SEPARATION OF CRACKED KEROSENE BY SOLVENT EXTRACTION

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1. Introduction

Cracked oil is one fraction obtained from heavy oil and contains various compounds such as aromatic compounds. nitrogen alkanes. compounds, and so on. If cracked oil was used as feedstock of fuel oil, these chemicals have to be removed not to produce contaminants with be burned. Besides, aromatic compounds are useful for raw materials of chemical industry. On the other hand, demands for fuel oils including refined oil from cracked oil has been declined recently. So, it could be new use of cracked oils to separate aromatic compounds and utilize them as raw materials of chemical industry.

The way of separating aromatic hydrocarbons has been studied. According to study on separation of coal tar fractions, nitrogen compounds and aromatic compounds could be separated from them by aqueous methanol solution^{1,2,3)}. Moreover, there are industrialized processes such as sulfolane process, furfural process, etc⁴⁾.

Then, the objective of this study is to investigate liquid-liquid equilibrium relationship between cracked kerosene and some kinds of solvents, and to discuss the feasibility of separation. In this paper, the separation of aromatic compounds is mainly discussed.

2. Experimental

Specific amounts of feed oil, R_0 , and solvents phase, E_0 , were brought into contact and were shaken at 298 K for 72 hours. These conditions are set with reference to the previous work about absorption oil⁵. The equilibrated oil, R_1 , and solvent phase, E_1 , were split into each other by separation funnel. The compositions of these phases were determined by the analysis with a gas chromatograph.

The conditions of material systems are summarized in **Table 1**.

Table 1 Conditions of material systems

| Cracked kerosene |
|--|
| Mass, R₀[kg] |
| 0.4 |
| Aqueous solution of methanol |
| Aqueous solution of sulfolane |
| Furfural |
| Mass fraction of water, $y_{w,0}$ [-] |
| 0, 0.3, 0.5, 0.7 |
| Mass ratio of solvent to feed, E_0/R_0 [-] |
| 1 |
| |

3. Results and Discussion

3.1 Composition of cracked kerosene

The gas chromatograms and composition of cracked kerosene are shown in **Fig.1** and **Table 2**, respectively. There were numbers of components in cracked kerosene as found in the chromatograms.

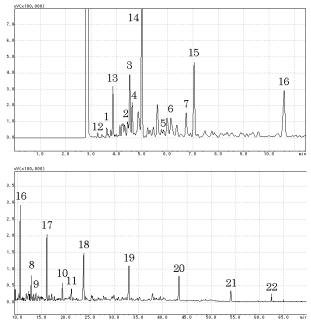


Fig.1 Gas chromatograms of cracked kerosene

| Table 2 Mass fraction and normal boiling points of |
|--|
| components in cracked kerosene |

| $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | | | | Mass | Boiling |
|--|----|------------------------|-------|----------|---------|
| 1 Toluene TOL 0.0026 110.63 2 Ethylbenzene EB 0.0067 136.19 3 m,p-Xylene M,PX 0.0233 139.1, 138.35 4 o-Xylene OX 0.0175 144.41 5 Propylbenzene PB 0.0041 159.22 6 1,3,5-Trimethylbenzene M 0.0142 164.72 7 1,2,4-Trimethylbenzene PC 0.0131 169.20 8 Tetraline T 0.0094 207.57 9 Naphthalene N 0.0044 217.96 10 Hexylbenzene HB 0.0091 226.00 11 2-Methylnaphthalene ZMN 0.0080 241.05 12 Heptane C7 0.0017 98.43 13 Octane C8 0.0168 125.67 14 Nonane C9 0.0671 150.80 15 Decane C11 0.0337 174.12 | | Components | | Fraction | Point |
| 2 Ethylbenzene EB 0.0067 136.19 3 m,p-Xylene M,PX 0.0233 139.1, 138.35 4 o-Xylene OX 0.0175 144.41 5 Propylbenzene PB 0.0041 159.22 6 1,3,5-Trimethylbenzene M 0.0142 164.72 7 1,2,4-Trimethylbenzene PC 0.0131 169.20 8 Tetraline T 0.0094 207.57 9 Naphthalene N 0.0044 217.96 10 Hexylbenzene HB 0.0094 226.00 11 2-Methylnaphthalene ZMN 0.0080 241.05 12 Heptane C7 0.0017 98.43 13 Octane C8 0.0168 125.67 14 Nonane C9 0.0671 150.80 15 Decane C10 0.0337 174.12 16 Undecane C11 0.0311 216.28 <td></td> <td></td> <td></td> <td>[-]</td> <td>[°C]</td> | | | | [-] | [°C] |
| 3 m,p-Xylene M,PX 0.0233 139.1, 138.35 4 o-Xylene OX 0.0175 144.41 5 Propylbenzene PB 0.0041 159.22 6 1,3,5-Trimethylbenzene M 0.0142 164.72 7 1,2,4-Trimethylbenzene PC 0.0131 169.20 8 Tetraline T 0.0094 207.57 9 Naphthalene N 0.0044 217.96 10 Hexylbenzene HB 0.0091 226.00 11 2-Methylnaphthalene 2MN 0.0080 241.05 12 Heptane C7 0.0017 98.43 13 Octane C8 0.0168 125.67 14 Nonane C9 0.0671 150.80 15 Decane C10 0.0337 174.12 16 Undecane C11 0.0311 216.28 17 Dodecane C12 0.0311 216.28 | 1 | Toluene | TOL | 0.0026 | 110.63 |
| 3 m,p-Xylene M,PX 0.0233 138.35 4 o-Xylene OX 0.0175 144.41 5 Propylbenzene PB 0.0041 159.22 6 1,3,5-Trimethylbenzene M 0.0142 164.72 7 1,2,4-Trimethylbenzene PC 0.0131 169.20 8 Tetraline T 0.0094 207.57 9 Naphthalene N 0.0044 217.96 10 Hexylbenzene HB 0.0091 226.00 11 2-Methylnaphthalene ZMN 0.0080 241.05 12 Heptane C7 0.0017 98.43 13 Octane C8 0.0168 125.67 14 Nonane C9 0.0671 150.80 15 Decane C10 0.0337 174.12 16 Undecane C11 0.0319 195.89 17 Dodecane C12 0.0311 216.28 <tr< td=""><td>2</td><td>Ethylbenzene</td><td>EB</td><td>0.0067</td><td>136.19</td></tr<> | 2 | Ethylbenzene | EB | 0.0067 | 136.19 |
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| 5 Propylbenzene PB 0.0041 159.22 6 1,3,5-Trimethylbenzene M 0.0142 164.72 7 1,2,4-Trimethylbenzene PC 0.0131 169.20 8 Tetraline T 0.0094 207.57 9 Naphthalene N 0.0044 217.96 10 Hexylbenzene HB 0.0091 226.00 11 2-Methylnaphthalene 2MN 0.0080 241.05 12 Heptane C7 0.0017 98.43 13 Octane C8 0.0168 125.67 14 Nonane C9 0.0671 150.80 15 Decane C10 0.0337 174.12 16 Undecane C11 0.0319 195.89 17 Dodecane C12 0.0311 216.28 18 Tridecane C13 0.0357 235.44 19 Tetradecane C14 0.0254 253.57 | | пі,р-Хуіепе | | | 138.35 |
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| 7 1,2,4-Trimethylbenzene PC 0.0131 169.20 8 Tetraline T 0.0094 207.57 9 Naphthalene N 0.0044 217.96 10 Hexylbenzene HB 0.0091 226.00 11 2-Methylnaphthalene 2MN 0.0080 241.05 12 Heptane C7 0.0017 98.43 13 Octane C8 0.0168 125.67 14 Nonane C9 0.0671 150.80 15 Decane C10 0.0337 174.12 16 Undecane C11 0.0319 195.89 17 Dodecane C13 0.0357 235.44 19 Tetradecane C14 0.0254 253.57 20 Pentadecane C15 0.0194 270.63 21 Hexadecane C17 0.0026 301.82 22 Heptadecane C17 0.0026 301.82 24 Total aromatic - 0.2740 - | | Propylbenzene | PB | 0.0041 | 159.22 |
| 8 Tetraline T 0.0094 207.57 9 Naphthalene N 0.0044 217.96 10 Hexylbenzene HB 0.0091 226.00 11 2-Methylnaphthalene 2MN 0.0080 241.05 12 Heptane C7 0.0017 98.43 13 Octane C8 0.0168 125.67 14 Nonane C9 0.0671 150.80 15 Decane C10 0.0337 174.12 16 Undecane C11 0.0319 195.89 17 Dodecane C12 0.0311 216.28 18 Tridecane C13 0.0357 235.44 19 Tetradecane C15 0.0194 270.63 21 Hexadecane C16 0.0086 286.79 22 Heptadecane C17 0.0026 301.82 - Total aromatic compounds - 0.2740 - | | | | | - |
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| 13 Octane C8 0.0168 125.67 14 Nonane C9 0.0671 150.80 15 Decane C10 0.0337 174.12 16 Undecane C11 0.0319 195.89 17 Dodecane C12 0.0311 216.28 18 Tridecane C13 0.0357 235.44 19 Tetradecane C14 0.0254 253.57 20 Pentadecane C15 0.0194 270.63 21 Hexadecane C16 0.0086 286.79 22 Heptadecane C17 0.0026 301.82 - Total aromatic - 0.2740 - | 11 | 2-Methylnaphthalene | 2MN | 0.0080 | 241.05 |
| 14 Nonane C9 0.0671 150.80 15 Decane C10 0.0337 174.12 16 Undecane C11 0.0319 195.89 17 Dodecane C12 0.0311 216.28 18 Tridecane C13 0.0357 235.44 19 Tetradecane C14 0.0254 253.57 20 Pentadecane C15 0.0194 270.63 21 Hexadecane C16 0.0086 286.79 22 Heptadecane C17 0.0026 301.82 - Total aromatic compounds - 0.2740 - | 12 | Heptane | C7 | 0.0017 | 98.43 |
| 15 Decane C10 0.0337 174.12 16 Undecane C11 0.0319 195.89 17 Dodecane C12 0.0311 216.28 18 Tridecane C13 0.0357 235.44 19 Tetradecane C14 0.0254 253.57 20 Pentadecane C16 0.0086 286.79 21 Hexadecane C17 0.0026 301.82 Total aromatic compounds | 13 | Octane | C8 | 0.0168 | 125.67 |
| 16 Undecane C11 0.0319 195.89 17 Dodecane C12 0.0311 216.28 18 Tridecane C13 0.0357 235.44 19 Tetradecane C14 0.0254 253.57 20 Pentadecane C15 0.0194 270.63 21 Hexadecane C16 0.0086 286.79 22 Heptadecane C17 0.0026 301.82 Total aromatic compounds | 14 | Nonane | C9 | 0.0671 | 150.80 |
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| 18 Tridecane C13 0.0357 235.44 19 Tetradecane C14 0.0254 253.57 20 Pentadecane C15 0.0194 270.63 21 Hexadecane C16 0.0086 286.79 22 Heptadecane C17 0.0026 301.82 Total aromatic compounds | 16 | Undecane | - · · | 0.0319 | 195.89 |
| 19 Tetradecane C14 0.0254 253.57 20 Pentadecane C15 0.0194 270.63 21 Hexadecane C16 0.0086 286.79 22 Heptadecane C17 0.0026 301.82 Total aromatic compounds | | | - | 0.0311 | 216.28 |
| 20 Pentadecane C15 0.0194 270.63 21 Hexadecane C16 0.0086 286.79 22 Heptadecane C17 0.0026 301.82 Total aromatic compounds - 0.2740 - | - | Tridecane | | | 235.44 |
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| 22 Heptadecane C17 0.0026 301.82 Total aromatic compounds - 0.2740 - | - | Pentadecane | | 0.0194 | 270.63 |
| Total aromatic - 0.2740 - | | Hexadecane | | 0.0086 | 286.79 |
| compounds - 0.2740 - | 22 | Heptadecane | C17 | 0.0026 | 301.82 |
| compounds | _ | Total aromatic | | 0 2740 | |
| Total alkanaa 0 1125 | - | | - | 0.2740 | - |
| - Total alkanes - 0.1125 - | - | Total alkanes | - | 0.1125 | - |

3.2 Conditions at equilibrium

The cracked kerosene and aqueous furfural solution $(y_{w,0}=0.5)$, the other solvents formed three phases, two phases respectively.

In the case of $y_{w,0}=1$ (water), any components were not detected in the extract phase.

3.3 Numerical relationships

The distribution coefficient of component i, m_i , and the separation selectivity relative to component j, $\beta_{i,i}$, were defined by,

$$m_{i} = y_{i,1}/x_{i,1}$$
(2)

$$\beta_{i,j} = m_{i}/m_{j}$$
(3)

 $(y_{i,1}, x_{i,1}: \text{the mass fractions of constituent i in respective phases})$

3.4 Distribution coefficients

The distribution coefficients derived by Eq.(2) were plotted against the carbon number of components in **Fig.2.** The m_is of aromatic compounds were higher than those of alkanes in all material systems. It confirmed that aromatic compounds in cracked kerosene could be separated. In this condition, yield of toluene was 0.35. The carbon number lowered m_i.

The m_{is} were also plotted against the kind of solvent and the water content in the extract phase, $y_{w,1}$, in **Fig.3**. The $y_{w,0}$ lowered m_i . This effect on m_i may be attributed principally to the polarities of materials.

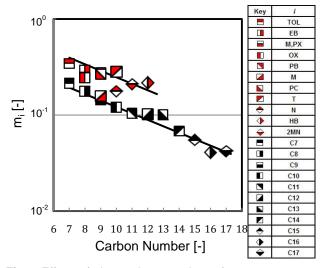


Fig.2 Effect of the carbon number of components on distribution coefficients, m_i. (Solvent: Methanol, y_{w,0}=0)

The m_is of methanol measured 35~330. The water content in the raffinate phase, $x_{w,1}$, measured 0 in all conditions. Therefore, the leakage of water from the solvent to the raffinate phase was favorably low.

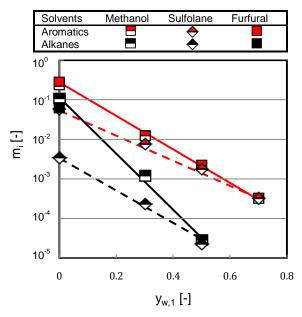


Fig.3 Effects of the kind of solvent and water content in aqueous phase, $y_{w,1}$, on distribution coefficients, m_i

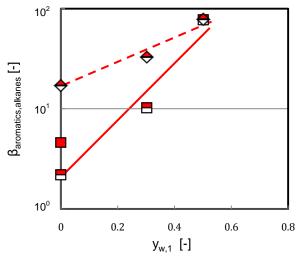


Fig.4 Effects of the kind of solvent and $y_{w,1}$, on selectivity relative to alkanes of aromatic compounds, $\beta_{aromatics,alkanes}$.

3.5 Selectivity

The separation selectivity relative to alkanes of aromatic compounds derived by Eq.(3) were plotted against $y_{w,1}$ in **Fig.4**. The $y_{w,1}$ raised β s. In the case of the sulfolane solvent, the β s were almost higher than the other solvents.

4. Conclusion

Cracked kerosene could be separated into aromatic compounds and the other hydrocarbons by three kinds of solvents (aqueous solution of methanol, sulfolane, furfural).

Literature Cited

- 1) Ukegawa, K., et al. J. of JPI, 33, (4), 250 (1990)
- 2) Kodera, Y., et al., Fuel, 70, (6) 765 (1991)
- 3) Matsumura, A., J. of NIRE, 4,(2), 43(1995)
- 4) Process of the refinement of crude oil, JPI (1998)
- 5) Egashira, R., et al., J. of JPI, 43, (5), 339 (2000)