Comparing the Methods to Estimate Critical Properties of Fatty Acids and Fatty Acids Esters

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***Abstract:* Biodiesel is a very promising alternative fuel and the estimation of the properties of biodiesel requires the estimation of the properties of the constituents components of biodiesel. Present work focuses on estimating the critical properties of Fatty Acid and Fatty Acid Methyl Ester (FAME). Total Ten methods for T_c and P_c and nine methods for acentric factor have been compared and best method is recommended.**

***Index Terms*: Biodiesel, Fatty Acid, FAME, Critical Properties**

I. INTRODUCTION

Biodiesel is a renewable, environmentally friendly substitute for petroleum-based diesel fuel. It is produced from vegetable oils, animal fats, or wastes cooking oils and fats, and can be used in existing diesel engines without any expensive modifications.[1] Biodiesel can also be added to petroleum diesel to create a biodiesel blend with favorable performance attributes and environmental benefits roughly proportional to the biodiesel fraction.

The fatty acid and their methyl ester plays an important role in the biodiesel composition and hence their properties will intern affect the properties of biodiesel. Fig. 1 shows the reaction for biodiesel production. Transesterification also called alcoholysis refers to a reaction involving displacement of alcohol from an ester by another alcohol to yield fatty acid alkyl esters (i.e. biodiesel and glycerol as a byproduct.

Triglycerides are the main components of any crude vegetable oil and depending upon the origin of the oil, the fatty acid distribution and the triglyceride composition can vary widely. Triglycerides and their fatty acid esters are important raw materials in the pharmaceutical, food, and chemical industries

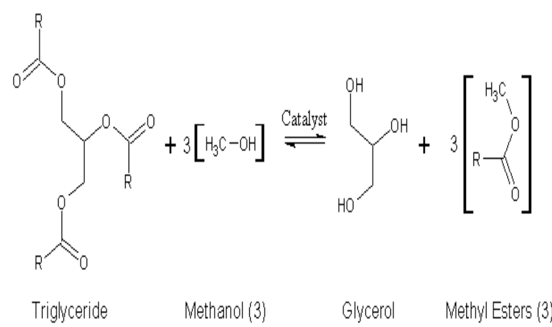

Fig 1. Reaction for Biodiesel Production[2]

As fundamental knowledge, the phase equilibria for the systems containing alcohol or CO_2 triglyceride, and fatty acid alkyl ester are required to design and develop biodiesel production processes. Thus phase equilibrium studies of Fatty acids and their esters are very important. Estimating the phase equilibrium of such system by means of Equation of state is most suitable path as it requires merely the knowledge of the pure component properties. Such property includes, Critical Temperature T_c, Critical Pressure P_c, Acentric factor. The biggest problem in determining such properties of pure fatty acids and their esters is that before reaching such critical state they decompose and hence it is not possible to determine them experimentally. However, for some of them the data is available in the open literature. In the present work different methods for estimating such properties are collected and have been compared with the reference values available in the literature. The work is divided in three

Table I Estimation Methods for Critical Temperature and Critical Pressure

Code	Methods	Equations
TcPc1.	Magoulas and Tassios [3]	$\ln(959.98 - T_c) = 6.81536 - 0.211145 N_c^{2/3}$
		$\ln P_c = 4.3398 - 0.3155 N_c^{0.6032}$
TcPc2.	Teja [3]	$\ln(1143.8 - T_c) = 7.15908 - 0.303158 N_c^{0.469609}$
		$\ln(P_c - 0.84203) = 1.75059 - 0.196383 N_c^{0.890006}$
TcPc3.	Hu [3]	$T_c = \dfrac{0.38106 + N_c}{0.0038432 + 0.0017607 N_c^{0.5} + 0.00073827 N_c}$
		$P_c = \dfrac{10}{0.19694 - 0.059777 N_c^{0.5} + 0.46718 N_c}$
TcPc4.	Morgan and Kobayashi [3]	$T_c = 981.38 - 10^{\left(2.95993 - 0.0860146 N_c^{0.6667}\right)}$
		$P_c = 10^{\left(0.84888 - 0.0112727 N_c^{0.6667}\right)}$
TcPc5.	Wilson and Jasperson [4]	$T_c = \dfrac{T_b}{\left\{0.048271 - 0.019846 N_r + \sum_k N_k (\Delta t_{ck}) + \sum_j M_j (\Delta t_{cj})\right\}^{0.2}}$
		$P_c = \dfrac{0.0186233 \times T_c}{\{-0.96601 + e^y\}}$
TcPc6.	Ambrose [3]	$\dfrac{T_b}{T_c} = \dfrac{1.242 + 0.138 N_c}{2.242 + 0.138 N_c}$
		$P_c = MW\,(0.339 + 0.226 N_c)^{-2}$
TcPc7.	Joback and Reid [4]	$T_c = T_b / \{A_M + B_M \sum n\Delta T_M - (\sum n\Delta T_M)^2$
		$P_C = M / (C_M + \sum n\Delta P_M)^2$
TcPc8.	Constantinou	$T_c = 186.481 \ln\left[2 \times 1.3788 + (N_c - 2) \times 3.1136\right]$

	and Gani [3]	$P_c = \frac{1}{\left(0.1068 + 2\times 0.018377 + \left(N_c - 2\right)\times 0.00903\right)^2}$
TcPc9.	Nakanishi [3]	$\frac{1}{T_c} = 0.000702 + \frac{0.004192}{N_c^{2/3}}$
		$P_c = \frac{80.37\times 1.01325}{N_c^{2/3}[1 + 0.1675 N_c^{2/3}]}$
TcPc10	Marrero and Pardillo [4]	$T_c = \frac{T_b}{\left\{0.5851 - 0.9286\left(\sum_k N_k * t_{cbk}\right) - \left(\sum_k N_k * t_{cbk}\right)^2\right\}}$

Table II Methods considered for Acentric factor estimation.

Sr. No.	Methods	Equations
W1.	Magoulas and Tassios [3]	$\omega = 0.194778 + 3.15382 N_c \times 10^{-2} + 1.73473 N_c^2 \times 10^{-4} - 1.13389 N_c^3 \times 10^{-6} + 8.96972 N_c^4 \times 10^{-9}$
W2.	Koniogeorgis [3]	$\omega = -3.91118 + 0.895296 \ln\left(6.8781 + 10.2306 N_c\right)$
W3.	Hoshino [3]	$\omega = 0.092 + \left[0.0527 - 0.0004\left(N_c - 2\right)\right]\left(N_c - 2\right)$
W4.	Morgan and Kobayashi [3]	$\omega = -0.0358 + 0.06348 N_c - 1.2549 N_c^2 \times 10^{-3} + 1.464 N_c^3 \times 10^{-5}$
W5.	Han and Peng [3]	$\omega = 0.004423\left[\ln\left(3.3063 + 3.4381 N_c\right)\right]^{3.651}$
W6.	Constantinou [3]	$\exp\left(\left(\frac{\omega}{0.4085}\right)^{0.505}\right) - 1.1507 = 0.29602\times 2 - \left(N_c - 2\right)\times 0.14691$
W7.	Joback and Reid [4]	$\omega = \frac{\left(T_b - 43\right)\left(T_c - 43\right)}{\left(T_c - T_b\right)\left(0.7 T_c - 43\right)} \log \frac{P_c}{P_b} - \frac{\left(T_c - 43\right)}{T_c - T_b} \log \frac{P_c}{P_b} + \log \frac{P_c}{P_b} - 1$
W8.	Wilson and Jasperson [4]	$\omega = \frac{\left(T_b - 43\right)\left(T_c - 43\right)}{\left(T_c - T_b\right)\left(0.7 T_c - 43\right)} \log \frac{P_c}{P_b} - \frac{\left(T_c - 43\right)}{T_c - T_b} \log \frac{P_c}{P_b} + \log \frac{P_c}{P_b} - 1$
W9.	Marrero and Pardillo [4]	$\omega = \frac{\left(T_b - 43\right)\left(T_c - 43\right)}{\left(T_c - T_b\right)\left(0.7 T_c - 43\right)} \log \frac{P_c}{P_b} - \frac{\left(T_c - 43\right)}{T_c - T_b} \log \frac{P_c}{P_b} + \log \frac{P_c}{P_b} - 1$

Table III Reference Values of Critical Properties for Fatty Acids and their Methyl Esters[6,7]

Fatty Acids/Esters	**Symbol**	**Tc (K)**	**Pc (bar)**	**ω**
Oleic acid	F1	781	13.9	1.187
Butyric acid	F2	628	44.2	0.604
Hexanoic acid	F3	667	33.5	0.67
Octanoic acid	F4	692	26.9	0.779
Decanoic acid	F5	713	22.5	0.877
Dodecanoic acid	F6	734	19.4	0.967
Tetradecanoic acid	F7	756	17	1.025
Hexadecanoic acid	F8	776	15.1	1.083
Linoleic Acid	F9	775	14.1	1.176
Stearic Acid	F10	799	13.6	1.084
Methyl Caprylate	FM1	646.850	25.49	0.562
Methyl Laurate	FM2	711.85	20.25	0.756
Methyl Myristate	FM3	738.850	18.50	0.844
Methyl Palmitate	FM4	762.850	16.50	0.924
Methyl Stearate	FM5	784.850	15.00	0.994
Methyl Oleate	FM6	763.850	12.80	1.049
Methyl Linoleate	FM7	749.433	21.05	0.570

classes as finding best possible methods for all the above properties for Fatty Acids, for the esters of Fatty acids and for Fatty Acid and their esters combined.

II. Estimation Methods

Most of the methods proposed for the estimation of T_c and P_c can be divided in two categories. First, the method with no finite limiting value/or limiting behavior for Tc and Pc. Second, the method with a finite limiting behavior for the critical temperature and a zero or a non- zero limiting value for the critical pressure. Table I shows the estimation methods for critical temperature and pressure considered in the present work.

Table IV Results for the critical temperature estimation

Method	%AAD FA	%AAD Esters	%AAD Combined
TcPc1	11.0621	3.7910	8.0681
TcPc2	12.7197	3.7168	9.0126
TcPc3	12.7556	3.7411	9.0438
TcPc4	12.6930	3.7313	9.0029
TcPc5	10.4951	8.4267	9.6434
TcPc6	8.4987	5.5137	7.2696
TcPc7	10.0736	5.3026	8.1091
TcPc8	13.4071	4.1526	9.5964
TcPc9	11.7199	*3.1375*	8.1860
TcPc10	*4.4502*	6.9720	*5.4886*

Table V Results for the critical Pressure estimation

Method	%AAD FA	%AAD Esters	%AAD Combined
TcPc1	7.5387	18.5300	12.0646
TcPc2	90.8194	91.8482	91.2430
TcPc3	90.5485	92.1860	91.2228
TcPc4	67.9212	66.2176	67.2197
TcPc5	10.5078	16.4726	12.9639
TcPc6	12.2336	*10.5298*	*11.5320*
TcPc7	*2.9392*	312.678	130.4787
TcPc8	78.4940	79.0751	78.7333
TcPc9	56.7078	63.9788	59.7017
TcPc10	7.7563	19.8366	12.7305

Table VI Results for the acentric factor estimation

Method	%AAD FA	%AAD Esters	%AAD Combined
W1	36.1706	*20.5902*	*29.7552*
W2	67.4431	31.9409	52.8246
W3	40.5034	21.6201	32.7279
W4	42.0943	23.0137	34.2376
W5	40.9019	22.0167	33.1256
W6	42.2195	23.5109	34.5160
W7	*5.3698*	105.9228	46.7740
W8	26.5171	58.1685	34.6597
W9	18.2035	38.9119	31.6208

III. REFERENCE DATA BASE

Data for seventeen components have been obtained [7] Reference critical property values for Fatty acids were obtained from Yaws and that for Esters were obtained from Aspen Hysys [6]. The values of T_c, P_c and w for all the components are listed in Table III.

IV RESULTS AND DISCUSSION

The methods listed for critical temperature and critical pressure in Table I were used to estimate the critical pressure and temperature. Microsoft Excel® was used for the calculation. The results are shown in Table IV, V and VI. They are compared based on %AAD with reference values the best methods are selected. Methods as per critical temperature, pressure and acentric factor are shown in table VII.

Table VII Most suitable Methods

Property	FA	Ester	Combined
Tc	Marrero and Pardillo	Nakanishi	Marrero and Pardillo
Pc	Joback and Reid	Ambrose	Ambrose
ω	Joback and Reid	Magoulas and Tassios	Magoulas and Tassios

In the recent work ten methods each for critical temperature and critical pressure were compared for ten fatty acids and seven fatty acid methyl esters. The best method for acid, ester and for fatty acid and ester combined are obtained after comparing the data with reference values. At the same time nine methods for acentric factor estimation also are compared for all the components. The work will be helpful for the better prediction of phase equilibrium of systems containing fatty acids and/or fatty acid esters using equation of state approach.

VI. REFERENCES

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