Journal of Energy and Environment Technology ISSN 2392-5701
http://jeet.siamtechu.net Research Article

แนวทางเชิงประจักษ์สำหรับการประมาณค่าความหนาแน่นและความหนืดของกรดไขมันเอทิลเอสเทอร์ บริสุทธิ์ที่อุณหภูมิต่าง ๆ

An Empirical Approach for Estimation Density and Viscosity of Pure Fatty Acid Ethyl Ester at Various Temperatures

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บทคัดย่อ

ความหนาแน่นและความหนืดจลน์เป็นสมบัติทางกายภาพที่สำคัญของเชื้อเพลิงเหลว ในการศึกษานี้เสนอสมการสมการเชิงประจักษ์สำหรับประมาณค่าความหนาแน่นและความหนืดจลน์ของกรดไขมันเอทิลเอสเทอร์ที่อุณหภูมิต่างๆ จากจำนวนอะตอมคาร์บอน และจำนวนพันธะคู่ ซึ่งสมการทั้ง 2 ขยายความสัมพันธ์จากกฎพลังงานควบรวมอิสระ ในการศึกษาใช้ข้อมูลจากเอกสารอ้างอิงมาใช้ในการศึกษาและสนับสนุนเพื่อยืนยันความถูกต้องแม่นยำของสมการที่จะนำไปใช้ จากการศึกษาพบว่าสมการที่นำเสนอง่ายต่อการใช้งานและมีความถูกต้องแม่นยสำหรับการประมาณความหนาแน่นและความหนืดจลน์ของกรดไขมันเอทิลเอสเทอร์ที่อุณหภูมิต่างๆ

คำสำคัญ: กรดไขมันเอทิลเอสเทอร์ ความหนาแน่น ความหนืดจลน์

Abstract

Density (ρ) and kinematic viscosity (μ) are important physical properties of a liquid fuel. In this work, two empirical models were proposed. One for estimation density and the other for estimation kinematic viscosity of fatty acid ethyl ester (FAEE) at different temperatures from its carbon numbers and number of double bond(s). Both models were the expansion of Martin's rule of free energy additivity. Data collected from literatures were used to validate, and support the proposed models. The proposed equations are easy to use and the estimated density and kinematic viscosity values of FAEEs at different temperatures agree well with the literature values.

Keywords: Fatty Acid Ethyl Ester, Density, Kinematic Viscosity

1. INTRODUCTION

Biodiesel is an alternative of renewable energy obtained from animal fat or vegetable oil reacts with a short chain alcohol by the transesterification to be converted into alkyl-esters and glycerine. Vegetable oils are the major sources for biodiesel production but types of oils are varied and depended upon their availabilities. Therefore, the feed stocks 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 of biodiesel compared to petrodiesel include their higher flash point, also is non-toxic, and essentially free of surfer and aromatics.[1, 2]

Density and viscosity of fatty acid ethyl ester (FAEE) or biodiesel are important properties for liquid fuel. They are required for calculation related to storage facilities, fluid flow, distillation units, separation process, storage tanks, design of reactors, and process piping.[3-6]

Experimental determinations of density and viscosity of FAEEs or biodiesels at various temperatures from different sources and processes are time consuming, but their values are necessary for mathematical calculations. Thus, good mathematical models would provide not only the accurate of density and viscosity values but they should also correlate the properties to chemical structure of the estimated substance for further development or refinement of the model [7].

The classical Rackett's equation (Eq.1) had been modified by Spencer and Danner[8] and it was successfully used by Basso et al.[9] to estimated density of FAEEs.

$$\rho = \frac{M}{\frac{RT_c}{P_c} Z_{RA}^{[1+(1-T/T_c)]^{2/7}}} \tag{1}$$

where M, T_c and P_c is molecular weight, critical temperature and pressure of the fatty acid ethyl esters, respectively. R is universal gas constant, and Z_{RA} is the Rackett compressibility factor[10, 11].

$$Z_{RA} = \left[\frac{MP_c}{\rho RT_c} \right]^{\left[1+(1-T_r)^{2/7}\right]^{-1}} \tag{2}$$

Phankosol et al. [3] expanded the Martin's rule of free energy additivity [12] to cover the free energy of volumetric expansion and successfully estimated density of pure saturated, unsaturated fatty acid methyl esters (FAMEs) and their mixture or biodiesel at different temperatures.

$$ln\rho = a + bz + \frac{c}{T} + \frac{dz}{T} + en_d + \frac{fn_d}{T} \tag{3}$$

where *a, b, c, d, e* and *f* are entropic and enthalpic constants and n_d is number of double bonds.

For kinematic viscosity, Krisnangkura et al [13] extended the rule of free energy additivity to cover the activated free energy of viscous flow [12] and Eq.4 was obtained for estimation of kinematic viscosity of pure saturated FAMEs [13].

$$ln\mu = a + bz + \frac{c}{T} + \frac{dz}{T} \quad (4)$$

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 FAEE would decrease the kinematic viscosity of the unsaturated ester by 1.5 carbon atoms from the saturated ethyl ester. Thus, Eq.5 was proposed for estimation dynamic viscosity of saturated and unsaturated FAEEs.

$$ln\eta = a + b(z - 1.5n_d) + \frac{c}{T} + (z - 1.5n_d)\frac{dz}{T} \quad (5)$$

However, when the free energy contribution from the double bonds was added to the Krisnangkura et al model (Eq.4), Eq.6 was obtained for estimation of viscosity of both saturated, unsaturated FAMEs and their mixture. [14].

$$ln\mu = a + bz + \frac{c}{T} + \frac{dz}{T} + en_d + \frac{fn_d}{T} \quad (6)$$

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

In this work, the Martin's rule of free energy of additivity was extended to estimate density and kinematic viscosity of FAEE at different temperatures from its carbon numbers and number of double bonds. This work, present and evaluate a simple model, based on that presented by Phankosol et al.[3, 14], applied to describe the density and kinematic viscosity of ethyl esters using the carbon number and number of double bonds present in ethyl ester molecule.

2. METHODOLOGY

2.1 Density and viscosity data

The density values of pure FAEEs are obtained from Pratas et al.[15, 16]. The densities were measured by using a digital density meter and viscosity were measured by using a rotary viscometerc.

2.2 Numeric constants of Eq. 3 and Eq. 6

The four numeric values of Eq.3 and Eq.6 (*a*, *b*, *c* and *d*) for saturated FAEEs were solved according to Krisnangkura et al.[13]. Two additional constants in Eq.3 and Eq.6, *e* and *f*, are solved according to Phankosol et al. [3, 17].

2.3 Statistical analysis

Statistical analysis was performed on Microsoft Excel 2010. The average absolute deviation (AAD) was calculated from Eq.7.

$$AAD = \sum_{i=1}^{n}[\frac{|lit. - cal.|}{lit.} \text{x}100\%] / N \quad (7)$$

where *lit*. and *cal*. Stand for literature and calculated values, respectively. *N* is the number of data points.

3. Results and discussion

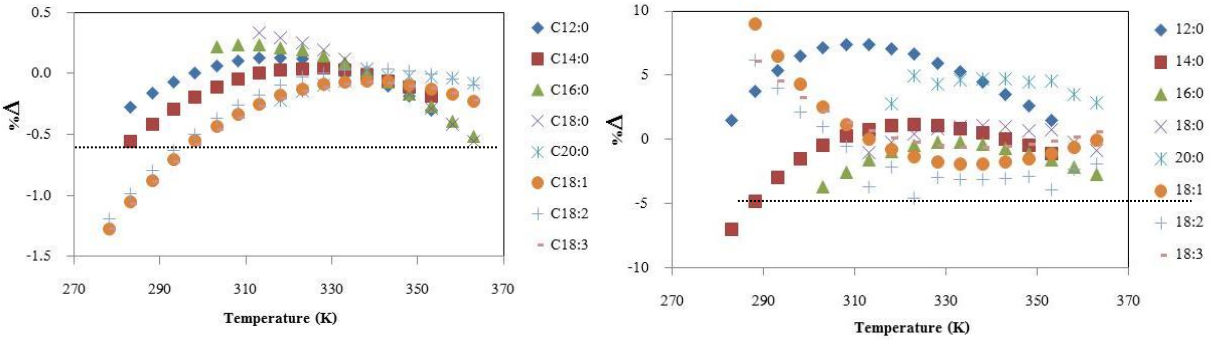
3.1 Density and viscosity of saturated FAEEs

The four numeric values of Eq.3 for saturated FAEE are -0.4297, -0.003, 80.85 and 1.03 and Eq.6 are -4.485, -0.014, 1241 and 44.5, respectively. Substitution these numeric values into Eq.3 and Eq.6, Eq.8 and Eq.9 are obtained, respectively.

$$ln\rho = -0.4297 + -0.003z + \frac{80.85}{T} + \frac{1.03z}{T} \quad (8)$$

$$ln\mu = -4.485 - 0.014z - \frac{1241}{T} + \frac{44.5z}{T} \quad (9)$$

The calculated densities and viscosities of FAEEs by Eqs.8 and 9 agreed well with those reported in literatures [15, 16]. Percent differences between the literature and calculated densities and kinematic viscosities of saturated FAEEs are shown in Fig. 1. The AAD of density and kinematic viscosity from were 0.166% and 2.59%, respectively.



(*a*) (*b*)

Fig. 1 Relative deviation between predicted density (Eq.8) and literature values (Figure 1*a*) and predicted kinematic viscosity (Eq.9) and literature values (Figure1*b*) of FAEEs at different temperatures. Literature data were obtained from Pratas et al. [15, 16].

3.2 Density and viscosity of unsaturated FAEEs

For unsaturated FAEEs, there are two additional constants, *e* and *f*. These two constants (in Eq.3 and Eq.6) were simply solved by simultaneous equations. Their numeric values are shown in Eq.10 and Eq.11, while the four constants (a, b, c and d) have the same for both saturated and saturated FAEEs. For saturated FAEE where number of double bond is zero, Eq.10 and Eq.11 are reduced to Eqs.8 and 9, respectively.

$$ln\rho = -0.4297 - 0.003z + \frac{80.85}{T} + \frac{1.03z}{T} + 0.0144n_d - \frac{1.23n_d}{T} \quad (10)$$

$$ln\mu = -4.485 - 0.014z + \frac{1241}{T} + \frac{44.5z}{T} + 0.454n_d - \frac{168.15n_d}{T} \quad (11)$$

The numeric values for Eqs.10 and 11 are slightly different from those of FAMEs [15, 16]. However, estimation of densities and viscosities of eight types of saturated and unsaturated FAEEs at 10-90°C agreed well with the literature values as listed in Table 1. The percent differences between the calculated and literature densities and kinematic viscosities values are listed in the parentheses. The calculated densities and kinematic viscosities values for both saturated and unsaturated FAEEs agree well with the literature values. The AAD of unsaturated FAEEs density and kinematic viscosity were 0.24% and 2.20, respectively.

The plot between the calculated (cal) and literature (lit) values of density and viscosity are linear with the intercept, slope, R^2 and standard error of -0.049, 1.060, 0.992 and 0.0022, respectively and 0.286, 0.920, 0.990 and 0.1474, respectively (Fig. 2).

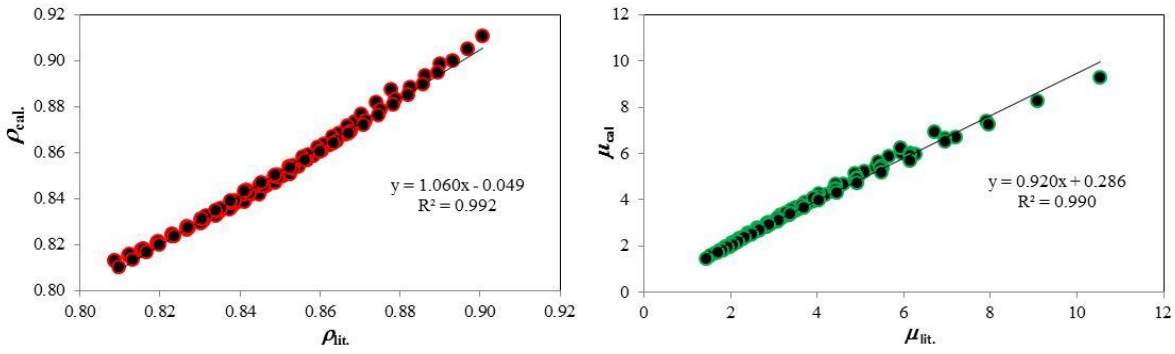


Fig. 2 The plots between estimated and literature values: a, density and b, kinematic viscosity of saturated and unsaturated FAEEs at 10-90°C.

4. Conclusion

Free energy is an extensive property and the free of a molecule can be summed from atoms or group of atoms in the mole (additivity). The free energy is, in turn, correlated to many physical properties. Density and kinematic viscosity are two of the examples. FAME and FAEE are only different in the methyl

and ethyl group. Therefore, their physical properties can be estimated by the same equation but differed in the numeric constants. In this work, density and kinematic viscosity of pure saturated and unsaturated FAEEs at various temperatures (10-90°C) are estimated with good accuracy.

Table 1. Estimated Densities (g/cm^3) and kinematic viscosities (cSt) of FAEEs at 20−90 °C

FAEEs (z:n_d)		Temperature (K)															
		293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15	348.15	353.15	358.15	363.15	368.15
C12:0	ρ	0.8630	0.8584	0.8540	0.8498	0.8457	0.8418	0.8380	0.8343	0.8308	0.8274	0.8241	0.8209	0.8178	0.8148	0.8119	0.8630
		(-0.06)	(0.01)	(0.07)	(0.11)	(0.13)	(0.14)	(0.12)	(0.09)	(0.04)	(-0.02)	(-0.09)	(-0.18)	(-0.29)	(-)	(-)	(-)
	μ	4.06	3.67	3.33	3.03	2.76	2.52	2.32	2.13	1.96	1.82	1.68	1.56	1.45	1.35	1.26	4.06
		(5.35)	(6.48)	(7.14)	(7.38)	(7.34)	(7.08)	(6.62)	(5.96)	(5.30)	(4.46)	(3.52)	(2.61)	(1.51)	(-)	(-)	(5.35)
C14:0	ρ	0.8635	0.8588	0.8543	0.8500	0.8458	0.8418	0.8379	0.8341	0.8305	0.8270	0.8236	0.8203	0.8172	0.8141	0.8111	0.8635
		(-0.30)	(-0.19)	(-0.11)	(-0.05)	(0.00)	(0.03)	(0.04)	(0.05)	(0.02)	(-0.01)	(-0.06)	(-0.11)	(-0.19)	(-)	(-)	(-)
	μ	5.35	4.81	4.34	3.93	3.57	3.25	2.97	2.72	2.49	2.30	2.12	1.96	1.82	1.69	1.57	5.35
		(-2.97)	(-1.53)	(-0.47)	(0.27)	(0.78)	(1.06)	(1.15)	(1.10)	(0.84)	(0.52)	(0.06)	(-0.48)	(-1.11)	(-)	(-)	(-)
C16:0	ρ	0.8587	0.8546	0.8506	0.8468	0.8432	0.8396	0.8362	0.8329	0.8298	0.8267	0.8237	0.8208	0.8180	0.8153	0.8127	0.8587
		(-)	(-)	(0.23)	(0.24)	(0.24)	(0.22)	(0.20)	(0.15)	(0.09)	(0.03)	(-0.06)	(-0.16)	(-0.26)	(-0.39)	(-0.51)	(-)
	μ	7.05	6.31	5.66	5.10	4.61	4.18	3.80	3.46	3.17	2.91	2.67	2.46	2.27	2.10	1.95	7.05
		(-)	(-)	(-3.70)	(-2.53)	(-1.56)	(-0.91)	(-0.45)	(-0.24)	(-0.23)	(-0.40)	(-0.69)	(-1.09)	(-1.56)	(-2.13)	(-2.76)	(-)
C18:0	ρ	0.8566	0.8527	0.8490	0.8454	0.8419	0.8386	0.8354	0.8323	0.8292	0.8263	0.8235	0.8208	0.8182	0.8156	0.8131	0.8566
		(-)	(-)	(-)	(-)	(0.34)	(0.30)	(0.25)	(0.20)	(0.13)	(0.04)	(-0.05)	(-0.16)	(-0.28)	(-0.41)	(-0.55)	(-)
	μ	9.29	8.26	7.38	6.62	5.95	5.37	4.86	4.42	4.02	3.68	3.37	3.09	2.84	2.62	2.43	9.29
		(-)	(-)	(-)	(-)	(-1.05)	(-0.21)	(0.42)	(0.85)	(1.03)	(1.05)	(0.97)	(0.69)	(0.76)	(-0.21)	(-0.82)	(-)
C20:0	ρ	0.8662	0.8612	0.8564	0.8517	0.8473	0.8430	0.8388	0.8348	0.8310	0.8272	0.8236	0.8201	0.8167	0.8135	0.8103	0.8662
		(-)	(-)	(-)	(-)	(-)	(-0.21)	(-0.13)	(-0.09)	(-0.05)	(-0.03)	(-0.01)	(-0.01)	(-0.02)	(-0.03)	(-0.08)	(-)
	μ	12.24	10.83	9.63	8.59	7.69	6.91	6.23	5.63	5.11	4.65	4.24	3.88	3.56	3.27	3.01	12.24
		(-)	(-)	(-)	(-)	(-)	(2.76)	(4.95)	(4.28)	(4.62)	(4.75)	(4.68)	(4.45)	(4.52)	(3.53)	(2.89)	(-)
C18:1	ρ	0.8766	0.8717	0.8669	0.8624	0.8579	0.8537	0.8496	0.8456	0.8418	0.8381	0.8346	0.8311	0.8278	0.8245	0.8214	0.8766
		(-0.71)	(-0.55)	(-0.43)	(-0.33)	(-0.25)	(-0.17)	(-0.13)	(-0.09)	(-0.07)	(-0.06)	(-0.07)	(-0.10)	(-0.13)	(-0.17)	(-0.23)	(-0.71)
	μ	7.40	6.65	6.00	5.42	4.92	4.48	4.09	3.74	3.44	3.16	2.92	2.70	2.50	2.32	2.16	7.40
		(6.47)	(4.28)	(2.52)	(1.14)	(0.04)	(-0.80)	(-1.33)	(-1.71)	(-1.91)	(-1.92)	(-1.79)	(-1.49)	(-1.11)	(-0.65)	(-0.08)	(6.47)
C18:2	ρ	0.8881	0.8831	0.8783	0.8737	0.8692	0.8650	0.8608	0.8568	0.8530	0.8492	0.8456	0.8422	0.8388	0.8355	0.8324	0.8881
		(-0.63)	(-0.49)	(-0.36)	(-0.25)	(-0.17)	(-0.09)	(-0.02)	(0.01)	(0.04)	(0.05)	(0.04)	(0.03)	(0.00)	(-0.04)	(-0.09)	(-0.63)
	μ	5.90	5.35	4.87	4.45	4.07	3.74	3.44	3.17	2.93	2.72	2.53	2.35	2.20	2.05	1.92	5.90
		(3.96)	(2.15)	(1.03)	(-0.53)	(-3.69)	(-2.14)	(-4.60)	(-2.94)	(-3.11)	(-3.14)	(-3.05)	(-2.90)	(-3.91)	(-2.32)	(-1.93)	(3.96)
C18:3	ρ	0.8997	0.8947	0.8899	0.8852	0.8807	0.8764	0.8722	0.8682	0.8643	0.8605	0.8569	0.8534	0.8500	0.8467	0.8435	0.8997
		(-0.72)	(-0.58)	(-0.46)	(-0.36)	(-0.27)	(-0.20)	(-0.15)	(-0.11)	(-0.09)	(-0.07)	(-0.08)	(-0.10)	(-0.12)	(-0.16)	(-0.22)	(-0.72)
	μ	4.70	4.31	3.96	3.64	3.37	3.12	2.89	2.69	2.51	2.34	2.19	2.05	1.93	1.82	1.71	4.70
		(4.53)	(3.25)	(2.18)	(1.34)	(0.65)	(0.13)	(-0.25)	(-0.48)	(-0.60)	(-0.62)	(-0.53)	(-0.35)	(-0.12)	(0.21)	(0.59)	(4.53)

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