DENSITY ESTIMATION FOR WASTE COOKING OIL BIODIESEL

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Abstract - This paper focuses on the biodiesel density predictive models and examines the accuracy of the HCC methodology which bases on Rackett equation modified by Spencer and Danner to estimate the density of waste cooking oil (WCO) biodiesel in a wide range of temperature based on its fatty acid methyl ester components. The calculated results are compared with experimental measurements for the density aiming to validate the chosen method. The analysis results obtained show that this method does not, in all cases, yield high accuracy even though its use is simple. Particularly, in case of the biodiesel derived from waste cooking oil (WCO), this method is not accurate enough to predict its density with the deviations between experimental data and calculated density getting relatively high, around 3.4%

Key words - waste cooking oil; biodiesel; density; FAME; prediction

1. Introduction

According to the latest report issued by the Intergovernmental Panel on Climate Change within the recent Climate Change Conference COP24, a relentless emission of greenhouse gases such as CO_2 when fossil fuels are consumed is making the global warming more and more severe and is bringing up challenges for humanity. In parallel, humanity is facing up the depletion of fossil energy sources while the demand for energy worldwide is rising. In response to this crisis, seeking a renewable and environmentally friendly alternative energy source becomes an increasingly urgent need. Biodiesel which is well-known as a renewable, environmentally friendly bio-fuel owning less particular emissions [1] and good lubrication properties [2] as well as the friendly properties such as non-toxic, biodegradable and contains essentially no sulphur or aromatics [3], has been taking up a growing market share in the global energy market, and is also a research trend for each country, especially in developing ones. Vietnam has a great potential to develop this kind of bio -fuel we know how to make good use of industrial / agricultural waste materials. The study of biodiesel production from these raw materials, namely waste cooking oil (WCO), collected mainly from the catering industry will have great significance in scientific research and industrial practice because of its potential low-cost biodiesel feedstock. The use of biodiesel from WCO could resolve environmental as well as economic and social problems in comparison with the first generation biodiesel which are derived from edible oils.

The bio-diesel spray and combustion analysis require knowledge of its thermo-physical properties influencing these processes. Density is one of the important properties of a fuel that affects spray atomization. The changes in fuel density also affect the start of the dynamic injection event. The density of a fuel is found to relate to other properties, such as the heating value and cetane number [4]. A predictive methodology for density prediction is essential in process modeling applications, wherein density variations with temperature are required, such as spray atomization in engines.

Up to now, three main methods for estimating liquid densities of pure fluids include: (1) the first one are based on the corresponding states theory (i.e., the Rackett equation and the Spencer and Danner method [5]) which has a limited predictive capability because of the requirement of critical properties and the use of experimental data adjusted parameters; (2) The second method is based on mixing rules, such as Kay's method, that allows the estimation of a mixture density provided that the composition of the fuel and the densities of the pure compounds are known [6]. They are only applicable to simple mixtures being of a nearly ideal behavior; (3) the last method is to use group contribution models that only require information on chemical structure of molecule under study. Many recent studies follow the latter in combination with a thermodynamic model [7-9].

The goals of the present study are to measure densities biodiesel derived from waste cooking oil in temperatures up to 353 K; present and evaluate a simple model, based on the methodology proposed by Halvorsen et al. [10] to calculate the densities of fatty acid methyl esters constituent to WCO biodiesel (HCC method).

2. Calculation Methodology

Because biodiesel is a mixture of mono-alkyl esters of long-chain fatty acids of which the carbon number ranges from C8 to C24 (most commonly between C14 and C18), this study, firstly bases on the available equations in literature to estimate the density of each fatty acid methyl ester containing the biodiesel. Then the corresponding properties of the biodiesel are determined with some mixing rules in terms of the weight percent of each pure fatty acid methyl ester in the biodiesel fuel.

A methodology proposed by Halvorsen et al. [10], called HCC, was be used to calculate the density of pure liquids for alkyl esters and biodiesel fuels. The results obtained should be evaluated and analyzed in comparison with other expressions and measured data in the same conditions to measure the predictive accuracy of the used formulae.

2.1. Estimation of Normal Boiling Point, Critical Parameters and Acentric Factor of pure component

The estimation methods for physical properties of heavy components, particularly the density of alkyl ester whose constituent biodiesel fuels are proposed in terms of normal boiling point, critical parameters and acentric factor of these components along with the understanding of their molecular weight. Therefore, these parameters are estimated first based on the published methods which have

been verified to have the best or better accuracy.

The normal boiling point *T*b is estimated by Constantinou- Gani correlation which yields the smaller errors analyzed by Anand *et al* [11].

$$T_{nb} = 204.359 \ln\left[\sum_k N_k (t_{b1k}) + W \sum_j M_j (t_{b2j})\right] \quad (1)$$

in which t_{b1k} and t_{b2j} are the values of contribution groups at the "First Order" and "Second Order" level according to the definition of this method [12]. N_k and M_j are the number of these groups.

The critical parameters (T_c, P_c, V_c) of the fatty acid methyl esters are predicted by Joback method [13] which produces the smaller error for the estimation of the critical parameters of alkyl ester as recommended by Anand *et al* [11].

$$T_c(K) = T_{nb}\left[0.584 + 0.965\sum_k N_k (t_{ck}) - \left\{\sum_k N_k (t_{ck})\right\}^2\right]^{-1} \quad (2)$$

$$P_c(bar) = \left[0.113 + 0.0032 N_{Atoms} - \left\{\sum_k N_k (p_{ck})\right\}\right]^{-2} \quad (3)$$

where the contributions are indicated as t_{ck}, p_{ck}.

The acentric factor ω is predicted by Lee-Kestler correlation which yields the higher accuracy [11]

$$\omega = \frac{-\ln P_c - 5.97214 + 6.096448\theta^{-1} + 1.28862\ln\theta - 0.169347\theta^6}{15.2518 - 15.6875\theta^{-1} - 13.4721\ln\theta + 0.43577\theta^6} \quad (4)$$

where $\theta = T_{nb}/T_c$

2.2. Density Estimation of the Biodiesel (HCC methodology)

The biodiesel is a mixture of fatty acid methyl esters, hence, the estimation of densities of biodiesel fuels can easily be made by estimating the densities of the fatty acid methyl ester (FAME) constituents. Densities of pure FAMEs and biodiesel were calculated using a systematized and fully predictive methodology, based on the method described by Halvorsen et al. [10].

$$\rho(g.cm^{-3}) = \frac{\sum_i x_i MW_i}{R\left(\sum_i \frac{x_i T_{c,i}}{P_{c,i}}\right)\left(\sum_i x_i Z_{RA,i}\right)^{\left[1+(1-T_r)^{2/7}\right]}} \quad (5)$$

where ρ is the biodiesel density, x_i is the molar fraction of component i, MW_i is the molar weight of component i, R is the ideal gas constant, $T_{c,I}$ and $P_{c,I}$ is the critical temperature and critical pressure of component i, T_r is the reduced temperature in relation to the studied temperature and $Z_{RA,i}$ is the Rackett's parameter of component i which is calculated by the following equation:

$$Z_{RA,i} = \left[\frac{MW_i . P_{c,i}}{\rho_i R T_{c,i}}\right]^{\left[(1+(1-T_r)^{2/7}\right]^{-1}} \quad (6)$$

where ρ_i is the reference density of component i.

The reference density at 298 K was determined using the predictive method proposed by Constantinou et al. [14] for calculating the liquid molar volume of pure fatty acid alkyl esters as recommended by Rodrigo Correa Basso et al. [15].

3. Experimental Methodology

3.1. WCO-Biodiesel Synthesis

Waste cooking oil (WCO) used as a feedstock for biodiesel synthesis in this study was procured from a local restaurant in Vietnam. The WCO sample was obtained by the way of collecting after being used once for cooking various dishes and then filtered to remove any inorganic residues and suspended matters. The first phase of the study was concerned with the analysis of the WCO sample.

Taking into consideration the average acid value of 3.96 mg KOH/g, corresponding to the weight percent of Free Fatty Acid (%FFA) lower than 2%, the methods used for biodiesel production from WCO are very similar to the conventional transesterification process with alkali-catalyst. The transesterification procedure was carried out following the steps detailed in the research of Basak Burcu Uzun and depicted in detail in the previous study [8].

Fatty acid methyl esters (FAME)s in biodiesel prepared from waste cooking oil were estimated using Thermo Scientific™ ISQ™ LT Single Quadrupole GC-MS System. For identification of FAME library search was carried out using NIST, NBS and Wiley GC-MS library. The individual peaks of the gas chromatogram were analyzed, and the fatty acids were identified using MS database. Relative percentage of fatty acid esters was calculated from total ion chromatography by computerized integrator.

3.2. Density measurement

Density was measured as a function of pressure and temperature using an ANTON-PAAR vibrating tube densimeter equipped with a high pressure cell (DMA HPM). This high-pressure densimeter cell enables measurements over broad ranges of pressure (0.1 to 140) MPa and temperature (283.15 to 403.15) K. The well-known measurement principle consists of determining the oscillation period of a U-shaped tube, which contains the sample. The square of this period is correlated to the density through a linear relationship. The parameters of this linear law were determined using water and decane as a reference liquid.

The dataset for density of WCO biodiesel were presented in the earlier work [8] that will be reused in this study to valid the accurate of the predictive model.

4. Results and discussion

4.1. WCO biodiesel: relative compositions of fatty acid methyl ester contents

Table 1 shows the fatty acid methyl ester composition of the biodiesel derived from waste cooking oil.

The oleic acid (C18:1) and palmitic acid (C16:0) are the major fatty acids in WCO-biodiesel with 37.59 wt% and 25.14 wt% respectively, followed by stearate acid (C18:0)–

13.18 wt%, linoleic acid (C18:2) – 9.76 wt% and palmitoleic acid (C16:1) – 7.16 wt%. The long chain fatty acids are present as minor constituents.

Table 1. *FAME profile of the WCO biodiesel*

RT (min)	FAME	wt.%
3.39	Methyl myristate (C14:0)	3.22
6.26	Methyl palmitoleate (C16:1)	7.16
6.78	Methyl palmitate (C16:0)	25.14
10.91	Methyl linoleate (C18:2)	9.76
11.24	Methyl oleate (C18:1)	37.59
11.97	Methyl stearate (C18:0)	13.18
16.29	Methyl eicosadienoate(C20:2)	0.53
16.38	Methyl eicosenoate(C20:1)	1.77
16.84	Methyl eicosanoate(C20:0)	0.62

Their FAME analysis showed that the fatty acids of these biodiesels were composed primarily of oleic acid and palmitic acid, followed by linoleic acid. These components able to improve not only certain of important fuel properties like cetane number, heat of combustion, oxidative stability and kinematic viscosity (C18:1, C16:0) but also the cold flow properties of biodiesel (C18:2) as shown in the works of Knothe G [16]. Based on this profile of fatty acid composition it is clearly assumed that waste cooking oil is suitable for biodiesel production.

4.2. Predicted property of pure FAME

The estimated results of the normal boiling point, critical parameters and acentric factors of pure FAME constituting in WCO biodiesel by using methods mentioned in section 2.1 are shown in Table 2.

Table 2. *The normal boiling point, critical parameters and acentric factors of pure FAME constituting in WCO biodiesel*

FAME	MW	T_{NB}	T_C	P_C	ω
C14:0	242	569.7	723.9	14.208	0.6449
C16:1	268	621.5	772.1	13.127	0.5341
C16:0	270	621.5	766.9	12.355	0.5474
C18:2	294	624.4	798.3	11.625	0.8056
C18:1	296	624.4	774.2	11.223	0.8155
C18:0	298	624.5	775.4	10.842	0.8205
C20:2	322	644.1	797.1	10.091	0.8937
C20:1	324	643.9	797.1	9.873	0.9152
C20:0	326	643.7	797.1	9.591	0.9375

These calculated values are reasonably accepted in comparisons with the other methods mentioned in the study of P. Saxena et. Al [17]. From the estimated values of critical properties, prediction of density was done.

The reference densities of pure fatty acid methyl esters presented in WCO biodiesel were calculated by the methodology depicted in section 2.2, and when compared to the published values [18, 19]. The calculated results and deviations were obtained within acceptable range with the overall average relative deviations(ARD) equal to 0.4631%, as reported in Table 3.

Table 3. *Calculated Densities, Rackett Parameters, and Deviations between Experimental Measurements and this Methodology for Pure Ester Densities*

FAME	ρ_{ref}(g/cm^3)	Z_{RA}	ARD (%)
C14:0	0.86344	0.227560613	0.6993
C16:1	0.87206	0.223481152	0.8875
C16:0	0.86258	0.220145961	0.7191
C18:2	0.87936	0.220141801	0.2810
C18:1	0.87047	0.219823375	0.4206
C18:0	0.86187	0.215789234	0.7563
C20:2	0.87018	0.214610198	0.1418
C20:1	0.86915	0.210377107	0.1654
C20:0	0.86128	0.210157863	0.0972
	Overall		**0.4631**

4.3. Estimated Density of WCO biodiesel

The density of WCO biodiesel is calculated by the mixing rule based on the density of each FAME comprising in biodiesel and their molar fraction in the mixture. Hence, we need to estimate the density of pure diesel at different temperatures than calculate the one of biodiesel and compare it with the experimental data.

Table 4 resumes the results of pure FAME density and the density of biodiesel at the range of temperatures 20, 40, 60, 80^{o}C respectively.

Table 4. *Calculated density of pure FAME and biodiesel at the range of temperatures 20, 40, 60, 80^{o}C*

		20^{o}C	40 ^{o}C	60 ^{o}C	80 ^{o}C
FAME	xi		ρ(g/cm^3)		
C14:0	0.0384	0.8996	0.8842	0.8686	0.8527
C16:1	0.0771	0.9064	0.8922	0.8777	0.8631
C16:0	0.2687	0.8886	0.8744	0.8599	0.8453
C18:2	0.0958	0.8827	0.8693	0.8558	0.8420
C18:1	0.3664	0.8810	0.8670	0.8529	0.8385
C18:0	0.1276	0.8860	0.8718	0.8575	0.8429
C20:2	0.0047	0.8813	0.8677	0.8539	0.8399
C20:1	0.0158	0.9006	0.8866	0.8723	0.8579
C20:0	0.0055	0.8820	0.8683	0.8543	0.8401
WCO BD		0.8868	0.8728	0.8586	0.8440

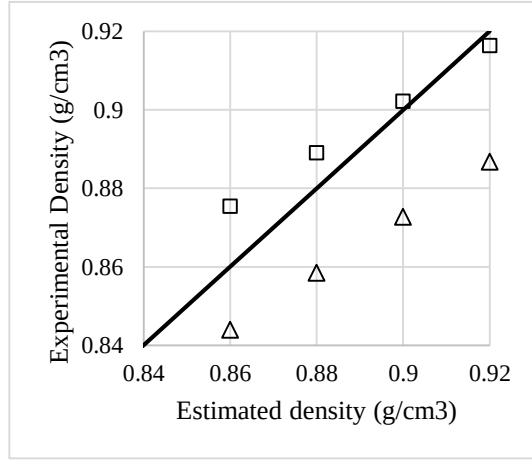

Figure 1. *Experimental data [8](□) and calculated densities (Δ) of WCO biodiesel at different temperatures*

Figure 1 represents the comparison between the experimental data [8] and calculated densities of WCO biodiesel at different temperatures in which the overall percentage average relative deviation is around 3.4%.

These results reveal that even if the HCC methodology is sample for estimation the density of pure FAME comprising in biodiesel, the use of this method is sometimes not accurate enough to predict the density of biodiesel, because of the requirement of critical properties as well as the experimental data adjusted parameters to reach higher correctness.

This will be explained by two reasons:

- This estimation method depends heavily on the critical properties of each component of methyl ester in the biodiesel mixture. These properties are calculated by the group contribution method via adding properties of chemical groups included in the methyl ester substance constituent biodiesel by formula proposed by Joback. Although evaluated as less error, however, for heavy component with a long chain molecular and high chemical group number, the error will be malfunctioned.

- Biodiesel produced from waste cooking oil has a variety of methyl ester component and the difference in mass fraction between them is also relatively large, while analytical method is difficult to evaluate all. Therefore, it leads to the error in the calculation according to the mixing rule and results in the deviations between experimental data and calculated density getting relatively high, around 3.4%

5. Conclusion

The density of the waste cooking oil biodiesel is predicted using the HCC methodology which bases on the Rackett equation modified by Spencer and Danner. The analysis results obtained show that this method does not, in all cases, yield high accuracy even though its use is simple. In case of the WCO biodiesel, this method is not accurate enough to predict its density. This is the reason why we try to develop a more efficient methodology based on an equation of state (EoS) coupling with the group contributions. An empirical approach proposed founded on the modified group-contribution PC-SAFT developed in our previous work [20] clearly has shown that, provided that the biodiesel alkyl ester composition is known, the predictive method investigated here can be used to predict liquid density of biodiesel fuels in a wide range of temperatures and pressure with overall deviations of 0.71%.

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