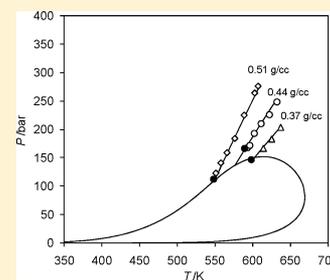


# Prediction of Volumetric Data in Supercritical Reactors

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**ABSTRACT:** Pressure-intensified processes are characterized by handling mixtures whose density is highly dependent on the operating conditions. In addition, fluid behavior in this type of equipment is clearly nonideal. Therefore, the frequent assumption of ideal mixing for calculating the mixture density is inaccurate. Prediction of volumetric information on mixtures is important for the design of continuous supercritical reactors and other process equipment such as heat exchangers, high-pressure pumps, compressors, etc. The isochoric method is a simple and reliable procedure to measure mixture densities and find conditions of homogeneous operation of supercritical chemical reactors at high temperature and pressure. Moreover, it also provides  $PvT$  properties simultaneously. It is well-known that the two-parameter equations of state (2P-EoS), like Soave–Redlich–Kwong or Peng–Robinson, have limitations to describe accurately the  $PvT$  properties of different fluids together with the phase transitions. The three-parameter RK-PR equation of state (3P-EoS), known as the generalized Redlich–Kwong–Peng–Robinson, is able to correlate and predict volumetric properties of size-asymmetric mixtures. In this work, RK-PR, coupled with the standard quadratic mixing rules, is used to model volumetric experimental data of nonreacting size-asymmetric binary systems. Moreover, on the basis of that modeling, we predict volumetric properties of reacting mixtures in the context of supercritical biodiesel production.



## 1. INTRODUCTION

Volumetric properties play an important role in the design of continuous supercritical reactors. Because composition, pressure, and temperature highly affect the density of a mixture near the critical region, it becomes a critical variable for proper reactor operation control. Moreover, many practical applications require homogeneous conditions to achieve the main advantages of supercritical reactors. For instance, it has been shown that homogeneous operation can highly enhance reaction rate and control of the selectivity, allowing important intensification of these high-pressure reactors. Velez et al.<sup>1</sup> have shown the convenience of using indirect methods, because the direct observation of the reacting system may result in technical difficulties. They showed that the isochoric method gives a very simple and robust experimental procedure for detecting phase transitions in complex reacting systems. In addition to phase envelope diagrams, the method provides  $PvT$  data for the reactants and products mixtures needed for the design of supercritical reactors. Their results can be directly applied to the selection of pressures and temperatures that guarantee homogeneous conditions for different reactions. This methodology can also be used to select cosolvents for the operation of reactors in the supercritical region.

In 1994, the group of Prof. Kenneth Hall published in this Journal,<sup>2</sup> based on the Ph.D dissertation of Yurttas,<sup>3</sup> the development of a semiautomated isochoric apparatus. They showed that the apparatus can be used to measure not only  $PvT$  properties but also vapor pressures for pure components and phase boundaries of mixtures. Because Prof. Hall's main studies involved natural gas mixtures, his contribution dealt with high pressures but moderate to cryogenic temperatures. In the isochoric method, a sample of known mass and composition is

introduced in a constant volume cell and the variation of pressure with temperature is recorded. When the system is homogeneous, the known feed density at the corresponding temperatures and pressures is obtained. As said before, the method can also provide an indirect way to determine the conditions of phase transition (bubble or dew points) of a mixture from the intersection of the pressure versus temperature isochoric straight lines<sup>2</sup> of the heterogeneous and homogeneous phase regions. Since the 1970s, Prof. Hall has been publishing novel applications of the isochoric method, taking full advantage of a simple theory to acquire useful information for the natural gas processing field. Besides many contributions on  $PvT$  and vapor–liquid equilibrium (VLE) measurements, more recently, in 2013, he reported a new methodology for determining residual energies and entropies for fluid samples,<sup>4</sup> based on isochoric and isothermal data. In summary, Prof. Hall honors with these contributions the fact that “there is nothing more practical than a good theory” (quoting L. Boltzmann).

In a pioneer contribution in 1975, Prof. Kenneth Hall and co-workers<sup>5</sup> proposed for the first time the method of intersecting isochores as a new technique for collecting binary VLE data without sampling. In the scope of this work, Prof. Hall highlighted that the most vexing experimental problem in VLE studies is sampling the phases for composition analysis. Those of us working in the development of pressure-intensified technologies know that, even more than 40 years later, this

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statement is still valid. Problems to obtain representative samples are many: fractionation and absorption in lines, adsorption in interfaces, plugging due to precipitation, and changing the equilibrium by sampling. These troubles become even more difficult to overcome when dealing with highly asymmetric systems, like those typical of supercritical technologies.

It is not within the scope of this work to review the pros and cons of the well-known synthetic methods. Besides the direct observation, which shows limitations for extreme condition experiments, there are many alternatives for detecting phase transitions at high temperature and pressure. In nonvisual methods other physical properties can be monitored. In fact, changes in X-ray transmission (instead of visible light), relative dielectric permittivity, sound speed, acoustic echo signal, or isochoric heat capacity are the basis for new phase detection. Also, if either the total volume of a variable-volume cell or the system density can be measured accurately, the appearance of a new phase can be obtained from the abrupt change in the slope on the pressure–density line.<sup>6–8</sup> Nevertheless, none of these methods are as simple, fast, and inexpensive as the isochoric method, which only needs instruments to sense temperature and pressure.

Of course, for design purposes, it is always desired to have a predictive tool for simultaneous modeling  $PvT$  and phase transitions. The high-pressure condition calls for the use of equations of state (EoS). Barrufet and Eubank<sup>9</sup> were the first to propose the use of isochoric lines to set constraints for developing fluid mixture EoS and tuning mixture combining rules. On the other hand, Cismondi and Mollerup<sup>10</sup> showed that the limitations of classic cubic equations of state (CEoS), like Soave–Redlich–Kwong<sup>11</sup> or Peng–Robinson,<sup>12</sup> are a consequence of their two-parameter density dependence rather than of their empirical character. It is a well-known feature of two-parameter cubic equations of state (2P-EoS) that the critical compressibility factor ( $Z_c$ ) is a characteristic constant of each model. In addition, a 2P-EoS will predict a unique universal  $PvT$  behavior for all fluids in terms of reduced variables, like in the corresponding state theory, which is not in agreement with the properties of real fluids. An extra degree of freedom given by a third parameter, generalizing for instance the attractive term of a CEoS, makes the equation be compound-specific and able to model  $PvT$  properties. On the basis of this fact, the authors generalized and compared several CEoS, putting special emphasis on volumetric properties of pure fluids. As a consequence, they were able not only to reproduce densities but also show that the improvement on volumetric properties gained from a 3P approach is associated with an improvement on the correlative and predictive capabilities for phase equilibria calculations in asymmetric systems. It is important to highlight that, regarding asymmetric systems, the authors state that the van der Waals repulsive term might be more able to follow the global  $PvT$  behavior of real fluids than the Carnahan–Starling (CS) repulsive term, when combined with the generalized van der Waals simple attractive contribution. However, the authors note that this does not mean that a more complex density dependence could be found for the attractive term, such that combined with the CS repulsive term would lead to better results. This is likely to be the case of the SAFT equations using the CS term.<sup>13,14</sup> Cismondi and Mollerup<sup>10</sup> showed that, among all the evaluated cubic three-parameter density dependence, the generalized Redlich–Kwong–Peng–Robinson (RK-PR) equation offers

the best performance. Interestingly, Prof. Hall also evaluated this model just after it was developed.<sup>15</sup> The authors concluded that RK-PR is a more accurate alternative to traditional cubic and to complex molecular-based EoS like PC-SAFT. In this contribution, synthetic mixtures of light gases were studied, and they highlighted the ability to correlate and predict volumetric and VLE data, considering RK-PR simplicity.

In summary, the aim of this work is to challenge RK-PR to fully predict density of mixtures based on the fitting of pure compound and binary interaction parameters to (1) vapor pressure and saturated liquid density data and (2) binary mixture saturation points, respectively. The latter ensures that the model correctly follows the phase transition, as needed in the design of supercritical reactors. First, we will show results on nonreacting binary mixtures; second, we will apply the model for predicting the behavior of a supercritical reactor used to carry out the transesterification of sunflower oil.

## 2. RK-PR EQUATION OF STATE

In this work, we choose the RK-PR cubic equation of state because of its simplicity and proven accuracy to represent volumetric properties. The three-parameter cubic equation of state<sup>10</sup> is as follows:

$$P = \frac{RT}{\nu - b} - \frac{a}{(\nu + \delta_1 b) \left( \nu + \frac{1 - \delta_1 b}{1 + \delta_1 b} \right)} \quad (1)$$

and

$$a = a_c \left( \frac{3}{2 + T/T_c} \right)^k \quad (2)$$

where  $P$  is the pressure,  $R$  the universal gas constant,  $T$  the temperature,  $\nu$  the molar volume,  $b$  the repulsive parameter,  $a$  the attractive parameter,  $\delta_1$  the third parameter in RK-PR,  $a_c$  the critical attractive parameter of pure compound,  $T_c$  the critical temperature of pure compound, and  $k$  a pure compound parameter that influences the temperature dependence of the attractive parameter. The RK-PR model matches the critical temperature ( $T_c$ ) and critical pressure ( $P_c$ ), and also a vapor pressure data point of the pure compound, while leaving one degree of freedom for the adjustment of volumetric properties. The third parameter can be calculated so the equation reproduces the critical compressibility ( $Z_c$ ), or it can also be fitted to give a better agreement at high densities (approach followed in this work). Cubic equations of state allow for the explicit calculation of  $a_c$  and  $b$  once the third parameter is obtained (see Mollerup and Michelsen<sup>16</sup>). In the RK-PR equation, the fitted  $Z_c$  is related to  $\delta_1$  by the following equation:

$$Z_c = \frac{y}{3y + d_1 - 1} \quad (3)$$

where  $d_1$  and  $y$  are intermediate variables:

$$d_1 = \frac{1 + \delta_1^2}{1 + \delta_1} \quad (4)$$

$$y = 1 + [2(1 + \delta_1)]^{1/3} + \left( \frac{4}{1 + \delta_1} \right)^{1/3} \quad (5)$$

The repulsive parameter and the critical value of the attractive parameter are calculated as follows:

**Table 1.** Pure Compound Critical Properties,<sup>18</sup> RK-PR Parameters, and Percent Average Relative Deviations (ARD%) in Vapor Pressure and Saturated Liquid Density

compound	$T_c$ (K)	$P_c$ (bar)	$a_c$ (barm <sup>6</sup> ·kmol <sup>-2</sup> )	$b$ (lt·mol <sup>-1</sup> )	$\delta_1$	$k$	ARD% <sup>a</sup>	
							$P$	$\rho$
<i>n</i> -octadecane	747	12.7	148.3381	0.3388	3.8180	3.6483	6.49	4.73
naphthalene	748.4	40.5	44.3276	0.1167	2.6961	2.2593	4.32	3.32
methyl oleate	764	12.8	152.0987	0.3514	3.5457	4.3953	11.74	4.83
methanol	512.5	80.8	11.1283	0.0355	4.1596	2.7827	3.28	6.23
glycerol	850	75	31.0529	0.0709	2.8126	3.2164	13	3.47

<sup>a</sup>Deviations in the range of 350 K up to each critical point.

$$b = \Omega_b \frac{RT_c}{P_c} \quad (6)$$

$$a_c = \Omega_a \frac{(RT_c)^2}{P_c} \quad (7)$$

where  $\Omega_a$  and  $\Omega_b$  are functions of the third parameter:

$$\Omega_a = \frac{3y^2 + 3yd_1 + d_1^2 + d_1 - 1}{(3y + d_1 - 1)^2} \quad (8)$$

$$\Omega_b = \frac{1}{3y + d_1 - 1} \quad (9)$$

Finally, in this contribution, we apply the RK-PR EoS to mixtures using the well-known quadratic mixing rules (QMRs) with the classical combination rules:<sup>17</sup>

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij} \quad (10)$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad (11)$$

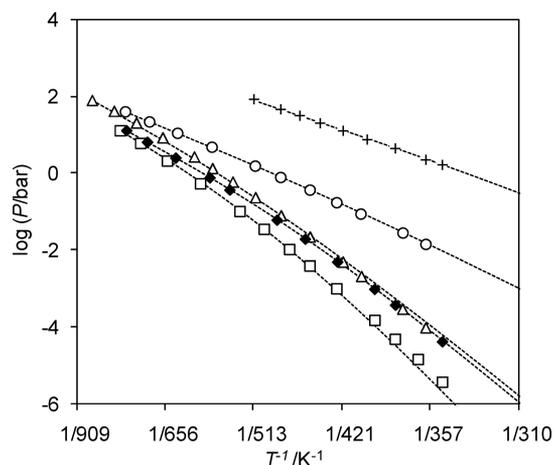
$$b = \sum_{i=1}^N \sum_{j=1}^N x_i x_j b_{ij} \quad (12)$$

$$b_{ij} = (1 - l_{ij}) \frac{b_i + b_j}{2} \quad (13)$$

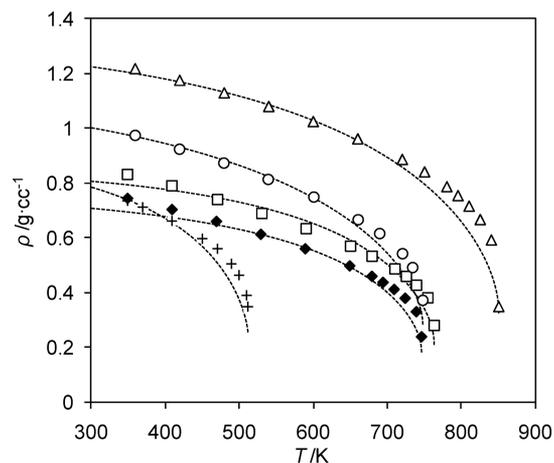
where  $N$  is the number of components in a multicomponent mixture;  $i$  and  $j$  are the components of the mixture, and  $x_i$  and  $x_j$  the mole fraction of each component. Parameters  $k_{ij}$  and  $l_{ij}$  are the attractive binary interaction parameter and the covolume binary interaction parameter, respectively. On the other hand, a linear mixing rule is set for the third parameter  $\delta_1$  ( $\sum_{i=1}^N x_i \delta_i$ ).

### 3. RESULTS AND DISCUSSION

**3.1. Pure Compound Modeling.** Pure compound parameters of the RK-PR EoS were fitted against experimental vapor pressures and saturated liquid densities. The fitted parameters are  $k$  and  $\delta_1$ , while  $a_c$  and  $b$  are calculated with the explicit expressions provided in the previous section. Table 1 reports the parameters corresponding to each compound, together with the percent average deviations in vapor pressure and liquid density compared with those given in the DIPPR database.<sup>18</sup> Figures 1 and 2 show the accuracy of RK-PR to correlate vapor pressure and saturated liquid density of all the compounds under study in this work.



**Figure 1.** Vapor pressure of *n*-octadecane (◆), naphthalene (○), methyl oleate (□), methanol (+), and glycerol (△). Symbols: experimental data.<sup>18</sup> Dashed lines: RK-PR correlations.



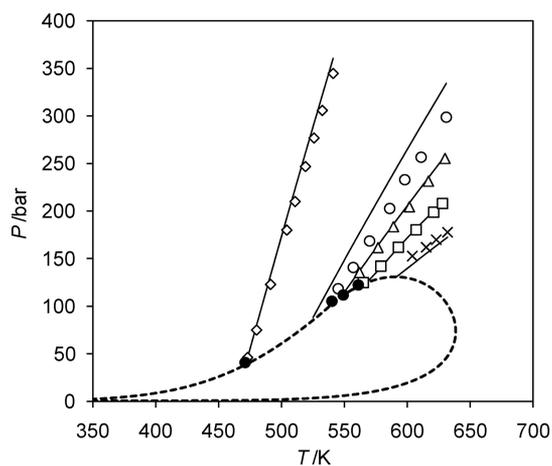
**Figure 2.** Saturated liquid density of *n*-octadecane (◆), naphthalene (○), methyl oleate (□), methanol (+), and glycerol (△). Symbols: experimental data.<sup>18</sup> Dashed lines: RK-PR correlations.

**3.2. Binary Nonreactive Mixtures.** Velez et al.<sup>1</sup> used the isochoric method to acquire  $PvT$  data of three nonreactive binary mixtures of methanol with *n*-octadecane, naphthalene, and methyl oleate. On the basis of the change of slope of the pressure–temperature line, at constant density, the authors also reported the phase transition conditions, above which the system is homogeneous. The experiments were carried out in the range of 0.25–0.6 g·cc<sup>-1</sup> and up to 650 K. As we mentioned in the Introduction, RK-PR binary interaction parameters were fitted only to the phase transition points. Table 2 reports the binary interaction parameters and summarizes the pressure

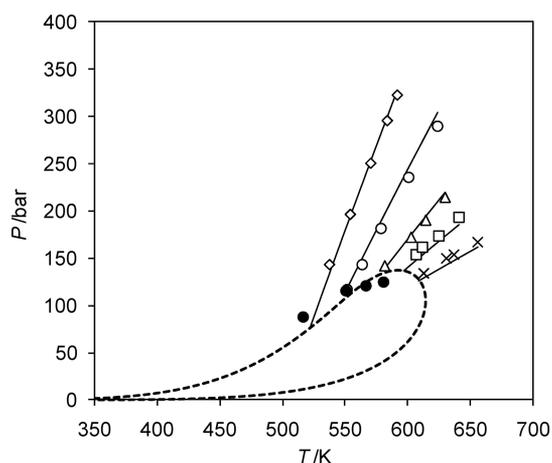
**Table 2.** RK-PR Binary Interaction Parameters Correlated with Phase Transition (PT) Points; Percent Average Relative Deviations in Pressure, ARD( $P$ )%, of Correlated and Predicted Experimental Data<sup>1</sup>

compound				PT correlation		$PvT$ prediction	
1	2	$k_{12}$	$l_{12}$	ARD( $P$ )%		ARD( $P$ )%	
methanol	<i>n</i> -octadecane	0.21	0.33	2.09		5.85	
methanol	naphthalene	0.25	0.35	8.77		3.29	
methanol	methyl oleate	0.162	0.38	2.9		2.77	

deviations in phase transition points and  $PvT$  data for each binary system. Figures 3–5 depict the correlation together with

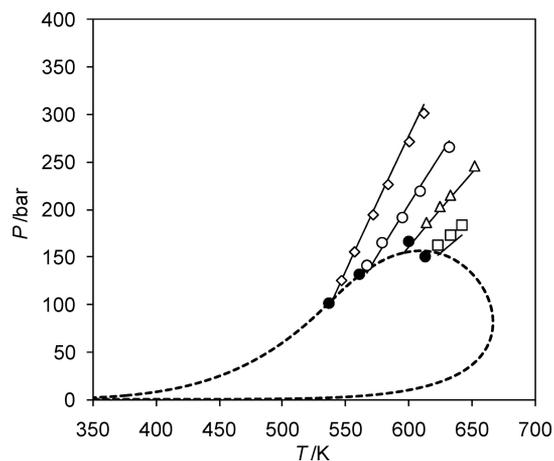


**Figure 3.**  $PvT$  data and phase transition points (●) of methanol + *n*-octadecane binary mixture (11.9:1 molar ratio) at 0.27 g·cc<sup>-1</sup> (x), 0.33 g·cc<sup>-1</sup> (□), 0.38 g·cc<sup>-1</sup> (△), 0.44 g·cc<sup>-1</sup> (○), and 0.60 g·cc<sup>-1</sup> (◇). Symbols: Experimental data.<sup>1</sup> Dashed line: RK-PR correlation. Solid lines: RK-PR prediction.



**Figure 4.**  $PvT$  data and phase transition points (●) of methanol + naphthalene binary mixture (6:1 molar ratio) at 0.22 g·cc<sup>-1</sup> (x), 0.29 g·cc<sup>-1</sup> (□), 0.37 g·cc<sup>-1</sup> (△), 0.48 g·cc<sup>-1</sup> (○), and 0.57 g·cc<sup>-1</sup> (◇). Symbols: Experimental data.<sup>1</sup> Dashed line: RK-PR correlation. Solid lines: RK-PR prediction.

the prediction of the isochores reported by Velez et al.<sup>1</sup> in the homogeneous region. As can be seen, based on phase transition correlation, RK-PR predicts accurately the volumetric data of the studied asymmetric-mixtures.



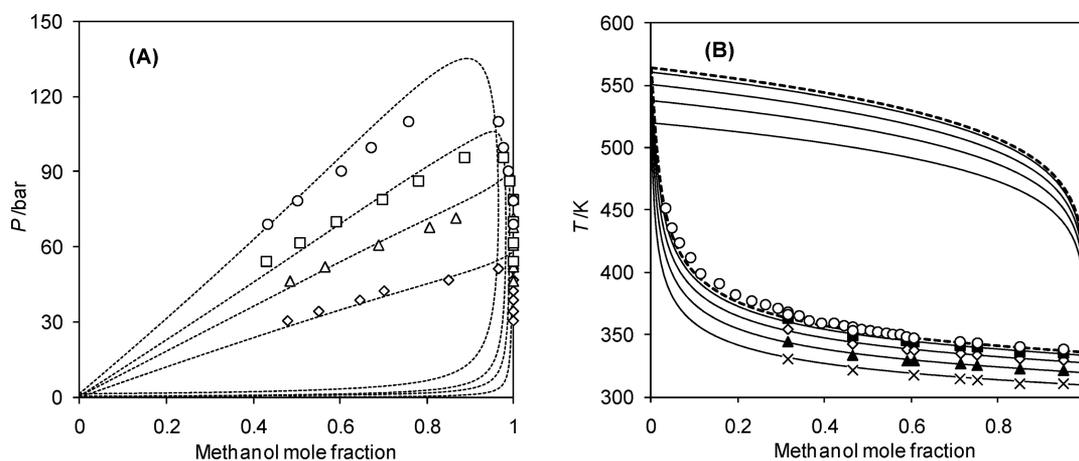
**Figure 5.**  $PvT$  data and phase transition points (●) of binary methanol + methyl oleate mixture (12.4:1 molar ratio) at 0.29 g·cc<sup>-1</sup> (□), 0.37 g·cc<sup>-1</sup> (△), 0.44 g·cc<sup>-1</sup> (○), and 0.51 g·cc<sup>-1</sup> (◇). Symbols: Experimental data.<sup>1</sup> Dashed line: RK-PR correlation. Solid lines: RK-PR prediction.

### 3.3. Modeling Sunflower Oil Transesterification Reactive Mixture.

Biodiesel production has grown rapidly over the past decade because it is an attractive replacement or additive for petroleum diesel. It is compatible with existing diesel engines, reduces GHG emissions, and is biodegradable. Biodiesel is a mixture of fatty acids alkyl esters commonly derived from the transesterification of refined vegetable oils with methanol or ethanol in the presence of an alkali or acid catalyst.<sup>19</sup> Moreover, recent interest in using alternative feedstock, such as crude vegetable oils or waste cooking oils, has grown considerably because of the high cost of using refined edible vegetable oils.<sup>20</sup> The noncatalytic supercritical alcohol technology for the processing of low-quality feedstocks has been under study during the past decade and has been shown to be a feasible alternative for economic biodiesel production.<sup>21</sup> The supercritical transesterification of lipids is a viable technology that has less impact on the environment, reduces the volume of water in the purification steps after the reaction, and allows the processing of low-cost oils because it is not affected by the presence of water and free fatty acids.<sup>22,23</sup>

The reaction takes place between 553 and 623 K. However, the conversion is not complete near the lower bound and the products undergoes thermal degradation above the upper bound.<sup>24</sup> It is known that when the alcohol:oil ratio changes from 10:1 to 40:1, the reaction conversion increases; however, the change from 40:1 to 70:1 has no significant effects.<sup>25</sup> It is noteworthy that the maximum temperature, the methanol content, and residence time affect in combination the biodiesel yield because of thermal degradation, i.e., at a given temperature and lower methanol content, the residence time should be lower to avoid unwanted products. In this regard, Velez et al.<sup>26,27</sup> measured  $PvT$  data of reacting mixtures made up of sunflower oil with methanol in the 553–660 K temperature range, 100–320 bar pressure range, and alcohol-to-oil molar ratio (MR) of 25 and 40. They show that the yield toward biodiesel is between 75 and 90% when the MR is 25, while the yield is above 90% when MR is 40. These experiments were carried out for 3–4 h, the time required to equilibrate each recorded  $PvT$  data point.

Velez et al.<sup>28</sup> also studied the continuous supercritical transesterification of sunflower oil. The residence time in a continuous reactor depends on the volumetric flow rate over



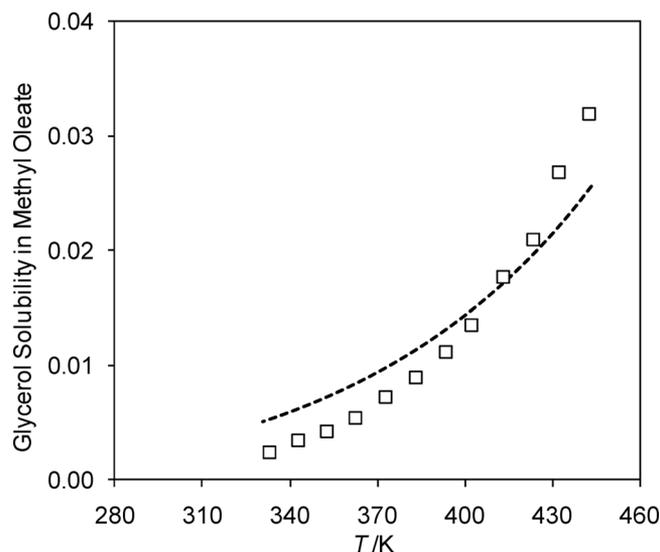
**Figure 6.** Vapor–liquid equilibrium for methanol + glycerol ( $k_{12} = -0.01$  and  $l_{12} = 0.03$ ). (A) Isothermal VLE data:<sup>31</sup> 493 K ( $\diamond$ ), 523 K ( $\triangle$ ), 543 K ( $\square$ ), 573 K ( $\circ$ );  $\text{ARD}(P) = 6.54\%$ . (B) Isobaric VLE data:<sup>32,33</sup> 1 bar ( $\circ$ ), 0.9 bar ( $\blacksquare$ ), 0.7 bar ( $\diamond$ ), 0.5 bar ( $\blacktriangle$ ), 0.3 bar ( $\times$ );  $\text{ARD}(T) = 0.52\%$ . Dashed lines: RK-PR correlation. Solid lines: RK-PR prediction.

the reactor volume. In this sense, the reacting mixture specific volume at the operating pressure, temperature, and composition plays a very important role in supercritical reactors. This parameter has been overestimated in most cases in the open literature. Velez et al.<sup>28</sup> showed the impact of using pure component density and ideal mixing hypothesis to estimate the system volumetric properties. Depending on reaction temperature, errors in the reactive mixture residence time can reach 65%.<sup>28</sup> Considering that the reaction conversion is almost complete<sup>29,30</sup> at temperatures higher than 560 K and the modeled  $PvT$  data is at higher temperatures, we model the reactive system assuming that the mixture comprises only the reaction products (data with high excess of methanol, i.e., alcohol to oil MR of 40). This is a ternary mixture containing biodiesel, glycerol, and the excess of methanol. It is important to highlight that the main constituent of the sunflower oil is the  $C_{18}$  fatty acids; consequently, the biodiesel will be mainly methyl oleate, which was modeled in the previous section. To assess the reactive mixture, additional binary interaction parameters are needed for the binaries of methanol + glycerol and glycerol + methyl oleate. Figures 6 and 7 show the model performance for each additional binary, both correlation and prediction. Interaction parameters and average deviation are reported in the figure captions. RK-PR correlation of the binary glycerol + methyl oleate is not as accurate as that of the glycerol + methanol. Notably, the solubility of glycerol in methyl oleate increases 1 order of magnitude in the temperature range of Figure 7. We can improve the accuracy of the model using temperature-dependent  $k_{ij}$ ; nevertheless, we prefer keeping the same approach of the other binaries so the model extrapolation is safer.

Finally, Figure 8 depicts RK-PR accuracy to predict the phase transition boundary of the reactive system and the volumetric properties for the data discussed earlier, which show a high yield toward biodiesel, i.e., a mixture of methanol and sunflower oil (MR of 40) fed to an isochoric reactor, more often called batch reactors. The model predicts with high accuracy the data measured with the isochoric method.

#### 4. CONCLUSIONS

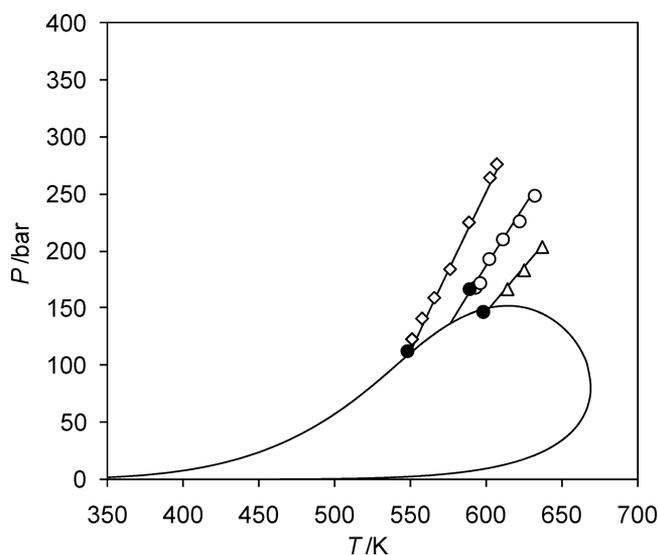
The design of supercritical reactors calls for knowledge on the boundary of homogeneous regions of reactive system and volumetric properties. As is well-known, volumetric properties



**Figure 7.** Solubility of glycerol in methyl oleate ( $k_{12} = 0.177$  and  $l_{12} = 0.32$ ); average absolute deviation in molar fraction  $\text{AAD}(x) = 2.65 \times 10^{-3}$ . Symbols: Experimental data.<sup>34</sup> Dashed line: RK-PR correlation.

are very sensitive to operating conditions and compositions in the near critical region. Therefore, accurate prediction of volumetric properties is needed, not only for the direct and obvious calculation of mixture residence time but also because transport property correlations usually request volumetric properties as well. Measurement of volumetric properties under extreme conditions may require very expensive equipment. Nevertheless, the underutilized isochoric method is a simple and inexpensive experimental procedure for detecting phase transitions in complex reacting and nonreacting systems. It is criticized for its low accuracy for both the phase transition and the volumetric data. However, the uncertainties that we have found are far below the security margins that are used for designing high-pressure equipment.

To model isochoric data, we choose the RK-PR EoS because it was particularly well-suited for modeling volumetric properties. In this work we show with several nonreactive asymmetric binary systems that RK-PR is able to accurately predict  $PvT$  data based on the correlation of a few experimental points of phase transition. Moreover, we also study a reactive system



**Figure 8.**  $PvT$  data and phase transition points (●) of the binary reactive mixture methanol + sunflower oil (40:1 molar ratio) at  $0.37 \text{ g}\cdot\text{cc}^{-1}$  ( $\Delta$ ),  $0.44 \text{ g}\cdot\text{cc}^{-1}$  ( $\circ$ ),  $0.51 \text{ g}\cdot\text{cc}^{-1}$  ( $\diamond$ );  $\text{ARD}(P) = 2.91\%$ . Symbols: Experimental data.<sup>26</sup> Solid lines: RK-PR predictions.

based on the catalyst-free transesterification of sunflower oil. Again, based on binary equilibrium data correlation, RK-PR was also able to predict volumetric properties of a multicomponent system.

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### Notes

The authors declare no competing financial interest.

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