Vapor-liquid equilibria for methanol + fatty acid methyl ester binary systems near critical temperature of methanol

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ABSTRACT

In biodiesel production processes using supercritical methanol, the phase equilibria for methanol + fatty acid methyl ester systems near the critical temperature of methanol (T_c = 512.6 K) are required as the fundamental data. A flow type method was applied to measure the vapor-liquid equilibria for methanol + fatty acid methyl ester binary systems at 493 – 543 K. The phase behavior was studied by changing the kind of fatty acid methyl esters. The mole fractions of methanol in vapor phase are close to unity for the systems. The present vapor-liquid equilibrium data were correlated by Peng-Robinson Stryjek-Vera equation of state with a modified conventional mixing rule. Inter-molecular parameters in the mixing rule were determined by fitting to the present experimental data obtained in this work. The correlated results are in good agreement with the experimental data.

Keywords: vapor – liquid equilibrium, methanol, fatty acid methyl ester

1. INTRODUCTION

Biodiesel fuel, consisting of fatty acid methyl esters produced by transesterification of vegetable oils with alcohol, has an ability to solve the problem of the fossil fuel limitation. Some techniques for production of the biodiesel have been reported over the last few years. Supercritical methanol has been utilized for the transesterification of the vegetable oils without the catalysts [1– 4]. The methanol used in this process can be recycled after the reaction. The phase equilibria for the mixtures containing methanol and fatty acid methyl esters near the critical point of methanol (T_c = 512.64 K) are highly useful for the design and the optimization of the operation conditions.

To elucidate the phase behavior for the mixtures, the vapor-liquid equilibria for methanol + fatty acid methyl ester systems were measured at 493 – 543 K by a flow method. Methyl laurate and methyl myristate with carbon atom chain lengths C_{12} and C_{14} were focused here. The present vapor-liquid equilibrium data were correlated by Peng-Robinson Stryjek-Vera PRSV equation of state [5] with a modified conventional mixing rule [6].

2. EXPERIMENTAL

2.1 Materials

Methanol, methyl laurate and methyl myristate used in this work were supplied by Wako Pure Chem. Ind. Their purities were checked with a gas chromatograph. The peak area percentages of the main compounds for methanol, methyl laurate and methyl myristate were more than 99.8, 98.0 and 95.0 %, respectively. These materials were used without further purification.

2.2 Apparatus and Procedure

A flow-type apparatus was adopted to avoid thermal decomposition of fatty acid methyl esters and pressure fluctuation caused by sampling. The schematic diagram of the experimental apparatus is shown in **Fig. 1**. The apparatus was quite similar to that used in the previous work [7]. The system was heated to the desired temperature by electric heaters. The mixture of methanol and methyl ester was supplied by a non-pulsating HPLC pump (PUS / PUD, GL sciences) (3). The measurements were performed in the range of the feed rates from 4.15 to 7.40 ml min^{-1} for methanol + methyl laurate system and from 3.90 to 8.10 ml min^{-1} for methanol + methyl myristate system. The phase behavior in an equilibrium cell (11) was observed with a video camera attached to a telescope of 42
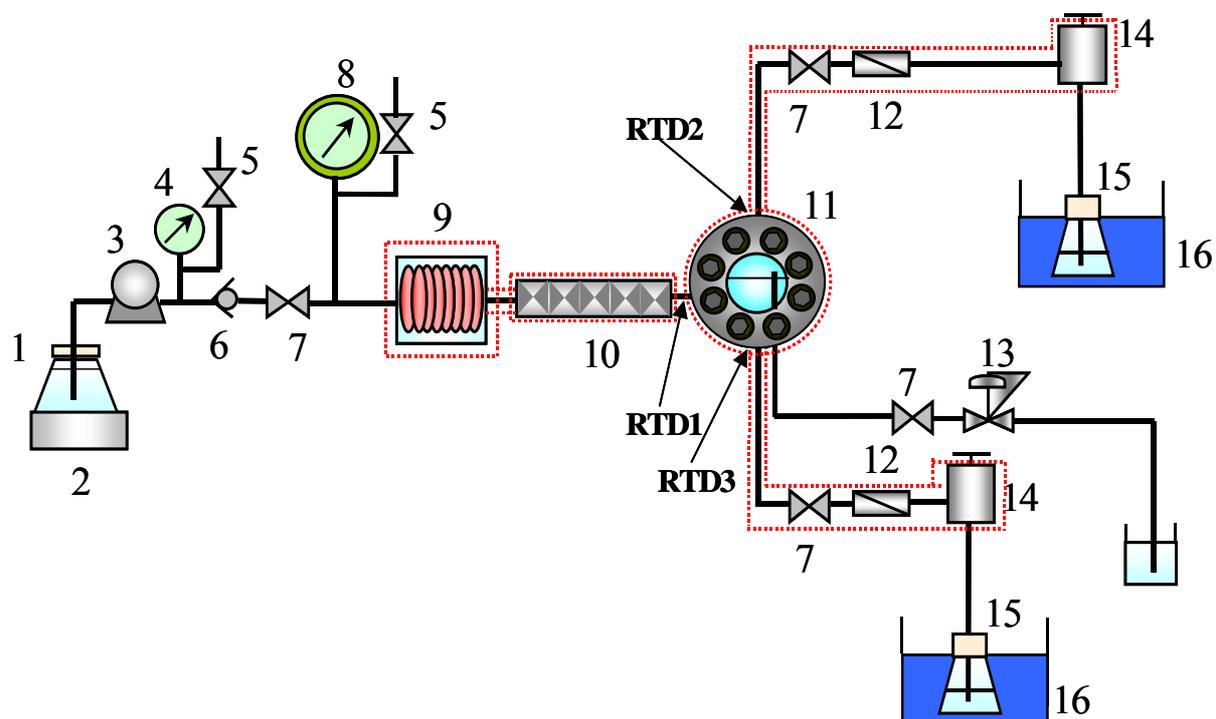
Fig. 1 Schematic diagram of experimental apparatus: (1) methanol + fatty acid methyl ester mixture; (2) electronic balance; (3) feed pump; (4) pressure gauge; (5) safety valve; (6) check valve; (7) stop valve; (8) precision pressure gauge; (9) preheating coil; (10) line mixer; (11) equilibrium cell; (12) filter; (13) back-pressure-regulator; (14) expansion valve; (15) sampling bottle; (16) water bath; (RTD1 – RTD3) resistance temperature detector; (– – –) heater

modifications (CCD-TR3300, SONY). The residence times in the equilibrium cell (11) were about 4.2 to 7.4 min for methanol + methyl laurate system and about 3.8 to 7.9 min for methanol + methyl myristate system. The temperatures of entrance, top and bottom of the cell were controlled within ±0.5 K. The pressure fluctuation was held to ±0.02 MPa. The effluents from vapor and liquid phases were depressurized through expansion valves (14). Samples in vapor and liquid phase were trapped into sampling bottles (15). The compositions in vapor and in liquid phases were analyzed by a gas chromatograph (GC) with a thermal conductivity detector (GC309, GL sciences). It is verified that methyl laurate and methyl myristate were not decomposed during measurement, because no other components were detected in GC analysis.

2.3 Results and Discussion

The experimental results of vapor-liquid equilibria for methanol + methyl laurate and methyl myristate systems at 493 – 543 K are shown in **Figs. 2 and 3**. The mole fractions of methanol in vapor phase at 493 – 543 K are very close to unity for both systems as shown in **Figs. 2 and 3**. **Fig. 4** shows the comparison between vapor-liquid equilibria for methanol + methyl laurate and methanol + methyl myristate systems. The mole fractions of methanol in liquid phase are almost the same for both systems. The mole fractions of methanol in vapor phase for methanol + methyl laurate system at higher pressure are lower than those for methanol + methyl myristate system. The difference of the saturated vapor pressures of both methyl esters may cause the difference of the mole fraction of methanol in vapor phase.

3. CORRELATION

3.1 Peng-Robinson Stryjek-Vera Equation of State

The present vapor-liquid equilibrium data were correlated by Peng – Robinson Stryjek – Vera equation of state (PRSV EOS) [5]. PRSV EOS is given by the followings.

$$p = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2} \tag{1}$$

$$a = 0.457235 \frac{R^2 T_c^2}{p_c} \alpha \tag{2}$$

$$b = 0.077796 \frac{RT_c}{p_c} \tag{3}$$

$$\alpha = \left[1 + \kappa \left\{ 1 - \left(\frac{T}{T_c} \right)^2 \right\} \right]^2 \tag{4}$$

$$\kappa = \kappa_0 + \kappa_1 \left\{ 1 + \left(\frac{T}{T_c} \right)^{0.5} \right\} \left\{ 0.7 - \left(\frac{T}{T_c} \right) \right\} \tag{5}$$

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{6}$$

where p is the pressure, R is the gas constant, T is the temperature and v is the molar volume. The parameters a and b the are the energy and size parameters, respectively. The subscript c denotes the critical properties. ω is the acentric factor, κ_1 is the substance parameter determined by fitting the saturated vapor pressures for pure substance. The critical temperature of methyl myristate and the critical pressures of methyl laurate and methyl myristate were predicted by a group contribution method [8]. The critical properties and substance parameters in PRSV EOS are listed in **Table 1**.

3.2 Mixing Rule

A modified conventional mixing rule [6] and a conventional mixing rule were adopted to the energy and size parameters of the equation of state as given by the following equations.

$$a = \sum_i \sum_j x_i x_j a_{ij} , \quad a_{ij} = \left[1 - k_{ij} + m_{ij}(x_i - x_j)\right]\sqrt{a_i a_j} \tag{7}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} , \quad b_{ij}^{1/3} = (1 - l_{ij}) \frac{b_i^{1/3} + b_j^{1/3}}{2} \tag{8}$$

wehere, k_{ij}, m_{ij} and l_{ij} are the inter-molecular parameter as $k_{ii}=0$, $k_{ij}=k_{ji}$, $m_{ii}=0$, $m_{ij}=-m_{ji}$, $l_{ii}=0$, $l_{ij}=l_{ji}$.

3.3 Results and Discussion

The inter-molecular parameters in the mixing rules were optimized from the present experimental data for methanol (1) + fatty acid methyl ester (2) systems. k_{12} was dependent on temperature, and m_{12} and l_{12} were independent of temperature. The values of these parameters are listed in **Table2**.

The correlated results for methanol + methyl laurate and methanol + methyl myristate systems are shown in **Figs. 2 and 3**. As shown in **Figs. 2 and 3**, the correlated results give good reproductions in vapor and liquid phases at 493 – 543 K.

Table 1 Critical properties and substance parameters in PRSV EOS [5]

Substance	T_c [K]	p_c [MPa]	ω [-]	κ_1 [-]
Methanol	512.64 [9]	8.097 [9]	0.56533 [9]	-0.16816
Methyl laurate	712.15 [10]	1.67 [8]	0.6849 [11]	-0.04289
Methyl myristate	718.1 [8]	1.55 [8]	0.9498 [11]	-0.26522

Table 2 Inter-molecular parameters for methanol (1) + fatty acid methyl ester (2) systems

(2)	k_{12}	m_{12}	l_{12}
Methyl laurate	$2.473 - 0.310 \ln T$	-0.397	0.141
Methyl myristate	$1.874 - 0.213 \ln T$	-0.409	0.134
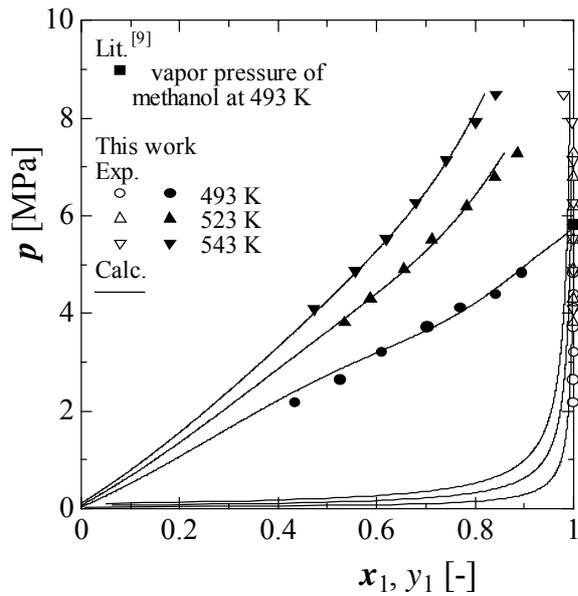
Fig.2 Vapor-liquid equilibria for methanol(1) + methyl laurate(2) system
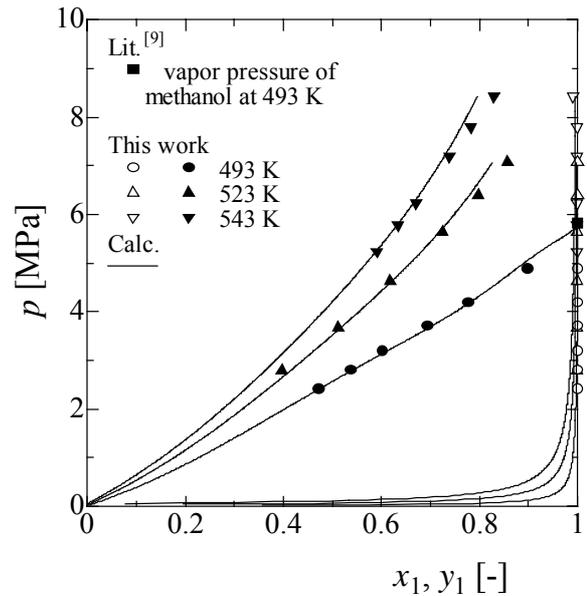
Fig.3 Vapor-liquid equilibria for methanol(1) + methyl myristate(2) system
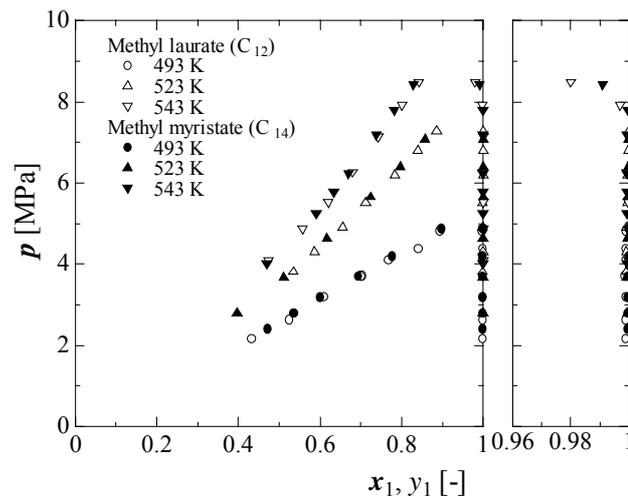
Fig.4 Comparison of vapor-liquid equilibria for methanol(1) + fatty acid methyl ester(2) systems

4. CONCLUSION

The vapor-liquid equilibria for methanol + methyl laurate and methanol + methyl myristate systems were measured at 493 – 543 K by a flow method. The mole fractions of methanol in vapor phase are very close to unity. Therefore, in biodiesel production processes, the phase separation after the transesterification reaction can be performed by only pressure control in order to recycle methanol used in the reaction. The mole fractions of methanol in liquid phase for both binary systems are almost the same at each temperature.

Peng – Robinson Stryjek – Vera equation of state with the modified conventional mixing rule was adopted to correlate the present experimental data for methanol + fatty acid methyl ester systems. Inter-molecular parameters were determined from the experimental data in this work. The correlated results are in good agreement with the experimental data.

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