Correlation of isentropic compressibility of biodiesel to its saponification number and iodine value

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Abstract. Isentropic compressibility is important injection timing of liquid fuel. The isentropic compressibility of biodiesels are correlated to number of carbon atoms, number of double bond(s) and temperature. In this work, an empirical approach for isentropic compressibility of biodiesels can be estimated by using saponification number (*SN*) and iodine value (*IV*). The proposed equations are easy to use and the estimated isentropic compressibility values of biodiesels at different temperatures agree well with the literature values. The average absolute deviation of estimated isentropic compressibility values of biodiesels at 288.15 to 353.15 K is 1.19%. The isentropic compressibility outside temperature between 288.15 and 353.15 K may be possibly estimated by this model but accuracy may be lower.

1. Introduction

Biodiesel is a mixture of saturated and unsaturated fatty acid alkyl esters (FAMEs) obtained by the transesterification of vegetables oils and animal fats with methanol or ethanol in a catalytic process [1,2]. Isentropic compressibility (K_S) is an important property for a hydraulic fluid, such as fuel injection system and combustion [3]. Also, the difference in the compressibility between biodiesel and petroleum diesel has been suspected for the increment in nitrogen oxide (NOx) emission [4,5]. Douheret *et al.* [6] pointed out that the more practical and reliable approach to determining K_S of a solution and liquid mixture were from the speed of sound and density data via the Newton-Laplace equation,

$$K_S = \frac{1}{\rho U^2} \tag{1}$$

where K_S, isentropic compressibility (Pa^{-1}); U, speed of sound ($m.s^{-1}$); ρ, density ($kg.m^{-3}$).

Krisanangkura *et al.* [5] proposed Gibbs free energy method for estimate K_S of fatty acid methyl ester and biodiesel were correlated to number of carbon atoms, number of double bond(s), shown as in equations (2) and (3):

$$\ln K_S = \ln A + \frac{\Delta G_{K_S}}{RT} \quad (2)$$

$$\ln K_S = -18.549 - 0.0248z - 0.0340n_d \frac{-727.83 + 3.156z + 5.1419n_d}{T} \quad (3)$$

where ΔG_{Ks} is Gibbs free energy (associated with isentropic compression); z is number of carbon atoms; n_d is number of double bond(s); T is absolute temperature; R is universal gas constant; A is numeric constant of thermodynamic.

Equation (3) is a good and simple model for estimation of biodiesel at different temperature, determination of the z and n_d requires the knowledge of fatty acid composition. The analysis must be done with a GC or a HPLC [7]. Saponification number (SN) and iodine value (IV) have long been used for characterization of fat and oil and they require no special instrumentation. However, both SN and IV can also be calculated from fatty acid composition. This work, an empirical approach for estimation K_S of biodiesel by a single empirical equation can be estimated without the prior knowledge of the K_S of an individual fatty acid methyl ester and can be predicted by using SN and IV.

2. Theory

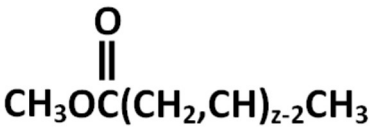

Figure 1. Chemical structure of fatty acid methyl ester.

Figure 1 shows chemical structure of fatty acid methyl ester can be written molecular weight mathematical as:

$$M_{\text{FAME}} = \text{COOCH}_3 + (z\text{-}2)\ [\text{CH}_2, \text{CH}] - n_d\ (2\text{H}) + \text{CH}_3 \quad (4)$$

With the substitution of molecular weight of C=12, O=16 and H=1 into equation (4) it yields:

$$z = \frac{M + 2n_d - 46}{14} \quad (5)$$

The saponification value (SV) and iodine value (IV) in the above equation were calculate using the following equations [7]:

$$SN = \frac{56,000}{M} \quad (6)$$

$$IV = \frac{25,400(n_d)}{M} \tag{7}$$

Equation (8) was derived from equation (3) with equations (5), (6) and (7) and can be used to estimate K_S of biodiesel at different temperatures from the SN and IV value.

$$K_S = -18.549 - \frac{0.0248}{SN} - \frac{727.83}{T} + \frac{3.156}{SN(T)} - \frac{0.034(IV)}{SN} + \frac{5.1419(IV)}{SN(T)} \tag{8}$$

3. Materials and Methods

3.1. Experimental data

Experimental speed of sound in biodiesel and their density data at different temperatures were obtained from Freitas *et al.* [8] and Lope *et al.* [9] (187 data). The experimental K_S for each biodiesel was calculated from density and speed of sound according to equation (1).

3.2. Statistical analysis

The deviations (D), absolute deviations (AD), average absolute deviations (AAD), Bias, standard error ($\sigma_{\bar{x}}$) and coefficient of determination (R^2) were calculated by equations (9) to (14), respectively:

$$\mathrm{D}(\%) = \frac{\mathrm{P_{exp}} - \mathrm{P_{cal}}}{\mathrm{P_{exp}}} 100\% \tag{9}$$

$$\mathrm{AD}(\%) = \left| \frac{\mathrm{P_{exp}} - \mathrm{P_{cal}}}{\mathrm{P_{exp}}} \right| 100\% \tag{10}$$

$$\mathrm{AAD}(\%) = \frac{100}{\mathrm{N}} \sum_{i=1}^{\mathrm{N}} \left[\left| \frac{\mathrm{P_{exp}} - \mathrm{P_{cal}}}{\mathrm{P_{exp}}} \right| \right] \tag{11}$$

$$\mathrm{Bias}(\%) = \frac{100}{\mathrm{N}} \sum_{i=1}^{\mathrm{N}} \left[\frac{\mathrm{P_{exp}} - \mathrm{P_{cal}}}{\mathrm{P_{exp}}} \right] \tag{12}$$

$$\sigma_{\bar{\mathrm{x}}} = \frac{\sigma}{\mathrm{N}} \tag{13}$$

$$\mathrm{R}^2 = \left[\frac{\mathrm{N} \sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{P_{exp}} \mathrm{P_{cal}} - \left(\sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{P_{exp}} \right) \left(\sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{P_{cal}} \right)}{\left(\left[\sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{P_{exp}^2} - \left(\sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{P_{exp}} \right)^2 \right] \left[\sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{P_{cal}^2} - \left(\sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{P_{cal}} \right)^2 \right] \right)^{\frac{1}{2}}} \right]^2 \tag{14}$$

where $\mathrm{P_{exp}}$ stands for experimental value reported elsewhere, $\mathrm{P_{cal}}$ is the calculated value and N is the number of data points.

4. Results and Discussion

Biodiesels are mixture of FAMEs of different compositions and vary according to the sources. Table 1 summarizes the *SN* and *IV* of neat and blended biodiesels, the range of *SN* and *IV* are 189.783 - 196.967 and 53.251 - 131.627, respectively. The estimated K_S of neat and blended biodiesels at 288.15 to 353.15 K by equation (8) are shown relative deviation (D (%)) in figure 2. The estimated K_S values for 16 biodiesels agrees well with the literature values. The Bias and AAD (%) were -0.28% and 1.19%, respectively. The K_S of biodiesels estimated by equation (8) were very close to those calculated using the z and n_d in using equation (3) (AAD = 1.18%). The correlation between the reported experiment K_S and estimated values using equation (8) (figure 3.) is linear with the slope, intercept, R^2 and standard error of 1.070, 0.000, 0.990, and 0.000, respectively.

Table 1. *SN*, *IV* and statistic values of estimated K_S by equation (8).

Biodiesels	*SN*	*IV*	N_{data}	Temperature (K)	AD (%)	Bias (%)	AAD (%)
Soy 1(S)	191.28	130.62	12	288.15 - 343.15	0.16 − 2.67 (1.19)*		
Rapeseed (R)	189.78	108.96	12	288.15 - 343.15	0.18 − 2.53 (1.14)		
Palm (P)	196.97	53.25	12	288.15 - 343.15	0.22 − 2.67 (1.21)		
SR	190.85	119.49	12	288.15 - 343.15	0.11 − 2.63 (1.26)		
PR	193.45	80.73	12	288.15 - 343.15	0.17 − 2.67 (1.22)		
SP	193.64	92.70	12	288.15 - 343.15	0.19 − 2.84 (1.13)		
SRP	192.79	97.83	12	288.15 - 343.15	0.20 − 2.69 (1.21)		
Sun flower	190.59	131.63	12	288.15 - 343.15	0.07 − 2.53 (1.17)		
Soybean +Rapeseed	191.18	117.57	12	288.15 - 343.15	0.12 − 2.93 (1.11)	-0.28	1.19
Soy 2	192.30	111.47	12	288.15 - 343.15	0.12 − 2.64 (1.23)		
Cotton 1	194.44	107.07	11	303.15 - 353.15	0.30 − 4.20 (1.16)		
Beef tallow	192.60	98.88	11	303.15 - 353.15	0.11 − 4.91 (1.08)		
Poultry fat	194.18	81.65	11	303.15 - 353.15	0.33 − 4.41 (1.01)		
Yellow grease1	190.87	64.11	11	303.15 - 353.15	0.07 − 5.05 (0.80)		
Yellow grease2	195.19	55.27	11	303.15 - 353.15	0.19 − 5.00 (0.83)		
Cotton 2	194.43	105.24	12	298.15 - 353.15	0.10 − 2.16 (1.99)		

* average AD(%)

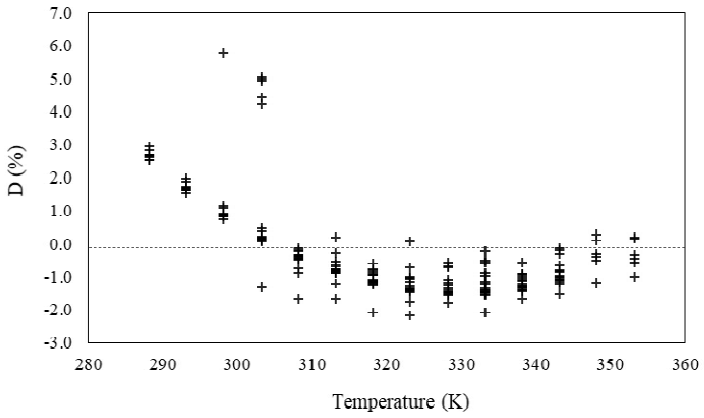

Figure 2. Relative deviations (D(%)) between K_S of biodiesels by equation (8) and the experimental values reported by Freitas *et al.* [8] and Lope *et al.* [9].

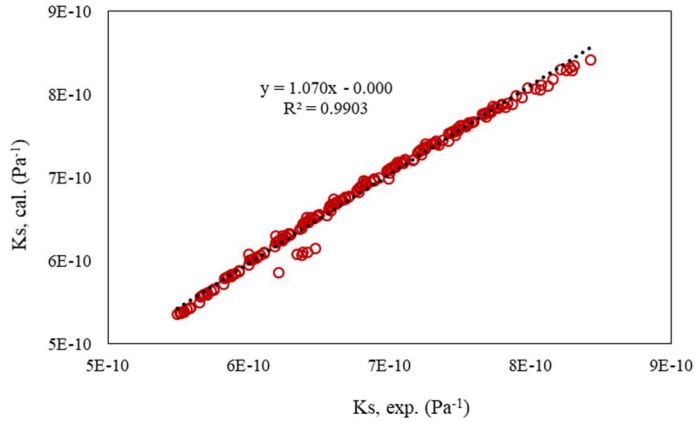

Figure 3. Correlation of the estimated ($K_{S,cal}$) to the experiment values ($K_{S,exp}$) [8,9] biodiesels at 288.15 to 353.15K.

5. Conclusions

Isentropic compressibility of biodiesel can be estimate from the *SN* and *IV* with a good accuracy at different temperatures (288.15 to 353.15K). Although, the validation was conducted between 288.15 and 353.15K, extrapolation is possible but it was not tested. The advantage of the proposed method is all the physical constants are well defined and related to the chemical molecule structure, which facilitates further refinement of the equations.

Acknowledgments

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