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LOGARITHMIC AND RATIONAL MODELS TO PREDICT KINEMATIC VISCOSITIES OF SUNFLOWER BIODIESEL-DIESEL FUEL BLENDS

M. Gülm̄^{1*}, A. Bilgin²

^{1,2}Karadeniz Technical University, Mechanical Engineering Department, Trabzon, Turkey

*E-mail address:gulum@ktu.edu.tr

ABSTRACT

Viscosity is a key fuel property because it affects atomization quality, size of fuel droplets, jet penetration length and hence engine performance, combustion characteristics and exhaust emissions in internal combustion engines. Researches about the usage of biodiesel-diesel fuel blends in diesel engines have been still continued in the literature. Therefore, developing reliable models to predict viscosities of biodiesel-diesel fuel blends is helpful to (1) know whether the blends meet standard specifications for diesel fuels or not (2) simulate injection and combustion processes in any engine modeling study. In this context, in this study, first, sunflower biodiesel was produced, and mixed with commercially available diesel fuel at the different volume ratios of 5, 10, 15, 20, 50 and 75%. The densities and kinematic viscosities of the prepared blends were measured in accordance with ISO 4787 and DIN 53015 standards, respectively. Finally, the logarithmic and rational models were derived to estimate viscosities of sunflower biodiesel, diesel fuel and their blends.

Keywords: Sunflower oil biodiesel, Transesterification, Fuel property, Biodiesel-diesel blends, Viscosity, Prediction, Model

INTRODUCTION

In recent years, dwindling known reserves of fossil fuels, their associated environmental problems, and global warming have become major issues in the world [1,2]. Researchers think that the use of renewable biomass fuels such as vegetable oils, biodiesel and ethanol etc. can help resolve such issues [2]. Among these fuels, biodiesel offers a number of important technical advantages over conventional diesel fuel including lower toxicity, negligible sulfur content and aromatics, derivation from a renewable and domestic feedstock, superior flash point and biodegradability, higher lubricity and cetane number and lower exhaust emissions [3-6]. However, important disadvantages of biodiesel include higher feedstock cost, viscosity and generally NO_x emissions, inferior storage and oxidative stability, lower volumetric energy content and inferior low-temperature operability [3,7,8].

Transesterification is one of the accepted processes to produce biodiesel, and the process involves a reaction between ester (here triglyceride) and alcohol in the presence of eligible catalysts to form new ester (biodiesel) and alcohol (glycerol) [9]. In other words, transesterification is a chemical process of changing triglycerides with alcohols into alkyl-ester and glycerol in the presence of homogeneous (alkalis and sulfuric acids) or heterogeneous catalysts (metal oxides) [10,11]. Different types of alcohols such as, methanol, ethanol, propanol and butanol have been used in transesterification [9,12]. Higher chain alcohols such as propanol and butanol result in production of biodiesel with higher viscosity and increased production cost [10]. On the other hand, methanol and ethanol are the most widely used, particularly methanol owing to its low price and availability [9, 13]. Fig. 1

shows transesterification reaction with methanol to produce fatty acid methyl ester (FAME or biodiesel) and glycerol [10].

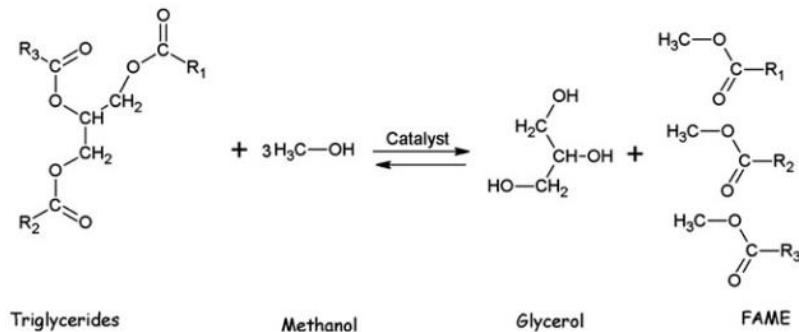


Figure 1. Transesterification of vegetable oil with methanol [10].

Viscosity is one of the most important fuel properties; modern diesel engines have fuel-injection systems that are sensitive to viscosity changes [14]. High viscosity leads to choking of the injectors, ring carbonization, larger droplets and poor atomization [14,15]. Moreover, viscosity affects fuel lubricating capacity, ensuring fuel pumps and injectors' lubrication [16].

Because biodiesel can be easily mixed with diesel fuel at any proportional, researchers have often investigated the usage of their blends in diesel engines in the literature. They can easily comment about engine performances, combustion characteristics and exhaust emissions results when important fuel properties (such as density, viscosity, higher heating value, cetane number etc.) of their blends are known [17]. Additionally, some of these properties are required as input data for predictive and diagnostic engine combustion models [18]. In this context, an a priori prediction of blend properties with regression models have emerged when measuring difficulties for each blending ratio and/or temperature at every turn are taken into account. Although several models have been proposed to estimate these properties in the literature [14,15,17,18,20-23], there will be always needed for new models having higher accuracy for different biodiesel-diesel fuel blends. Therefore, in this study, (1) sunflower biodiesel was synthesized by means of transesterification, (2) the produced biodiesel was blended with commercially available diesel fuel at the volume ratios of 5, 10, 15, 20, 50 and 75% which are called as B5, B10, B15, B20, B50 and B75 as usual, (3) densities and kinematic viscosities of each blend were measured at 10°C, 20 °C, 30°C, 40°C, 50°C and 60°C by following international ISO 4787 and DIN 53015 standards, and (4) the two-term rational and three-term logarithmic models were derived to characterize viscosity-temperature and viscosity-biodiesel fraction variations.

MATERIALS AND METHODS

Biodiesel Production

Transesterification reaction was performed using 99% purity methanol, potassium hydroxide and anhydrous sodium sulphate purchased from Merck. Reaction parameters were selected as follows according to [24]: 1.00% catalyst concentration, 40°C reaction temperature, 180 minutes reaction time and 6:1 alcohol/oil molar ratio.

Density Measurement

The densities of pure fuels (diesel and produced biodiesel) and blends were determined by means of pycnometer in accordance with ISO 4787 standard. Details of the measurements were given in [25-27].

Viscosity Measurement

The dynamic viscosities of pure fuels and blends were determined in accordance with DIN 53015 standard using universal Haake Falling Ball Viscometer, Haake Water Bath and stopwatch. Details of the measurements can be seen in [25-27]. The kinematic viscosity was calculated by dividing dynamic viscosity to density at the same temperature, as well-known.

Uncertainty Analysis

Uncertainties of the measured and calculated physical quantities such as dynamic and kinematic viscosities and densities were determined using the method proposed by Kline and McClintock given in [28]. According to this method, if the result R is a given function of the independent variables $x_1, x_2, x_3, \dots, x_n$ and $w_1, w_2, w_3, \dots, w_n$ are the uncertainties of each independent variables, then the uncertainty of the result w_R is calculated by using the equation:

$$w_R = \left[\left(\frac{\partial R}{\partial x_1} \cdot w_1 \right)^2 + \left(\frac{\partial R}{\partial x_2} \cdot w_2 \right)^2 + \left(\frac{\partial R}{\partial x_3} \cdot w_3 \right)^2 + \dots + \left(\frac{\partial R}{\partial x_n} \cdot w_n \right)^2 \right]^{1/2} \quad (1)$$

The highest uncertainty for all calculated properties was computed as 0.0817%, means that the results are highly reliable and accurate.

RESULTS AND DISCUSSION

Effect of Biodiesel Fraction on Kinematic Viscosity

The variation in viscosities of sunflower biodiesel-diesel fuel blends with respect to biodiesel fraction for different temperatures (10°C , 20°C , 30°C , 40°C , 50°C and 60°C) is shown in Fig. 2 where points and lines represent measurement and calculated values coming from the three-term logarithmic model:

$$v = v(X) = a + b \cdot \ln(X - c) \quad (2)$$

where v is kinematic viscosity (mm^2/s), a , b and c are regression constants, and X is volume fraction (v/v) of biodiesel in the blends.

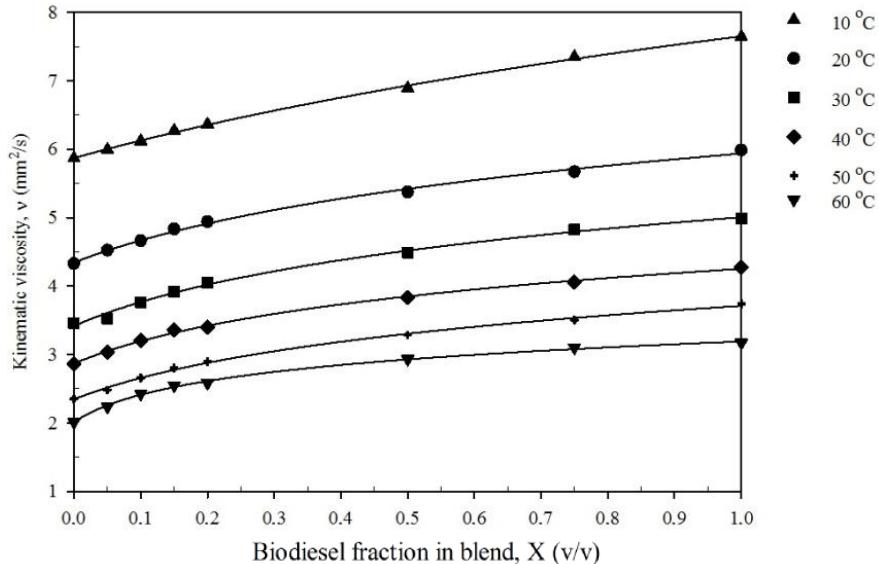


Figure 2. Changes of viscosity vs. biodiesel fraction in blend

As shown in Fig. 2, viscosities of blends non-linearly increase with increase of biodiesel fraction for all tried temperatures, and viscosities decrease with increasing temperature at a fixed biodiesel content in the mixture, as expected. The qualitative and quantitative characterization of viscosity-biodiesel fraction variation was done by means of the three-term logarithmic model (Eq. 2). Table 1 lists measured viscosities, regression parameters and % relative errors between measured and calculated viscosities at the measurement points from Eq. 2. According to regression analysis result in this table, the maximum % relative error and the minimum correlation coefficient (R) were computed as 2.3042% and 0.9974, respectively. These results indicate that the logarithmic model properly fits the data and represents perfectly kinematic viscosity-biodiesel fraction relationship.

Table 1. Measured viscosities by the authors, errors of measured and calculated viscosities from Eq. (2) and regression parameters for different temperatures

Temp. T (°C)	Measured, v (mm ² /s)							
	Biodiesel fraction, X (v/v)							
	0	5	10	15	20	50	75	100
10	5.870	5.991	6.118	6.271	6.364	6.891	7.347	7.641
20	4.328	4.523	4.663	4.833	4.941	5.374	5.669	5.986
30	3.460	3.527	3.764	3.921	4.055	4.493	4.827	4.988
40	2.866	3.033	3.204	3.361	3.402	3.832	4.057	4.279
50	2.355	2.483	2.661	2.800	2.897	3.284	3.504	3.740
60	2.015	2.238	2.428	2.548	2.584	2.933	3.103	3.171

Table 1 (Continued)

Temp. T (°C)	Regression constants			R
	a	b	c	
10	6.2610	2.2710	-0.84230	0.9994
20	5.6870	1.0340	-0.27370	0.9982
30	4.8260	0.9206	-0.21640	0.9974
40	4.1350	0.7306	-0.17640	0.9988
50	3.5780	0.7504	-0.19340	0.9987
60	3.1670	0.4111	-0.05997	0.9988

Table 1 (Continued)

Temp. T (°C)	Relative errors (%)			
	Biodiesel fraction, X (v/v)			
	0	5	10	15
10	0.0213	0.1872	0.1313	0.4394
20	0.4441	0.0506	0.1336	0.7020
30	1.2455	2.3042	0.0696	0.4925
40	0.0491	0.5516	0.2648	1.3092
50	0.4205	1.3954	0.1185	0.8597
60	0.2382	0.9597	0.5952	0.8886
				1.1289

Table 1 (Continued)

Temp. T (°C)	Relative errors (%)		
	Biodiesel fraction, X (v/v)		
	50	75	100
10	0.5594	0.4026	0.0997
20	0.8877	0.7448	0.8160
30	0.5779	0.6725	0.3677
40	0.4529	0.5459	0.5914
50	0.5859	0.8641	0.7841
60	0.1495	0.7297	0.6289

Effect of Temperature on Kinematic Viscosity

Fig. 3 illustrates changes of blends' (B75, B50, B20, B15, B10 and B5) and pure fuels' (B100 and D) viscosities as a function of temperature. The dots represent the experimental data while lines represent the predicted viscosity values from the two-term rational model:

$$v = v(T) = 1/(a + b \cdot T) \quad (3)$$

where v is kinematic viscosity (mm²/s), a and b are regression constants, and T is temperature of the blends in °C.

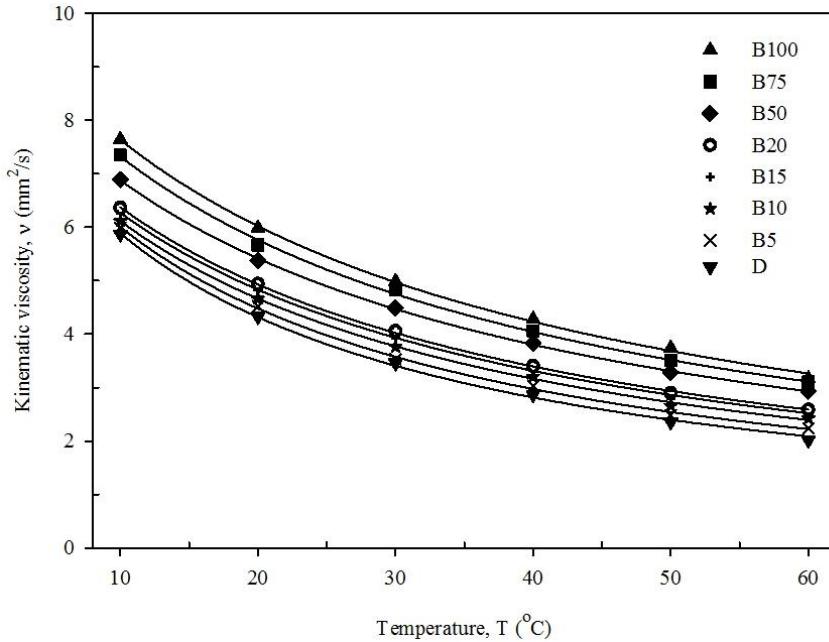


Figure 3. Changes of viscosity vs. temperature

All blends and fuels reveal the same qualitative change behavior: viscosities non-linearly decrease with increasing temperature, as seen in Fig. 3. The increase in temperature leads to decrease in the cohesive attraction and increase in kinetic energy of molecules and hence the viscosity of blend decreases [15]. Moreover, Table 2 lists measured viscosities, % relative errors between measured and calculated viscosities from Eq. 3 and regression parameters. The maximum error was computed for diesel fuel at 60°C as 3.6633% and the minimum correlation coefficient was determined as 0.9994. These results and Fig. 3 show that the high accuracy agreement of the calculated and measured viscosity values is quantitatively and qualitatively captured by the rational model for the investigated temperature ranges.

Table 2. Measured viscosities by the authors, errors of measured and calculated viscosities from Eq. (3) and regression parameters for different temperatures

Biodiesel fraction X (v/v)	Measured, v (mm ² /s)					
	Temp. T (°C)					
	10	20	30	40	50	60
0	5.870	4.328	3.460	2.866	2.355	2.015
5	5.991	4.523	3.527	3.033	2.483	2.238
10	6.118	4.663	3.764	3.204	2.661	2.428
15	6.271	4.833	3.921	3.361	2.800	2.548
20	6.364	4.941	4.055	3.402	2.897	2.584
50	6.891	5.374	4.493	3.832	3.284	2.933
75	7.347	5.669	4.827	4.057	3.504	3.103
100	7.641	5.986	4.988	4.279	3.740	3.171

Table 2 (Continued)

Biodiesel fraction X (v/v)	Regression constants	
	a	b
0	5.870	4.328
5	5.991	4.523
10	6.118	4.663
15	6.271	4.833
20	6.364	4.941
50	6.891	5.374
75	7.347	5.669
100	7.641	5.986

Table 2 (Continued)

Biodiesel fraction X (v/v)	R	Relative errors (%)					
		Temp. T (°C)					
		10	20	30	40	50	60
0	0.9994	0.3344	0.2273	1.4837	1.7574	1.8416	3.6633
5	0.9994	0.1783	0.9621	1.3103	2.0130	2.4520	0.6432
10	0.9996	0.0013	0.0720	0.1979	1.2311	2.4393	1.3977
15	0.9996	0.0152	0.0149	0.2819	1.4016	2.2746	1.0527
20	0.9998	0.1491	0.2031	0.8407	0.2224	1.3758	0.1545
50	0.9998	0.1879	0.8133	0.5370	0.7604	0.7800	0.1149
75	0.9994	0.3514	1.6527	1.5689	0.3728	0.3651	0.3046
100	0.9994	0.0741	0.6001	0.3325	1.0754	1.4559	2.9169

CONCLUDING REMARKS

The models evaluated in this study can be easily used for predicting viscosity of biodiesel-diesel fuel blends, providing useful information on the preparation of mixtures respecting the viscosity limitations of quality standards for diesel fuels or for fuel injection and combustion process modeling. The following conclusions can be drawn from this study:

- 1) The three-term logarithmic model as a function of biodiesel percentage provides an opportunity to estimate kinematic viscosities of sunflower biodiesel, diesel fuel and their blends at different temperatures with quite well accuracy. The logarithmic model has the maximum relative error and minimum correlation coefficient of 2.3042% and 0.9974, respectively.
- 2) The good correlation is obtained using the two-term rational model for the kinematic viscosity-temperature variation with quite high accuracy. From the rational model, the maximum relative error and the minimum correlation coefficients is computed as 3.6633% and 0.9994.

REFERENCES

- [1] Abebe K. Endalew, Yohannes Kiros, Rolando Zanzi, "Heterogeneous catalysis for biodiesel production from Jatropha curcas oil (JCO)", Energy, Vol. 36, 2011, pp. 2693-2700.
- [2] Tsutomu Sakai, Ayato Kawashima, Tetsuya Koshikawa, "Economic assessment of batch biodiesel production processes using homogeneous and heterogeneous alkali catalysts", Bioresource Technology, Vol. 100, 2009, 3268-3276.
- [3] Xinhai Yu, Zhenzhong Wen, Ying Lin, Shan Tung Tu, Zhengdong Wang, Jinyue Yan, "Intensification of biodiesel synthesis using metal foam reactors", Fuel, Vol. 89, 2010, 3450-3456.
- [4] Surbhi Semwal, Ajay K. Arora, Rajendra P. Badoni, Deepak K. Tuli, "Biodiesel production using heterogeneous catalysts", Bioresource Technology, Vol. 102, 2011, 2151-2161.
- [5] D. Y. C. Leung, B .C. P. Koo, Y. Guo, "Degradation of biodiesel under different storage conditions", Bioresource Technology, Vol. 97, 2006, 250-256.
- [6] Hem Joshi, Bryan R. Moser, Joe Toler, Terry Walker, "Preparation and fuel properties of mixtures of soybean oil methyl and ethyl esters", Biomass and Bioenergy, Vol. 34, 2010, 14-20.
- [7] Ali Keskin, Abdulkadir Yasar, Metin Gürü, Duran Altiparmak, "Usage of methyl ester of tall oil fatty acids and resinic acids as alternative diesel fuel", Energy Conversion and Management, Vol. 51, 2010, 2863-2868.
- [8] Meltem Conk Dalay, Seda Gunes, "Biodiesel from microalgae: a renewable energy source", Middle-East Journal of Scientific Research, Vol. 21, 2014, 2308-2314.
- [9] Masoud Zabetti, Wan Mohd Ashri Wan Daud, Mohamed Kheireddine Aroua, "Activity of solid catalysts for biodiesel production: a review", Fuel Processing Technology, Vol. 90, 2009, 770-777.
- [10] Abebe K. Endalew, Yohannes Kiros, Rolando Zanzi, "Inorganic heterogeneous catalysts for biodiesel production from vegetable oils", Biomass and Bioenergy, Vol. 35, 2011, 3787-3809.
- [11] Y. A. Elsheikh, Zakaria Man, M. A. Bustam, Suzana Yusup, C. D. Wilfred, "Bronsted imidazolium ionic liquids: synthesis and comparison of their catalytic activities as pre-catalyst for biodiesel production through two stage process", Energy Conversion and Management, Vol. 52, 2011, 804-809.
- [12] Anastopoulos, Dodos, Kalligeros, Zannikos, "CaO loaded with Sr(NO₃)₂ as a heterogeneous catalyst for biodiesel production from cottonseed oil and waste frying oil", Biomass Conversion and Biorefinery, Vol. 3, 2013, 169-177.
- [13] M. E. Borges, L. Diaz, "Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: a review", Renewable and Sustainable Energy Reviews, Vol. 16, 2012, 2839-2849.

- [14] Saeid Baroutian, Mohamed K. Aroua, Abdul A. A. Raman, Nik M. N. Sulaiman, “Viscosities and densities of binary and ternary blends of palm oil+palm biodiesel+diesel fuel at different temperatures”, *J. Chem. Eng. Data*, Vol. 55, 2010, 504-507.
- [15] Narayan Gaonkar, R. G. Vaidya, “Engineering of viscosity of biodiesel blends: a novel approach”, *Energy Efficient Technologies for Sustainability (ICEETS)*, 2016, doi: 10.1109/ICEETS.2016.7582889.
- [16] Istvan Barabas, Adrian Todorut, Doru Baldean, “Performance and emission characteristics of an CI engine fueled with diesel-biodiesel-bioethanol blends”, *Fuel*, Vol. 89, 2010, 3827-3832.
- [17] Ertan Alptekin, Mustafa Canakci, “Determination of the density and the viscosities of biodiesel-diesel fuel blends”, *Renewable Energy*, Vol. 33, 2008, 2623-2630.
- [18] Pedro Benjumea, John Agudelo, Andres Agudelo, “Basic properties of palm oil biodiesel-diesel blends”, *Fuel*, Vol. 87, 2008, 2069-2075.
- [19] Narayan Gaonkar, R. G. Vaidya, “A simple model to predict the biodiesel blend density as simultaneous function of blend percent and temperature”, *Environmental Science and Pollution Research*, Vol. 23, 2016, 9260-9264.
- [20] Mustafa E. Tat, Jon H. Van Gerpen, “The specific gravity of biodiesel and its blends with diesel fuel”, *Journal of the American Oil Chemists' Society*, Vol. 77, 2000, 115-119.
- [21] R. E. Tate, K.C. Watts, C. A. W. Allen, K. I. Wilkie, “The densities of three biodiesel fuels at temperatures up to 300°C”, *Fuel*, Vol. 85, 2006, 1004-1009.
- [22] Sibel Geacai, Olga Lulian, Irina Nita, “Measurement, correlation and prediction of biodiesel blends viscosity”, *Fuel*, Vol. 143, 2015, 268-274.
- [23] Istvan Barabas, “Predicting the temperature dependent density of biodiesel-diesel-bioethanol blends”, *Fuel*, Vol. 109, 2013, 563-574.
- [24] A. B. M. S. Hossain, A. N. Boyce, “Biodiesel production from waste sunflower cooking oil as an environmental recycling process and renewable energy”, *Bulgarian Journal of Agricultural Science*, Vol. 15, 2009, 312-317.
- [25] Mert Gülbüm, Atilla Bilgin, “Density, flash point and heating value variations of corn oil biodiesel–diesel fuel blends”, *Fuel Processing Technology*, Vol. 134, 2015, 456-464.
- [26] Mert Gülbüm, Atilla Bilgin, “Two-term power models for estimating kinematic viscosities of different biodiesel-diesel fuel blends”, *Fuel Processing Technology*, Vol. 149, 2016, 121-130.
- [27] Mert Gülbüm, Atilla Bilgin, Abdülvahap Cakmak, “Comparison of optimum reaction parameters of corn oil biodiesels produced by using sodium hydroxide (NaOH) and potassium hydroxide (KOH)”, Vol. 30, *Journal of the Faculty of Engineering and Architecture of Gazi University*, 2015, 503-511.
- [28] J.P. Holman, “Experimental Methods for Engineers”, seventh ed., McGraw-Hill, New York , 2001.