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Predicting the vapor pressure of fatty acid esters in biodiesel by group contribution method

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ABSTRACT

In this study, a group contribution method based on the Riedel equation was developed to predict the vapor pressures of fatty acid methyl, ethyl, propyl, and butyl esters. A CH_2 (ester) group was introduced to distinguish the fatty acid methyl, ethyl, propyl, and butyl esters. The group parameters were regressed based on a total of 4687 vapor pressure data. The results show that, the proposed group contribution method illustrates much better performance in predicting the vapor pressures of fatty acid methyl and ethyl esters, and comparable accuracy in predicting the vapor pressures of fatty acid propyl and butyl esters in comparison with Ceriani's group contribution method (Ceriani et al., 2013). A test set of 2584 experimental data was used to further verify the reliability of the proposed method and its superiority in accurately predicting the vapor pressure within the whole temperature range over Ceriani's group contribution method. By using these two group contribution methods, vapor pressures of ten biodiesels were also predicted, and the proposed group contribution method has a better accuracy with the overall average relative deviation of 5.49%. The temperature dependency of biodiesel vapor pressure is also well reproduced by the proposed method.

1. Introduction

Biodiesel is oxygenated, biodegradable, nontoxic, and environmentally friendly, and has received substantial attention as a renewable alternative to petroleum diesel [1,2]. Biodiesel is a mixture of long chain fatty acid alkyl esters, which can be produced from various edible and non-edible feedstocks through the transesterification reaction with alcohols [3,4]. Physical and chemical properties have a significant influence on the spray, combustion, and emission characteristics of engines fueled with biodiesel, and temperature-dependent properties over a wide temperature range are required for accurate modeling of biodiesel spray and combustion processes [5–7]. However, the properties of biodiesels derived from different sources differ from one another due to the variation of fatty acid compositions. Therefore, the knowledge of properties of fatty acid alkyl esters is crucial for the determination of biodiesel properties.

Vapor pressure (or equilibrium vapor pressure), the pressure of a vapor in thermodynamic equilibrium with its condensed phases (liquid in case of liquid fuel) in a closed container [8], is an important fluid property because of its direct relation with the fuel vaporization process in engines [9]. Temperature-dependent vapor pressures of biodiesel are required for accurate spray and combustion modeling as well as the estimation of phase equilibrium in the oil and gas industry [6]. Although efforts have been devoted to experimentally determining the vapor pressures of biodiesels and fatty acid alkyl esters [10,11], it is impractical to provide all the necessary data over a wide temperature range for the various biodiesels from different sources by experiment [6,10–12]. Moreover, the accuracy decreases when measuring the relatively low vapor pressure of low-volatility compounds with large molecular weights such as the long chain esters found in biodiesel fuels [13,14], and there is a poor agreement between different reported data on such low vapor pressures [11]. Additionally, the unsaturated compounds would be subjected to oxidation or decomposition with increasing temperature during the experiment [11,12]. Therefore, vapor pressure prediction methods for fatty acid esters in biodiesel are of great interest, and an increasing number of relevant studies can be found in the recent literature.

Ceriani and Meirelles [15] developed a group contribution method to correlate the vapor pressure and temperature for fatty compounds, and Yuan et al. [12] applied this group contribution method to determine the Antoine parameters for unsaturated fatty acid methyl esters (FAMEs) due to the lack of experimental vapor pressure data. The aforementioned methods developed by Ceriani and Meirelles [15], and Yuan et al. [12] were evaluated together with a cubic-plus-association equation of state (CPA EoS) method by Freitas et al. [10] using the experimental vapor pressures of ten biodiesel fuels. The method by Yuan et al. [12] and the CPA EoS method [10] were found to be superior to the method by Ceriani and Meirelles [15]. An and Yang [6] proposed a

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new generalized correlation for vapor pressure prediction based on the Lee–Kesler's method, where a fuel dependent parameter 'A' is introduced, which requires the critical temperature, normal boiling temperature, and the acentric factor of the fluid as the input. Díaz et al. [13] developed a vapor pressure model applicable for predicting the FAME vapor pressures of moderate temperatures based on the Cox equation. More recently, Ceriani et al. [16] improved the vapor pressure model of Ceriani and Meirelles [15], and a more accurate group contribution model was obtained with extended temperature range. From the review of the previous prediction methods, the group contribution methods [15,16] are able to predict the temperature-dependent vapor pressure with only the structural groups of the molecule as the input, while the methods based on theoretical correlations [6,10] require the input of physical properties, which are usually unavailable for long chain fatty acid esters. However, the recent comparison work by Wallek et al. [17] shows that the group contribution model recently proposed by Ceriani et al. [16] showed large deviations for the prediction of the vapor pressures lower than 1.0 kPa of FAMEs. Therefore, further refinement of the vapor pressure prediction method is needed for a more accurate description of the vapor pressures of fatty acid esters in biodiesel fuels.

Biodiesels derived from various sources are composed of fatty acid alkyl esters with different carbon numbers [18]. Besides methanol, other alcohols like ethanol, propanol, isopropanol, n-butanol, and its isomers can also be used to produce biodiesel [19–22]. Therefore, this study aims at developing a group contribution method that is able to predict vapor pressure over a wide temperature range for fatty acid methyl, ethyl, propyl, and butyl esters. The proposed group contribution method was also used to predict the vapor pressures of biodiesels reported by Freitas et al. [10]. Moreover, the proposed model was compared with the group contribution model proposed by Ceriani et al. [16], which has the lowest deviation in predicting the vapor pressures of FAMEs among various group contribution and corresponding state vapor pressure prediction methods recently investigated by Wallek et al. [17].

2. Experimental data

Property model development requires reliable experimental data, and for temperature-dependent properties, the temperature range should be as wide as possible [23,24]. In this study, the experimental data of vapor pressure were taken from the National Institute of Standard and Technology (NIST) ThermoData Engine (TDE) with the implementation of the dynamic data evaluation concept [25]. The experimental data from the TDE-SOURCE database [26,27] were firstly evaluated dynamically, and the data with relatively large deviations were detected and rejected using its internal algorithm. Then, duplicate data points were identified and removed. Considering the practical temperature range of engine operation, vapor pressures of temperature lower than 273 K were also excluded. Furthermore, the available data were carefully rechecked for some conflicting data, which were not considered in the development of the prediction method. The classes of compound are FAMEs, fatty acid ethyl esters (FAEEs), fatty acid propyl esters (FAPEs), fatty acid butyl esters (FABEs), and hydrocarbons (HCs). The summary of the experimental database of vapor pressure used for model development can be found in Table 1.

It should be noted that the fatty acid alkyl esters in the database are all esters of naturally occurring fatty acids with even-carbon-number [28], and the unsaturated fatty acid esters all have *cis* carbon-carbon double bond configuration, and the HCs are also with even-carbon-number. Although the reduced temperature range in Table 1 appears to be up to or near the critical point, it is not the case for all the compounds, especially for fatty acid esters. Therefore, critical temperatures and critical pressures of these compounds predicted by the method of Marrero and Gani [29] were also used together with the experimental database to develop the prediction method. In total, the complete data used to develop the vapor pressure prediction method has 4687 data points including 4635 experimental vapor pressures and critical pressures for 52 compounds.

Table 1
Experimental database for vapor pressures of fatty acid alkyl esters and HCs.

Class of compound	Number of data	Carbon number	Temperature range (K)	Reduced temperature range
FAME	935	5–25	273–666	0.36–1.00
FAEE	264	6–20	273–582	0.41–0.98
FAPE	226	7–21	316–593	0.49–0.99
FABE	188	8–22	346–577	0.43–0.77
HC	3022	6–20	273–768	0.41–1.00

Table 2
Group parameters for the proposed group contribution method.

Group	A_k	B_k	C_k	D_k
CH_3	15.51893	6.29760	−4.92892	0.43968
CH_2	0.47917	0.46162	−0.27395	−0.00316
CH_2 (ester)	−1.30518	−1.73993	3.15768	−0.42464
CH═	1.92278	2.22903	−3.39461	0.30846
COO	1.37943	1.05560	−0.29666	−0.03915

3. Group contribution model development

A good description of the temperature dependency is important for the vapor pressure prediction method. In this study, the Riedel equation [30] was used to describe the temperature dependency of vapor pressure because of its well-known capability of predicting the complete vapor pressure curve [31]. The original Riedel equation is formulated as

$$\ln(P_r) = A - B/T_r + C\ln T_r + DT_r^6 \quad (1)$$

where P_r and T_r are the reduced pressure and reduced temperature, respectively. The equation parameters A, B, C, and D are determined through theoretical correlations of the normal boiling point, critical

Table 3
ARDs (%) of vapor pressures predicted by Ceriani's group contribution method and the proposed group contribution method in this work for esters of fatty acids with carbon number ≤ 18.

	FAME		FAEE		FAPE		FABE	
	Ceriani[a]	This work	Ceriani	This work	Ceriani	This work	Ceriani	This work
C4:0[b]	5.82	3.68	9.44	8.14	1.15	3.74	13.12	3.82
C6:0	4.00	2.97	6.55	6.38	8.23	4.40	13.26	9.44
C8:0	1.84	2.01	14.27	5.06	15.12	4.39	26.07	12.89
C10:0	4.88	4.57	23.52	8.45	11.23	3.60	7.35	23.98
C12:0	9.13	5.15	16.63	2.98	10.30	20.64	12.95	19.76
C14:0	12.56	4.42	22.17	2.20	6.84	21.64	41.18	30.65
C16:0	18.81	6.96	9.79	4.90	7.05	11.78		
C18:0	22.83	4.22	44.21	17.14	12.40	2.54	70.49	9.43
C18:1	16.60	6.01	9.47	10.75				
C18:2	9.53	9.80	11.52	11.24				
C18:3	19.58	12.31	12.32	14.59				
Overall	11.42	5.65	16.35	8.35	9.04	9.09	23.05	13.74

[a] Ceriani = Ceriani's group contribution method.
[b] Cx:y is the nomenclature for fatty acids, where x and y denote the carbon number and unsaturation degree, respectively.