Prediction of Density of Fatty Acid Alkyl Esters (Biodiesel) by Various Group-Contribution Methods

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Abstract—**Biodiesel is a promising alternative for petro-diesel fuel. Density of biodiesel (Fatty acid alkyl esters or FAAEs) plays an important role in the fuel injection in a diesel engine and is also an important parameter for correlating cetane number, viscosity and heating value of a liquid fuel. Methods for the prediction of density of various types of biodiesel are required. Various versions of Group contribution methods GCVOL have been developed and used for the prediction of density of FAAEs. In the present study, density of seven fatty acid methyl esters and three fattyacid ethyl esters was predicted by using three versions of GCVOL methods (GCVOL-Elbro, GCVOL-Ihmels, GCVOL-Pratas). Total 152 data points for the experimental values of density of FAMEs and FAEEs were used to find the best method for the prediction of density of FAAE. GCVOL-Elbrogave percentage overall relative deviation of 8.53 for FAMEs and 5.25 for FAEEs and hence this method is being proposed as the best group contribution method for the prediction of density of FAAEs.**

Keywords—*biodiesel, FAME, FAEE, density, GCVOL*

I. INTRODUCTION

Due to the rapid depletion of resources of petroleum fuels to meet the increasing demands of energy has created a need for the search of alternative fuels. Biodiesel is a promising alternative for petro-diesel. Biodiesel is composed of fatty acid alkyl esters (FAAE) obtained by the transesterification of triglycerides compounds, using a short chain alcohol, such as methanol or ethanol, in the presence of a catalyst. The common feedstocks for biodiesel production include vegetable oils like palm, rapeseed, soybean, sunflower, canola and jatropha. Biodiesel offers advantages such as biodegradability, nontoxicity, lower emissions, and it is miscible with petroleum diesel at any proportion and thus compatible with the modern diesel engine [1],[2]. Density of biodiesel is an important property and it directly influences the fuel injection process, as it determines the actual amount of mass of fuel to be injected in diesel engine. Moreover, density is an important parameter for liquid fuel to correlate the cetane number, heating value andviscosity[3].Several studies on the density measurements and predictions for biodiesel (fatty acid methyl ester; FAME and fatty acid ethyl esters; FAEE) have been conducted. Gouw et al. [4] correlated densities of saturated FAMEs at 293K and 313K. Pratas et al. [5],[6] applied group contribution model (GCVOL) to predict

densities of ten FAEEs and fifteen FAMEs from 273K to 373K. Ramirez-Verduzco et al. [7]developed empirical correlation based on molecular structure. Biodiesel densities were usually measured over a temperature range below 373K. In this study, density of seven fatty acid methyl esters (FAMEs) and three FAEEs were predicted by three versions of group contribution methods (GCVOL). The experimental data for density as reported by Pratas [6] was used for this study. Total 102 experimental density data points for seven FAMEs and 50 experimental density data points for three FAEEs were used in the temperature range of 278.15K-373.15K.

II. DENSITY PREDICTION METHODS

Various GCVOL group contribution methods used in this study are discussed below.

A. GCVOL-Elbro Method

The GCVOL method is a group contribution method for predicting saturated liquid density, which was developed by Elbro et al. [8] in which density of a pure compound can be calculated by

$$\rho = 1000 \times \frac{MW}{V} = 1000 \times \frac{MW}{\sum n_i \Delta v_i} \qquad (1)$$

where ρ is the density in kgm^{-3}; MW is the molecular weight in g mol^{-1}; V is the molar volume in cm^3 mol^{-1}; n_i is the number of groups i and Δv_i is the molar group volume in cm^3 mol^{-1}, which is defined as

$$\Delta v_i = A_i + B_i T + C_i T^2 \qquad (2)$$

where T is in K; A_i, B_i and C_i are group volume temperature constants (i.e. group parameters). The group parameters needed for fatty acid alkyl ester density prediction are listed in Table 1 in which the application temperature range recommended is from the melting point to the normal boiling point of the compound.

Following Eqn. (1) the biodiesel density can be calculated as

$$\rho_m = 1000 \times \frac{\sum x_j MW_j}{\sum x_j V_j} \quad (3)$$

where ρ_m is the biodiesel density in kg m^{-3}; MW_j is the molecular weight of component j; V_j is the molar volume of component j and x_j is the molar fraction of component j.

B. GCVOL-Ihmels Method

Ihmels and Gmehling[9]extended and revised the GCVOL-Elbro method by adding other new group parameters and those are presented in Table 1.

C. GCVOL-Pratas Method

Pratas et al. [10]further optimized the values of the constants for the double bond group parameter (CH=, as reported in Table 1), while other paramters remain the same as those of the GCVOL-Elbro method.

Table I. Group Parameters For Fatty Acid Alkyl Ester Density Prediction In Gcvol

Methods	Parameters	A	B	C
GCVOL-Elbro	CH$_2$	12.52	12.94	0
	CH$_3$	18.96	45.58	0
	CH=	6.761	23.97	0
	COO	14.23	11.93	0
GCVOL-Ihmles	CH$_2$	12.04	14.1	0
	CH$_3$	16.43	55.62	0
	CH=	-1.651	93.42	-14.39
	COO	61.15	-248.2	36.81
GCVOL-Pratas	CH=	11.43	6.756	0

III. PREDCITION OF DENSITY

Density of seven FAMEs and three FAEEs was predicted at various temperatures (278.15 K -373.15 K) by GCVOL group contribution methods as discussed above. The calculations were done in Microsoft Excel®. These predicted values of density were compared with their experimental values and % Overall average relative deviation (% OARD) was calculated by using Eqn. (4).

$$\%OARD = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{\rho_{i\,exp} - \rho_{i\,pred}}{\rho_{i\exp}} \right| \times 100 \quad (4)$$

where $\rho_{i\,exp}$ is the experimental value and $\rho_{i\,pred}$ is the predicted or calculated value of density of FAME or FAEE in Kg m^{-3}; N is the number of data points for a given FAAE. For this study, total 152 (102 for FAMEs and 50 for FAEEs)

data points for experimental values of density were used in the temperature range of 278.15 K-373.15 K.

IV. PREDCITION OF DENSITY

The % OARD values of FAMEs and FAEEs for various methods are reported in Table II and Table III.

Table II. % OardFor Fames For Various Gcvol Methods

FAME	No. of data points	%OARD		
		GCVOL-Elbro	GCVOL-Ihmel	GCVOL-Pratas
C16:1	18	8.09	16.46	10.37
C18:3	18	3.2	14.8	10.1
C20:0	11	8.96	23.86	8.96
C20:1	20	7.61	14.72	9.54
C22:0	9	17.44	30.24	17.44
C22:1	18	7.01	13.56	8.81
C24:0	8	7.43	20.99	7.43
Global % OARD for all the seven FAMEs		**8.53**	**19.23**	**10.38**

From Table II and Table III, it can be interpreted that for the density prediction GCVOL-Elbro gave the least global % OARD of 8.53 for FAMEs and 5.25 for FAAEs, followed by GCVOL-Pratas with global % OARD of 10.38 and 9.74 respectively. GCVOL-Ihmel gave quite high deviation for both FAMEs and FAEEs. However, literature reportsGCVOL-Pratas as the best method for the prediction of density of FAAEs in comparison to the other two. But in the present study, GCVOL-Elbro was found to be better as compared to GCVOL-Pratas for the FAAEs under consideration. The reason for this may be due to the different esters and their density data points used in the prediction of density. Hence, GCVOL-Elbro method is being proposed as the best group contribution method for the prediction of density of FAAEs.

Table III. % OARD FOR Fames FOR VARIOUS GCVOL METHODS

FAEE	No. of data points	%OARD		
		GCVOL-Elbro	GCVOL-Ihmel	GCVOL-Pratas
C18:2	18	5.19	2.87	9.4
C18:3	20	2.4	16.11	8.61
C20:0	12	8.17	22.62	11.21
Global % OARD for three FAEEs		**5.25**	**13.87**	**9.74**

V CONCLUSIONS

Density is an important property of biodiesel and the prediction of density of biodiesel is required. GCVOL Group

contribution methods have been developed for the prediction of density of FAAEs. In the present study, three version of GCVOL methods (GCVOL-Elbro, GCVOL-Ihmels, GCVOL-Pratas) were used for the prediction of density of seven fatty acid methyl esters and three fatty acid ethyl esters and it was found that GCVOL- Elbro gave the best prediction with global % OARD of 8.53 for FAMEs and 5.25 for FAEEs. This study can be extended by predicting density for these FAAEs by other methods available in literature like based on Rackett equation, empirical correlations based on molecular structure and development of empirical correlation based on regression of experimental data.

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