



Research article

Gibbs energy additivity approaches to QSPR in modeling of high pressure density and kinematic viscosity of FAME and biodiesel



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ARTICLE INFO

Article history:

Received 19 April 2016

Received in revised form 18 September 2016

Accepted 21 September 2016

Available online 28 September 2016

Keywords:

Biodiesel

Density

Fatty acid methyl ester

Gibbs energy

Kinematic viscosity

Model

Pressure

ABSTRACT

Density (ρ) and kinematic viscosity (μ) are important physical properties of biodiesel. They are directly affected by both temperature and pressure. Accordingly, models which correlate density and kinematic viscosity of fatty acid methyl ester (FAME) and biodiesel to their carbon numbers, number of double bonds of fatty acid are proposed. Gibbs free energy additivity is used as an alternative approach to quantitative structure-property relationship (QSPR) in estimating density and kinematic viscosity at high temperature and pressure of FAME and biodiesel. It is one of the best models for estimating density of FAME, mixtures of FAMES or biodiesels and biodiesel blends at different temperatures (283.15–333.15 K) and pressures (0.2–40 MPa).

For kinematic viscosity, the model is simply derived from the sum (or subtraction) of the Gibbs energies of dynamic viscous flow and volumetric expansion. Thus, this is the first model proposed for prediction of kinematic viscosity of FAME and biodiesel at different temperatures and pressures. Because there is no experimental value in the literature, the accuracy of the model is tested against the experimental density and experimental dynamic viscosity (η) via the classical equation ($\mu = \eta/\rho$).

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1. Introduction

Biodiesel is an important renewable liquid fuel, which has been widely accepted as an alternative fuel for use in high speed diesel engine. It is generally produced by alkaline catalyzed transesterification of vegetable oils or animal fats with monohydric low molecular weight alcohols [1], but commercial biodiesels are mainly fatty acid methyl esters (FAME). Types of oils selected for biodiesel feedstocks depend upon their availabilities and quality of the derived biodiesels. Density and viscosity are two of the main properties, which vary with raw materials used for its production and they have been included in most national or international standard for commercial biodiesel. They are specified at atmospheric pressure and at fixed temperatures. However, modern high speed diesel engines generally inject fuel into the combustion chamber at very high pressure. Under these extreme high pressure

conditions both density and viscosity vary significantly and at a certain point will pressure-freeze [2,3]. Both density and viscosity are changed with temperature and pressure. Hence, the correct knowledge of these properties is of great importance for fuel injection, atomization, volumetric flow through the pipe line, thermal efficiency of the engine and emissions [4–7]. The measurements of density and viscosity at atmospheric pressure are simple but data at high pressure and temperature require sophisticated instrumentation and time consuming experiments. In addition, measurements of these properties at the point of injection are almost not possible. Accordingly, mathematical models are much more convenient. There were numerous models for estimation density [8–12] and viscosity [11,13–21] of fatty acid methyl ester (FAME) and biodiesel at atmospheric pressure, but models for estimation of density [22–24] and viscosity [3,25–28] at high pressure are few compared to those for atmospheric pressure.

Schedemann et al. [29] reported that densities of methyl linoleate estimated by using the VTPR (Volume Translated Peng–Robinson) group contribution equation of state at different temperatures and pressures were more precise than the Triden (three dimensional density correlation system). Prieto et al. [23] correlated the experimental

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cottonseed biodiesel density data to the 4PGMA EoS (4 path Goharshadi–Morsali–Abbaspour equation of state) within $0.2 \text{ kg}\cdot\text{m}^{-3}$ corresponding to average relative deviations within 0.02%.

In case, when there is no model for prediction of kinematic viscosity at high pressures, it can be determined from the relationship in Eq. (1),

$$\eta = \mu \times \rho \quad (1)$$

where η , μ and ρ are dynamic viscosity, kinematic viscosity and density, respectively.

Paton and Schaschke [28] reported that the viscosity of biodiesel could be computed with the modified cubic PR EoS (Peng–Robinson equation of state). Based on the concept of free volume, the empirical relationship between dynamic viscosity and pressure was shown in Eq. (2) [27],

$$\eta_p = \eta_0 e^{p/\beta} \quad (2)$$

where β , η_p and η_0 are regression constant, dynamic viscosity at pressure p and 0.1 MPa, respectively.

Also, Robertson and Schaschke [3] measured viscosity of sunflower biodiesel at different temperatures (273–294 K) and found that data fitted well to Eq. (2) with the β constant varied with temperatures. Eq. (2) does not have the temperature term. Thus, it can be used at isotherm. On the other hand, Duncan et al. [25] used the hybrid Tait–Litovitz equation (Eq. (3)) to correlate viscosity at elevated pressures for a series of biodiesels,

$$\eta_p = Ae^{(B/RT^3)} \frac{(D+p)}{(D+0.1)^E} \quad (3)$$

where R is gas constant, p is pressure, T is absolute temperature and A , B , D and E are the fitting constants.

Data regression was performed using a Newton–Gaussian nonlinear method. Eq. (3) could be used for both petrodiesel and biodiesel but the numeric constants were different for different types of liquids. Therefore, prediction power of Eq. (3) is very limited.

Alternatively, Eq. (4) was proposed by Freitas et al. [26] for estimation of viscosity at high pressure for soybean oil, rapeseed oil and mixture of soybean and rapeseed oil biodiesels. Eq. (4) is simple and has only two fitting parameters (a and b). The values for a and b were 1.2 and 0.84 for all three biodiesels. Accordingly, the slopes of the plot between $\ln(\eta_p)$ and p were parallel at all T . The overall AAD for these biodiesels were 3.90% at all T and P ,

$$\ln \eta_p = \ln \eta_0 + a \frac{(p-p_0)}{T^b} \quad (4)$$

where a and b are fitting parameters, p_0 is reference p (atmospheric pressure).

In this study, Gibbs energy additivity was proposed as an alternative approach to QSPR model for estimation of density and kinematic viscosity of FAME and biodiesel. Densities and kinematic viscosity at different temperatures and pressures are easily estimated from its carbon numbers and numbers of double bonds.

2. Background

Quantitative structure–property relationship (QSPR) is very useful technique for estimation of the physicochemical properties of a compound. It assumes a strong correlation between structure and property of the compound considered [30]. Group contribution method based on fragments has been widely used as the correlation tool [10,29,31–34]. The development of alternative approaches to find quantitative mathematical relationships between the intrinsic molecular structure and observable properties of chemical compounds would be of increasing importance in the chemistry of the 21st century [30]. Gibbs free energy

additivity is similar to group contribution method, in which molecule is divided into atom or group of atoms [35]. The difference between the two methods is, Gibbs energy is assigned for each divided group of atoms (ΔG_i). The Gibbs energy of the whole molecule (ΔG) is derived from the sum of Gibbs energy of all the contribution groups,

$$\Delta G = \sum_{i=1}^z \Delta G_i \quad (5)$$

Thus, structure and property of a molecule is correlated via ΔG . Eq. (5) can be substituted into equation that relates Gibbs energy to physical property. The Andrade equation on viscosity is a good example (Eq. (5)),

$$\eta = Ae^{-\Delta G/RT} = Ae^{\left(\sum_{i=1}^z -\Delta G_i\right)/RT} \quad (6)$$

where η is dynamic viscosity; A is regression constant.

For saturated and unsaturated fatty acid methyl ester, Eq. (6) is expanded to Eq. (7) [36],

$$\ln \eta = \frac{\Delta S_f}{R} + \ln A - \frac{\Delta H_f}{RT} + \frac{z\Delta S_i}{R} - \frac{z\Delta H_i}{RT} + \frac{n_d\Delta S_d}{R} - \frac{n_d\Delta H_d}{RT} \quad (7)$$

or

$$\ln \eta = s_0 + s_1z + s_2n_d - \frac{h_0 + h_1z + h_2n_d}{T} \quad (8)$$

where $s_0 = \frac{\Delta S_f}{R} + \ln A$; $s_1 = \frac{\Delta S_i}{R}$; $s_2 = \frac{\Delta S_d}{R}$; $h_0 = \frac{-\Delta H_f}{R}$; $h_1 = \frac{-\Delta H_i}{R}$; $h_2 = \frac{-\Delta H_d}{R}$; ΔS and ΔH are entropy and enthalpy, respectively; z and n_d are number of carbon atoms and number of double bond of fatty acid; i and f stand for group of atom i th and fatty acid arbitrarily having zero carbon atom.

There are other physical properties of FAME and biodiesel, which are related to Gibbs energies in the form of Eq. (6). For example; density (ρ) and kinematic viscosity (μ) of FAME and biodiesel could be estimated by Eq. (8), but numeric values for the six coefficients are different and the η on the left hand side is replaced by ρ or μ , accordingly.

However, Eq. (8) is limited to the dynamic viscosity of FAME and biodiesel at atmospheric pressure. For dynamic viscosity at higher pressure, it is postulated that the Gibbs energy of viscous flow expansion is simply derived from the sum of Gibbs energy from atmospheric pressure and Gibbs energy contributed from the change in pressure factor (p') as shown in Eq. (9),

$$\Delta G_p = \Delta G_{atm} + p' \sum_{i=1}^z \Delta G_{p,i} \quad (9)$$

where $\Delta G_{atm} = \sum_{i=1}^z \Delta G_i$, $p' = \frac{p_i - p_{atm}}{p_{atm}}$.

Substitutions the Gibbs energy term in Eq. (9) into Eq. (6), Eq. (10) is obtained,

$$\ln \eta_p = \ln \eta_{atm} - \frac{p'(\Delta G_{p,f} + z\Delta G_{p,i} + n_d\Delta G_{p,d})}{RT} \quad (10)$$

Expanding the ΔG to its enthalpy and entropy forms,

$$\ln \eta_p = \ln \eta_{atm} + p' \left(s_{p,\eta 0} + s_{p,\eta 1}z + s_{p,\eta 2}n_d + \frac{h_{p,\eta 0} + h_{p,\eta 1}z + h_{p,\eta 2}n_d}{T} \right) \quad (11)$$

where $s_{p,\eta 0} = \frac{\Delta S_{p,f}}{R}$, $s_{p,\eta 1} = \frac{\Delta S_{p,i}}{R}$, $s_{p,\eta 2} = \frac{\Delta S_{p,d}}{R}$, $h_{p,\eta 0} = -\frac{\Delta H_{p,f}}{R}$, $h_{p,\eta 1} = -\frac{\Delta H_{p,i}}{R}$, and $h_{p,\eta 2} = -\frac{\Delta H_{p,d}}{R}$.

Eq. (11) was proposed for estimation of dynamic viscosity of FAME and biodiesel at different temperatures and pressures [37]. In the case

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