Separation of aromatic hydrocarbons from cracked kerosene
by O/W/O emulsion liquid membrane

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1. Introduction
Cracked kerosene (CK) is one of the by-products from the process of cracking of heavier oil fraction to produce cracked gasoline in petroleum refinery. Nowadays, the supply of ordinary gasoline is decreasing. Because of this, whereas the quantity of cracked gasoline is decreasing, that of cracked kerosene is increasing. There are many kinds of chemical compounds contained in cracked kerosene, the alkanes such as octane (C8), nonane (C9), decane (C10); the aromatic hydrocarbons such as m,p-xylene (M,PX), pseudo cumene (PC), tetraline (T), etc. Since the content of aromatic hydrocarbons in the cracked kerosene is so high that this fraction does not meet the specification for the ordinary kerosene, the cracked kerosene is used as a low-value heavy oil blendstock. On the other hand, aromatic hydrocarbons are useful as raw materials of chemical industry. It is, therefore, desired to separate aromatic hydrocarbons from the cracked kerosene. The liquid-liquid equilibrium extraction has been widely used for aromatics separation, such as, sulfolane process. The liquid membrane permeation is expected as an alternative to the extraction. The liquid membrane separation is governed by the difference in permeation rates of the components through the membrane and the difference is attributed mainly to the solubilities of the components into the aqueous membrane liquid. In general, the solubility of aromatic hydrocarbon in water is about 200 times larger than that of alkane hydrocarbon, so that aromatic hydrocarbon permeates through the aqueous membrane preferentially rather than alkane hydrocarbon to be separated. In O/W/O emulsion liquid membrane process, the feed oil phase is emulsified in an aqueous solution of surfactant to prepare the stable O/W emulsion. This O/W emulsion is dispersed in a solvent oil phase to form O/W/O dispersion system, where the internal feed and external solvent oil phases are divided by the aqueous phase. This aqueous phase plays a role of the liquid membrane, through which the permeate transfers from feed to solvent phase and the separation takes place.

In this work, the separation of CK by the O/W/O emulsion liquid membrane technique was conducted. The effect on experimental condition for emulsion liquid membrane separation was studied.

![Fig. 1 Apparatuses for batch emulsion liquid membrane permeation (a) emulsifier with high-speed homogenizer (b) permeator](image)

Table 1  Experimental condition of batch permeation

<table>
<thead>
<tr>
<th>Feed</th>
<th>Cracked kerosene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Hexane</td>
</tr>
<tr>
<td>Membrane</td>
<td>Aqueous solution of surfactant</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Polyoxyethylene (20) sorbitan monoleate (Tween 80)</td>
</tr>
</tbody>
</table>

| Stirring velocity in emulsification | \( N_{e} \) [h\(^{-1}\)] | \( 1.1 \times 10^{4} \) |
| Stirring velocity in permeation    | \( N_{p} \) [h\(^{-1}\)] | \( 1.8 \times 10^{4} \sim 3.6 \times 10^{4} \) |
| Total volume of liquid in permeator| \( V_{p} \) [m\(^{3}\)] | \( 4.0 \times 10^{-1} \) |
| Volume fraction of inner oil phase in O/W emulsion | \( f_{	ext{oil}} \) [-] | \( 0.5 \) |
| Volume fraction of O/W emulsion in O/W/O emulsion | \( f_{	ext{O/W}} \) [-] | \( 0.25 \) |
| Concentration of surfactant in a membrane liquid | \( C_{s} \) [-] | \( 0.005 \sim 0.2 \) |
| Operation time                       | \( t \) [h] | \( 0 \sim 0.5 \) |
| Operation temperature                | \( T \) [K] | \( 293 \pm 5 \) |

Table 2  Components in cracked kerosene

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass fraction [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>0.03</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>0.006</td>
</tr>
<tr>
<td>m,p-xylene</td>
<td>0.024</td>
</tr>
<tr>
<td>o-xylene</td>
<td>0.016</td>
</tr>
<tr>
<td>propylbenzene</td>
<td>0.004</td>
</tr>
<tr>
<td>mesitylene</td>
<td>0.015</td>
</tr>
<tr>
<td>pseudocumene</td>
<td>0.013</td>
</tr>
<tr>
<td>tetraline</td>
<td>0.009</td>
</tr>
<tr>
<td>naphthalene</td>
<td>0.004</td>
</tr>
<tr>
<td>hexylbenzene</td>
<td>0.01</td>
</tr>
<tr>
<td>2-methyl naphthalene</td>
<td>0.008</td>
</tr>
<tr>
<td>Aromatics</td>
<td>0.111</td>
</tr>
<tr>
<td>Alkanes</td>
<td>0.291</td>
</tr>
</tbody>
</table>
2. Experimental

CK was used as an inner oil phase. Aqueous membrane solution consisted of ion-exchanged water and polyoxyethylene (20) sorbitan monooleate as an emulsifying agent. Hexane was used as external solvent phase. The feed CK and aqueous membrane solution were stirred by a commercial high-speed homogenizer to prepare the stable emulsion. This prepared emulsion was brought into contact with the solvent by stirring vessel which was made of Pyrex glass equipped with a six-flat-blade turbine type impeller and four baffles. Figure 1 shows appearance of the apparatuses for batch emulsion liquid membrane permeation (a) emulsifier with high-speed homogenizer (b) permeator. Stirring started to begin a permeation run (t=0) and continued for a specified operating time. The extract phases were sampled for analysis by a gas chromatograph (GC-2010, Shimazu Corp.). This operation was repeated for the several different times to obtain the time courses of the compositions in the extract phase etc. Table 1 gives the detailed experiment conditions.

3. Results and Discussion

Cracked kerosene contained a number of hydrocarbon components. Table 2 summarizes several representative components and the respective contents identified, determined by gas chromatography.

The mass fraction in raffinate phase, $x_i$, can be calculated by mass balance as follows:

$$ R_0 x_{i,0} + E_0 y_{i,0} = R x_i + E y_i $$

(1)

$E$ and $R$ were obtained from the experimental data. Yield of component $i$, $Y_i$, was defined as,

$$ Y_i = \frac{E \cdot y_i}{R_0 \cdot x_{i,0}} $$

(2)

where $x_{i,0}$ and $y_i$ denote the mass fraction of component $i$ in the inner oil phase at $t=0$ and that in the external extract oil phase after a run, respectively. $R_0$ refers to the initial mass of inner oil phase and $E$ expresses the mass of out oil phase after the run.

Mass transfer rate of component $i$ through ideal emulsion liquid membrane was expressed as,

$$ \frac{dE y_i}{dt} = P_D a(x_i - y_i)V_f $$

(4)

In this equation, $P_D a$ expressed overall volumetric permeation coefficient.

When overall mass transfer is governed by permeation through the membrane, the overall permeation coefficient is qualitatively expressed as

$$ P_l \propto D_i \cdot m_i $$

(5)

Separation selectivity of total aromatics by the ratio of overall volumetric permeation coefficients relative to total alkane was defined as,

$$ \beta = \frac{P_{\text{aromatic}}}{P_{\text{alkane}}} \cdot \frac{a}{a} = \frac{P_{\text{aromatic}}}{P_{\text{alkane}}} $$

(6)

Figure 2 shows the time courses of mass of raffinate and extract phase. The mass of raffinate phase

![Figure 2 Time course of mass of raffinate and extract phase](image)

![Figure 3 Time course of mass fraction in extract phase](image)

![Figure 4 Time course of mass fraction in raffinate and extract phase](image)

![Figure 5 Time course of yield](image)
increased as the mass of extract phase decreased with time. The extract phase transferred to raffinate phase. The variation of surfactant concentration didn’t have much effect on $R$ and $E$.

**Figure 3** shows the time courses of mass fraction in extract phase. The mass fractions of all components which were identified by gas chromatography are shown on this figure. All of the mass fractions of extract phase increased with time. From next figure, the total aromatics and total alkane are shown to explain. Their variations are almost same as each compound.

**Figure 4** shows the time courses of mass fraction in raffinate and extract phase about total aromatics, total alkane and hexane. The mass fraction of total aromatics and total alkane in raffinate phase decreased as those in extract phase increased with time. The mass fraction of hexane in raffinate phase increased as that in extract phase decreased with time. So the mass fraction of raffinate and extract phase approached each other. The difference of mass fraction which is driving force of permeation decreased with time.

**Figure 5** shows the time courses of yields about total aromatics and total alkane. Under all conditions, $Y_i$ of aromatic compounds were larger than those of alkane compounds, namely, it was confirmed that these compounds were separated into each other by the emulsion liquid membrane. The yield increased with time. This figure also shows comparison between emulsion liquid membrane and liquid-liquid extraction on yields. The yields in the case of liquid-liquid extraction method$^{[1]}$ about total aromatics and total alkane are expressed in a straight lines. The yields in the case of emulsion liquid membrane method were higher than those of liquid-liquid extraction. The yield of liquid-liquid extraction was 0.065 and that of emulsion liquid membrane was 0.30 at maximum about total aromatics.

**Figure 6** shows the time courses of overall volumetric permeation coefficient, $P_{at}$. In any case, $P_{at}$ decreased with stirring time. $P_{at}$ of the aromatic compounds was larger than those of alkane compounds. Aromatic compounds were selectively transferred through liquid membrane to extract phase and could be separated from alkane compounds.

**Figure 7** shows the time courses of separation selectivity by the ratio of overall permeation coefficients, $\beta$. The separation selectivity decreased with time. This figure also shows comparison between emulsion liquid membrane and liquid-liquid extraction on separation selectivity. The separation selectivity in the case of liquid-liquid extraction method$^{[1]}$ about total aromatics is expressed in a straight line. The separation selectivity in the case of emulsion liquid membrane method was higher than that of liquid-liquid extraction. The separation selectivity of liquid-liquid extraction was 12 and that of emulsion liquid membrane was 17 at maximum about total aromatics. Aromatic compounds were selectively

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![Fig.6 Time course of overall volumetric permeation coefficient](image6.png)

![Fig.7 Time course of separation selectivity](image7.png)

![Fig.8 Effect of surfactant concentration on overall volumetric permeation coefficient](image8.png)

![Fig.9 Effect of surfactant concentration on separation selectivity](image9.png)
transferred through liquid membrane to extract phase and could be separated from alkane compounds.

**Figure 8** shows the effect of surfactant concentration on overall volumetric permeation coefficient, \( P_\alpha \). While \( C_i \) was lower, \( P_\alpha \) increased with \( C_i \). And then while \( C_i \) was larger, \( P_\alpha \) decreased with \( C_i \). \( P_\alpha \) had maximum value around \( C_i = 0.05 \).

**Figure 9** shows the effect of surfactant concentration on separation selectivity by the ratio of overall permeation coefficients, \( \beta \). The surfactant concentration didn’t have much effect on separation selectivity.

**Figure 10** shows the effect of surfactant concentration on interfacial tension between inner oil and surfactant solution phase and the effect of surfactant concentration on viscosity in surfactant solution from previous work[5]. The surfactant was Tween 20 in the previous work. The interfacial tension decreased with surfactant concentration. The decreasing trend became smaller from CMC (critical micelle concentration). The viscosity increased with surfactant concentration from CMC. While surfactant concentration was lower, it was supposed that the inner oil droplet decreased due to the decrease of interfacial tension. Therefore the \( P_\alpha \) increased. While surfactant concentration was higher, it was supposed that diffusivity at liquid membrane decreased due to increase of viscosity from Wilke-Chang equation. Therefore the \( P_\alpha \) decreased. The Wilke-Chang equation is shown as below.

Wilke-Chang equation

\[
D_{\text{saturated water}} = \frac{2.946 \times 10^{-11} (\alpha M_{\text{water}}) \mu T}{\mu_{\text{water}} V_{\text{b, surfactant}}}^{0.6}
\]

4. Conclusions

The aromatic hydrocarbon compounds were separated from cracked kerosene by the emulsion liquid membrane. Then the highest yield and separation selectivity were 0.3 and 17. These were higher than those of liquid-liquid equilibrium extraction. There was the appropriate surfactant concentration range.

**Nomenclatures**

- \( a \) = specific interfacial area between O/W emulsion and extract phase [m\(^{-1}\)]
- \( C_i \) = mass fraction of surfactant in membrane liquid [-]
- \( E \) = mass of extract phase [kg]
- \( N_E \) = stirring velocity in emulsification [h\(^{-1}\)]
- \( N_F \) = stirring velocity in permeator [h\(^{-1}\)]
- \( P_e \) = overall permeation coefficient [kg/h/m\(^2\)]
- \( R \) = mass of raffinate phase [kg]
- \( T \) = operation temperature [K]
- \( t \) = operation time [h]
- \( V_{FR} \) = total volume of liquid in permeation vessel [m\(^3\)]
- \( x \) = mass fraction in raffinate phase [-]
- \( y \) = mass fraction in extract phase [-]

**Greek**

- \( \beta \) = separation selectivity of total aromatics by ratio of overall volumetric permeation coefficient relative to total alkane [-]
- \( \phi_{Oi,0} \) = volume fraction of inner oil in O/W emulsion [-]
- \( \phi_{Oi,0} \) = volume fraction of O/W emulsion in total liquid [-]

**Subscript**

- 0 = at initial state
- \( i \) = component \( i \)
- CK = cracked kerosene
- M, PX = m-p-xylene
- PC = pseudocumene
- T = tetraline
- C8 = octane
- C9 = nonane
- C10 = decane

**Literature Cited**