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Prediction of vapor pressure of fatty acid methyl esters

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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. Alternative fuels are needed and Biodiesel can be a promising alternative for diesel fuels. Vapor Pressure is a very important property of biodiesel because volatility, safety and stability of fuel depend on it. In this study, vapour pressure prediction of few fatty acid methyl esters (FAME) is done using Peng-Robinson Equation of State (PR-EOS) at zero pressure condition. For critical properties, four different groups of prediction methods were used. The estimated critical properties were used to predict the vapour pressure of FAMEs by using PR-EOS. Based on the predicted critical properties, vapor pressure of FAME was predicted using PR-EOS. The results showed that, none of the methods gave good results for vapour pressure.

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Keywords: Fatty Acid Methyl Ester; Vapor Pressure; Prediction Models, PR-EOS, 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
MP	Marrero and Pardillo
LK	Lee Kesler
WJ	Wilson and Jasperson

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Greek symbols	
ϕ	Fugacity coefficient
f	Fugacity
ω	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 rapid rate. Biodiesel can be a promising alternative for petroleum-based fuels which are made from vegetable oils and animal fats. The main advantages of biodiesel are: it is biodegradable, is produced from renewable energy sources, nontoxic, and it gives fewer emissions of pollutant gases. The transesterification is the most widely used method for biodiesel production, as the physical characteristics of biodiesel are very close to diesel fuel and the process is relatively simple[1]. There are three kinds of catalysts that can be used in transesterification reaction, a strong alkaline catalyst, a strong acid, and an enzyme. The main advantage of using a strong alkali as a catalyst are less reaction time and lower amount of catalyst required in the trans-esterification reaction [1].

Vapor 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 vapor pressure can favour the evaporative emissions and a lower value leads to delayed ignition, poor atomization, and problematic combustion. Biodiesel has lower vapor 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 feed oils take place at high temperature [2, 3]. Lack of experimental data for vapor pressure gave rise to the need of development of accurate models for the prediction of vapour pressure.

2. Literature Review

A rigorous literature search revealed that, only few data are available on the vapor pressure of FAMEs especially in the low vapor pressure range which prompted us to undertake this study. Several model equations for FAME were used for the estimation of vapor pressure. Various model equations and their details have been compiled in Table 1:

Table 1. Methods for Vapor Pressure of FAME

Sr. No	Name of Model	Model Equation	Requirement for model	Reference
1.	Antoine Equation	$\log(P_v) = A - \frac{B}{T+C}$	A,B,C = Antoine Constants T = Temperature in Kelvin (K)	[3]
2	Ceriani et. al.	$\ln P_{i,vp} = \sum_k N_k \left[A_{1k} + \frac{B_{1k}}{T^{1.5}} - C_{1k}\ln(T) - D_{1k}(T)\right] + \left[M_i \sum_k N_k \left(A_{2k} + \frac{B_{2k}}{T^{1.5}} - C2klnT - D2kT + Q\right.\right.$ $Q = f_0 + N_c f_1 \left(\alpha + \frac{\beta}{T^{1.5}} - \gamma \ln T - \delta T\right) + (S_0 + N_{cs} S_1)$	$P_{i,vp}$ = Vapor Pressure (Pa) T = Temperature (K) N_k = Number of groups k in the molecule M_i = Component molecular weight Q = Correction Term A_{1k}, B_{1k}, C_{1k}, D_{1k} = Ceriani constants obtained from the regression of the experimental data. N_c = The total number of carbon atoms in the molecule N_{cs} = The number of carbons of the alcohol side chain f_0, f_1, s_0, and s_1 = optimized constants, α, β, γ, and δ =optimized parameters obtained by regression of the databank	[4]

3	Lee-Kestler Equation	$\ln(P_r) = \ln P_r^{(0)} + \omega \ln P_r^{(1)}$ $P_r = (P_v/P_c)$	P_r = Reduced vapor pressure P_v = Vapor pressure in kPa P_c = Critical Pressure ω =Accentric factor	[2]
4	Tu	$\ln(P_v * MW) = A + \frac{B}{T} - C \ln T - DT$	P_v = Vapor pressure in kPa MW = Molecular Weight T = T(K)/100 A,B,C,D = Tu constants	[2]
5	Pitzer	$\ln(P_{vpr}) = f^{(0)}(T_r) + f^{(1)}(T_r)$ $f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln(T_r) + 0.169347 T_r^6$ $f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln(T_r) + 0.43577 T_r^6$	P_{vpr} = Reduced vapor pressure (P_v/P_c) $T_r = T/T_c$ $f^{(0)}$, $f^{(1)}$ = Poling Correlations	[2]

3. Prediction of Critical Properties

Critical properties like critical temperature (T_c), critical pressure (P_c), critical volume (V_c) and eccentric factor (ω) play a key role in the prediction of vapor pressure. Manuel et. al. [5] has discussed several models for prediction of such properties and divided them in three packages as shown in Table 2. We have used these packages to predict critical properties. We have also used Nakanishi, Ambrose and Margoulus & Tassios (NAM) models for the prediction of critical temperature, critical pressure and eccentric factor respectively which is compiled in Table 3.

Table 2. Methods used for prediction of each property [5, 6]

Property	Package1	Package2	Package3
T_{nb}	CG	MP	CG
T_c	CG	MP	A
P_c	WJ	WJ	A
ω	LK	LK	LK

Table 3. Method for the prediction of critical properties

Property	Method	References
T_c	Nakanishi	[6]
P_c	Ambrose	[6]
ω	Margoulus &Tassios	[6]

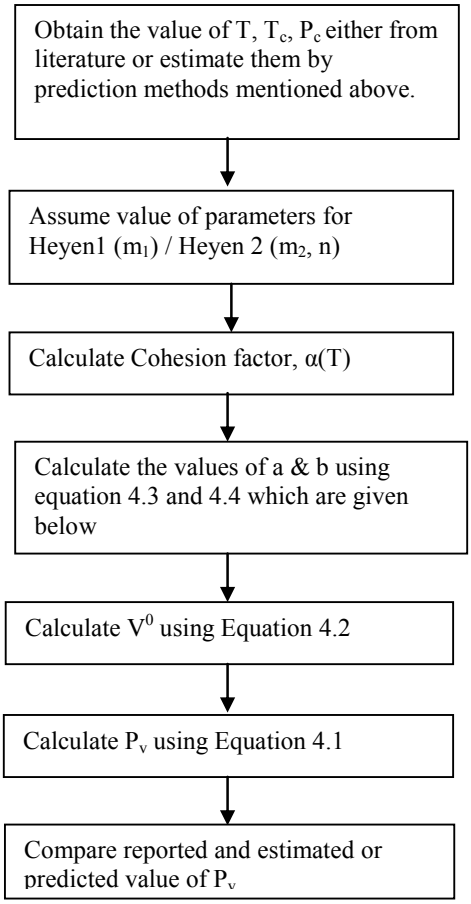
4. Prediction of Vapor Pressure

In the present work, vapor pressure prediction was done by using PR-EOS, which is based on the equality of fugacities of vapor and liquid phases that coexist at equilibrium. The fundamental equation of vapor liquid phase equilibrium for a pure substance that is the equality of fugacities $f^V = f^L$, can be also expressed in terms of the fugacity coefficient at saturation $\phi = f/P_v$ since P_v is the same in both phases: $\phi^V(T, P_v) = \phi^L(T, P_v)$ [7].

Check for your symbols

At low pressures, the vapor phase can be considered as an ideal gas, so its fugacity coefficient $\phi^V = f^V/P_v$ is equal to 1.0. Therefore, $\phi^L = f^L/P_v = 1$ and $P_v = f^L$. The liquid phase fugacity f^0 at low pressure ($P \rightarrow 0$) is equal to the vapor pressure: $P_v \approx f^0$ [5]. In this study, PR-EOS is used for the vapour pressure prediction of FAME at zero pressure fugacity.

Fig 1 given below gives the algorithm used for the prediction of vapor pressure by PR- EOS. Various equations used for the prediction are given below Fig 1.



$$P_v = \frac{RT}{V^0 - b} \exp\left[\frac{a}{2\sqrt{2}RTb} \ln\left(\frac{V^0 + (1-\sqrt{2})b}{V^0 + (1+\sqrt{2})b}\right) - 1\right] \tag{4.1}$$

$$V^0 = \left(\frac{a}{2RT}\right) - b - \frac{b}{2}\sqrt{\left(\frac{a}{bRT} - 1\right)^2 + 6\left(1 - \frac{a}{bRT}\right) + 1} \tag{4.2}$$

$$b = 0.0778 \frac{RT_c}{P_c} \tag{4.3}$$

$$a = 0.45724 \frac{(RT_c)^2}{P_c} \alpha(T) \tag{4.4}$$

$$\alpha(T) = \exp\left[m_2\left\{1 - \left(\frac{T}{T_c}\right)^n\right\}\right] \tag{4.5}$$

$$\alpha(T) = \exp\left[m_1\left\{1 - \left(\frac{T}{T_c}\right)\right\}\right] \tag{4.6}$$

Fig. 1. An algorithm for prediction of vapor pressure using zero pressure fugacity [7].

4. Results and Discussion

Critical properties are estimated by using methods mentioned above in Table 4. From the estimated values of critical properties, prediction of vapor pressure was done by using PR-EOS. The prediction was done for various FAMEs and compared with the experimental values [8, 9] reported in literature at given temperature.

Based on these estimated and reported data % ARD was calculated which is shown in Table 5. Percentage Average Relative Deviation is calculated by:

$$\mathrm{ARD} = \frac{1}{N}\sum_{i}^{N}\left|\frac{X_{exp}-X_{cal}}{X_{exp}}\right| \times 100 \quad (7)$$

Where 'X_{exp}' is experimental value, 'X_{cal}' is calculated value and 'N' is number of data points

Table 4. Estimated critical properties by various methods

Method	Property	C8:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2
Package1	T_c(K)	733.94714	773.32528	790.20917	805.65255	819.88202	820.63504	821.38494
	P_c(bar)	26.822141	18.758761	16.113626	16.428541	12.293349	12.534776	12.782841
	ω	1.1568301	1.1069327	1.075823	1.1699329	1.0012039	1.0070448	1.0129838
Package2	T_c(K)	563.89952	651.33929	698.05283	748.19626	802.95557	809.6683	790.40707
	P_c(bar)	20.607741	15.799713	14.234411	13.009639	12.039553	12.367265	12.300746
	ω	1.2921092	0.8626542	0.644939	0.4368249	0.2451657	0.3415754	0.4216223
Package3	T_c(K)	796.64539	811.10513	818.06343	824.84665	831.45697	831.43971	831.42245
	P_c(bar)	28.100582	19.959932	17.431846	15.471334	13.906738	13.812821	13.718908
	ω	0.5473319	0.7180695	0.7990975	0.8767181	0.9508209	0.945549	0.9402415
Nakanishi	T_c(K)	598.495	684.831	718.792	748.476	774.753	774.753	774.753
Ambrose	P_c(bar)	28.1012	19.9604	17.4323	15.4717	13.9071	13.8132	13.7193
Margoulus &Tassios	ω	0.4919	0.6319	0.7035	0.7762	0.85	0.85	0.85

Table 5. Calculated % ARD for vapor pressure

FAME	%ARD			
	NAM *	Package 1	Package 2	Package 3
Methyl Caprylate(C8:0)	18.77265	28.358	25.8255377	38.93725
Methyl Laurate(C12:0)	18.191316	23.99575	31.3571728	30.5091
Methyl Myristate(C14:0)	16.601845	22.76671	21.1248587	29.61374
Methyl Palmitate(C16:0)	10.578869	12.96967	5.26684393	20.83733
Methyl Stearate(C18:0)	6.4405576	13.33288	8.40191613	14.04022
Methyl Oleate(C18:1)	8.4543752	15.21876	13.4607169	15.83749
Methyl Linoleate(C18:2)	2.1058559	7.68753	2.65822229	8.46603

* N = Nakanishi, A = Ambrose, M = Margoulus & Tassios

Table 5 shows that the for the prediction of vapor pressure, amongst the all models, the NAM model gives lesser %ARD for most of the FAMEs except for Methyl Palmitate for which Package 2 gives better value. All the models given above

yield good result for Methyl Linoleate, the lowest % ARD of 2.10 is for the NAM model. Also for Methyl Stearate, NAM model and Package 2 gave good result, while the other two yielded higher %ARD values.

5. Conclusion

Vapor pressure is very important property of any biodiesel. Here vapor pressure is estimated using different critical properties which are predicted using various methods. Vapor pressure prediction is done by PR-EOS at zero pressure fugacity. Every model gave good results for methyl linoleate in which NAM model gave less than 2.5%. Also critical properties predicted by NAM model gave better results for vapor pressure than others. But there are variations in results of ARD calculation. So more study is required and more work to be done on prediction of vapor pressure.

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