

# Thermodynamic modeling of vapor-liquid equilibrium systems including biodiesel in high and low pressures using cubic equations of state

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## Abstract

In the work, vapor-liquid equilibrium (VLE) of pure and binary mixtures of the systems including fatty acid Ethyl or Methyl esters and alcohols is analyzed by two simple cubic equations of state; Cubic-Square-Well (CSW EoS) and the Peng-Robinson (PR EoS). To achieve this purpose, first, the parameters of equations of state for pure systems are optimized using experimental vapor pressure and liquid density. Two models show accepted accuracy, however, the PR EoS with AARD=1.01% demonstrates better results for pure systems. Then the results of the pure systems are used to correlate the phase behavior of the binary mixtures in low and high pressure using one binary interaction parameter in equilibrium systems. The results for binary fatty acid ester systems show deviations as AARD=0.45% and AARD=0.23% for PR and CSW EoSs, respectively. For alcohol+fatty acid ester binary systems the pressure deviations are AARD=5.04% and AARD=14.14% for PR and CSW EoSs, respectively. Therefore, the results show that the CSW and PR equations of state can be applied to calculate the phase behavior of these types of systems with good accuracy and simplicity, therefore, can be used in designing, modeling, and optimization of the biodiesel units.

**Keywords:** Biodiesel, Vapor-liquid Equilibrium, Cubic-Square-Well (CSW), Peng-Robinson (PR), Equation of state.

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## 1. Introduction

Biodiesel fuel is one of the clean and renewable fuels. In reality, biodiesel is a mixture of fatty acid esters including methyl or ethyl ester. Fatty acids are widely used in various industries such as cosmetics [1], pharmaceuticals [2], food industries [3], etc. This fuel is produced from materials such as animal fat, vegetable oil (edible – Nonedible), restaurant waste [4,5]. That is why it is popular.

There are several ways to produce this fuel, but the most commonly used method is the transesterification method. In this method, the oil reacts with alcohol and processes several two Biodiesel and glycerin products are produced [6,7]. Because the decline in oil reserves and the increase in environmental contamination are rising information and physicochemical properties of the components of equilibrium systems are important for the designing, modeling, and optimization of the production of Biodiesel fuel [8]. biodiesel production and consumption. For this reason, the possession of thermodynamic Many articles has been published on the correlation of phase behavior of (VLE) systems with determining the coefficient of activity and determining the fugacity coefficient. Silva et al. [9] determined the VLE data for the systems: ethyl palmitate + ethyl stearate, ethyl palmitate + ethyl oleate and ethyl palmitate + ethyl linoleate at pressure range 5.3329-9.3326 kPa. Tang et al. [8] measured the vapor-liquid equilibria of the system ethyl myristate + ethyl palmitate at 0.5, 1, and 1.5 kPa and applied the NRTL and two UNIFAC based models to describe the experimental data. Shimoyama et al. [10], determined the vapor-liquid equilibrium for methanol + methyl laurate and methanol + methyl myristate systems near critical temperature of methanol with Peng-Robinson equation of state. Oliveira et al. [11] determined the VLE data for the low-pressure systems with the Cubic-Plus-Association (CPA) equation of state and in the other work, Oliveira et al. [12] measured the vapor-liquid equilibrium of the systems fatty acid ester + alcohol at pressure 2-12 MPa with the Cubic-Plus-Association (CPA) equation of state.

In this work, the parameters of the two equations of state (PR, CSW) for the fatty acid ethyl or methyl ester and methanol, ethanol systems are obtained using correlation of the vapor pressure and liquid density. Then equilibrium data for six binary systems including fatty acid ethyl or methyl ester at low pressure [8,16,17,18] and four binary systems including fatty acid ethyl/methyl ester + alcohol at high pressure [10,15] are correlated by two equations of state. In addition to determining the preferable model to describe the phase behavior of equilibrium systems. The novelty of this work is to explore the ability of the simple cubic equations of state (PR and CSW) for pure and binary systems including biodiesel and obtain the parameters of these models and comparison of the performance of the simple cubic EoSs to each other and the complex equation of state such as CPA [11].

## 2. Thermodynamic Modeling

The VLE analysis in this work was done based on the two cubic equations of state namely PR EoS, and CSW EoS.

### 2-1. Peng-Robinson equation of state:

After the publication of the Van der Waals (VdW) and SRK equations of state, Peng and Robinson made a comprehensive study for the evaluation of hydrocarbon systems. They showed that the ability of (SRK) equation of state requires correction in predicting fluid properties, especially along the critical area. Finally, they proposed the following equation [10]:

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + 2bV - b^2} \quad (1)$$

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha^2 \quad (2)$$

$$\alpha = \left(1 + k(1 - \sqrt{T_r})\right) \quad (3)$$

$$k = 0.37464 + 1.54226\omega - 0.266992\omega^2 \quad (4)$$

$$b = 0.0778 \frac{RT_c}{P_c} \quad (5)$$

In the above equations: R is gas constant, T is temperature,  $T_c$  is critical temperature and  $P_c$  is critical pressure, V is molar volume. Parameters a and b are the energy and size parameters, respectively.  $\omega$  is the acentric factor and the subscript c denotes the critical properties. In the original form of the PR equation of state, the parameters of the model are calculated from critical properties and therefore there are no adjustment parameters for pure systems. However, some researchers are attempted to directly obtain the model parameters using experimental VLE data similar to the CPA EoS [11]. Also, for a fair comparison between the ability of the EoSs for the description of the VLE data the second approach is used and the parameters of the PR and SRK EoSs are directly are obtained using Pure VLE data. Therefore, the equation is described as follows:

$$P = \frac{RT}{V - b_0} - \frac{a}{V^2 + 2b_0V - b_0^2} \quad (6)$$

$$a = a_0 * \alpha^2 \quad (7)$$

$$\alpha = \left(1 + k(1 - \sqrt{T_r})\right) \quad (8)$$

In the above equations, the parameters  $a_0$  and  $b_0$  and k are considered as adjustable parameters of the models.

### Cubic-Square-Well equation of state:

The pressure equation of the CSW equation of state was obtained as [13]:

$$P_{CSW} = \frac{RT}{v - 4\tau v_0} + \frac{zRT}{2} \frac{(1 - m - w)mv_0}{(mv + v_0w)(mv + v_0(1 - m))} \quad (9)$$

$$m = 4\sqrt{2}\pi\lambda^3 - 3/4\sqrt{2}\pi(\lambda^3 - 1) \quad (10)$$

$$v_0 = N_A \sigma_i^3 / \sqrt{2} \quad (11)$$

$$Z = (4\sqrt{2}\pi/3)\lambda^3 - 1 \quad (12)$$

$$w = \exp\left(\frac{\varepsilon}{kT}\right) - m \quad (13)$$

where,  $\varepsilon$  is the square –well potential depth,  $N_A$  is Avogadro is number,  $z$  is maximum attainable coordination number,  $v_0$  is the closed packed volume,  $m$  is an orientational parameter,  $\lambda$  is the square –well potential parameter,  $\tau = \sqrt{2}\frac{\pi}{6}$ ,  $v$  is molar volume and  $\sigma$  id the diameter of the particle. The parameters of pure components are  $\varepsilon$ ,  $\sigma$ ,  $\lambda$  that can be obtained by optimization of the thermodynamic properties of the pure systems.

The following mixing rules are used to calculate the parameters of mixtures based on pure parameters and extend the application field of equations of state to the mixtures. In the study of phase equilibrium for binary systems, it has been tried to determine the binary interaction parameter ( $k_{ij}$ ) according to equations of state by applying appropriate mixing rules.

**Mixing rules for PR and SRK EoSs:**

$$b = \sum_{i=1}^N x_i b_i \quad (14)$$

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij} \quad (15)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad k_{ij} = k_{ji}$$

**Mixing rules for CSW EoS:**

$$m = \sum_i \sum_j x_i x_j m_{ij} = 4\sqrt{2}\pi\lambda_{ij}^3 - 3/4\sqrt{2}\pi(\lambda_{ij}^3 - 1) \quad (16)$$

$$v_{0i} = N_A \sigma_i^3 / \sqrt{2} \quad (14)$$

$$Z_i = (4\sqrt{2}\pi/3)\lambda_{ii}^3 - 1 \quad (17)$$

$$w = \sum_i \sum_j x_i x_j w_{ij} = \sum_j \sum_i x_i x_j \left( \exp\left(\frac{\varepsilon_{ij}}{kT}\right) - m_{ij} \right) \quad (18)$$

$$z = \sum_i x_i z_i \quad (19)$$

$$v_0 = \sum_i x_i v_{0i} \quad (20)$$

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_i \varepsilon_j} \quad (21)$$

$$\lambda_{ij} = \frac{\lambda_i \sigma_i + \lambda_j \sigma_j}{\sigma_i + \sigma_j} \quad (22)$$

The expression of the chemical potential and fugacity coefficient of PR and CSW EoS is given in Appendix A.

The systems studied in this work are shown in Table 1 with details of pressure. The low-pressure systems are at a pressure range of 0.5 – 13.3 KPa and the high-pressure systems are in the pressure range of 2 – 9 MPa.

Table1 Details of the vapor-liquid equilibrium systems used in this work.

	System	Pressure (MPa)	No. of data point	Ref.
<b>High Pressure</b>	Ethanol-Ethyl laurate	2.23-7.09	22	[15]
	Ethanol-Ethyl myristate	2.11-6.93	19	[15]
	Methanol-Methyl laurate	2.16-8.49	20	[10]
	Methanol-Methyl myristate	2.41-8.42	19	[10]
<b>Low Pressure</b>		Pressure (kPa)		
	Ethyl palmitate-Ethyl oleate	5.3,9.3	22	[17]
	Ethyl palmitate-Ethyl linoleate	9.3	11	[17]
	Ethyl palmitate - Ethyl stearate	5.3	9	[17]
	Methyl laurate-Methyl myristate	3.9, 5.3, 6.6, 13.3	20	[18]
	Ethyl myristate-Ethyl palmitate	0.5, 1, 1.5	42	[8]
	Methyl myristate -Methyl palmitate	0.5, 1, 1.4, 3.9, 5.3, 6.6, 13.3	54	[17, 18]

### 3. Results and Discussion

#### 3.1 Pure systems

Each of the two EoSs which are considered in this work has three parameters. The parameters of the PR EoS for pure systems are  $a_0$ ,  $b$  and  $k$ , also for CSW EoS are  $\varepsilon, \sigma, \lambda$ , that are obtained by simultaneous optimization of the saturated vapor pressure and the liquid density of the pure components. The objective function to be minimized is as follows:

$$oF_1 = \frac{1}{N} * \sum_i \left| \frac{p^{exp} - p^{cal}}{p^{exp}} \right| * 100 \quad (23)$$

$$oF_2 = \frac{1}{N} * \sum_i \left| \frac{\rho^{exp} - \rho^{cal}}{\rho^{exp}} \right| * 100 \quad (24)$$

$$OF = 0.3 * oF_1 + 0.7 * oF_2 \quad (24)$$

In the above relation, N is the number of calculated experimental points, and symbols exp and cal represent experimental data and calculated value, respectively. Cubic EoSs show better results in predicting the vapor phase properties than the liquid phase properties. Therefore, weights 0.3 and 0.7 were used for vapor pressure and liquid phase density, respectively, in the objective function to improve the correlating results for liquid phase density. The parameters of the equation

of state for pure compounds have been studied along with a wide range of temperatures that are given as reduced temperature in Tables 2-3. To check the accuracy of the equations of state and determine the deviation of the model results with experiments, the average absolute relative deviation (AARD<sub>Total</sub>) is used.

Table 2 PR pure compound parameters and reduced temperatures of studied systems.

Compound	$T_r$	$a_0(m^6 \cdot Pa/mol^2)$	$b_0(m^3/mol)$	k
Methyl myristate	0.55-0.90	10.97	0.00028	1.32
Ethyl caprate	0.55-0.90	7.87	0.00020	1.24
Methanol	0.54-0.89	0.94	0.00003	1.00
Ethanol	0.54-0.90	1.29	0.00005	1.23
Ethyl palmitate	0.55-0.90	13.42	0.00034	1.56
Methyl palmitate	0.55-0.90	12.60	0.00032	1.43
Methyl stearate	0.55-0.90	14.87	0.00036	1.50
Ethyl linoleate	0.55-0.90	13.98	0.00036	1.68
Methyl linoleate	0.55-0.90	13.92	0.00034	1.52
Ethyl laurate	0.55-0.90	9.61	0.00026	1.37
Methyl laurate	0.55-0.90	8.81	0.00024	1.25
Ethyl myristate	0.55-0.90	11.50	0.00030	1.41
N-Tetradecane	0.55-0.90	8.829	0.00020	1.22
Methyl linolenate	0.55-0.90	13.61	0.00030	1.51
Ethyl stearate	0.55-0.90	15.17	0.00038	1.62
Methyl oleate	0.55-0.90	14.19	0.00035	1.53
Ethyl oleate	0.55-0.90	15.18	0.00037	1.49

Table 3 CSW pure compound parameters and reduced temperatures of studied systems.

Compound	$T_r$	$\sigma(m)$	$\epsilon/k(K)$	$\lambda$
Methyl myristate	0.55-0.90	5.81E-10	2562.09	1.05
Ethyl caprate	0.55-0.90	5.43E-10	2083.78	1.08
Methanol	0.54-0.89	2.96E-10	1190.00	1.17
Ethanol	0.54-0.90	3.30E-10	1534.67	1.08
Ethyl palmitate	0.55-0.90	6.14E-10	3208.95	1.02
Methyl palmitate	0.55-0.90	6.02E-10	2901.35	1.04
Methyl stearate	0.55-0.90	6.26E-10	3207.94	1.03
Ethyl linoleate	0.55-0.90	6.24E-10	3447.86	1.02
Methyl linoleate	0.55-0.90	6.16E-10	3188.70	1.03
Ethyl laurate	0.55-0.90	5.66E-10	2529.81	1.05
Methyl laurate	0.55-0.90	5.57E-10	2202.73	1.08
Ethyl myristate	0.55-0.90	5.92E-10	2759.05	1.04
N-Tetradecane	0.55-0.90	5.63E-10	2074.59	1.08
Methyl linolenate	0.55-0.90	6.09E-10	3206.51	1.03
Ethyl stearate	0.55-0.90	6.35E-10	3426.56	1.02
Methyl oleate	0.55-0.90	6.20E-10	3217.26	1.02
Ethyl oleate	0.55-0.90	6.31E-10	3177.06	1.03

Tables 4-5 represent the percentage of  $AARD_{Total}$  calculated based on vapor pressure and fluid density by two state equations. The result of the comparison of the  $AARD_{Total}$  equations is shown in Fig. 1. According to Fig. 1, both equations have a good ability to predict simultaneously the vapor pressure and liquid density. The absolute average relative deviation calculated for each model is shown in Tables 4-5. In comparison, The PR EoS can provide better correlation respect to the CSW EoS for the pure systems. The better results of the PR EoS respect to the CSW EoS for pure section may be due to the fact that biodiesels are long-chain molecules, while the CSW equation developed based on small and spherical molecules.

Table 4 Vapor pressure deviation, liquid density deviation, and total deviation of the results of PR EoS respect to experiment.

Compound	%AARD <sub>P</sub>	%AARD <sub>density</sub>	%AARD <sub>Total</sub>
Methyl myristate	0.38	1.36	0.87
Ethyl caprate	0.20	0.91	0.56
Methanol	1.62	0.75	1.19
Ethanol	0.92	1.35	1.14
Ethyl palmitate	0.85	1.07	0.96
Methyl palmitate	0.70	1.04	0.87
Methyl stearate	2.58	1.30	1.94
Ethyl linoleate	2.42	0.95	1.69
Methyl linoleate	0.21	1.16	0.69
Ethyl laurate	0.54	0.88	0.71
Methyl laurate	1.46	0.63	1.05
Ethyl myristate	0.32	0.85	0.59
N-Tetradecane	0.85	0.55	0.70
Methyl linolenate	0.25	1.31	0.78
Ethyl stearate	0.72	1.18	0.95
Methyl oleate	0.82	1.19	1.01
Ethyl oleate	1.42	1.44	1.43
<b>AARD<sub>Total</sub></b>			<b>1.01</b>

Table 5 Vapor pressure deviation, liquid density deviation, and total deviation of the results of CSW EoS respect to experiment.

Compound	%AARD <sub>P</sub>	%AARD <sub>density</sub>	AARD <sub>Total</sub>
Methyl myristate	2.81	4.71	3.76
Ethyl caprate	1.83	4.35	3.09
Methanol	2.05	2.68	2.37
Ethanol	0.59	2.37	1.48
Ethyl palmitate	5.87	4.47	5.17
Methyl palmitate	4.46	4.54	4.50
Methyl stearate	7.25	4.75	6.00
Ethyl linoleate	7.87	4.42	6.15
Methyl linoleate	4.39	4.72	4.56
Ethyl laurate	2.31	4.39	3.35
Methyl laurate	2.9	3.90	3.40

Ethyl myristate	3.66	4.34	4.00
N-Tetradecane	2.14	3.43	2.79
Methyl linolenate	4.37	4.86	4.62
Ethyl stearate	5.37	4.37	4.87
Methyl oleate	5.42	4.67	5.05
Ethyl oleate	5.79	4.85	5.32
<b>AARD Total</b>			<b>4.14</b>

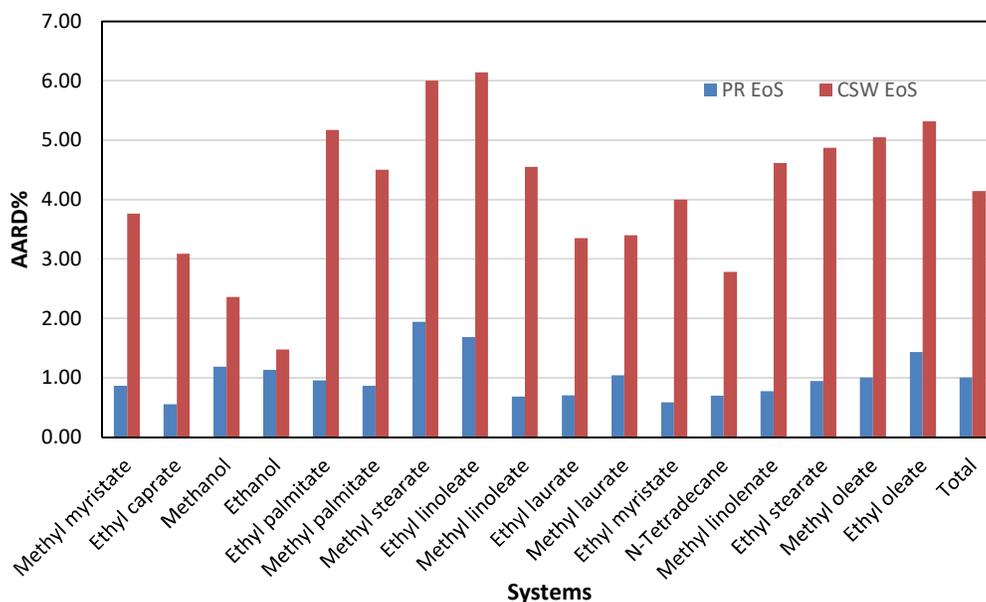


Fig. 1. Comparison of the results (AARD<sub>Total</sub>) of two models for pure systems.

### 3-2 binary systems

In this section, using only one interaction parameter the phase behavior of the binary systems are correlated based on PR and CSW EoS. Using the parameters obtained for pure systems for PR and CSW EoS, with the help of a logical program, the interaction parameter is estimated by calculating the bubble temperature for low-pressure systems and calculating bubble pressure for high-pressure systems. The results of calculating the binary interaction parameter ( $k_{ij}$ ) in Table 6 are reported for models. The results show that the obtained binary interaction parameters ( $k_{ij}$ ) value of the CSW EoS is close to zero. This means that the pure parameters of the CSW EoS are suitable and the mixing rules used in the model good describe the behavior of the binary systems. The AARD% calculations for systems are as follows:

For low-pressure systems:

$$\%AARD_T = oF_1 = \frac{1}{N} * \sum_i \left| \frac{T^{exp} - T^{cal}}{T^{exp}} \right| * 100 \quad (24)$$

For high-pressure systems:

$$\%AARD_p = oF_1 = \frac{1}{N} * \sum_i \left| \frac{p^{exp} - p^{cal}}{p^{exp}} \right| * 100 \quad (25)$$

$$\%AARD_y = oF_2 = \frac{1}{N} * \sum_i \left| \frac{y^{exp} - y^{cal}}{y^{exp}} \right| * 100 \quad (26)$$

Table 6 The binary interaction parameter ( $k_{ij}$ ) for PR and CSW EoSs.

Systems	PR	CSW
Ethyl palmitate - ethyl oleate	-0.027	0.009
Ethyl palmitate - ethyl linoleate	-0.024	0.008
Ethyl palmitate - ethyl stearate	-0.044	0.007
Ethyl myristate-ethyl palmitate	-0.044	0.018
Methyl Laurate-methyl Myristate	0.025	0.015
Methyl myristate -methyl palmitate	0.024	0.002
Ethanol -ethyl laurate	0.009	0.067
Ethanol -ethyl myristate	0.015	0.086
Methanol -methyl laurate	0.071	0.188
Methanol -methyl myristate	0.082	0.201

The first system studied was ethyl palmitate- ethyl oleate at 5.33 kPa and 9.33 kPa. All equations have made good correlations for these vapor-liquid equilibrium systems, as presented in Fig. 2. Global absolute average relative deviations are 0.53%, and 0.23% for bubble temperature obtained for these systems, respectively for PR and CSW. Fig. 3 shows the vapor-liquid equilibrium system correlation results for the ethyl palmitate-ethyl linoleate at pressure 9.3 kPa with all equations of state. The calculated  $\%AARD_T$  for each model is presented in Table 7. The global mean absolute average relative deviations of bubble temperature calculated by using the two models (PR and CSW) is 0.45% and 0.23% for PR and CSW, respectively. According to the results, the CSW model was introduced as the superior model in the correlation of bubble temperature for low-pressure equilibrium systems, and then the PR model was the superior model. In the year 2014, Oliveira et al. [ 11] used the CPA EoS to predict the phase behavior of low-pressure systems. The results of their work are shown in Table 7. The CPA EoS, in comparison with the CSW EoS has a lower ability to correlate the phase behaviors of systems. In general, the order of the superiority of these three models can be compared to each other in the following form: CSW > PR > CPA. Based on the comparison of the three equations, it could be

concluded that obtaining the best results by adding extra difficulty to the model is not always beneficial. In fact, the conditions of the study systems should be considered in improving the equations.

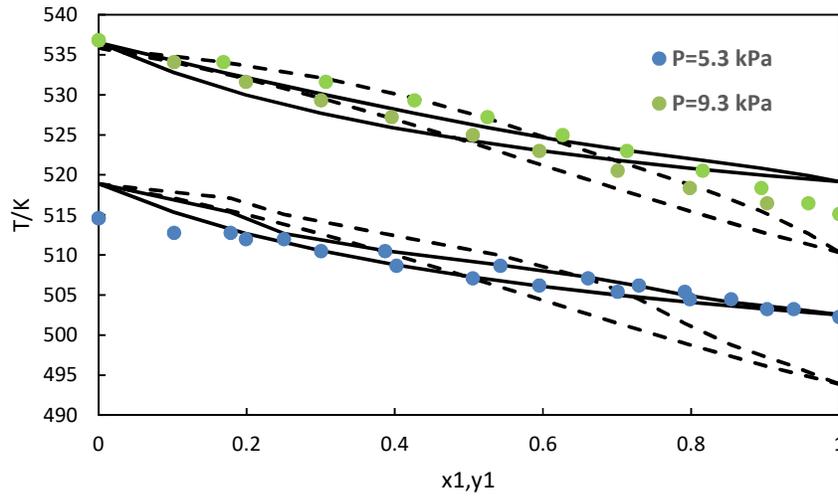


Fig. 2.  $T - x_1 - y_1$  diagram for ethyl palmitate - Ethyl oleate at 5.3 and 9.3 kPa:(●) experimental data [17]; (—) correlated results by the CSW EoS;(- -) predicted results by the PR EoS.

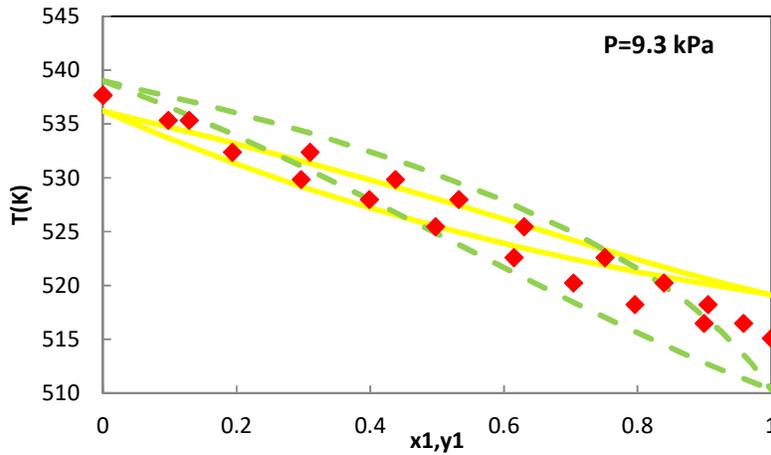


Fig. 3.  $T - x_1 - y_1$  diagram for Ethyl palmitate (1) - Ethyl linoleate (2) at 9.3 kPa:(◆) experimental data [17]; (—) correlated results by the CSW EoS;(- -) correlated results by the PR EoS.

Table 7 Absolute average relative deviations (AARD%) of PR and CSW EoSs for the binary fatty acid systems and comparison results with CPA EoS.

Systems	%AARD <sub>T</sub>		
	PR	CSW	CPA [11]
Ethyl palmitate - ethyl oleate	0.53	0.23	0.21
Ethyl palmitate - ethyl linoleate	0.35	0.34	0.19
Ethyl palmitate - ethyl stearate	0.56	0.09	0.10
Ethyl myristate-ethyl palmitate	0.49	0.24	0.47
Methyl Laurate-methyl Myristate	0.11	0.11	0.75
Methyl myristate -methyl palmitate	0.66	0.38	0.57
<b>Global mean %AARD<sub>T</sub></b>	<b>0.45</b>	<b>0.23</b>	<b>0.50</b>

After determining the bubble-temperature and choosing the best model, the bubble-pressure for vapor-liquid equilibrium systems including Ethanol-Ethyl laurate at 2-7 MPa, Ethanol-Ethyl myristate at 2-7 MPa, Methanol-Methyl laurate, and Methanol-Methyl myristate at 2-9 MPa, were estimated by equations of state and compared with experimental data. Fig 4. Shows the experimental data of the Ethanol-Ethyl laurate system at 2-7 MPa along with results calculated by PR and CSW equations of state. Global absolute average relative deviations of PR EoS are obtained as 3.2%, 2.3% for bubble-pressure and vapor mole fraction, respectively and %AARD of bubble-pressure and vapor mol fraction obtained for these systems, by CSW are 6.28%, 0.74%. The results for the bubble-pressure and vapor mol fraction calculations for Ethanol-Ethyl laurate, Ethanol-Ethyl myristate, Methanol-Methyl laurate and Methanol-Methyl myristate systems are shown in Table 8 by two models.

The accuracy of the CSW equation has been greater in correlating the phase behavior of these systems, so the value of the global mean average deviation for the vapor phase mol fraction obtained by the CSW model for alcohol-fatty acid binary systems is 0.53%. while the global mean absolute average relative deviation for the PR EoS model is 2.01%. The basis for choosing the best model in the calculation of high-pressure systems is a model that has the lowest deviation in the calculation of the vapor phase mole fraction and bubble pressure simultaneously. Although among the PR and CSW EoSs, the CSW EoS has the higher deviation in determining the bubble pressure of these systems, however, this model has the lower deviation in the calculation of the vapor mole fraction. In general, based on the results obtained from the global absolute average relative deviations, the PR EoS shows the lower deviation in two items as vapor phase mole fraction and bubble pressure simultaneously. However, It can be explicitly stated that two EoSs are suitable for correlating phase behavior of systems.

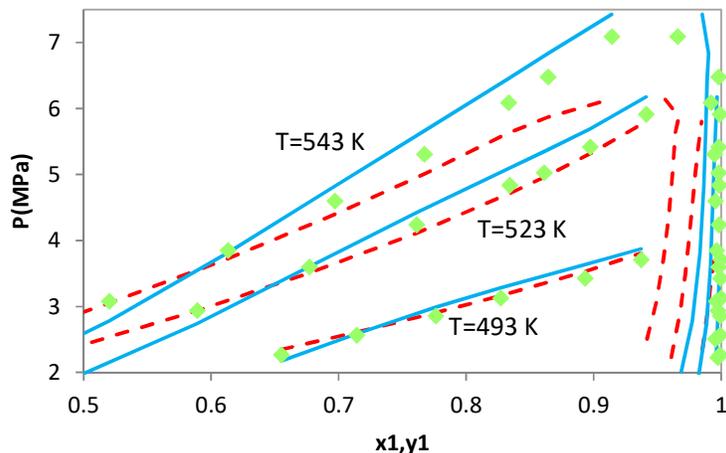


Fig. 4.  $P - x_1 - y_1$  diagram for Ethanol (1) - Ethyl laurate (2) at 493 K-523 K-543 K: ( $\diamond$ ) experimental data [15]; (-) correlated results by the CSW EoS; (- -) correlated results by the PR EoS.

Table 8 Absolute average relative deviations (AARD%) of PR and CSW EoSs for the alcohol-fatty acid binary systems.

system	%AARD <sub>p</sub>		%AARD <sub>y</sub>	
	PR	CSW	PR	CSW
Ethanol-ethyl laurate	3.23	6.28	2.37	0.74
Ethanol-ethyl myristate	2.77	12.76	1.43	0.31
Methanol-methyl laurate	7.05	7.73	2.60	0.81
Methanol-methyl myristate	7.14	29.80	1.65	0.27
<b>Global mean %AARD</b>	<b>5.04</b>	<b>14.14</b>	<b>2.01</b>	<b>0.53</b>

#### 4. Conclusion

Vapor-liquid equilibrium data for pure and binary systems containing methyl or ethyl ester and alcohol was explored by two simple cubic equations of state as PR EoS and CSW EoS. The results obtained from these two models (PR and CSW EoSs) are compared with each other and the CPA equation of state as an association EoS. The models were first examined by determining the parameters to be adjusted for pure systems and PR EoS was introduced with total absolute average relative deviations of 1.02% as the accurate model. Then, by determining the binary interaction parameters for all binary systems at low and high pressures, the CSW EoS with a global absolute average relative deviation of 0.23% for to calculate the bubble-temperature of the binary mixtures of the fatty acid shows the better results, however, the PR EoS in binary mixtures of alcohol-fatty acid with bubble-pressure AARD% as 5.04% and vapor mole fraction AARD% as 2.01 demonstrate better results as CSW EoS.

## Appendix A. The fugacity coefficient for each species, i, in the mixtures.

The fugacity coefficient for each species, i, in the mixtures for PR and CSW EoSs are as follows:

$$\ln\phi_{i,PR} = \frac{B_i}{B}(Z-1) - \ln(Z-B) + \frac{A}{2.828} \left[ \frac{B_i}{B} - \frac{2\sum_j y_j a_{ij}}{a} \right] + \ln \left[ \frac{Z+2.414}{Z-0.414B} \right] \quad \text{A.1}$$

$$A = \frac{aP}{(RT)^2}, \quad B = \frac{bP}{RT} \quad \text{A.2}$$

$$\ln\phi_{i,CSW} = \ln \left( \frac{RT}{Pv} \right) + \ln \left( \frac{v}{v-4\tau v_0} \right) + \frac{4\tau v_{oi}}{v-4\tau v_0} - \frac{z_i}{2} \ln \left( \frac{mv+v_0w}{mv+v_0(1-m)} \right) \\ - \frac{z}{2} \left( \frac{2v\sum_j x_j m_{ij} + wv_{oi} + 2v_0\sum_j x_j w_{ij}}{mv+v_0w} - \frac{2(v-v_0)\sum_j x_j m_{ij} + (1-m)v_{oi} + 2v_0}{mv+v_0(1-m)} \right) \quad \text{A.3}$$

### List of symbols

- k Boltzmann's constant ( $1.38066 \cdot 10^{-23} \text{JK}^{-1}$ )  
m Orientational parameter  
 $N_A$  Avogadro's number ( $6.02205 \cdot 10^{+23} \text{ mol}^{-1}$ )  
P Pressure (Pa-MPa)  
R Gas constant (8.314 J/mol.K)  
T Temperature(K)  
v Volume ( $m^3$ )  
z maximum attainable coordination number  
w A function of temperature defined in Eq. (18)  
 $v_0$  closed packed volume ( $m^3/mol$ )  
 $x_i$  Mole fraction of component i

### Greek letters

- $\sigma$  Size parameter(m)  
 $\varepsilon$  square-well potential depth  
 $\lambda$  the square-well potential parameter  
 $\phi$  Fugacity coefficient  
 $\tau$  Constant (0.7405)

### Subscripts

CSW Cubic square-well

### Superscripts

- cal Calculated properties  
exp Experimental properties

### References

- [1] Keng PS, Basri M, Zakaria MR, Rahman MA, Ariff AB, Rahman RA, Salleh AB. Newly synthesized palm esters for cosmetics industry. Industrial crops and products. 2009;29(1):37-44.

- [2] Pérez-Feás C, Barciela-Alonso MC, Sedes-Díaz A, Bermejo-Barrera P. Phthalates determination in pharmaceutical formulae used in parenteral nutrition by LC-ES-MS: importance in public health. *Analytical and bioanalytical chemistry*. 2010;397(2):529-35.
- [3] Kim J, Altreuter DH, Clark DS, Dordick JS. Rapid synthesis of fatty acid esters for use as potential food flavors. *Journal of the American Oil Chemists' Society*. 1998;75(12):1109-13.
- [4] de Lima da Silva N, Benedito Batistella C, Maciel Filho R, Maciel MR. Biodiesel production from castor oil: optimization of alkaline ethanolysis. *Energy & Fuels*. 2009;23(11):5636-42.
- [5] Silva C, Weschenfelder TA, Rovani S, Corazza FC, Corazza ML, Dariva C, Oliveira JV. Continuous production of fatty acid ethyl esters from soybean oil in compressed ethanol. *Industrial & engineering chemistry research*. 2007;46(16):5304-9.
- [6] Ma F, Hanna MA. Biodiesel production: a review. *Bioresource technology*. 1999;70(1):1-5.
- [7] Fukuda H, Kondo A, Noda H. Biodiesel fuel production by transesterification of oils. *Journal of bioscience and bioengineering*. 2001;92(5):405-16.
- [8] Tang G, Ding H, Hou J, Xu S. Isobaric vapor–liquid equilibrium for binary system of ethyl myristate+ ethyl palmitate at 0.5, 1.0 and 1.5 kPa. *Fluid Phase Equilibria*. 2013;347:8-14.
- [9] Silva LY, Falleiro RM, Meirelles AJ, Krähenbühl MA. Vapor–liquid equilibrium of fatty acid ethyl esters determined using DSC. *Thermochimica acta*. 2011;512(1-2):178-82..
- [10] Shimoyama Y, Iwai Y, Jin BS, Hirayama T, Arai Y. Measurement and correlation of vapor–liquid equilibria for methanol+ methyl laurate and methanol+ methyl myristate systems near critical temperature of methanol. *Fluid phase equilibria*. 2007;257(2):217-22..
- [11] Oliveira MB, Queimada AJ, Coutinho JA. Modeling of biodiesel multicomponent systems with the cubic-plus-association (CPA) equation of state. *Industrial & engineering chemistry research*. 2010;49(3):1419-27.
- [12] Oliveira MB, Queimada AJ, Coutinho JA. Prediction of near and supercritical fatty acid ester+ alcohol systems with the CPA EoS. *The Journal of Supercritical Fluids*. 2010;52(3):241-8.
- [13] Haghtalab A, Mazloumi SH. Electrolyte cubic square-well equation of state for computation of the solubility CO<sub>2</sub> and H<sub>2</sub>S in aqueous MDEA solutions. *Industrial & engineering chemistry research*. 2010;49(13):6221-30..
- [14] Wong DS, Sandler SI. A theoretically correct mixing rule for cubic equations of state. *AIChE Journal*. 1992;38(5):671-80..
- [15] Shimoyama Y, Iwai Y, Abeta T, Arai Y. Measurement and correlation of vapor–liquid equilibria for ethanol+ ethyl laurate and ethanol+ ethyl myristate systems near critical temperature of ethanol. *Fluid Phase Equilibria*. 2008;264(1-2):228-34..
- [16] Chen R, Ding H, Liu M, Qi J, Zhou H, Chen N. Isobaric vapor–liquid equilibrium for binary system of methyl myristate+ methyl palmitate at 0.5, 1.0 and 1.4 kPa. *Fluid Phase Equilibria*. 2014;382:133-8..

[17] Silva LY, Falleiro RM, Meirelles AJ, Krähenbühl MA. Vapor-liquid equilibrium of fatty acid ethyl esters determined using DSC. *Thermochimica acta*. 2011;512(1-2):178-82.

[18] Rose A, Supina WR. Vapor Pressure and Vapor-Liquid Equilibrium Data for Methyl Esters of the Common Saturated Normal Fatty Acids. *Journal of Chemical and Engineering Data*. 1961;6(2):173-9.

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