Estimation kinematic viscosity of biodiesel produced by ethanolysis

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ABSTRACT

Kinematic viscosity (μ) is an important physical property of biodiesel. It dictates fuel atomization and complete combustion in the diesel engine. The kinematic viscosity of biodiesel is correlated to number of carbon atoms, number of double bond(s) and temperature via the Martin's rule of free energy additivity. In this work, proposed an empirical approach for estimation the kinematic viscosity of biodiesel based on free energy of viscous flow by a single empirical equation. The single empirical equation can be estimated without the prior knowledge of the kinematic viscosity of an individual fatty acid ethyl ester and can be estimated by using the average number of carbon atoms (z_{ave}) and average number of double bonds ($nd_{(ave)}$) from its fatty acid composition. Data available in literatures are used to validate, and support the speculations derived from the proposed equation. The proposed equation is easy to use and the estimated kinematic viscosity values of fatty acid ethyl esters (FAEEs) at different temperatures agree well with the literature values.

Keywords: *Biodiesel, Fatty acid ethyl ester, Kinematic viscosity, Estimation, Thermodynamic parameters*

1. INTRODUCTION

Biodiesel is a mixture of alkyl esters that, an alternative of renewable energy obtained from animal fat or vegetable oil reacts with a short chain alcohol by the transesterification. Vegetable oils are the major sources for biodiesel production but types of oils are varied and depended upon their availabilities. Therefore, the feedstocks for biodiesel of different countries are different. The processes use ethanol in biodiesel synthesis is appealing because it is produced from biorenewable sources, resulting in a completely agricultural-based fuel obtained by ethanolysis, the advantages include higher miscibility with vegetable oils that allows better contact in the reaction step and lower toxicity [1], [2].

Nomenclature

η	dynamic viscosity (mPa·s)
μ	kinematic viscosity (mm^2/s)
ρ	density (kg/m^3)

Generally in a diesel engine, viscosity is one of the physical properties of a liquid fuel that is greatly affected by the atomization of fuel sprays. Combustion is initialized through the atomization of the fuel which is Atomization is the first stage of combustion in the diesel engine. Thus, higher viscous liquids, which tend to form larger droplet size, may enhance the polymerization reaction, especially oil of high degree of unsaturation. The use of a viscous fuel leads to the poor atomization which is responsible for premature injector cooking and poor fuel combustion [3] - [6]. Once, the method for predicting the viscosity is reliable, it is more convenient to develop the combustion model of biodiesel profoundly.

Krisnangkura equation [7], when the free energy of viscous flow term in the Andrade equation was expanded according to the Martin's rule of free energy additivity[8], Eq.1 was obtained for estimation of kinematic viscosity of pure saturated FAMEs [7].

$$\ln\mu = a + bz + \frac{c}{T} + \frac{dz}{T} \qquad (1)$$

where a, b, c and d are thermodynamics constant, z is the carbon number and T is absolute temperature.

Basso et al. [9] who observed that an additional double bond introduced to the fatty acid ethyl ester would decrease the kinematic viscosity of the unsaturated ester by 1 - 2 carbon atoms from the saturated ethyl ester. They developed Krisnangkura equation [7] by optimization non-linear regression method, a value of 1.5/double bond was obtained, show the equation as follows:

$$ln\mu = a + b(z - 1.5\,\mathrm{n_d}) + \frac{c}{T} + (z - 1.5\,\mathrm{n_d})\frac{dz}{T} \qquad (2)$$

Phankosol et al. [10] presented a set of equations for the determination of kinematic viscosity of pure methyl esters by based on thermodynamic parameters. They developed Krisnangkura equation [7] were expanded effected degree of unsaturation by the relationship of free energy of viscous flow with the phenomenon of kinematic viscosity (μ=η/ρ) depends will increase as the chain length is increased and show the general equation as follows:

$$ln\mu = a + bz + \frac{c}{T} + \frac{dz}{T} + en_d + \frac{fn_d}{T} \qquad (3)$$

where e and f are thermodynamics constant and n_d is number of double bonds.

This work, present and evaluate a simple model, based on that presented by Phankosol et al. [10], applied to describe the kinematic viscosity of ethyl esters using the number of carbon atoms and double bonds present in ethyl ester molecule.

2. METHODOLOGY

2.1 Viscosity data

The viscosity values of pure FAEEs and biodiesels are obtained from Pratas et al. [11], [12] and Baroutian et al. [13]. The *viscosities* were measured by using a rotary viscometer.

2.2 Numeric constants of Eq(3)

For saturated fatty acid esters, n_d is zero and Eq(3) is reduced to Eq(1). The 4 numeric values of Eq(1) or Eq(3) (a, b, c, and d) for fatty acid ethyl esters were solved according to Krisnangkura et al. [7]. Two additional constants, e and f, are solved by two simultaneous equations according to Phankosol et al. [14], [15].

2.3 Determination of average carbon numbers and number of double bonds

Biodiesel is the mixture of FAEEs and its density can be directly estimated without the prior knowledge of individual ester when the average carbon number (z_{ave}) and the average number of double bonds ($n_{\mathrm{d(ave)}}$) are used in place of z and n_{d}. The $\mathrm{z_{ave}}$ and $n_{\mathrm{d(ave)}}$ are calculated according to Eq(4) and Eq(5), respectively.

$${}_{?} = \frac{\sum\limits_{i=1}^{n} x_i z_i}{\sum\limits_{i-1}^{n} x_i} \qquad (4)$$

$$n_{d(ave)} = \frac{\sum\limits_{i=1}^{n} x_i n_{d(i)}}{\sum\limits_{i-1}^{n} x_i} \qquad (5)$$

where x_i, z_i and $n_{d(i)}$ are the percent composition, carbon numbers and number of double bonds of fatty acid ester i, respectively.

2.4 Statistical analysis

Statistical analysis was performed on Microsoft Excel 2010. The average absolute deviation (AAD) was calculated from Eq(6).

$$AAD = \sum_{i=1}^{n} [\frac{|\,\mu_{lit} - \mu_{cal}\,|}{\mu_{lit}} \mathrm{x}100\%] / N \qquad (6)$$

where μ_{lit} and μ_{cal} are the experimental and predicted viscosity, respectively. N is the number of data points.

3. RESULTS AND DISCUSSION

Short chain fatty acids are minor components found in naturally occurring fats and oils and they are not suitable for production of biodiesel. Long chain fatty acids are much more abundant in nature and they are feed stock for biodiesel. In addition, long chain fatty acids occurred in nature are both saturated and unsaturated with different number of double bonds.

Thus, Eq(3) was derived for unsaturated FAEEs, but it can be used for saturated FAEEs as well. The numeric constants for Eq(3)are listed in Eq(7).

$$ln\mu = -4.485 - 0.014z_{ave} + \frac{1241}{T} + \frac{44.5z_{ave}}{T} + 0.454n_{d(ave)} - \frac{168.15n_{d(ave)}}{T} \quad (7)$$

The estimated kinematic viscosity values by Eq(7) and the reported experimental values are included for comparison. The correlation between the reported experimental viscosities [13] and estimated values using Eq(7) (28 data points) was linear with the slope of 0.921 and intercept at 0.304. The R^2 and standard error are 0.988 and 0.311, respectively. The AAD for biodiesels were 4.22%, respectively. The values were lower than those estimated by Eq(2) (AAD=9.41%).

Table 1 *Absolute average deviation between the kinematic viscosity of biodiesel data available in literature [13] over the temperature range 283.15 to 353.15K and those estimated by Eq(2)*

Biodiesels	z_{ave}	$n_{(ave)}$	N_{exp}	Temperature range (K)	Eq(7)	Eq(2)
Palm	17.15	0.66	14	283.15-353.15	4.25	8.70
Jatropha	17.67	1.08	14	283.15-353.15	4.19	10.12
Total			28	AAD	4.22	9.41

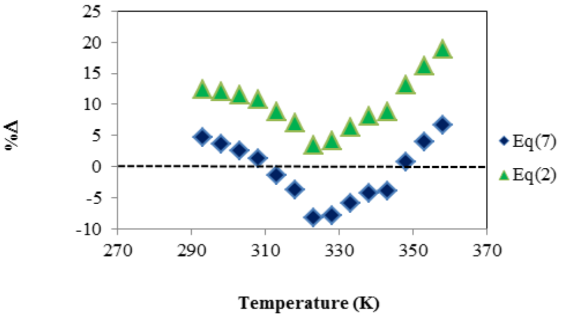

Fig. 1. *Relative deviation between kinematic viscosity of biodiesels predicted by Eqs(7) and (2) and experimental data of literature[13] as function of temperature.*

5. CONCLUSION

The kinematic viscosity of biodiesel at various temperatures (283.15-353.15 K) can be easily predicted. Besides the accuracy, the model provide two additional advantages: 1) viscosity of biodiesel can be estimated without a prior knowledge of the viscosities of individual fatty acid methyl esters, and 2)all the numeric values are well defined. This would allow further refinement of the models.

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