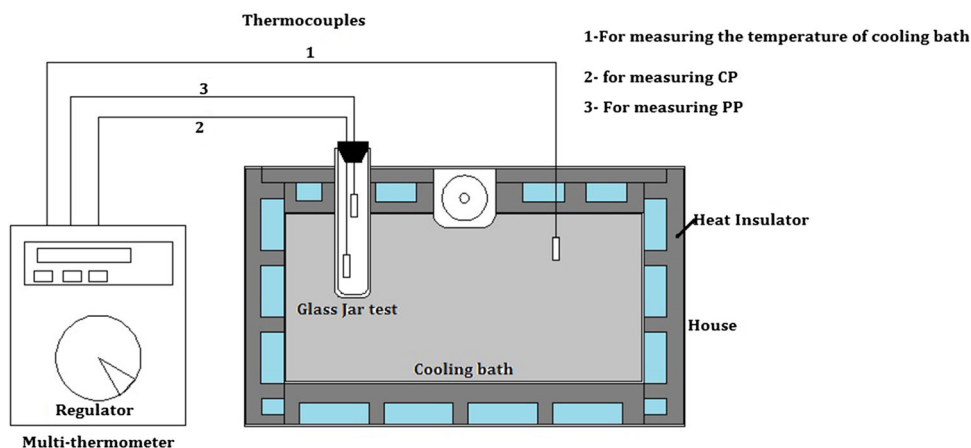
Japan) with a precision of $\pm 0.1\text{ mg}$. The density values of the samples were measured for temperatures between 20 to $270\text{ }^\circ\text{C}$. The experimental setup of measuring the density of biodiesel samples is shown in Fig. 1.

Cloud Point and Pour Point Setup

The biodiesel samples were tested as per American standard test method for Cloud Point and Pour Point, ASTM D2500, and ASTM D97, respectively. The setup mainly consisted of a cooling bath, glass test jar, thermocouples, multi-thermometer, and a regulator as depicted in Fig. 3. A glass test jar was placed in an aluminum cylinder inside the cooling bath liquid. The glass test jar

was isolated from the aluminum cylinder by means of a cork support, stopper and ring assembly. Also, the cylinder has been immersed into an 8-liter stainless steel cooling bath containing alcohol at $-25\text{ }^\circ\text{C}$. The cooling bath was put inside an 11 cm thick styrofoam block in order to isolate it from any vibrations and heat transfer to keep the cooling bath temperature at the required temperature during the test very cold for a long period of time. The entire system was covered by a 3 cm thick wooden box. Three T-type thermocouples were used to measure the temperature in the cooling bath; the first one to measure the temperature of the bath, the second one is used to measure Cloud Point, which was placed at the bottom of the glass test jar, while the last one to measure the Pour

Fig. 3 The schematic of the cloud point and pour point measurement apparatus



Point, which was placed in the upper part of the sample in the glass test jar.

Results and Discussion

Accuracy and Repeatability

To ensure the accuracy of the results, an accuracy and repeatability test was carried out. The kinematic viscosity of pure water at 30 °C was found to be 0.803 mm²/s. The value is given as 0.80908 mm²/s [71]. The percent error of the measured value was calculated to be less than 1 %. Table 4 shows the repeatability test results for some samples at specific temperatures. For each sample type, the measurement of the flow time was repeated at each specific temperature four times, and the average flow time was recorded for the calculation of kinematic viscosity. However, with accuracy and repeatability error less than 1 %, it can be concluded that the results to be discussed are 99 % accurate and precise. These measurements were carried out at different temperatures (see Table 4) and atmospheric pressure.

Kinematic Viscosity

From 20 to 270 °C Figure 4 shows the relationship between the kinematic viscosity and temperature of WFME, WCME, 25-WFME, 50-WFME, and 75-WFME, respectively. It can be seen that viscosity decreases as

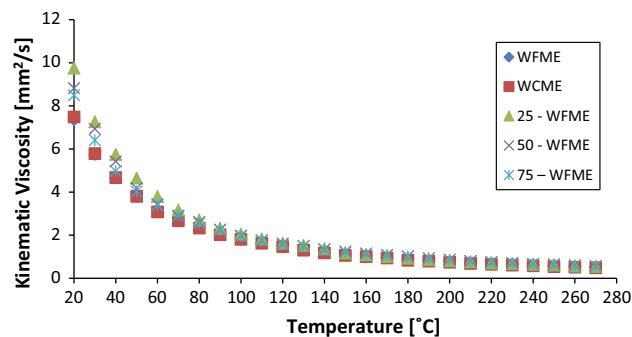


Fig. 4 Kinematic viscosity—temperature relationship for all samples

temperature increases and this behavior can be explained by kinetic molecular theory [72].

Figure 5 shows the change of the kinematic viscosity with the increase of the percentage of WFME to WCME. The x-axis represents the fraction of WCME, whereas the kinematic viscosity values are provided on the y-axis. It can be observed that the kinematic viscosity decreased as the percentage of WFME increased for each temperature considered.

From –10 to 20 °C Figure 6 and Table 5 provide the kinematic viscosity of biodiesel samples. The tests were initially conducted by 5 °C increments. Toward, the end of the tests 1 °C or 2 °C increments were taken to determine the highest kinematic viscosity of the samples.

It can be seen from Fig. 6 that decreasing the temperature leads to a rapid increase in the kinematic viscosity of

Table 4 Ubbelohde viscometer repeatability results for some of the biodiesel samples

Fluid type	Temperature (°C)	Measured kinematic viscosity (mm ² /s)	Average kinematic viscosity (mm ² /s)
WFME	40	4.670	4.665
		4.664	
		4.669	
		4.660	
		4.660	
WFME	80	2.355	2.353
		2.351	
		2.354	
		2.353	
WCME	40	4.699	4.678
		4.664	
		4.659	
		4.691	
50-WFME	40	5.422	5.421
		5.418	
		5.423	
		5.421	

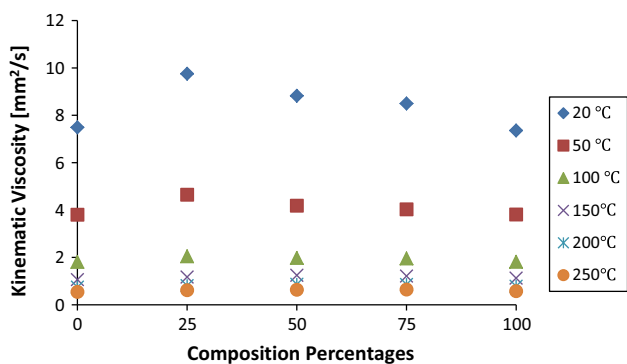


Fig. 5 Kinematic viscosity and percentage composition relationship

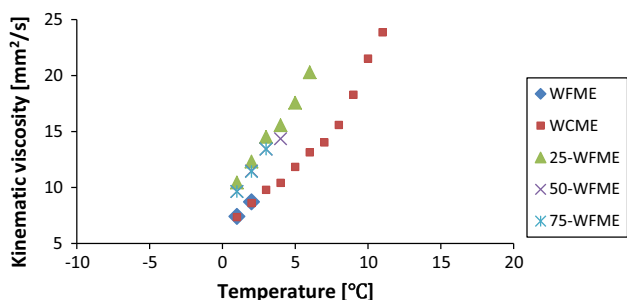


Fig. 6 Kinematic viscosity-temperature relationships of the biodiesel samples

biodiesel samples. The formation of crystals of biodiesel samples occurred at various temperatures depending on the percentage of WFME as shown in Table 5.

Density

The density of five samples of biodiesel was measured at a range of temperature, and the results are shown in Fig. 7. It

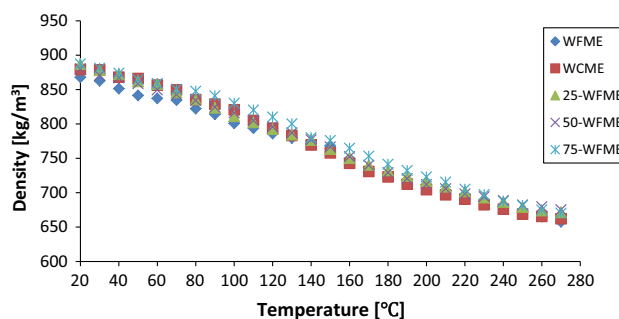


Fig. 7 Density—temperature relationship for all samples

was observed that the density of the blends increased with the percentage of WFME in the blend at all temperatures and decreased with the increase in temperature for all the tested biodiesel samples.

The relationship between the density of the sample and their relative composition percentage at some chosen temperature is shown in Fig. 8.

Dynamic Viscosity

Dynamic viscosity values were calculated from the density and kinematic viscosity by multiplying the measured density and the kinematic viscosity values. The variations in the dynamic viscosity of different blends of WFME and WCME with temperature are shown in Fig. 9. The results showed that, for each of the blends with different percent mixture composition, the viscosity decreased rapidly non-linearly with increasing temperature.

The change of the dynamic viscosity with the increasing of percentage of WFME to WCME at chosen temperatures is shown Fig. 10. The figure shows that the increase of the

Table 5 Kinematic viscosities of five biodiesel fuel samples in the temperature range –10–20 °C

Temperature (°C)	Kinematic viscosity (mm ² /s)				
	WCME	25-WFME	50-WFME	75-WFME	WFME
20	7.351	10.4399	9.637	9.637	7.415
15	8.612	12.315	11.472	11.426	8.711
10	9.788	14.519	13.42	13.42922	nd ^a
8	10.414	15.557	14.351	nd ^a	–
5	11.834	17.57	nd ^a	–	–
2	13.143	20.284	–	–	–
0	14.03	nd ^a	–	–	–
–3	15.59	–	–	–	–
–5	18.282	–	–	–	–
–7	21.516	–	–	–	–
–8	23.8629	–	–	–	–
–10	nd ^a	–	–	–	–

^a (not determined), Formation of crystals at this temperature

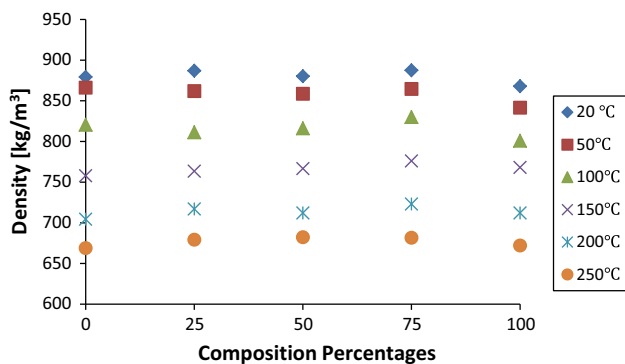


Fig. 8 Density and percentage composition relationship

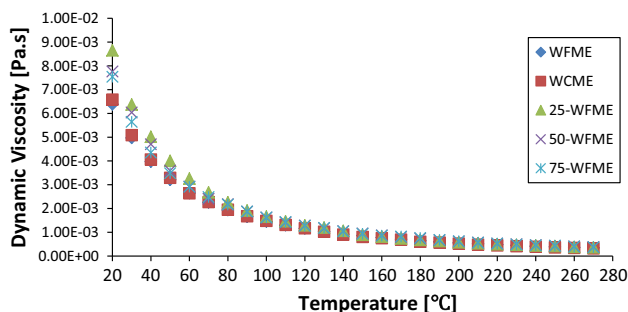


Fig. 9 Dynamic viscosity–temperature relationship for all biodiesel samples

percentage of WFME leads to a decrease in the dynamic viscosity of the biodiesel.

Cloud Point and Pour Point

Cloud point is the temperature at which small solid crystals are observed at first as the fuel is cooled [73]. In this experiment, the cloud point was definitely the temperature point when the character on the reverse side of the test tube was disappearing due to the formation of crystal wax. Pour Point was determined by cooling down the samples until the biodiesel was totally ceased, and then the degree before

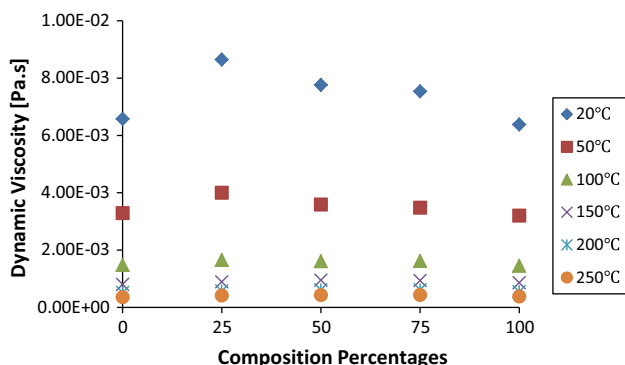


Fig. 10 Density and percentage composition relationship

the ceasing point was recorded. Pour Points and Cloud Points of biodiesel samples are shown in Table 6. It can be seen from Table 6 and Fig. 11 that increasing the percentage of WFME leads to an increase of the Pour Point and Cloud Point of the biodiesel samples.

Mathematical Models of Biodiesel Samples

A mathematical model is a simple description of physical, chemical or biological processes. Saxena et al. [74] reviewed various methods for the prediction of important thermophysical properties such as cetane number, kinematic viscosity, density, higher heating value, flash point, cloud point, pour point, cold filter plugging point and vapor pressure for various biodiesel feedstocks.

Sivaramakrishnan and Ravikumar [75] developed an equation to calculate cetane number of various vegetable oils and their biodiesel from their viscosity, density, flash point and higher calorific value. They concluded that this equation gives an accuracy of 90 %.

For vegetable oils, it has been shown that density decreases linearly with an increase in temperature. This correlation can be expressed mathematically as in [76],

$$\rho = a + bT \quad (2)$$

where ρ is the density expressed in g cm^3 , T is the temperature expressed in $^{\circ}\text{C}$, a is the intercept and b is a negative slope.

According to Krisnangkura et al. [77], viscosity may be considered the integral of the interaction forces of molecules. When heat is applied to fluids, molecules can then slide over each other more easily making the liquid to become less viscous. The effect of temperature on the kinematic viscosity of a given liquid is described by means of the Arrhenius equation

$$v = A_1 \exp\left(\frac{E_a}{RT}\right) \quad (3)$$

where v is the kinematic viscosity, mm^2/s , E_a the activation energy for flow, R the universal gas constant and T the absolute temperature, K . Additionally, $A_1 = \frac{N_A h}{V}$ where N_A , V and h are the Avogadro's number, the molecular volume and the Planck's constants, respectively. The SI physical unit of kinematic viscosity is $\text{m}^2 \text{s}^{-1}$. In the case of vegetable oils, Eq. (3) can be rewritten as in Eq. (4), which is known as the Andrade equation [76, 77]

$$v = A_1 \exp\left(\frac{B}{T}\right) \quad (4)$$

where T is the absolute temperature and A_1 and B are specific constants to be adjusted for each specific oil. By applying logarithms to both sides of Eq. (4) we get:

Table 6 Cloud point and pour point of the five biodiesel samples

Biodiesel samples	WFME (%)	Cloud point (°C)	Pour point (°C)
WCME	0	−1	−10.5
25-WFME	25	5.7	−1
50-WFME	50	11.5	3.5
75-WFME	75	14	7.7
WFME	100	17.8	11.3

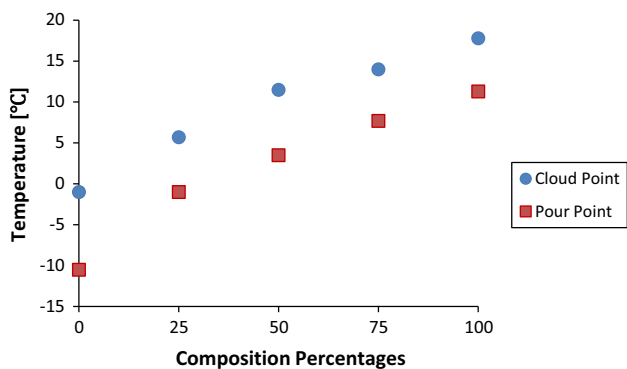


Fig. 11 The cloud and Pour Points of biodiesel samples

$$\ln(v) = A + \frac{B}{T} \tag{5}$$

Equation (4) allows us to linearize Eq. (4) by applying the least-squares method and making 1/T the independent variable. Additionally, Azian et al. [78] suggested modifying Eq. (5), which is especially useful when dealing with wide temperature ranges,

$$\ln(v) = A + \frac{B}{T} + \frac{C}{T^2} \tag{6}$$

Sometimes, the dynamic or absolute viscosity μ is applied, which can be calculated from the kinematic viscosity ν and the density ρ as,

$$\mu = \nu\rho \tag{7}$$

The SI physical unit of dynamic viscosity is the Pa s. The viscosity of biodiesel could be estimated by the empirical equations derived from Grunberg–Nissan’s equation at which the interaction term of the binary pairs of methyl ester has been neglected. These equations were proposed by Ramirez-Verduzco [79].

$$\rho_b = \sum_{i=1}^n w_i \left(1.069 + \frac{3.575}{M_i} + 0.0113N_i - 7.41 \times 10^{-4}T \right) \tag{8}$$

$$\ln\mu_b = \sum_{i=1}^n w_i \left(-18.354 + 2.362\ln M_i - 0.127N_i + \frac{2009}{T} \right) \tag{9}$$

w_i, M_i, N_i are the mass fraction (wt%/100), molecular weight in g/mol, and the number of double bond in the fatty acid chain respectively (refer to Table 1). T is the temperature in Kelvin, ρ_b is the density of the biodiesel in g/cm³, μ_b is the dynam viscosity in mPa s. The kinematic viscosity is estimated from Eqs. (8) and (9).

$$\nu_b = \frac{\mu_b}{\rho_b} \tag{10}$$

To predict the viscosities and densities of biodiesel samples at different temperature the correlation between viscosity and temperature and density and temperature, a statistical software package was used to analyze the data. The best correlation between viscosity and temperature as well as between density and temperature for each of biodiesel sample can generally be written as shown in Table 7. Overall, the empirical equations realize the best accuracy for the prediction kinematic viscosity, dynamic viscosity, and density of five samples with the highest correlation coefficient of 0.999. Furthermore, this shows that the empirical equations can be used confidently to predict the biodiesel properties (kinematic, dynamic viscosity and density).

The measurements of the cloud point and pour point were correlated as a function of percentage composition by empirical second order polynomial equations. From the regression coefficient, it was observed that the regression analysis of the data shows that the polynomial equation is better fitted for the measured values than a linear equation [80, 81].

The proposed equations for calculating cloud point and pour point as a function of composition respectively are shown in Table 7.

As both density and viscosity are highly temperature sensitive, it is possible to determine the dependence between them. According to Rodenbush et al. [75], when dealing with vegetable oils, the dependence between density and viscosity can be expressed as illustrated in

$$\rho = D + \frac{E}{\nu^{1/2}} \tag{11}$$

Equation (11) is particularly useful because it can be adjusted by means of a least-squares linear regression by choosing $1/\nu^{1/2}$ as an independent variable.

Table 7 General mathematical-physical model of the biodiesel samples based on the temperature

From 20 to 270°C				From -10 to 20°C			
Kinematic viscosity (mm ² /s)				Kinematic viscosity (mm ² /s)			
$\nu = \exp(A + B/T)$				$\nu = \exp(A + B/T)$			
	A	B	R ²		A	B	R ²
WFME	-3.709	1629.546	0.995	WFME	-7.275	2718.542	1.000
WCME	-3.856	1677.753	0.996	WCME	-8.704	3114.84	0.970
25-WFME	-3.953	1770.771	0.993	25-WFME	-7.635	2921.147	0.996
50-WFME	-3.678	1659.55	0.992	50-WFME	-6.998	2715.690	0.999
75-WFME	-3.626	1631.429	0.993	75-WFME	-7.120	2750.748	0.999

From 20 to 270°C				From 20 to 270°C			
Density (kg/m ³)				Dynamic viscosity (Pa.s)			
$\rho = A - BT$				$\nu = \exp(A + B/T)$			
	A	B	R ²		A	B	R ²
WFME	1127.348	0.872	0.997	WFME	-11.343	1812.064	0.998
WCME	1176.388	0.979	0.989	WCME	-11.539	1881.91	0.999
25-WFME	1156.379	0.92	0.994	25-WFME	-11.597	1961.845	0.997
50-WFME	1144.683	0.893	0.991	50-WFME	-11.309	1845.049	0.996
75-WFME	1170.283	0.935	0.994	75-WFME	-11.259	1822.509	0.997

From 20 to 270°C				From 20 to 270°C			
Density-kinematic viscosity				Cloud Point (°C)			
$\rho = \exp(A + B/\nu)$				$CP = A + By + Cy^2$			
	A	B	R ²	A	B	C	R ²
WFME	6.778	-0.158	0.993	-0.88	0.288	-0.001	0.995
WCME	6.794	-0.163	0.978	Pour Point (°C) $PP = A + By + Cy^2$			
25-WFME	6.787	-0.167	0.985				
50-WFME	6.788	-0.173	0.976	A	B	C	R ²
75-WFME	6.788	-0.180	0.988	-10.429	0.474	-0.005	0.999

T the temperature of biodiesel (K); y the percentage of biodiesel

Table 7 shows the relationship between the density and kinematic viscosity and indicates that equation is accomplished when dealing with the studied biodiesel prepared from waste oil obtained notably high R^2 values in all biodiesel samples.

Conclusions and Future Works

The biodiesel samples were prepared via the transesterification method to investigate the biodiesel properties. The kinematic viscosity and density of the prepared biodiesel samples were within the European biodiesel standard and with the exception of the American specifications. In this study, the biodiesel properties (kinematic viscosity, dynamic viscosity and density) and cold flow properties (CP and PP) and kinematic viscosity of the biodiesel samples were measured within the temperature range from

20 to 270 °C and –10 to 20 °C, respectively. The following points have been observed based on the results obtained from the experiments:

1. At high temperatures (above 250 °C), the value of the kinematic viscosity is almost equal and the difference between these values is about 3 %.
2. It has been noticed that the density and the viscosity of the biodiesel sample increase with the increase of the biodiesel fraction. It is also seen that the density and viscosity of each sample decrease with an increase in the temperature.
3. The cloud point and pour point of the WCME increased when the WFME contents of the mixture increase.
4. Empirical equations to predict the density and the viscosity of the biodiesel and its blends as a function of temperature have been developed. The empirical equations and the measured data closely match with

R^2 of 0.995 for density, kinematic viscosity, PP and CP model.

- As a result, it is suggested from the study that it is possible to use the biodiesel obtained from waste oils as an alternative fuel, which can be considered as renewable energy and environmental recycling process from waste oil after frying.

An interesting future study might measure the other properties of the biodiesel samples such as the specific gravity and cold filter plugging point. Moreover, to improve the cold flow properties of the biodiesel samples, some kind of improvers such as conventional diesel fuel (petrodiesel) or alkyl esters can be added.

Since biodiesel can degrade due to oxidation, contact with water, and/or microbial activity, the storage of biodiesel over extended periods may lead to degradation of its fuel properties. Consequently, this research suggests that the degradation process of biodiesel at different temperatures and exposure times should be studied in the future.

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References

- Bhale, P.V., Deshpande, N.V., Thombre, S.B.: Improving the Low temperature properties of biodiesel fuel. *Renew. Energ.* **34**, 794–800 (2009)
- Joshi, R.M., Pegg, M.J.: Flow properties of biodiesel fuel blends at low temperatures. *Fuel* **86**, 143–151 (2007)
- Knothe, G.: Biodiesel: current trends and properties. *Top. Catal.* **53**, 714–720 (2010)
- American Society for Testing and Materials (ASTM) Standard D 6751. Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. ASTM, Conshohocken
- Refaat, A.A.: Different techniques for the production of biodiesel from waste vegetable oil. *Int. J. Environ. Sci. Technol.* **7**(1), 183–213 (2010). doi:10.1007/bf03326130
- Yuan, W., Hansen, A.C., Zhang, Q.: Predicting the temperature dependent viscosity of biodiesel fuels. *Fuel* **88**, 1120–1126 (2009)
- Jiao, J., Gai, Q.Y., Wei, F.Y., Luo, M., Wang, W., Fu, Y.J., et al.: Biodiesel from forsythia suspense [(Thunb.) vahl (Oleaceae)] seed oil. *Bioresour. Technol.* **143**, 653–656 (2013)
- Chu, J., Xu, X., Zhang, Y.: Production and properties of biodiesel produced from *Amygdalus pedunculata* Pall. *Bioresour. Technol.* **134**, 374–376 (2013)
- Knothe, G.: Avocado and olive oil methyl esters. *Biomass Bioenergy* **58**, 143–148 (2013)
- Uzun, B.B., Kilic, M., Ozbay, N., Putun, A.E., Putun, E.: Biodiesel production from waste frying oils: optimization of reaction parameters and determination of fuel properties. *Energy* **44**, 347–351 (2012)
- Mejía, J.D., Salgado, N., Orrego, C.E.: Effect of blends of diesel and palm-caster biodiesels on viscosity, cloud point and flash point. *Ind. Crops Prod.* **43**, 791–797 (2013)
- Knothe, G.: Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Process. Technol.* **86**, 1059–1070 (2005)
- Mejía, J.D., Salgado, N., Orrego, C.E.: Effect of blends of diesel and palm-caster biodiesels on viscosity, cloud point and flash point. *Ind. Crops Prod.* **43**, 791–797 (2013)
- Knothe, G., Steidley, K.R.: A comparison of used cooking oils: a very heterogeneous feedstock for biodiesel. *Bioresour. Technol.* **100**, 5796–5801 (2009)
- Poling, B.E., Prausnitz, J.M., O’Connell, J.P.: The properties of gases and liquids, 5th edn. McGraw-Hill, New York (2001)
- Knothe, G., Krahl, J., Van Gerpen, J.H.: The biodiesel handbook, 2nd edn. AOCS Press, Champaign IL (2010)
- Hoekman, S.K., Broch, A., Robbins, C., Cenicerros, E., Natarajan, M.: Review of biodiesel composition, properties, and specifications. *Renew. Sustain. Energy Rev.* **16**, 143–169 (2012)
- Freitas, S.V.D., Pratas, M.J., Ceriani, R., Lima, A.S., Coutinho, J.A.P.: Evaluation of predictive models for the viscosity of biodiesel. *Energy Fuels* **25**, 352–358 (2011)
- Meng, X., Jia, M., Wang, T.: Predicting biodiesel densities over a wide temperature range up to 523 K. *Fuel* **111**, 216–222 (2013)
- Esteban, B., Riba, J., Baquero, G., Rius, A., Puig, R.: Temperature dependence of density and viscosity of vegetable oils. *Biomass Bioenerg* **42**, 164–171 (2012)
- Moradi, R., Karami, B., Mohadesi, M.: Densities and kinematic viscosities in biodiesel – diesel blends at various temperatures. *American chemical society. J. Chem. Eng. Data* (2012). doi:10.1021/je3008843
- Ustra, M., Silva, F., Ansolin, M., Balen, M., Cantelli, K., Alkimim, I., Mazutti, M., Voll, F., Cabral, V., Cardozo-Filho, L., Corazza, M., Vladimir Oliveira, J.: Effect of temperature and composition on density, viscosity and thermal conductivity of fatty acid methyl esters from soybean, castor and *Jatropha curcas* oils. *J. Chem. Thermodyn.* **58**, 460–466 (2013)
- Verma, P., Sharma, M.P., Dwivedi, G.: Prospects of bio-based alcohols for Karanja biodiesel production: an optimisation study by Response Surface Methodology. *Fuel* **183**, 185–194 (2016)
- Bilgin, A., Gülüm, M., Koyuncuoglu, İ., Nac, E., Cakmak, A.: Determination of transesterification reaction parameters giving the lowest viscosity waste cooking oil biodiesel. *Procedia Soc. Behav. Sci.* **195**, 2492–2500 (2015)
- Verma, P., Sharma, M.P.: Review of process parameters for biodiesel production from different feedstocks. *Renew. Sustain. Energy Rev.* **62**, 1063–1071 (2016)
- Dwivedi, G., Sharma, M.P.: Application of Box-Behnken design in optimization of biodiesel yield from *Pongamia* oil and its stability analysis. *Fuel* **145**, 256–262 (2015)
- Verma, P., Sharma, M.P.: Comparative analysis of effect of methanol and ethanol on Karanja biodiesel production and its optimisation. *Fuel* **180**, 164–174 (2016)
- Bryan, R.: Moser, impact of fatty ester composition on low temperature properties of biodiesel–petroleum diesel blends. *Fuel, Elsevier* **115**, 500–506 (2014)
- Mushtaq, M., Tan, I., Nadeem, M., Devi, C., Lee, S., Sagir, M.: A convenient route for the alkoxylation of biodiesel and its influence on cold flow properties. *Int. J. Green Energ.* **11**, 267–279 (2014). doi:10.1080/15435075.2013.772519
- Kim, J., Yim, E., Jeon, C., Jung, C., Han, B.: Cold performance of various biodiesel fuel blends at low temperature. *Int. J. Automot. Technol.* **13**(2), 293–300 (2012). doi:10.1007/s12239-012-0027-2

31. Rasimoglu, N., Temur, H.: Cold flow properties of biodiesel obtained from corn oil. *Energy* **68**, 57–60 (2014)
32. Nainwal, S., Sharma, N., Sharma, A., Jain, S., Jain, S.: Cold flow properties improvement of *Jatropha curcas* biodiesel and waste cooking oil biodiesel using winterization and blending. *Energy* **89**, 702–707 (2015)
33. Verma, P., Sharma, M.P., Dwivedi, G.: Impact of alcohol on biodiesel production and properties. *Renew. Sustain. Energy Rev.* **56**, 319–333 (2016)
34. Verma, P., Sharma, M.P.: Performance and emission characteristics of biodiesel fuelled diesel engines. *Int. J. Renew. Energy Res.* **5**(1), 2015
35. Verma, P., Sharma, M.P., Dwivedi, G.: Evaluation and enhancement of cold flow properties of palm oil and its biodiesel. *Energy Reports* **2**, 8–13 (2016)
36. Demirbas, A.: Progress and recent trends in biodiesel fuels. *Energy Conserv. Manag.* **50**, 14–34 (2009)
37. Bajpai, D., Tyagi, V.K.: Biodiesel: source, production, composition, properties and its benefits. *J. Oleo Sci.* **55**, 487–502 (2006)
38. Ma, F., Hanna, M.A.: Biodiesel production: a review. *Bioresour. Technol.* **70**, 1–15 (1999)
39. Poonam, N.S., Anoop, S.: Production of liquid biofuels from renewable resources. *Prog. Energy Combust. Sci.* **37**, 52–68 (2011)
40. Marchetti, J.M., Miguel, V.U., Errazu, A.F.: Possible methods for biodiesel production. *Renew. Sust. Energy Rev.* **11**, 1300–1311 (2007)
41. Helwani, Z., Othman, M.R., Aziz, N., Fernando, W.J.N., Kim, J.: Technologies for production of biodiesel focusing on green catalytic techniques: a review. *Fuel Process. Technol.* **90**, 1502–1514 (2009)
42. Govinda, R.: Timilsina, and Ashish Shrestha, how much hope should we have for biofuels? *Energy* (2010). doi:10.1016/j.energy.2010.08.023
43. Dunn, R.O.: Cold flow properties of biodiesel by automatic and manual analysis methods. *J. ASTM Int.* **7**(4), 1–15 (2010)
44. Ramos, M.J., Fernández, C.M., Casas, A., Rodríguez, L., Pérez, A.: Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresour. Technol.* **100**, 261–268 (2009)
45. Giakoumis, E.G.: A statistical investigation of biodiesel physical and chemical properties, and their correlation with the degree of unsaturation. *Renew. Energy* **50**, 858–878 (2013)
46. Hoekman, S.K., Broch, A., Robbins, C., Ceniceros, E., Natarajan, M.: Review of biodiesel composition, properties, and specifications. *Renew. Sust. Energy Rev.* **16**, 143–169 (2012)
47. Amani, M.A., Davoudi, M.S., Tahvildari, K., Nabavi, S.M., Davoudi, M.S.: Biodiesel production from *Phoenix dactylifera* as a new feedstock. *Ind. Crop Prod.* **43**, 40–43 (2013)
48. Moser, B.R.: Influence of blending canola, palm, soybean, and sunflower oil methyl esters on fuel properties of biodiesel. *Energy Fuel* **22**(6), 4301–4306 (2008)
49. Sahoo, P.K., Das, L.M.: Process optimization for biodiesel production from *Jatropha*, *Karanja* and *Polanga* oils. *Fuel* **88**, 1588–1594 (2009)
50. Sanford, S.D., White, J.M., Shah, P.S., Wee, C., Valverde, M.A., Meier, G.R.: Feedstock and biodiesel characteristics report. Renewable Energy Group Inc, Iowa (2010)
51. Tang, H., Salley, S.O., Simon, K.Y.: Fuel properties and precipitate formation at low temperature in soy, cottonseed, and poultry fat-based biodiesel blends. *Fuel* **87**, 3006–3017 (2008)
52. Usta, N., Aydoğan, B., Çon, A.H., Uğuzdoğan, E., Özkal, S.G.: Properties and quality verification of biodiesel produced from tobacco seed oil. *Energy Convers. Manag.* **52**, 2031–2039 (2011)
53. Al-Shanableh, F., Evcil, A., Savas, M.A.: Prediction of cold flow properties of biodiesel fuel using artificial neural network. *Procedia. Comput. Sci. PROCES10116* (in press)
54. Peel, M.C., Finlayson, B.L., McMahon, T.A.: Updated world map of the Köppen-Geiger climate classification. *Hydrol. Earth Syst. Sci.* **11**, 1633–1644 (2007). doi:10.5194/hess-11-1633-2007
55. FAO, IIASA, ISRIC, ISSCAS, JRC: Harmonized World Soil Database (version 1.1). FAO, Rome (2009)
56. ASTM Standard specification for biodiesel fuel (B100) blend stock for distillate fuels. In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D6751-08 (2008a)
57. Tomes, D.T., Lakshmanan, P., Songstad, D.: Biofuels: Global Impact on Renewable Energy, Production Agriculture, and Technological Advancements. Springer Science + Business Media LLC, New York (2011)
58. ASTM Standard specification for diesel fuel oil, biodiesel blend (B6 to B20). In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D7467-08a (2008b)
59. ASTM Standard specification for diesel fuel oils. In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D975-08a (2008c)
60. Can, O., Celikten, I., Usta, N.: Effects of ethanol addition on performance and emissions of a turbocharged indirect injection Diesel engine running at different injection pressures. *Energy Convers. Manag.* **45**, 2429–2440 (2004). doi:10.1016/j.enconman.2003.11.024
61. ASTM Standard specification for fuel oils. In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D396-08b (2008d)
62. Canakci, M., Van Gerpen, J.: Comparison of engine performance and emissions for petroleum diesel fuel, yellow grease biodiesel, and soybean oil biodiesel. *Trans. ASAE* **46**, 937–944 (2003)
63. Cennatek Bioanalytical Services.: Kinematic Viscosity According to ASTM D445. <http://cennatek.ca/analytical/biodiesel/kinematic-viscosity-according-to-astm-d445/>. (2013)
64. Freitas, Samuel V.D., Pratas, Maria Jorge, Ceriani, Roberta, Lima, Alvaro S., Coutinho, João A.P.: Evaluation of predictive models for the viscosity of biodiesel. *Energy Fuels* **2011**(25), 352–358 (2010). doi:10.1021/ef101299d
65. Van Jon, G.: The basics of diesel engines and diesel fuels. In: Knothe, G., Van Gerpen, J., Krahl, J. (eds) *The Biodiesel Handbook*, 2nd (edn). pp 25–33. ISBN: 978-1-893997-62-2 (2005)
66. Gerhard, K.: The history of vegetable oil-based diesel fuels. In: Knothe, G., Van Gerpen, J., Krahl, J. (eds) *The Biodiesel Handbook*, 2nd (edn). pp 12–24. ISBN: 978-1-893997-62-2 (2005a)
67. Dzida, M., Prusakiewicz, P.: The effect of temperature and pressure on the physicochemical properties of petroleum diesel oil and biodiesel fuel. *Fuel* **87**(10–11), 1941–1948 (2008)
68. ASTM D446 07: Standard Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers, Philadelphia 1966 (1966)
69. DIN 53012:2003-03: Viscosimetry—capillary viscosimetry of newtonian liquids—sources of errors and corrections, Berlin (2003)
70. Totten, G.E.: Fuels and lubricants handbook: technology, properties, performance, and testing, Glen Burnie, ISBN: 0-8031-2096-6 (2003)
71. Pritchard, P.J., Leylegian, J.C.: Introduction to fluid mechanics, eighth edition, united states of america, fox and mcdonald's, Wiley, New York, ISBN-13 9780470547557
72. Brown, T.L., LeMay, H.E., Bursten, B.E., Brunauer, L.S.: Chemistry: The Central Science, China (2014)
73. U.S. Department of Energy: Biodiesel Handling and use Guidelines, DOE/GO-102006-2358, 3rd edition (2006)
74. Saxena, P., Jawale, S., Joshipura, M.H.A.: Review on prediction of properties of biodiesel and blends of biodiesel. *Proc. Eng.* **51**, 395–402 (2013)

75. Sivaramakrishnan, K., Ravikumar, P.: Determination of cetane number of biodiesel and its influence on physical properties. *ARPN (ARPN)* **7**, 205–211 (2012)
76. Rodenbush, C.M., Hsieh, F.H., Viswanath, D.S.: Density and viscosity of vegetable oils. *J. Am. Oil Chem. Soc.* **76**, 1415–1419 (1999)
77. Krisnangkura, K., Yimsuwan, T., Pairintra, R.: An empirical approach in predicting biodiesel viscosity at various temperatures. *Fuel* **85**, 107–113 (2006)
78. Azian, M.N., Kamal, A.A.M., Panau, F., Ten, W.K.: Viscosity estimation of triacylglycerols and of some vegetable oils, based on their triacylglycerol composition. *J. Am. Oil Chem. Soc.* **78**, 1001–1005 (2001)
79. Ramírez-Verduzco, L.F.: Density and viscosity of biodiesel as a function of temperature: empirical models. *Renew. Sustain. Energ. Rev.* **19**, 652–665 (2013)
80. Joshi, R.M., Pegg, M.J.: Flow properties of biodiesel fuel blends at low temperatures. *Fuel* **86**, 143–151 (2007)
81. Enweremadu, C.C., Rutto, H.L., Oladeji, J.T.: Full length research paper investigation of the relationship between some basic flow properties of shea butter biodiesel and their blends with diesel fuel. *Int. J. Phys. Sci.* **6**(4), 758–767 (2011)