1. Introduction

Bioethanol (is one of the biofuel) is produced by fermentation of biomass-derived sugar and concentration of the fermentation broth up to the high purity enough for motor gasoline use, that is to say, higher than 0.994 by mass fraction. Purification of bioethanol using ordinary distillation is impossible because mixture of water and ethanol form an azeotropic mixture at 0.954 of mass of ethanol. The other techniques for ethanol separation have been studied for long time. Those technique were adsorption, membrane separation, extractive, and heterogeneous distillation and so on. However, these processes were relatively complex and difficult to operate.

A simple technique, solvent extraction, has been investigated for bioethanol purification. A large number of organic solvents have been examined, such as furfural, xylene, or ionic liquid. For most cases, the ethanol extraction was studied with the solvents giving relatively high yield of ethanol. However, it was impossible to concentrate ethanol up to the specified concentration for fuel use since ethanol and solvent mixtures were homogenous. It is necessary to study the application of the extraction with the solvents that formed heterogenous two phases with ethanol.

The objective of this study was to apply the solvent extraction technique to concentrate ethanol with solvent that formed heterogenous two phases. Liquid-liquid equilibrium for each solvent was experimentally measured and correlated with UNIFAC model. Countercurrent extraction process was computationally simulated under various operating conditions. The effects of the operating conditions such as solvent per feed flow ratio or reflux ratio were investigated to evaluate the yield and purity of the product.

2. Liquid-Liquid Equilibrium

2.1 Experimental

Table 1 Experimental conditions

<table>
<thead>
<tr>
<th>Feed</th>
<th>Ethanol + Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Tridecane</td>
</tr>
<tr>
<td></td>
<td>Tetradecane</td>
</tr>
<tr>
<td></td>
<td>Hexadecane</td>
</tr>
<tr>
<td>$F$ [kg]</td>
<td>0.020</td>
</tr>
<tr>
<td>$S/F$ [-]</td>
<td>1</td>
</tr>
<tr>
<td>$z_e$ [-]</td>
<td>0-1</td>
</tr>
<tr>
<td>$T$ [K]</td>
<td>298,303,308</td>
</tr>
<tr>
<td>Contacting time [h]</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 1 shows the experimental conditions for binary and ternary liquid-liquid equilibrium. Long chain alkane hydrocarbon (tridecane, tetradecane and hexadecane) were selected since it formed two liquid phases with ethanol. The compositions of liquid solution were measured with gas chromatography and Karl-Fischer titrator in term of mass fraction of ethanol, water and solvent.

2.2 Results and Discussion

Figure 1 shows the mutual solubility of ethanol and solvent when tridecane, tetradecane and hexadecane were used as solvent together with previous study [1]. The mutual solubility of the ethanol-solvent increased as temperature was elevated. The solubility of ethanol increased up to 0.165 with the increasing temperature by using tridecane as a solvent. Under the same temperature, the ethanol solubility increased with the decreasing the solvent’s carbon chain length. Since the mixture formed heterogenous two phases, the extraction operation in the high ethanol purity range could be carried out.

![Figure 1 Mutual solubility between ethanol and solvent](image)

Figure 2 show the effects of temperature on ternary system of ethanol, water, and solvent. The mass fraction of ethanol in extract phase increased up to 0.158 with the increase of ethanol concentration in raffinate phase. The mass fractions of ethanol and water in the extract phase and that of solvent in the raffinate phase increased with temperature. Figure 3 show the effects of solvent’s carbon chain length on liquid-liquid equilibrium. The mass fraction of ethanol and water in the extract phase and that of solvent in the raffinate phase increased with the decrease of carbon chain length in the solvent.
The liquid–liquid equilibrium especially the compositions in extract phase.

The distribution ratio of component $i$, $m_i$, was defined as,

$$m_i = \frac{y_i}{x_i}$$  \hspace{1cm} (1)

where $x_i$ and $y_i$ denote the mass fractions of component $i$ in the raffinate and extract phases at equilibrium, respectively. The separation selectivity of ethanol relative to water, $\beta_{e,w}$, was defines as,

$$\beta_{e,w} = \frac{m_e}{m_w}$$  \hspace{1cm} (2)

The LLE of the systems measured in this study were estimated by the UNIFAC method, one of the thermodynamic techniques to estimate activity coefficients with interaction parameters among functional groups. The interaction parameters were determined by fitting with the experimental results. Table 2 present the group of parameters for calculation of the LLE in this work. The calculated LLE were also shown in Figures 2 by lines. The UNIFAC method could favorably estimate

<table>
<thead>
<tr>
<th>a</th>
<th>CH₃</th>
<th>CH₂</th>
<th>OH</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>0</td>
<td>0</td>
<td>281.30</td>
<td>291.19</td>
</tr>
<tr>
<td>CH₂</td>
<td>0</td>
<td>0</td>
<td>281.30</td>
<td>291.19</td>
</tr>
<tr>
<td>OH</td>
<td>627.46</td>
<td>627.46</td>
<td>0</td>
<td>-153.55</td>
</tr>
<tr>
<td>H₂O</td>
<td>1265.41</td>
<td>1265.41</td>
<td>-41.56</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 2 Liquid-liquid equilibrium in different temperature (A) raffinate phase (B) extract phase

Figure 3 Liquid-liquid equilibrium in different solvent (A) raffinate phase (B) extract phase

Figure 4 shows the effects of mass fraction of ethanol in raffinate ($x_e$) on the distribution coefficient. Although $m_e$ decreased as $x_e$ increased until 0.5 and increased in the range of $x_e > 0.5$, $m_e$ was relatively small (less than 0.2) in
3. Bioethanol Purification Process

3.1 Process Description

The process scheme of a countercurrent solvent extraction for the separation of bioethanol are shown in Figure 6. Purification process consisted of the extractor (1) where 2 liquid phases were contacted counter currently, a solvent recovery 1 (2) for separating solvent and extract, and solvent removal 2 (3) for recovering solvent from the raffinate. Highly pure ethanol was produced in the enriching section between the feed entry point and the top of the extractor, where the ethanol was enriched up to nearly pure with the concentration higher than in azotrope by reflux operation. On the other hand, high solubility of ethanol in the solvent was required in the stripping section lower than the feed entry to improve the extraction yield. Although these two criteria of the solvent should conflict with each other, they could be satisfied at the same time by selecting different operating temperatures for the enriching and stripping sections. The enriching section was conducted in lower temperature to increase product purity and the stripping section was operated in relatively higher temperature for increasing product yield.

![Figure 6 Schematic diagram of a countercurrent multistage extraction](image)

### 3.2 Basic Equations for Process and Calculation

#### Table 3 Calculation Conditions

<table>
<thead>
<tr>
<th>Feed Mass Flow rate (F)</th>
<th>[kg/h]</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Stage (f)</td>
<td>[-]</td>
<td>2- (N-2)</td>
</tr>
<tr>
<td>Temperature (T)</td>
<td>[K]</td>
<td>298-323</td>
</tr>
<tr>
<td>Mass ethanol in Feed (x_e)</td>
<td>[-]</td>
<td>0.1-1</td>
</tr>
<tr>
<td>Number of Stage (N)</td>
<td>[-]</td>
<td>10</td>
</tr>
<tr>
<td>Reflux Ratio (r)</td>
<td>[-]</td>
<td>1-10</td>
</tr>
<tr>
<td>Mass Ratio of Solvent to Feed</td>
<td>[-]</td>
<td>1-40</td>
</tr>
<tr>
<td>(S/F)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purity (x_y)</td>
<td>[-]</td>
<td>0.994</td>
</tr>
<tr>
<td>Yield (Y)</td>
<td>[-]</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The material balances for all components and component i at each stage k are represented by,

\[
\sum_{i} x_{i,k} F + x_{i+1,k} R_{i,k} + y_{i,k} E_{k} = y_{i,k} E_{k} + x_{i,k} R_{i,k}
\]

where \( R_{i,k} \), \( E_{k} \), \( x_{i,k} \), and \( y_{i,k} \) represent the mass flow rates of the raffinate and extract, and the mass fraction of component i at the k stage. \( F \) and \( z \) are the mass flow rate and composition of feed. The constrains on the mass fractions of component i are shown as,

\[
\sum_{i} x_{i,k} = 1 \quad \sum_{i} y_{i,k} = 1
\]

The total yield of ethanol for this process was defined as,

\[
Y = \frac{x_{n,a} P}{x_{n,a} F}
\]

where \( P \) and \( x_{n,a} \) represent the product mass flow rate and purity respectively. The assumption of equilibrium stage was valid for each stage. These and others necessary equations were simultaneously solved using a program written in MATLAB. Liquid–liquid equilibrium was calculated by the UNIFAC model with the determined
parameters. Separation of solvent and extract components in solvent removal both in top and bottom product was assumed to be complete. The calculation conditions are shown in Table 3. The effect of operating conditions on yield and purity were investigated.

3.3 Results and Discussion

Figure 7 shows the variation in top product purity and yield by increasing reflux ratio. As the reflux ratio increased, the ethanol mass fraction in the product also increased. The higher reflux ratio leads to up to 0.996 of product purity. The reflux could enhance the purity of ethanol. On the other hand, the effect of reflux ratio in product yield was almost constant.

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Figure 7 Effect of reflux ratio to product purity and yield

Figure 8 shows the effect of solvent per feed flow ratio on product purity and yield. The increasing S/F ratio leaded to increase yield. Ethanol yield increased up to 1 with increasing S/F ratio. In case of purity, S/F ratio gave no effect.

Figure 8 Effect of S/F flow ratio to product purity and yield

Figure 9 shows the correlation of mass ethanol in feed with reflux and solvent per feed flow ratio. The effect of solvent per feed flow ratio on product purity and yield was investigated.

Figure 9 Correlation of mass ethanol in feed with reflux and solvent per feed flow ratio

4. Conclusion

The LLEs of ternary mixture of ethanol, water and solvent were experimentally measured. Pure ethanol and solvent formed heterogeneous two phases, that is to say, bioethanol could be concentrated up to fuel specification. The LLE was correlated using UNIFAC model with interaction parameters determined by the experimental data fitting. Bioethanol purification using countercurrent multistage extraction was computationally simulated based on the LLE above. The main factors for increasing yield and purity were solvent per feed mass flow and reflux ratio respectively. Both solvent per feed ratio and reflux ratio was relatively higher to get high purity and yield of ethanol. Since this value could be reduced in the high ethanol feed concentration, it is recommended to have an additional pre-concentration distillation. Then the process evaluation should be developed with both the pre-concentration and dehydration processes.

Nomenclature

\[ \begin{align*}
x & = \text{mass fraction in raffinate phase, } y = \text{mass fraction in extract phase, } z = \text{mass fraction in feed phase, } F = \text{Feed mass flow rate, } R = \text{Raffinate mass flow rate, } E = \text{Extract Flow rate, } r = \text{reflux ratio, } SF = \text{solvent per feed flow ratio, } P = \text{Product, } Y = \text{Yield, } x_p,e = \text{Purity, } a = \text{interaction parameter.} \\
T & = \text{Temperature, } N = \text{number of stage, } f = \text{feed stage. } m = \text{distribution coefficient, } \beta = \text{selectivity.} \\
\text{LLE} & = \text{Liquid-liquid Equilibrium,} \\
\text{Subscript: } e & = \text{ethanol, } w = \text{water, } s = \text{solvent, } i = \text{component, } k = \text{stage number, } m = \text{functional group, } n = \text{number of component} \end{align*} \]

References