

Correlation of Vapor-Liquid Equilibria of Supercritical Methanol + Glycerol System

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The α function in the original Peng-Robinson equation of state was modified and expressed as a temperature-dependent form. The vapor-liquid equilibria for methanol + glycerol system were correlated at high temperatures and pressures with the original Peng-Robinson equation of state with conventional mixing rules (PR EOS), the modified Peng-Robinson equation of state with conventional mixing rules (PR-M EOS), and the modified Peng-Robinson equation of state with Wong-Sandler mixing rules (PR-M-WS). The PR-M EOS greatly enhances the correlation accuracy both in liquid and vapor phases compared with PR EOS. In particular, the correlation accuracy of liquid phase has been further improved by PR-M-WS.

1. Introduction

Biodiesel is produced by transesterification of triglycerides from oils and fats with an excess of alcohol¹⁾. For the production of biodiesel fuels, supercritical methanol method is superior to the conventional alkaline and acid catalyst methods. Supercritical methanol can be conducted without catalyst. It requires very short reaction time²⁾.

The separation of products from biodiesel productions requires the knowledge of phase equilibria of binary and multi-component mixtures containing methanol, glycerol and/or fatty esters. In the previous work of the authors the vapor-liquid equilibria for methanol + methyl laurate and methanol + glycerol systems were measured from 493 to 573K. Cubic equations of states with several mixing rules have been applied to correlate the experimental data. However, good correlated results are not obtained in vapor phase.

In order to describe the phase behavior for methanol + glycerol system near the critical temperature of methanol, Peng-Robinson equation of state (PR EOS) is more suitable than the other cubic equations of states. It is difficult to accurately correlate both liquid and vapor phases at the same time. In this work, the authors proposed to modify the α function in the original Peng-Robinson equation of state as temperature-dependent form (PR-M EOS). Furthermore, PR-M EOS with Wong-Sandler mixing rules (PR-M-WS) were also applied to calculate the vapor-liquid equilibria of methanol + glycerol system at high temperatures and high pressures. NRTL model was used to calculate the excess Gibbs free energy G^E in Wong-Sandler mixing rules. The binary parameter τ_{ij} were optimized based on minimizing an objective function.

2. Calculation model

2.1 Peng-Robinson Equation of State

The Peng-Robinson equation of state is explained as follows.

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m(b + V_m) + b(V_m - b)} \quad (1)$$

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

$$b = \frac{0.0778RT_c}{P_c} \quad (3)$$

$$\alpha = (m(1 - \sqrt{T_r}) + 1)^2 \quad (4)$$

$$m = -0.26992\omega^2 + 1.54226\omega + 0.37464 \quad (5)$$

$$T_r = \frac{T}{T_c} \quad (6)$$

where p is the pressure, R is the gas constant, T is the temperature, and V_m is the molar volume. The parameters a and b are the energy and size parameters, respectively. The ω is the acentric factor. Subscript c means the critical property.

2.2 Modified α function

In order to improve the correlation accuracy in vapor phase for methanol + glycerol system, The α function was modified³⁾. In this work, the α function is explained by the following equation.

$$\alpha_i = \left(\frac{0.468992}{T_{R,i} - 0.3087282} + 0.350664 \right) \quad (7)$$

The equation of state used Eq. (7) instead of Eq. (4) is called as PR-M EOS in this work.

2.3 Parameters of pure compounds

The molecular weights M_w , acentric factors ω and the critical temperatures T_c and pressures P_c of the pure substances focused in this work are obtained from aspen plus database and are listed in Table 1.

Table 1 Critical properties and acentric factors of substances

Substance	M_w	T_c [K]	P_c [MPa]	ω
Methanol	32.04	512.5	8.084	0.5658
Glycerol	92.09	850	7.5	0.5127

2.4 Mixing rules

2.4.1 Conventional mixing rules

The following van der Waals one-fluid mixing rules are frequently used to correlate the vapor-liquid equilibria.

$$a_m = \sum_{i=1}^c \sum_{j=1}^c x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (8)$$

$$b_m = \sum_{i=1}^c x_i b_i \quad (9)$$

where k_{ij} is the binary interaction parameter.

2.4.2 Wong-Sandler mixing rules

The Wong-Sandler mixing rules were developed in order to reproduce the composition dependences of the second virial coefficients accurately. Using WS mixing rules, the energy and size parameters, a and b in PR equation of state can be obtained as follows:

$$b_m = \sum_{i=1}^c \sum_{j=1}^c x_i x_j \left[\frac{b_i + b_j}{2} - \frac{\sqrt{a_i a_j}}{RT} (1 - k_{ij}) \right] / \left[1 - \sum_{i=1}^c \frac{x_i a_i}{b_i RT} - \frac{G^E}{CRT} \right] \quad (10)$$

$$a_m = b_m \left(\sum_{i=1}^c \frac{x_i a_i}{b_i} + \frac{G^E}{C} \right) \quad (11)$$

$$C = \frac{\ln(\sqrt{2}-1)}{\sqrt{2}} = -0.623225$$

where G^E is the excess Gibbs free energy. In this work, G^E was calculated by NRTL model.

The NRTL model is given by

$$\frac{G^E}{RT} = \sum_{i=1}^c x_i \frac{\sum_{j=1}^c \tau_{ji} G_{ji} x_j}{\sum_{k=1}^c G_{ki} x_k} \quad (12)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (13)$$

where, α_{ij} is the non-randomness parameter which is fixed as 0.3 in this work, τ_{ij} are the binary parameters.

2.5 Objective function

The objective function used to optimize the binary parameters is explained by the following equation.

$$F(k_{ij}) = d(x) \times d(y) \quad (14)$$

where $d(x)$ and $d(y)$ represent the deviation functions in liquid and vapor phases, respectively.

$$d(x) = \sum \left[\frac{\sum |x_i^{\text{exp}} - x_i^{\text{cal}}|}{N_p} \right] / N_T \quad (15)$$

$$d(y) = \sum \left[\frac{\sum |y_i^{\text{exp}} - y_i^{\text{cal}}|}{N_p} \right] / N_T \quad (16)$$

Where x^{exp} and y^{exp} are the literature data in liquid and vapor phases, respectively, the superscript cal represents the calculated results, N_p is the number of pressure data at each temperature, N_T is the number of temperature data.

3. Results and discussion

3.1 $pV_m T$ relationship of methanol

The pressures at different temperatures of methanol were calculated by PR EOS and PR-M EOS at the constant molar volume 0.0002823 m³/mol (density = 113.5 kg/m³)⁴. The results are shown in Figure 1. The both models give almost identical trends; however, the deviation by PR-M EOS is slightly larger than that by PR EOS.

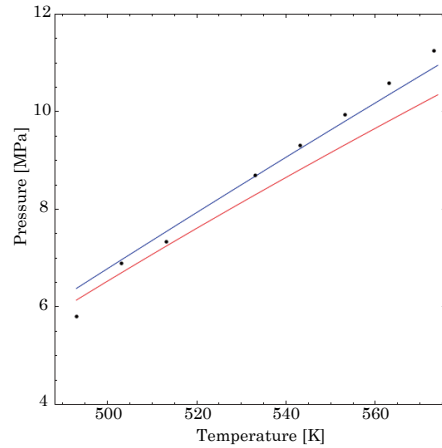


Fig. 1 Pressures of methanol at constant molar volume 0.0002823 m³/mol.

(●) Literature data⁴.

(—) Calculated results by PR EOS.

(—) Calculated results by PR-M EOS.

3.2 Saturated vapor pressures

PR EOS and PR-M EOS were adopted to calculate the saturated vapor pressures of methanol and glycerol. The results are shown in Figures 2 and 3. From Figure 3, the results by PR-M EOS are obviously lower than the experimental data for glycerol. It means that the α function of PR-M EOS gives stronger molecular interactions of glycerol in pure liquid glycerol. The reasons why the molecular interactions of glycerol in pure liquid glycerol should be stronger are explained in the following section.

3.3 Binary vapor- liquid equilibria

The binary parameters k_{ij} and τ_{ij} were optimized to give good correlated results of the vapor- liquid equilibria for methanol + glycerol system. The literature data² were used for the optimization of binary parameters. The objective function used in this work is presented in Eq. (14) - Eq. (16). The binary parameters are shown in Table 2.

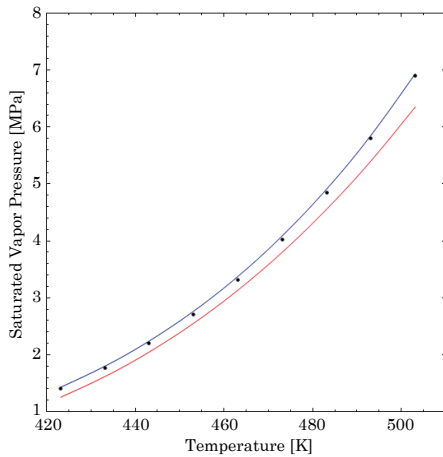


Fig. 2 Saturated vapor pressures of methanol.
 (●) Literature data⁴.
 (—) Calculated results by PR EOS.
 (—) Calculated results by PR-M EOS.

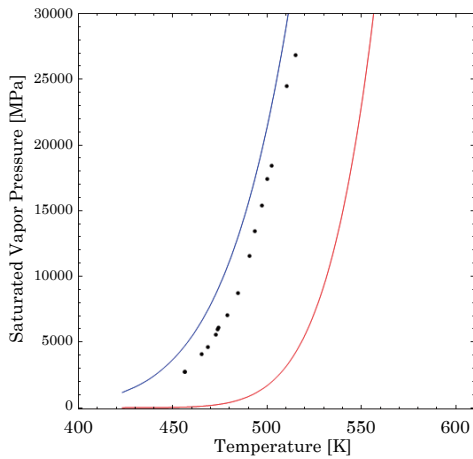


Fig. 3 Saturated vapor pressures of glycerol.
 (●) Literature data⁵.
 (—) Calculated results by PR EOS.
 (—) Calculated results by PR-M EOS.

Table 2 Binary parameters for methanol + glycerol system

EOS and mixing rule	k_{ij}	τ_{ij}
PR-EOS with conventional mixing rule	-0.027	—
PR-M EOS with conventional mixing rule	-0.035	—
PR-M EOS with Wong-Sandler mixing rule	-0.035	$\tau_{1,2}=6.41 - 0.01144T$ $\tau_{2,1}=-0.025$

The calculated results by using PR EOS with conventional mixing rules, PR-M EOS with conventional mixing rules and PR-M-WS are listed in Table 3, and shown in Figures 4, 5 and 6, respectively. The left slope of each the same color pair represents liquid phase

border and that of right slope represents vapor phase border. In other words, the vapor and liquid phases coexist in the region between both slopes. As shown in Table 3 and Figure 4, it is difficult to satisfy both liquid and vapor phase by using PR EOS with conventional mixing rules, although the binary parameter was optimized. Specially, the calculated results of mole fractions of methanol in vapor phase are low compared with the experimental data. In other words, the calculated mole fractions of glycerol in vapor phase are higher compared with the experimental data. The results cannot be improved even if the binary parameter was optimized. This means that the molecular interactions of glycerol may become stronger for the presence of methanol in the liquid phase. Table 3 and Figure 5 show that the results by PR-M EOS with conventional mixing rules are much better than those of PR EOS with conventional mixing rules. The calculated results in vapor phase are improved by PR-M EOS with conventional mixing rules. This means that the α function of PR-M EOS gives stronger molecular interactions of glycerol, and the mole fractions of glycerol are reduced in vapor phase. The hydrogen bond formations between glycerol and methanol molecules may be the reasons for the stronger molecular interactions of glycerol in liquid methanol + glycerol compared with those in pure liquid of glycerol. The α function should be modified to explain the strong interaction of glycerol in methanol + glycerol system, even if the calculated results of saturated vapor pressures for glycerol are low compared with the experimental data for pure glycerol.

From Table 3 and Figure 6, the results by PR-M-WS are almost the same as those by PR-M EOS with conventional mixing rules in vapor phase. However, the results by PR-M-WS are improved compared with those by PR-M EOS with conventional mixing rules in liquid phase. Specially, the calculated results in liquid phase at 493K by PR-M-WS are much improved compared with those by PR-M EOS.

Table 3 Deviations between literature and calculated results for methanol + glycerol system

$T[K]$	PR-EOS with conventional mixing rule		PR-M with conventional mixing rule		PR-M EOS with Wong-Sandler mixing rule	
	δx	δy	δx	δy	δx	δy
493	4.93	0.41	2.57	0.04	0.64	0.04
523	3.56	1.09	2.78	0.26	1.74	0.27
543	3.41	1.5	1.86	0.69	2.48	0.68
573	3.01	2.55	2.14	1.11	1.98	1.11
Σ	14.91	5.56	9.35	2.09	6.84	2.1

$$\delta(x) = \frac{100 \sum |x_i^{\text{exp}} - x_i^{\text{cal}}|}{N_p} \quad \delta(y) = \frac{100 \sum |y_i^{\text{exp}} - y_i^{\text{cal}}|}{N_p},$$

N_p is number pressure data at each temperature.

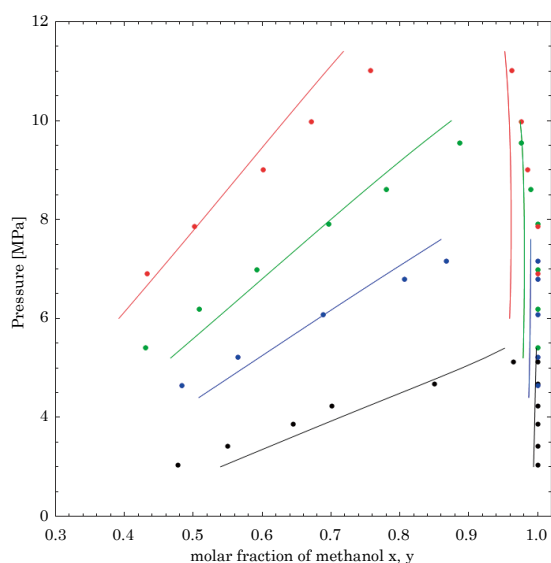


Fig. 4 Vapor-liquid equilibria for methanol + glycerol system calculated by PR EOS with conventional mixing rule. (●, ●, ●, ●) Literature data at 493, 523, 543, 573K, respectively²⁾. (—, —, —, —) Calculated results by PR EOS with conventional mixing rule at 493, 523, 543, 573K, respectively.

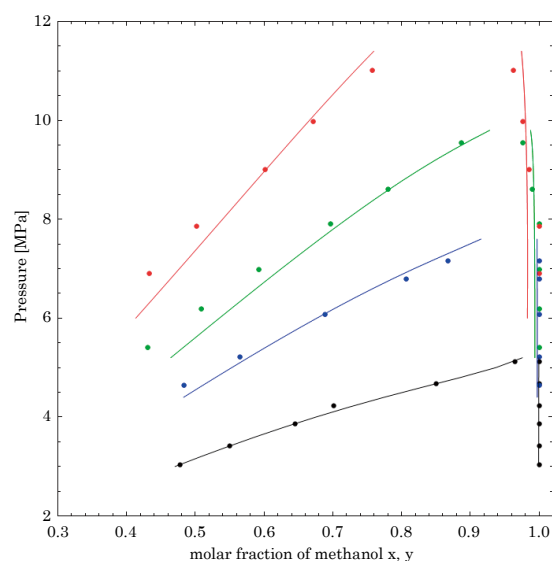


Fig. 6 Vapor-liquid equilibria for methanol + glycerol system calculated by PR-M EOS with Wong-Sandler mixing rule. (●, ●, ●, ●) Literature data at 493, 523, 543, 573K, respectively²⁾. (—, —, —, —) Calculated results by PR-M EOS with Wong-Sandler mixing rule at 493, 523, 543, 573K, respectively.

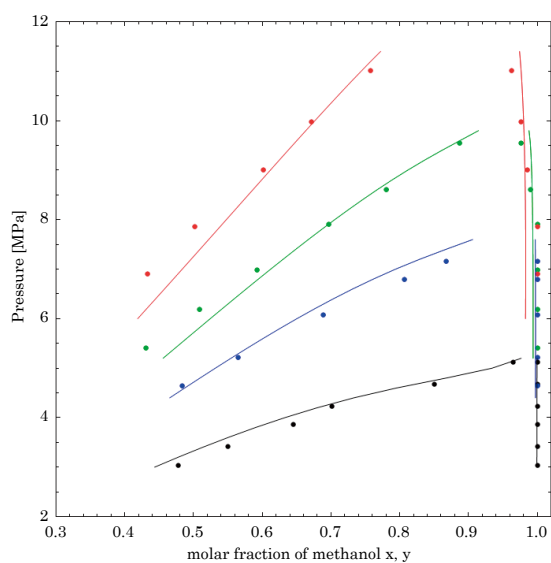


Fig. 5 Vapor-liquid equilibria for methanol + glycerol system calculated by PR-M EOS with conventional mixing rule. (●, ●, ●, ●) Literature data at 493, 523, 543, 573K, respectively²⁾. (—, —, —, —) Calculated results by PR-M EOS with conventional mixing rule at 493, 523, 543, 573K, respectively.

4. Conclusion

The authors proposed a new equation for α function in Peng-Robinson equation. The α function gives strong interaction for glycerol. The vapor-liquid equilibria for methanol + glycerol system are correlated by PR EOS, PR-M EOS, and PR-M-WS. The PR-M EOS with optimized binary interaction parameter greatly enhanced the correlation accuracy both in liquid and vapor phases. In particularly, the correlation accuracy of liquid phase has been further improved by using Wong-Sandler mixing rules. It can be applied to explore the operating conditions in the reactor and the separation process of biodiesel production plants.

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