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Full Length Article

Comparison of various methods for the estimation of vapor pressure of fatty acid methyl and ethyl esters (FAAE's)

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HIGHLIGHTS

- New generalized method for the estimation of vapor pressure of FAAE's is proposed.
- Seven methods for the estimation of vapor pressure of FAAE's have been critically compared.
- Total 299 experimental vapor pressure data points have been used in this study.

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ABSTRACT

Petroleum fuels are being used at a rapid rate and there is a need for renewable alternative fuels. Biodiesel (mainly a mixture of fatty acid alkyl esters FAAE's) is a potential alternative to petro-diesel. Combustion modeling of biodiesel requires vapor pressure data. The experimental determination of vapor pressure of FAAE's is difficult, therefore the estimation of vapor pressure of FAAE becomes important. In this study, various methods based on group contribution, equation of state (PR EOS) and correlations based were used to estimate the vapor pressure of nine FAME in the carbon chain range of C6 to C18 and four FAEE in the carbon chain range of C8–C13. The FAME's and FAEE's chosen for this study are the main constituents of real world biodiesels. These methods were compared on the basis of their ability to estimate the vapor pressure of FAAE's with accuracy and simplicity in the application of the method. Other than the methods which are already available in literature, two new methods, Othmer and Yu and Peng Robinson equation of state (PR EOS) at zero pressure were used in this study. For FAME's total 244 vapor pressure data points in the temperature range of 306–512 K were used where as for FAEE total 55 data points in the temperature range of 273–462 K were used. Amongst compound specific methods, Yuan and Othmer and Yu gave good prediction for both FAME's and FAEE's. For FAME's the % OARD for Yuan method was 4.83 and for Othmer and Yu it was 2.56. For FAEE's Yuan gave % OARD of 1.30, while Othmer and Yu gave % OARD of 2.85. Amongst generalized methods Ceriani, PR EOS and Othmer and Yu gave good estimation of vapor pressure for FAME's with least % OARD of 7.64 for Othmer and Yu. But, for FAEE's except Othmer and Yu (% OARD 19.19) all other methods gave very high deviation. In the present study strengths, weaknesses and applicability of selected methods have been highlighted.

1. Introduction

The depleting resources of petroleum fuels and the environmental concerns associated with them have created urgent needs for alternative fuels [1]. Biodiesel is a potential alternative to petroleum diesel fuel. It is composed of fatty acid alkyl esters (FAAE) obtained by the trans-esterification of triglycerides compounds, using a short chain alcohol, such as methanol or ethanol. The common feedstock for biodiesel production includes oils like palm, rapeseed, soybean, sunflower, canola and jatropha [2]. Amongst these, jatropha is a potential feedstock as it is non-edible and can be grown anywhere [3]. 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 [4]. The usefulness of biodiesel fuels depend upon the adequacy of their thermophysical properties, which must meet the standards such as ASTM D6751 and EN 14214. Vapor pressure express the volatility, safety and stability

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of a fuel. A higher value of vapor pressure can lead to evaporative emissions, while a lower value leads to delayed ignition, poor atomization and problematic combustion. As biodiesel fuels have lower vapor pressure such problems can occur. Combustion modeling requires vapor pressure of biodiesel in a wider range of temperature up to their critical temperature. The experimental determination of vapor pressure of biodiesel (FAAE's) is cumbersome and time-consuming. More importantly, FAAE's decompose before reaching their critical temperature therefore the estimation of vapor pressure becomes important [1]. Many researchers have used various models for the estimation of vapor pressure of FAAE. Yuan et al. [5] carried out the estimation of vapor pressure of methyl esters of fourteen fatty acids that are commonly present in biodiesel fuels by Antoine equation and group contribution method proposed by Ceriani and Meirelles. Freitas et al. [4] estimated the vapor pressure of three methyl esters and ten biodiesels using Yuan, Ceriani and cubic plus equation of state (CPA EOS). They reported that Yuan and CPA EOS gave better prediction compared to Ceriani model. Yang et al. [6] used Lee-Kessler, Ambrose-Walton and data compilation method for the estimation of vapor pressure of five methyl esters and they reported that Lee-Kessler and data compilation methods gave good results, but Ambrose-Walton method gave large errors in the entire temperature range. Anand et al. [1] used Lee-Kessler, Tu and Pitzer correlation for the estimation of vapor pressure of methyl esters. They reported that Lee-Kessler and Tu correlations gave better prediction in comparison to Pitzer.

The methods which have been used by the researchers for the estimation of vapor pressure of fatty acid alkyl esters fall basically in three categories based on the input data required for the estimation of vapor pressure. The models in the first category require the use of critical properties and acentric factor, the second category is based on the contribution of various structural groups and the third one requires the regression coefficients which are obtained by regressing the experimental values of vapor pressure. Category wise models with the required properties are mentioned in Table 1.

Different researchers have compared various methods, but to best of our knowledge no study is reported where all these methods were compared together. Moreover, researchers have used different experimental data for comparing the methods. Hence, there is no common conclusion about the suitable methods to estimate vapor pressure of FAAE's. This leads to the requirement of comparing the available methods using common database. We performed literatures search and found two new methods for estimating vapor pressures for high boiling compounds. Since, FAAE's are high boiling (and hence low vapor pressure) compounds these two new methods were also included in this study.

In this study nine fatty acid methyl esters (FAME's) in the carbon chain range of C6–C18 and four fatty acid ethyl esters (FAEE's) in the carbon chain range of C8–C13, which are the main constituents of real world biodiesel were selected. The experimental vapor pressure data for FAME's as reported by Scott et al. [8], Rose and Supina [9], Bonhorst et al. [10] and for FAEE's as reported by Benziane et al. [11] were used for this study. Total 244 data points for FAME's in the temperature range of 306–512 K and 55 data points for FAEE in the temperature range of 273–462 K were considered for the estimation of vapor pressure. Details about the data is reported in Table 2. All the methods listed in Table 1 were compared for the estimation of vapor pressure of FAAE's. Tu, Riedel and Ambrose-Walton methods gave very large deviation in the estimation of vapor pressure and hence they were not considered for the comparison. Apart from the listed methods, two new methods Othmer and Yu [12] and Peng Robinson equation of state (PR EOS) at zero pressure [13], were also used to estimate vapor pressure of FAAE's. Othmer and Yu method was originally proposed to be used for non-hydrocarbon organics whose vapor pressure is below 15 kPa. To the best of our knowledge, this method has never been used for FAAE's. Since FAAE's also have low vapor pressure, in this study Othmer and Yu method was used for the estimation of vapor pressure of FAEE's. There is not much literature available on the applicability of this method. Wisniak et al. [14] proved that the liquid phase fugacity f^0 at zero pressure ($P \rightarrow 0$) is equal to the vapor pressure, $P^{sat} \approx f^0$. Valderrama and Forero [13] successfully applied this principle to Peng-Robinson equation of state (PR EOS) at zero pressure to estimate vapor pressure of ionic liquids. This method gave very accurate prediction of low vapor pressure of ionic liquids. As FAAE also have low vapor pressure, hence in this study, this method was applied for the estimation of vapor pressure of FAAE's.

Table 1
Various models for estimation of vapor pressure of FAEE.

Category no.	Methods for estimation of vapor pressure	Requirements	References
1	Pitzer	Critical temperature, critical pressure, acentric factor	[6,7]
	Lee-Kessler		[6,7]
	Ambrose-Walton	Critical temperature, critical pressure, acentric factor, boiling point	[6,7]
	corresponding states		
	Riedel		[7]
2	Ceriani Meirelles	Group contributions	[5,7]
	Tu		[1]
3	Antonie/Yuan	Regression coefficients	[5]

Table 2
Experimental vapor pressure data of FAME's and FAEE's.

FAME/FAEE	No. of experimental data points for vapor pressure	Temperature range (K)	Pressure range (kPa)	Ref.
Methyl Caprylate (C8:0)	43	306–418	0.1–24.8	[8–10]
Methyl Decanoate (C10:0)	46	324–461	0.04–30.9	
Methyl Laurate (C12:0)	35	336–485	0.01–24.2	
Methyl Myristate (C14:0)	35	364–510	0.02–22.0	
Methyl Palmitate (C16:0)	26	378–508	0.017–8.2	
Methyl Stearate (C18:0)	28	398–512	0.018–4.8	
Methyl Oleate (C18:1)	11	401–458	0.02–0.62	
Methyl Linoleate (C18:2)	11	392–458	0.015–0.64	[8]
Methyl Linolenate (C18:3)	9	394–458	0.016–0.62	
Ethyl Octanoate (C8:0)	17	273–452	0.002–46.42	[11]
Ethyl Decanoate (C10:0)	12	303–462	0.004–22.350	
Ethyl Dodecanoate (C11:0)	12	313–462	0.002–8.48	
Ehyl Tetradecanoate (C13:0)	14	333–462	0.001–3.19	