Abstract—This study presents three different approaches to estimate bubble point pressures for the binary system of CO₂ and ethyl palmitate fatty acid ethyl ester. The first method involves the Peng-Robinson (PR) Equation of State (EoS) with the conventional mixing rule of Van der Waals. The second approach involves the PR EOS together with the Wong-Sandler (WS) mixing rule, coupled with the UNIQUAC GE model. In order to model the bubble point pressures with this approach, the volume and area parameter for ethyl palmitate were estimated by the Hansen group contribution method. The last method involved the Peng-Robinson, combined with the Wong-Sandler method, but using NRTL as the GE model. Results using the Van der Waals mixing rule clearly indicated that this method has the largest errors among all three methods, with errors in the range of 3.96-6.22%. The PR-WS-UNIQUAC method exhibited small errors, with average absolute deviations between 0.95 to 1.97 percent. The PR-WS-NRTL method led to the least errors, where average absolute deviations ranged between 0.65-1.7%.

Keywords—Bubble pressure, Gibbs excess energy model, mixing rule, CO₂ solubility, ethyl palmitate.

I. INTRODUCTION

As an alternative to petroleum-based diesel fuel, biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources [1]-[4]. Analogous to conventional diesel fuel, it can be used in diesel ignition engines. The cost of biodiesel, however, is the main constraint to the commercialization of the product. Algae and used cooking oil are raw materials which can decrease the process cost, by replacing edible oils as raw material. Other factors to increase the benefits of biodiesel production are the adaption of continuous processes for transesterification and a complete separation and the recovery of valuable by-products such as glycerol [2], [5].

Biodiesel can be defined as the monoalkyl esters from long-chain fatty acids (FAE). The term biodiesel can be attributed to both long-chain fatty acid methyl esters (FAME) and ethyl esters (FAEE) [6]. Nowadays, FAME is the most commercially available biodiesel, thanks to the relatively lower price of ethanol in EU countries, whereas in countries such as Brazil and Argentina, where biodiesel ethanol (EtOH) is abundantly available with lower prices, FAME leads the biodiesel markets [7].

There are four primary ways to make biodiesel: direct use and blending, microemulsions, thermal cracking (pyrolysis), and transesterification. The most commonly used method is the transesterification of vegetable oils and animal fats.

The transesterification reaction includes the exchange of the alkoxy group of a lipid oil or fat with an aliphatic alcohol (e.g. methanol and ethanol). This substitution will be completed in the presence of acids such as H₂SO₄ or alkalinities (e.g. KOH and NaOH) as the catalyst [8]. Fig. 1 represents the biodiesel reaction scheme.

Fig. 1 Biodiesel reaction scheme

The transesterification reaction is affected by the molar ratio of glycerides to alcohol, the catalyst, reaction temperature, reaction time, and the free fatty acids content and water content of the oils or fats.

Biodiesels produced from lipid sources are mainly comprised of six different FAE’s, consisting of palmitic acid (C16:0), steric acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2) and linoleic acid (C18:3) alkyl esters, with small amounts of palmitoleic acid (C16:1) also present. Ideal biodiesel fuels mainly contain high amounts of methyl oleate, methyl palmelate, and ethyl palmitate [1], [9]. In this study, the phase equilibria for mixtures of CO₂ + ethyl palmitate was investigated. Besides the potential for non-catalytic biodiesel production at high pressures (in the supercritical state), supercritical CO₂ also offers an exciting alternative to purification and glycerol separation in water-free processes [10], [11].

Ethyl palmitate fatty acid ethyl esters are produced in the palmitic acid transesterification process in the presence of ethanol.

Fig. 2 shows the molecular structure of ethyl palmitate.

Fig. 2 Molecular structure of ethyl palmitate FAEE
II. THERMODYNAMIC MODELING

The modeling of experimental equilibrium data was investigated using the PR (PR) equation of state, combined with two different mixing rules, consisting of the Van der Waals conventional mixing rule (vdW1) and the Wong-Sandler (WS) mixing rule. In order to predict the phase equilibrium for non-ideal systems, the WS mixing rule requires the use of a Gibb’s excess energy (GE) model, in order to combine a liquid activity model with an equation of state. Mixtures of CO2 and FAEE have non-ideal behavior due to the presence of a long-chained FAEE, together with the small CO2 molecule. As a result, the WS-GE mixing rule should be able to predict the phase behavior of this system accurately.

The classical vdW1f mixing rules, as well as activity coefficient models like the Margules and van Laar equations, use ‘average’ or ‘overall’ compositions. They are models based on ‘random mixing’ [12]-[14]. However, due to intermolecular forces, the mixing of molecules is never entirely random and a way to account for the non-randomness can lead to improved models and better descriptions of phase behavior [10], [12], [15], [16]. Therefore, local composition activity coefficient models have drastically changed the range of applicability of liquid phase models.

Some of the most common GE models include the NRTL and UNIQUAC models. The NRTL model is based on the critical properties of the components and the UNIQUAC model is based on area and volume parameters. FAEEs have known critical properties ($T_c$, $P_c$) and $\omega$, but determining their surface and volume parameters is more challenging. Because of this, different methods have been investigated for the determination of these two unknown variables. In this study, a group contribution method has been used to calculate the surface and volume parameters ($r$, $q$) for ethyl palmitate FAEE.

The thermodynamic models used, including the Peng-Robinson equation of state, and the mixing rules are presented below [12]:

A. PR Equation of State:

The Peng-Robinson EOS is used to predict the phase equilibria of the binary system of CO2 + ethyl palmitate. Equations (1) and (2) represent the Peng-Robinson EOS and its parameters.

$$ P = \frac{RT}{v-b} \left( \frac{a(T)}{v(v+b)+b(v-b)} \right) $$

(1)

where:

$$ a(T) = a_0 a $$

$$ a_0 = 0.45724 \left( \frac{RT}{P_c} \right)^{\frac{1}{2}} $$

$$ \alpha = (1 + m(1-\sqrt{T}))^{\frac{1}{2}} $$

$$ b = 0.07780 \frac{RT}{P_c} $$

$$ m = 0.37464 + 1.54225m - 0.20992$$

B. Van der Waals Mixing Rule

Equations (3) and (4) give the mixing rules and combining laws used in the vdW1 model.

$$ a = \sum_{i=1}^{n} x_i a_i $$

$$ b = \sum_{i=1}^{n} x_i b_i $$

(3)

where:

$$ a_i = \sqrt{a_0 a_i (1 - k_i)} $$

$$ b_i = \frac{b_i + b_i}{2} (1 - l_i) $$

(4)

in which $l_i$ and $k_i$ are binary interaction parameters that are optimized to the experimental phase equilibrium data for the CO2+FAEE system.

C. Wong Sandler Mixing Rule

The Wong-Sandler mixing rule, developed for cubic equations of state, equates the excess Helmholtz free energy at infinite pressure from an equation of state to that from an activity coefficient model [12], [17].

$$ G^E = A^E $$

where:

$$ A^E = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (b_i a_j + b_j a_i) $$

(5)

and $k_{ij}$ is an optimizing parameter.

D. Activity Models

The excess energy was calculated in this study by two different activity models, namely NRTL and UNIQUAC. Equations (7)-(11) represent these two activity models and the relations to calculate their parameters [12].

E. NRTL Activity Model

$$ g^E = x_i x_j (r_{ij} G_{ij} + \frac{\tau_{ij} G_{ij}}{x_i + x_j G_{ij}} + \frac{\tau_{ij} G_{ij}}{x_i + x_j G_{ij}}) $$

(7)

where:

$$ r_{ij} = \frac{\Delta G_{ij}}{RT} $$

$$ \tau_{ij} = \frac{\Delta G_{ij}}{RT} $$

$$ ln G_{ij} = -\alpha_{ij} r_{ij} $$

$$ ln G_{ij} = -\alpha_{ij} r_{ij} $$

$$ r_{ij} = r_{ij} $$

(8)

and $\Delta G_{ij}, \Delta G_{ij}, \alpha_{ij}$ are the binary parameters.
F. UNIQUAC Activity Mode

\[
g^e = g^e(\text{combinatorial}) + g^e(\text{residual})
\]

\[
g^e(\text{combinatorial}) = \frac{R T}{x_i} \ln \frac{x_i}{x_i + x_j} + \frac{x_j}{x_i + x_j} \ln \left( \frac{x_i}{x_i + x_j} \right) + \frac{x_j}{x_i + x_j} \ln \left( \frac{x_j}{x_i + x_j} \right)
\]

\[
g^e(\text{residual}) = -q_i x_i T \ln \left( T + q_i x_i T \right) - q_j x_j T \ln \left( T + q_j x_j T \right)
\]

where:

\[
\Phi_i = x_i \ln \left( \frac{x_i}{x_i + x_j} \right) + \frac{x_j}{x_i + x_j} \ln \left( \frac{x_i}{x_i + x_j} \right) + \frac{x_j}{x_i + x_j} \ln \left( \frac{x_j}{x_i + x_j} \right)
\]

\[
\Theta_i = x_i \ln \left( \frac{x_i}{x_i + x_j} \right)
\]

\[
\ln \frac{\Delta U_{ij}}{R T} = \ln \frac{\Delta H_{ij}}{R T} = \ln \frac{\Delta S_{ij}}{R}
\]

\[
r \text{ and } q \text{ are pure component parameters, the coordination number, } z, \text{ is taken to be 10, and } \Delta U_{ij}, \Delta H_{ij}, \text{ and } \Delta S_{ij} \text{ are binary parameters to be optimized.}
\]

The Hansen group contribution method for the estimation of \( r \) and \( q \) is [18]:

\[
e_i = \sum_k v_{i}^k R_k, \quad q_i = \sum_k v_{i}^k Q_k
\]

where \( v_{i}^k \) is the number of groups of type \( k \) in molecule \( i \) and \( R_k \) and \( Q_k \) are dimensionless surface and volume group parameters.

G. Optimizing Parameters

Each approach has parameters which are optimized to experimental data with an objective function as defined by equation (12) that calculates the minimum deviation between predicted values from the corresponding experimental data.

\[
\text{OF}_{\text{Temp}} = \left| \frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right| \times 100
\]

The thermodynamic models were programmed in MATLAB and the optimizing procedure was done using the Differential Evaluation (DE) algorithm.

The experimental bubble pressure data for a binary system of CO\(_2\)+ethyl palmitate at high pressures were taken from literature [11] in order to evaluate the models and optimize the interaction parameters. CO\(_2\) mole fractions were in the range of 0.5033 to 0.9913. Temperatures ranged from 313.15 to 353.15 K and pressure went up to 21 MPa [11].

Table I presents the properties of CO\(_2\) and FAEE which were used in the modeling [11].

III. RESULTS

The UNIQUAC volume and surface parameters, predicted by the group contribution method are given in Table II [18].

Each approach involved optimizing its own set of binary parameters. Table III shows the optimized parameters at each temperature.

The bubble pressure results of the three thermodynamic models were compared to experimental values from the literature. Figs. 3-7 show a comparison between the different approaches at various temperatures.

To compare the results, average absolute deviations, and average relative deviations were also calculated at different temperatures for each approach and the results are presented in Table IV.
**Table IV**

AVERAGE ABSOLUTE AND RELATIVE DEVIATIONS AT DIFFERENT TEMPERATURES FOR THE THREE MODELS

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature (K)</th>
<th>AAD</th>
<th>ARD%</th>
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<tr>
<td>NRTL</td>
<td>313.15</td>
<td>0.12</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td>323.15</td>
<td>0.08</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>333.15</td>
<td>0.05</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>343.15</td>
<td>0.11</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>353.15</td>
<td>0.09</td>
<td>0.87</td>
</tr>
<tr>
<td>UNIQUAC</td>
<td>313.15</td>
<td>0.11</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>323.15</td>
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<td>1.47</td>
</tr>
<tr>
<td></td>
<td>333.15</td>
<td>0.09</td>
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</tr>
<tr>
<td></td>
<td>343.15</td>
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<tr>
<td></td>
<td>353.15</td>
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</tr>
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<tr>
<td></td>
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<tr>
<td></td>
<td>353.15</td>
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<td>3.96</td>
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IV. CONCLUSIONS

The PR EOS with classical mixing rules shows the maximum deviations from experimental data, which can be related to the limitation of this EOS in modeling long-chained molecules such as FAEEs. This dramatic deviation can be seen at all temperatures.

The two approaches using the Wong-Sandler mixing rule showed that this approach has less errors than the conventional Van der Waals mixing rule. According to results, the NRTL model led to the least errors due to the accurate Van der Waals mixing rule. According to results, the NRTL showed higher errors, perhaps because of the non-accurate binary interaction parameters.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>a</td>
<td>energy term</td>
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<tr>
<td>A</td>
<td>Helmholtz energy</td>
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<tr>
<td>G</td>
<td>Gibbs free energy</td>
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<tr>
<td>g</td>
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<tr>
<td>kij</td>
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</tr>
<tr>
<td>v</td>
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</tr>
<tr>
<td>x1</td>
<td>molar composition of component i</td>
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<tr>
<td>z</td>
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Greek letters

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<tr>
<td>α12</td>
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<td>Φi</td>
<td>surface area fraction for component i in the mixture</td>
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<td>τ12</td>
<td>Boltzmann factor</td>
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<td>ω</td>
<td>acentric factor</td>
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<tr>
<td>Φ1</td>
<td>volume fraction for component 1 in the mixture</td>
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Superscripts and subscripts

<table>
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<tr>
<td>i,j</td>
<td>component</td>
</tr>
<tr>
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<td>denotes CO2 and FAEE</td>
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<tr>
<td>c</td>
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<tr>
<td>r</td>
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</tr>
<tr>
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<tr>
<td>Exp.</td>
<td>experimental data</td>
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</table>

REFERENCES