LIQUID-LIQUID EQUILIBRIUM DATA FOR THE PSEUDO-TERNARY BIODIESEL OF CHICKEN FAT + METHANOL + GLYCEROL


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ABSTRACT
Liquid-liquid equilibrium (LLE) data for the system biodiesel of chicken fat + methanol + glycerol was measured at 25 and 45 °C and atmospheric pressure. The zone of miscibility was found by means of the binodal curve, using the density of turbidity in each point for its construction. Tie lines were defined through the calibration curves of the biodiesel and glycerin phases. The distribution and selectivity coefficients for the system were determined. The validation of the equilibrium data was proved using the Othmer-Tobias and Hand correlations, with coefficients close to the unity. The LLE data were correlated with the UNIQUAC model for temperatures of 25 °C and 45 °C, with global mean deviation values of 0.78% and 0.89%, respectively.

KEYWORDS
liquid-liquid equilibrium; chicken fat biodiesel; methanol; glycerol

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had an average herd of 38, 578 million animals (Cherubini et al., 2015). With the trimming during the boning process, a significant amount of pork fat is obtained, and it can become an environmental problem if not handled correctly. Lee et al. (2016) studied the production of biodiesel from swine fat, using the transesterification method, obtaining a yield of 97.2% at 380 °C. Regarding beef cattle, Brazil has the largest herd of beef in the world, estimated at approximately 200 million animals (Cardoso et al., 2016). As a result, a lot of unused greasy residue is generated and, if it does not have the right destination, it can become a potential polluter.

The production of poultry meat is also of great relevance in Brazil. Consequently, the amounts of waste produced by this activity are also high, in particular, the unused parts of the chicken. According to the Brazilian Association of Animal Protein (Associação Brasileira de Proteína Animal - ABPA), in its latest annual report, the production of broiler chickens was 50,524,652 units, equivalent to 12.9 million tons, of which, 66% went to the domestic market (ABPA, 2017). Therefore, the production of biodiesel using the viscera of the chicken as raw material is considered of great importance. Literature provides relevant studies on the production of biofuel using the raw material in question. Kirubakaran and Selvan (2018) discussed the importance of fat for energy production, especially high-fat chicken, its advantages for biodiesel production, different forms of fat extraction, and its various techniques. Fayyazi et al. (2015) used an ultrasound system to optimize the production of biodiesel from chicken fat using a genetic algorithm and obtaining the response surface, obtaining a good conversion rate and with biodiesel properties in the ASTM D6751 standard.

The phase equilibrium is very important on the industrial process. In what concerns the production of biodiesel, two partially miscible phases are formed: one rich in glycerin and another, rich in biodiesel. The study of the LLE involving biodiesel produced from animal fat are presented in the literature. Sena and Pereira (2016) studied the tie lines and their respective models. Studies with methyl biodiesel from fish viscera were also analyzed, obtaining good results and a minimal global error in their
thermodynamic modeling (Maghami et al., 2016). This work reports LLE data for the ternary system composed by biodiesel of chicken fat + methanol + glycerol, at 25 and 45 °C and atmospheric pressure. Furthermore, UNIQUAC model was applied for correlating experimental data series.

2. MATERIALS AND METHODS

2.1 Reagents

The reagents used to obtain biodiesel and to obtain the equilibrium data were: melted chicken fat supplied by the city market in Apodi, situated in the state of Rio Grande do Norte (Brazil), methanol (Neon, 99.8%) glycerol PA (Neon, 99.7%), potassium hydroxide (Impex, 86%), and sodium sulfate anhydrous (Sigma-Audrich, 99%).

2.2 Biodiesel production

Initially, since the chicken fat was in solid state, it was necessary to melt it down. Then, the transesterification process began with the preparation of potassium methoxide from potassium hydroxide (KOH) and methanol. To obtain this, 40mL of methyl alcohol and 2g of potassium hydroxide (KOH) were used under constant stirring until complete homogenization.

The transesterification reaction was carried out by mixing the obtained potassium methoxide to 100g of chicken fat in a molar ratio (1:6), at a constant stirring using magnetic plate, showing satisfactory results for the procedure. This reaction mixture was stirred for 60 minutes at room temperature for the transesterification reaction. To get the alkyl esters mixture from excess methanol and glycerol, a separation funnel was applied.

The acidity index obeyed the methodology proposed by Pregnolato and Pascuet (1985) and was obtained by titrimetric methods. The experiment used three Erlenmeyer flasks. During the process, 2 g of the chicken methyl biodiesel were added to 25mL of an ether-alcohol solution (2:1), and 2 drops of the phenolphthalein indicator titrated with the standard solution of 0.1M NaOH until the appearance of pink coloration that remained for at least 30 seconds. All procedures were done in triplicate. The value of the acidity index of 0.286 mg of KOH/g was satisfactory; considering that the maximum allowed limit is 0.5 mg of KOH/g (ANP, 2014).

2.3 Gas chromatography

To determine the composition of the biodiesel produced, gas chromatography coupled to mass spectrometry was performed. The equipment used was the GCMS-QP2010 SE-SHIMADZU, with a 30m long capillary column, 0.25mm diameter and 0.25μm thickness. The solution was diluted 1% with acetone and the sample injection was 1 μl. Helium was used as gas during the operation, with a flow rate of 2 mL/min. The temperature of the injector was set at 250 °C. Table 1 shows the profile of methyl esters present in the chicken fat methyl biodiesel.

2.4 Equilibrium data

A glass cell with magnetic stirring and temperature control was used. The apparatus used to maintain operating temperatures was SP Labor Ultra-Spectacular Bath SP-152. The methodology available through literature was used to obtain the binodal curves (Sena & Pereira, 2016). Initially, mixtures with known glycerol and methanol compositions were titrated with biodiesel. Each time the cloud point was reached, the

<table>
<thead>
<tr>
<th>Methyl Esters</th>
<th>Mass Composition (%)</th>
<th>Molar Mass (g/mol)</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl tetradecanoate</td>
<td>0.56</td>
<td>242.40</td>
<td>C15H30O2</td>
</tr>
<tr>
<td>Methyl Hexadec-9-Enoate</td>
<td>0.32</td>
<td>268.44</td>
<td>C17H32O2</td>
</tr>
<tr>
<td>Methyl Palmitoleate</td>
<td>3.21</td>
<td>268.44</td>
<td>C17H34O2</td>
</tr>
<tr>
<td>Methyl Palmitate</td>
<td>22.19</td>
<td>270.45</td>
<td>C17H36O2</td>
</tr>
<tr>
<td>Methyl Linoleate</td>
<td>27.06</td>
<td>294.47</td>
<td>C18H32O2</td>
</tr>
<tr>
<td>Methyl Oleate</td>
<td>40.91</td>
<td>296.49</td>
<td>C19H36O2</td>
</tr>
<tr>
<td>Methyl stearate</td>
<td>5.76</td>
<td>298.51</td>
<td>C20H40O2</td>
</tr>
</tbody>
</table>
The experimental procedure was stopped and the density of the resulting mixture was measured. Then, the same procedure was performed by titrating with glycerol a previously known mixture of biodiesel and methanol. The densities were taken obeying the same criteria already placed, when the turbidity was detected. All experimental measurements were performed in triplicate. All density measurements were performed using an ANTON PAAR, DMA 35 PORTABLE DENSITY METER, properly calibrated.

With the values of the known densities and compositions for each point, calibration curves were constructed for the three components, both in the glycerin and in the biodiesel rich phase (Sena & Pereira, 2016). It is noteworthy that the term glycerol is used for the pure compound while glycerin refers to the phase obtained after separation. As the curves found were polynomials of the second degree, one of the roots had to be discarded, considering only one with a physical-chemical sense. With the binodal curves plotted, 6 points below these were chosen, a region that has two phases. A fixed mass of 40g for each point, with previously known composition, was used. The mixture was stirred for three hours and allowed to stand for 12 hours, so that phase separation was guaranteed. The whole procedure was performed with temperature control (25 °C and 45 °C). Then, the densities of the phases rich in biodiesel and glycerin were measured. With the aid of the calibration curves, it was possible to find the values of the tie lines. Both binodal and tie lines curves were plotted using the Python computational tool (Harper et al., 2015), generating diagrams with good quality.

With the values of the tie lines, it was possible to calculate the distribution ($\beta_2$ and $\beta_3$) and selectivity (S) coefficients, which serve to prove the extraction power of the solvent. The calculation of these parameters is represented by equations (1), (2) and (3).

$$\beta_2 = \frac{w_{21}}{w_{23}}$$  \hspace{1cm} (1)

$$\beta_3 = \frac{w_{31}}{w_{33}}$$  \hspace{1cm} (2)

$$S = \frac{\beta_2}{\beta_3}$$  \hspace{1cm} (3)

Where:

$\beta_2$ = coefficient of methanol distribution;

$\beta_3$ = glycerin distribution coefficient;

S = coefficient of selectivity;

$w_{21}$ = mass fraction of methanol in the biodiesel rich phase;

$w_{23}$ = mass fraction of methanol in the glycerin-rich phase;

$w_{31}$ = mass fraction of glycerin in the biodiesel-rich phase;

$w_{33}$ = mass fraction of glycerin in the glycerol-rich phase.

Then, the Othmer-Tobias and Hand correlations are described by Equations (4) and (5), respectively.

$$\ln\left(\frac{1-w_{33}}{w_{33}}\right) = a_1 + b_1 \ln\left(\frac{1-w_{11}}{w_{11}}\right)$$ \hspace{1cm} (4)

$$\ln\left(\frac{w_{23}}{w_{33}}\right) = a_2 + b_2 \ln\left(\frac{w_{21}}{w_{11}}\right)$$ \hspace{1cm} (5)

Where:

$w_{11}$ = mass fraction of biodiesel in the biodiesel-rich phase.

2.5 Application of the thermodynamic model

With the found experimental data, a classic correlation reported in the literature was used to calculate the compositions, according to each thermodynamic model. The model chosen was UNIQUAC. For this, the Regress computational tool was used (Stragevitch, 1994). The values of the parameters of the UNIQUAC model, $r$, $q$, and $q'$ were found by the sum of the parameters of each subgroup that compose the molecule of each component (Prausnitz, 1999). For the biodiesel, the compounds found in highest concentrations were methyl palmitate, methyl linoleate, and methyl oleate. Each percentage was parameterized, since the other components presented negligible composition. Biodiesel characterization using three constituents (methyl palmitate, methyl linoleate, and methyl oleate) was found to be coherent considering that biodiesel-rich phase is predominantly composed by biodiesel and glycerin-rich phase presents biodiesel in dilute concentration. In other words, it is important to
point out the separation efficiency of the biodiesel constituents in the upper phase. Equations (6) and (7) represent the group contributions UNIFAC structural parameters to the UNIQUAC model:

\[ r_i = \sum_k v_k^{(i)} R_k \]  
\[ q_i = \sum_k v_k^{(i)} Q_k \]  

Where:

- \( i \) = species of the system;
- \( k \) = identification of subgroups;
- \( v_k^{(i)} \) = number of subgroups of type \( k \) in a molecule of species \( i \);
- \( R_k \) = value of the UNIFAC volume parameter;
- \( Q_k \) = value of the UNIFAC surface parameter.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Binodal curves

The points of the binodal curves are presented in Table 2 for temperatures of 25 °C and 45 °C.

Figure 1 shows the arrangements thereof. It is possible to notice a large area with two phases just below the experimental points, characteristic of systems that have biodiesel (\( w_1 \)), methanol (\( w_2 \)), and glycerol (\( w_3 \)) in their mass compositions (Sena & Pereira, 2016).

Observing Figure 1, one can observe the influence of temperature on the system. The area of miscibility increased when the temperature of 45 °C was used, when compared to the temperature of 25 °C.

![Figure 1. Binodal curves for the biodiesel + methanol + glycerol system at 25 °C and 45 °C.](image)
Table 3. Liquid-liquid equilibrium data for the system biodiesel ($w_1$), glycerol ($w_2$), and methanol ($w_3$) at 25 and 45 °C; compositions are in mass fraction*.

<table>
<thead>
<tr>
<th>T = 25 °C</th>
<th></th>
<th>T = 45 °C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$w_1$</td>
<td>$w_2$</td>
<td>$w_3$</td>
<td>$w_1$</td>
</tr>
<tr>
<td>0.8876</td>
<td>0.0982</td>
<td>0.0142</td>
<td>0.3335</td>
</tr>
<tr>
<td>0.8977</td>
<td>0.0880</td>
<td>0.0143</td>
<td>0.0282</td>
</tr>
<tr>
<td>0.9165</td>
<td>0.0690</td>
<td>0.0145</td>
<td>0.0154</td>
</tr>
<tr>
<td>0.9176</td>
<td>0.0679</td>
<td>0.0145</td>
<td>0.0195</td>
</tr>
<tr>
<td>0.9382</td>
<td>0.0470</td>
<td>0.0148</td>
<td>0.0119</td>
</tr>
<tr>
<td>0.9414</td>
<td>0.0438</td>
<td>0.0148</td>
<td>0.0107</td>
</tr>
</tbody>
</table>

*The estimated average experimental uncertainty in mass fraction is: $u(w) = 0.0005$

Table 4. Parameters of the Othmer-Tobias and Hand correlations at 25 °C and 45 °C.

<table>
<thead>
<tr>
<th>T = 25 °C</th>
<th></th>
<th>T = 45 °C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Othmer-Tobias</td>
<td></td>
<td>Hand</td>
</tr>
<tr>
<td>A</td>
<td>b</td>
<td>$R^2$</td>
<td>a</td>
</tr>
<tr>
<td>0.37</td>
<td>-2.3567</td>
<td>0.9911</td>
<td>0.1439</td>
</tr>
<tr>
<td>0.4528</td>
<td>-2.5281</td>
<td>0.9882</td>
<td>0.1986</td>
</tr>
</tbody>
</table>

3.2 Tie-lines, distribution, and selectivity coefficients

Table 3 shows the compositions of the tie lines, both in the glycerin-rich and biodiesel-rich phases, for temperatures of 25 °C and 45 °C, respectively. With this, it was possible to assemble the diagrams with the tie lines obtained, as can be seen in Figures 2 (a) and (b).

By the slopes of the tie lines, one can conclude that methanol has more affinity for glycerol than for biodiesel, because hydroxyl (OH) is present in its molecular formula, corroborating with results of Sena & Pereira (2016). Figures 3 and 4 show the graphs he distribution coefficients and selectivity for temperatures of 25 °C and 45 °C with respect to alcohol, in this case, methanol.

The values of selectivity found had values higher than 1, implying a good solvent extraction capacity, in this case methanol, corroborating with Mesquita et al. (2012).
The reliability of the tie lines was confirmed by the correlations of Othmer-Tobias and Hand. The settings determined for both equations have similar values and are close to the unit. Table 4 presents the parameters found for such correlations. Figures 5 and 6 show the charts relevant to the models.

![Figure 3. Methanol Selectivity according to their mass fractions (w₂).](image1)

![Figure 4. Methanol distribution coefficients according to their mass fractions (w₂).](image2)
3.3 Thermodynamic correlation of the experimental data

The correlation of the experimental data was performed using the UNIQUAC model. The computational tool Regress 2.0 was used for the respective estimations. The values of the structural parameters \( r, q, \) and \( q' \) are presented in Table 5 (Prausnitz, 1999). Parameters \( A_i \) of the UNIQUAC correlation were estimated and are presented in Table 6. For the biodiesel, the weighted average of the structural parameters was considered, taking into account the mass compositions of palmitic, oleic, and linoleic species. Figures 7 and 8 show the tie lines obtained experimentally and those obtained by each one of the models for temperatures of 25 °C and 45 °C, respectively.

From the diagrams presented by Figures 7 and 8, one can see that the UNIQUAC model correlated very well with the experimental data. This is proven by the values of global mean deviations. At 25 °C, the deviation was 0.78%, whereas at 45 °C the value was 0.89%.

![Figure 5. Othmer-Tobias correlation for biodiesel and glycerin rich phases compositions at 25 °C and 45 °C.](image)

![Figure 6. Hand correlation for biodiesel and glycerin rich phases compositions at 25 °C and 45 °C.](image)
Table 5. Parameters r, q, and q’.

<table>
<thead>
<tr>
<th>Component</th>
<th>r</th>
<th>Q</th>
<th>q’</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodiesel</td>
<td>12.35</td>
<td>10.18</td>
<td>10.18</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.4311</td>
<td>1.432</td>
<td>0.96</td>
</tr>
<tr>
<td>Glycerol</td>
<td>4.7957</td>
<td>4.908</td>
<td>4.908</td>
</tr>
</tbody>
</table>

Table 6. Parameters $A_{ij}$ (Kelvin) for the UNIQUAC model for biodiesel (1), methanol (2), and glycerol (3).

<table>
<thead>
<tr>
<th></th>
<th>$T = 25 , ^\circ C$</th>
<th>$T = 45 , ^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{12}$</td>
<td>239.36</td>
<td>620.61</td>
</tr>
<tr>
<td>$A_{21}$</td>
<td>442.66</td>
<td>277.31</td>
</tr>
<tr>
<td>$A_{13}$</td>
<td>157.29</td>
<td>140.07</td>
</tr>
<tr>
<td>$A_{31}$</td>
<td>4.0235</td>
<td>31.841</td>
</tr>
<tr>
<td>$A_{23}$</td>
<td>-35.161</td>
<td>-35.247</td>
</tr>
</tbody>
</table>

Figure 7. Experimental tie lines predicted by the UNIQUAC model for the biodiesel system of chicken fat + methanol + glycerol at 25 °C.

Figure 8. Experimental tie lines predicted by the UNIQUAC model for the biodiesel system of chicken fat + methanol + glycerol at 45 °C.
4. CONCLUSIONS

Biodiesel derived from chicken fat becomes a viable alternative for the production of biofuel given the high amount of waste that the chicken slaughtering activity generates and the fact that Brazil is one of the largest producers of chicken in the world. The LLE data for the system composed by biodiesel of chicken fat + methanol + glycerol presented thermodynamic consistency, as evidenced by the correlations of Othmer-Tobias and Hand. The slope of the tie lines showed that methanol has a better affinity for glycerol than for biodiesel due to the presence of the hydroxyl group. The classic correlation reported in the literature, UNIQUAC, was used for the predictions of tie lines at 25 °C and 45 °C, with mean global deviation values lower than 1%.

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5. REFERENCES


