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Prediction of vapor pressure of fatty acid methyl esters using cubic equation of state

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Abstract

Fossil fuels are depleting at a rapid rate, due to their ever increasing demand and so there is a need for alternative and sustainable fuel. Biodiesel can be a promising alternative for petroleum based diesel fuels. Biodiesel is a mixture of fatty acid alkyl esters produced by the trans-esterification of vegetable oils/animal fats with alcohol in the presence of catalyst. Vapour pressure of biodiesel (FAMEôs) is a very important property because combustion characteristics, volatility, safety and stability of fuel depend on it. In the present work, prediction of vapour pressure of nine fatty acid methyl esters (FAMEôs) was done using Peng-Robinson Cubic Equation of State (PR-CEOS) at zero pressure fugacity condition. The estimation of critical properties like critical temperature (T_c) and critical pressure (P_c) was also done as they are used as input for the prediction of vapour pressure using PR- CEOS at zero pressure fugacity condition. Eight cohesion factor models were used in PR CEOS for the prediction of vapour pressure. The estimated values of vapor pressure were compared with the experimental values (244 data points) of vapor pressure obtained from literature. In this work, Heyen1 and SRK type cohesion factor models are being proposed for the prediction of vapour pressure of FAMEôs by PR- CEOS.

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Keywords: Fatty Acid Methyl Ester; Vapor Pressure; Prediction Models, PR CEOS, Critical Properties

Nomenclature

FAME	Fatty Acid Methyl Ester
T	Temperature
P	Pressure
R	Gas constant
a	Force constant in the PR equation of state
b	volume constant in the PR equation of state
V^0	Volume for zero pressure at constant temperature
m_1	Parameter of the Heyen-1 function
m_2	Parameter of the Heyen-2 function
n	Parameter of the Heyen-2 function
CG	Constantinou and Gani
A	Ambrose

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MP	Marrero and Pardillo
LK	Lee Kesler
Greek symbols	
ẅ	Fugacity coefficient
ä	Fugacity
ɤ	Accentric factor
Subscripts	
v	vapor
L	Liquid
nb	Normal boiling point
c	critical

1. Introduction

The fossil fuels are the major sources of energy all over the world, but these sources are limited and depleting at a very rapid rate and hence there is a need for an alternative and sustainable fuel. Biodiesel can be a promising alternative for petroleum-based fuels which are made from vegetable oils and animal fats. Biodiesel is a mixture of fatty acid alkyl esters, obtained by the trans-esterification of vegetable oils with an alcohol like methanol or ethanol in the presence of a catalyst. The catalyst can be acidic, basic or enzymatic. The main advantages of biodiesel are: it is biodegradable, is produced from renewable energy sources, nontoxic, and it gives fewer emissions of pollutant gases. Vapour pressure is an important physicochemical property for fuels, because the volatility, safety, and stability of a fuel depend on it. It is also important in the development of separation processes [1]. A higher value of vapour pressure can favour the evaporative emissions and a lower value leads to delayed ignition, poor atomization, and problematic combustion. Biodiesel has a lower vapour pressure, which might cause these problems. For using biodiesel in diesel engines alone or in the form of blend with petrodiesel, vapour pressure of biodiesel must be adjusted by changing the composition of biodiesel to satisfy the standard specifications (ASTM). But it is impractical to measure the vapour pressure experimentally, as it is time taking, expensive and most importantly, the decomposition of FAMEôs take place at high temperature [2,3]. Lack of experimental data for vapor pressure of FAMEôs gave rise to the need of development of accurate models for the prediction of vapour pressure.

2. Prediction of Critical Properties

Critical properties like critical temperature (T_c), critical pressure (P_c), critical volume (V_c) and accentric factor (ɤ) play a key role in the prediction of vapor pressure. In the present work, Tc and Pc are the important input parameters in the prediction of vapor pressure. Also normal boiling point (T_{nb}) of Fatty acid methyl ester (FAME) was calculated as it is required for the estimation of T_c and P_c.

Table 1. Prediction models for normal boiling point and critical properties

Sr. No.	Property	Model	Reference
1	Normal Boiling Point	Yuan (Y)	[4,5]
2	Critical Temperature	Joback (J)	[4,5,6]
3	Critical Pressure	Marrero and Pardillo (MP)	[4,7]
4	Accentric factor	Constantinou and Gani (CG)	[5,6,7]

3. Prediction of Vapor pressure

Prediction of vapor pressure was done for nine FAMEôs using various models as listed in Table 2. The estimated values were compared with the experimental values obtained from literature and global percent average relative deviation (Global % ARD) was calculated for each model as shown in Table 2.

Table 2. Global % ARD for vapour pressure of FAMEôs

Sr. No.	Method	Global % ARD
1	Lee Kesler	56.1712
2	Pitzer	72.9645
3	Ceriani	1666.547
4	Riedel	4294.892
5	Ambrose-Walton	20016.22

$$\%ARD = \frac{1}{N}\left|\frac{\exp erimentalv\ alue - estimatedv\ alue}{\exp erimentalv\ alue}\right| \times 100$$

global % ARD is calculated by the summation of % ARD of FAMEôs divided by the number of FAMEôs. The global %ARD values show that none of the above model gave good prediction of vapor pressure. The present work focuses on the use of Peng-Robinson cubic equation of state (PR CEOS) at zero pressure fugacity for the prediction of vapor pressure of FAMEôs.

3.1 Prediction of vapor pressure using PR CEOS at zero pressure fugacity

Prediction of vapor pressure was carried out for nine different FAMEôs as listed in Table 4. The reason for selecting these FAMEôs was that mostly these are the major constituents of biodiesel obtained from various sources. For prediction of vapour pressure PR CEOS was used at zero pressure fugacity condition [8]. At low pressures (P Ÿ 0), the vapour phase can be considered as an ideal gas so its fugacity coefficient $\phi^v = f^v / P_v$ is equal to 1.0. Therefore, $\phi^L = f^L / P_v$ and $P_v = f^L$. Wisniak et al. [9] states that the liquid phase fugacity ä^0 at low pressure (P Ÿ 0) is equal to the vapor pressure: P_v å ä^0.
Fig 1 gives the algorithm used for the estimation of compound specific parameter for the cohesion factor using PR CEOS at zero pressure fugacity. Various equations used for the prediction are also given in Fig 1.

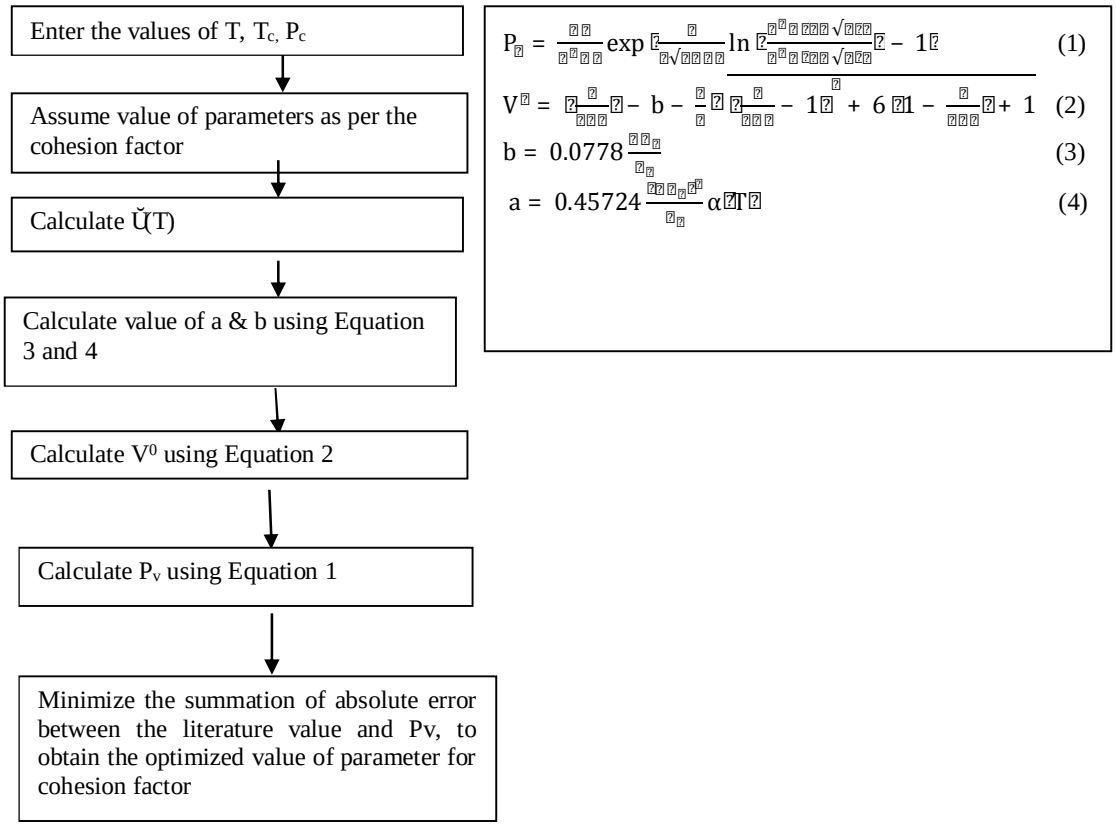

Fig. 1 An algorithm for estimation of compound specific parameter [8]

In equation 4, Ψ(T) is a cohesion factor and using the above method, eight different cohesion factors as shown in Table 3 were used for the prediction of vapor pressure and determination of compound specific parameters.

Table 3. List of cohesion factors used in vapour pressure prediction

Sr. No	Cohesion Factor	Equation	Reference
1	Heyen1	$\Psi = \alpha \left(1 - \frac{T}{T_c}\right)$	[8]
2	Heyen2	$\Psi = \alpha \left(1 - \frac{T}{T_c}\right)^{\beta}$	[8]
3	SRK Type	$\Psi = \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2$	[10]
4	Harmens & Knapp	$\Psi = \left[1 + m\left(1 - T_r^{0.5}\right) - n\left(1 - \frac{1}{T_r}\right)\right]^2$	[11]
5	Polishuk	$\Psi = \frac{1}{1 + m\left(T_r^{n} - 1\right)}$	[12]
6	Melhem	$\Psi = \exp\left[1 + l\left(1 - T_r^{0.5}\right) + m\left(1 - T_r^{0.5}\right)^2\right]$	[13]
7	Twu	$\Psi = T_r^{(n(m-1))} \exp\left[l\left(1 - T_r^{(nm)}\right)\right]$	[14,15]
8	Wilson	$\Psi = \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2$	[16]

4. Results and Discussions

The Table 4 shows the values of compound specific parameters (m_1) for Heyen1 cohesion factor model and it also shows the % ARD in the prediction of vapour pressure of nine FAMEôs.

Table 4. Values of compound specific parameter and % ARD for vapour pressure of FAMEôs

FAME	No. of experimental data points (244) for vapour pressure	Temperature Range (K)	m_1	%ARD
Methyl Caprylate (C8:0)	43	306-418	1.16672	5.04
Methyl Decanoate (C10:0)	46	324-461	1.23227	4.72
Methyl Laurate (C12:0)	35	336-485	1.31208	3.13
Methyl Myristate (C14:0)	35	364-510	1.38674	2.80
Methyl Palmitate (C16:0)	26	378-508	1.46748	2.82
Methyl Stearate (C18:0)	28	398-512	1.53745	2.21
Methyl Oleate (C18:1)	11	401-458	1.475	9.82
Methyl Linoleate (C18:2)	11	392-458	1.45347	3.97
Methyl Linolenate (C18:3)	9	394-458	1.440313	5.71

Similar work was carried out for other cohesion factor models as listed in Table 3. For each cohesion factor model global% ARD was calculated for the prediction of vapor pressure. The results for the same are summarized in the Table 5.

Table 5 Global % ARD for different cohesion factor models

Sr. No	Model	Global % ARD
1	Heyen1	4.7665
2	Heyen2	8.2635
3	SRK Type	4.3810
4	Harmens & Knapp	3.6228
5	Polishuk	7.3769
6	Melhem	66.842
7	Twu	3.6437
8	Wilson	17.265

The above results show that except Melhem and Wilson model, all the other models gave good prediction of vapour pressure. Harmens & Knapp and Twu gave the best result, followed by SRK type and Heyen1. Heyen1and SRK type model require only one parameter, while Harmens & Knapp and Twu require more than one parameters, which makes the estimation of other properties mathematically complex. Hence, in the present work Heyen1 and SRK type cohesion factors are being proposed for the prediction of vapour pressure using PR- CEOS at zero fugacity condition.

5. Conclusions

In the present work, prediction of vapour pressure of nine FAMEôs was done by various methods and the predicted values of vapour pressure were compared with the experimental values (244 data points) available in literature and global % ARD was calculated. PR-CEOS at zero pressure fugacity condition with various types of cohesion factors was used for the prediction of vapour pressure. Heyen1 and SRK type cohesion factors, which are one parameter models in comparison to models which require more than one parameters (Harmens & Knapp, Twu) are being proposed for the prediction of vapour pressure of FAMEôs (global % ARD less than 5%) by PR- CEOS at zero pressure fugacity conditions.

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