



Measurement and correlation of ternary vapor-liquid equilibria for methanol + glycerol + fatty acid methyl ester (methyl laurate, methyl myristate, methyl palmitate) systems at elevated temperatures and pressures



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ABSTRACT

The phase behaviors for three ternary systems (methanol + glycerol + methyl laurate/methyl myristate/methyl palmitate) were studied at elevated temperatures (about 493.0 K, 523.0 K) and pressures by a flow-type method. The results demonstrated that the mole fractions of methanol in liquid phase increase and the mole fractions of glycerol and FAME decrease with increasing pressure. The influences of FAME molecular chain length on mutual solubility between methanol, glycerol and FAME in vapor phase were discussed. The experimental data were regressed by Redlich-Kwong-Soave equation of state (RKS EOS), RKS EOS combined with Boston and Mathias function (RKS-BM EOS) and Redlich-Kwong-Soave Aspen equations of state (RKS-Aspen EOS) with van der Waals (vdW) mixing rule. The correlated results with RKS-Aspen EOS are more accurate than other EOSs. The vapor-liquid equilibria (VLE) experimental data can be employed for designing the methanol process and phase separation in biodiesel production technology.

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1. Introduction

Biodiesel is considered as an alternative diesel fuel for traditional fuel due to its renewable and environmental benefits, such as biodegradable, nontoxic, low emission and renewable. The most usual technology for biodiesel production is transesterification, which was defined as the reaction of various oils (such as vegetable oil, animal fats or waste oil) with alcohol. The product of transesterification was biodiesel (fatty acid alkyl esters, FFAE) and glycerol [1]. All of these oils are composed by triacylglycerols, minor amounts mono and diacylglycerols and free fatty acids in refined progress. Alcohols can be methanol, ethanol, 1-propanol, 1-butanol. Among the alcohols, transesterification yield was decreased in the order: methanol > ethanol > 1-propanol > 1-butanol as reported in the literature [2]. So, methanol is the most frequently and widely used.

The transesterification reaction has been developed using alkaline and acidic catalysts in previous research. Recently, Saka and Kusdiana [3] firstly reported a supercritical methanol transesterification without catalyst. The separation of the products and the catalysts was not needed. Moreover, supercritical methanol method is an environmentally friendly technology in biodiesel production process. Many scholars pay great attention to its excellent performances including shorter reaction time, non-catalysts and simpler separation process. In recent years, a continuous transesterification process of vegetable oil using supercritical methanol was designed by He et al. [4]. Wang et al. [5] have made focus on methanol recovery through flash evaporation in continuous production of biodiesel via supercritical methanol. Continuous transesterification process is a great progress for the industrialized development of biodiesel with supercritical methanol method, among which, the phase separation of products (fatty acid methyl esters, FAME and glycerol) and methanol is very important. It is crucial to know the phase behavior of the reaction mixtures for detailed process design.

Up to now, some researchers have reported the phase equilibria studies of some binary systems near supercritical temperature of

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methanol. Tang [6], Glisic [7] and Hegel [8] reported VLE data of methanol + triglycerides systems. Shimoyama's group [9,10] measured the VLE of methanol + glycerol/methyl laurate/methyl myristate systems. The phase equilibria data for methanol + C18 methyl esters at 523–573 K in the pressure ranges of 2.45–11.45 MPa were reported by Fang [11]. However, only Fang et al. [12] measured the phase equilibria data for ternary system (methanol + C18 FAME + α -tocopherol) at high temperatures and pressures. Therefore, the experimental VLE data of the relevant systems including methanol, glycerol and FAME are still severely insufficient for the detailed design and operation of the biodiesel production process with methanol.

In this work, an apparatus was designed and manufactured for measuring the vapor-liquid phase behavior at elevated temperatures and pressures by our research group. And a flow-type method was used to measure VLE data of three ternary systems (methanol + glycerol + methyl laurate/methyl myristate/methyl palmitate) at elevated temperatures and pressures. The experimental VLE data were correlated using the Redlich-Kwong-Soave equation of state [13] (RKS EOS), RKS EOS combined with Boston and Mathias function [14] (RKS-BM EOS) and Redlich-Kwong-Soave-Aspen equations of state [15] (RKS-Aspen EOS). The van der Waals (vdW) [16] mixing rule with EOSs was used to regress the experimental data.

2. Experimental section

2.1. Materials

The suppliers and purities of the materials used in this work were listed in Table 1. Their purities were checked by a gas chromatography. These chemicals were adopted without further purification.

2.2. Apparatus and procedure

A vapor-liquid phase equilibria apparatus was designed and manufactured by our research group, and the schematic diagram is presented in Fig. 1. The preheater, high pressure liquid circulating pump (HPCP) and equilibria cell are the major components of this apparatus. The phase behavior inner the equilibria cell can be discerned through two sapphire glass windows. A detailed description of the equilibria cell was given in our previous work [17,18]. In this study, the thermocouples and pressure transducer in the apparatus were recalibrated.

First of all, the binary mixtures of glycerol and FAME with the mole fraction (0.25, 0.50, 0.75) of glycerol were made. Suitable amounts of methanol were added into the binary mixtures until the ternary mixtures (methanol, glycerol and FAME) become one phase. Different amounts of methanol were loaded into 200 ml ternary mixtures in order to get different initial feed compositions.

The preheater and equilibria cell were heated to the specified temperature firstly. The feed was pumped into the preheater by HPCP with keeping the valve 8 and 9 closed. The HPCP and valve 4 were closed when the liquid level reached to the middle of the

equilibria cell, which can be seen through the sapphire glass window. After the temperature and pressure of the equilibria cell were stable, the valve 4 and pump were opened. The pressure of the system was maintained stable by adjusting the valve 8 and 9 and the flow rate of pump. In order to keep the phase interface stable and avoid entrainment happening, the flow rate of HPCP is restricted to the range of 0.60–1.5 ml/min. After the temperature and pressure of the system have been well stabilized for 30 min, the position of the phase interface was also well stabilized. Then the samples of vapor and liquid phase were trapped into 10 ml sample bottles every 10 min for 1 h. The temperature of the system were measured by two thermocouples with the accuracy of 0.4%. The average of the two thermocouples was used as the temperature of the systems. The fluctuation of pressure was controlled within ± 0.025 MPa. The sample bottles were cooled in ice-water bath to prevent methanol volatilization. The compositions of samples were analyzed by gas chromatograph with a hydrogen flame detector (GC1100) using OV-17 capillary column (50 m \times 0.32 mm \times 0.1 μ m). The temperature of sample injector, detector and column were 280 $^{\circ}$ C, 300 $^{\circ}$ C and 230 $^{\circ}$ C, respectively. Every sample was analyzed at least three times to insure the accuracy, and the uncertainties of the mole fractions were ± 0.002 .

3. Model

The experimental VLE data were regressed by the RKS EOS [13], RKS-BM EOS [14] and RKS-Aspen EOS [15]. The equations of state are shown by the following expressions:

RKS EOS

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

$$\text{With } a(T) = 0.42747 \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (2)$$

$$\alpha(T) = \left[1 + \left(0.48508 + 1.551714\omega - 0.15613\omega^2 \right) \left(1 - \left(\frac{T}{T_c} \right)^{0.5} \right) \right]^2 \quad (3)$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (4)$$

RKS-BM EOS

Boston and Mathias [14] (BM) modified the temperature dependent function $\alpha(T)$ in attractive force parameter, and combined the new $\alpha(T)$ with RKS EOS. The modified $\alpha(T)$ item is pressed as following:

$$\alpha(T) = \left[\exp \left[c \left(1 - \left(\frac{T}{T_c} \right)^d \right) \right] \right]^2 \quad (5)$$

$$d = 1 + \frac{0.37464 + 1.54226\omega - 0.26992\omega^2}{2} \quad (6)$$

$$c = 1 - \frac{1}{d} \quad (7)$$

where p is the pressure (Pa), V is the molar volume ($\text{m}^3 \cdot \text{mol}^{-1}$), T is the temperature (K), R is the gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). The

Table 1
Suppliers and purities of the used chemicals.

Chemical	Purity	Supplier
Methanol	>99.8 wt%	Tianjin Guangfu
Glycerol	>99.5 wt%	Tianjin Guangfu
Methyl laurate	>99.0 wt%	Tianjin Guangfu
Methyl myristate	>98.0 wt%	Shanghai Jingchun Scientifical Co., Ltd.
Methyl palmitate	>97.0 wt%	Shanghai Jingchun Scientifical Co., Ltd.

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