Improvement of Process for Reducing the Benzene Content in Motor Gasoline Using an Emulsion Liquid Membrane and Distillation

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The process for removing toxic benzene from reformate based on an emulsion liquid membrane and distillation was improved and the calculation results of the new and old processes were compared. In the new process, benzene and non-aromatic hydrocarbons with boiling points close to that of benzene are removed from the reformate by two ordinary distillators to yield low-benzene reformate. The benzene and non-aromatic hydrocarbons are separated by the liquid membrane. The process calculation was carried out based on the previous empirical correlation of the mass transfer coefficient in the packed column permeator. Low-benzene reformate of the same flow rate and benzene content as in the previous process could be obtained by distillators with practical numbers of stages and operating conditions. The total aromatics content in the low-benzene reformate was higher than that of the original reformate, in contrast to the previous process. The octane number of the low-benzene reformate is thus higher than that of the original reformate. The yield of benzene was almost the same and the mass fraction of benzene in the product considerably increased. The flow rate of the stream to the permeator, consisting of the benzene and non-aromatics removed from the reformate, was naturally smaller than that in the previous process, where the original reformate was fed directly to the permeator. Therefore, the new process can treat larger amounts of the reformate than the previous process with the equivalent size of permeator. In the solvent recovery step, both the number of distillation stages and the heat energy required could be reduced. Solvent recovery absorbed the major part of the energy for the whole process. The energy requirement for the whole process was therefore lowered.

1. Introduction

Benzene is well known to be harmful to the human body, e.g. carcinogenic, so reduction of the benzene content in motor gasoline is very desirable and the removed benzene should be purified for use as raw materials for industrial purposes. Liquid membrane separation of hydrocarbons1)2) is based principally upon the difference between the distribution coefficients of hydrocarbons into an aqueous membrane phase. The distribution coefficient of aromatics is markedly higher than those of other hydrocarbon families. Therefore, this separation technique provides quite high selectivity especially for the separation of aromatics from other hydrocarbon families, which is difficult to achieve by an ordinary distillation because of the similar boiling points and azeotropic mixtures of these families. This technique is expected to be of practical use as an alternative to common aromatics separation techniques such as the sulfolane process.

Previously, we developed a process based on an emulsion liquid membrane permeator using a packed column and distillators to decrease the benzene content in motor gasoline as shown in Fig. 1(a)3). In this process, benzene was removed by the liquid membrane permeator (PT3 in the figure) directly from reformate ($F$), which has a higher benzene content than other blend stocks used in motor gasoline. The low-benzene reformate ($R$) obtained instead of the original reformate was blended with the other stocks to manufacture low-benzene motor gasoline.

In this study, the process was modified and the calculation results of this new process were compared with those of the previous process.

2. Outline of the Modified Process

Figure 1(b) shows the schematic diagram of the modified process. In this new process the mixture of benzene and non-aromatic hydrocarbons with boiling points close to that of benzene, $D_o$, are removed from the reformate, $F$, by two ordinary distillators, DT1 and
DT2. The distillate from the former distillator, D1, and bottom product from the latter, W2, are mixed by MX6 to make the low-benzene reformate, M6. The mixture of benzene and non-aromatics removed from the reformate, D2, was introduced to the liquid membrane part for separation. The liquid membrane part consists of two emulsifiers, EMs, a liquid membrane permeator, PT3, a demulsifier, DEM, and a distillator for solvent recovery, DT4. The reflux, R5, leads to the permeator. Gas oil was selected as a solvent of the liquid membrane separation because of the sufficiently high boiling range relative to that of the reformate, low distribution coefficient into the aqueous phase and low cost. In the permeator, benzene, which has a higher distribution coefficient into the membrane liquid, permeates preferentially to the non-aromatics from the raffinate phase through the liquid membrane to the extract phase. The solvent and membrane liquid are recycled and reused. From this part, the products of benzene, P5, and the non-aromatic hydrocarbons, R3, are obtained. Japanese commercial processes to lower benzene content using sulfolane extraction are operated by the same procedure: the mixture of benzene and paraffin removed from the reformate by distillators is separated by sulfolane extraction.

3. Equations for the Process, and Calculation

3.1. Equations for the Process

The basic equations representing the process are the material balances and the restrictions for the equipment, the constraints of mass fractions for the streams, some definitions, and so on. The restriction for the permeator is the permeation rate equation,

\[ \frac{d(E \cdot x_E, i)}{dz} = -P_i \cdot a \cdot (x_R, i - x_E, i) \cdot \frac{D^2}{4} \]  

with the appropriate boundary conditions. In this equation, \( P_i \cdot a \) is the overall volumetric permeation coefficient. The reflux ratio for the permeator, \( r_3 \), was defined as,

\[ r_3 = R_5 / P_5 \]

The yield of benzene, \( Y_B \), was represented as follows:

\[ Y_B = P_5 \cdot x_E, B \cdot (F \cdot x_F, B) \]  

(3)

The other equations are omitted here, but were reported in detail previously.

3.2. Calculation

3.2.1. Specifications and Conditions

The composition of the feed reformate and the conditions used for the process calculation are shown in Tables 1 and 2, respectively.

The components contained in the reformate were the same as those used in the previous study, that is, twelve hydrocarbons with respective mass fractions in real reformate of more than 0.01. The composition and flow rate were also the same. According to the previous study, the flow rate and benzene content were specified for the product of low-benzene reformate, M6, as follows:

\[ M_6 = 386 \text{ kg·h}^{-1} \]  

(4)

\[ x_{m,b} = 0.0010 \]  

(5)

The flow rate of distillate from DT1, D1, was arbitrarily determined as,

\[ D_1 = 60 \text{ kg·h}^{-1} \]  

(6)

The extract, E3, was separated into the pure solvent,

<table>
<thead>
<tr>
<th>Component (i)</th>
<th>Mass fraction, ( x_{E,i} ) [—]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene (B)</td>
<td>0.0679</td>
</tr>
<tr>
<td>Toluene (T)</td>
<td>0.2370</td>
</tr>
<tr>
<td>Xylene (X)</td>
<td>0.2543</td>
</tr>
<tr>
<td>Ethylbenzene (EB)</td>
<td>0.0518</td>
</tr>
<tr>
<td>Trimethylbenzene (TMB)</td>
<td>0.0981</td>
</tr>
<tr>
<td>Butane (B)</td>
<td>0.0264</td>
</tr>
<tr>
<td>Pentane (P)</td>
<td>0.0372</td>
</tr>
<tr>
<td>2-Methylbutane (2MB)</td>
<td>0.0534</td>
</tr>
<tr>
<td>Hexane (H)</td>
<td>0.0363</td>
</tr>
<tr>
<td>2-Methylpentane (2MP)</td>
<td>0.0410</td>
</tr>
<tr>
<td>3-Methylpentane (3MP)</td>
<td>0.0314</td>
</tr>
<tr>
<td>Heptane (Hp)</td>
<td>0.0652</td>
</tr>
<tr>
<td>Aromatics (A)</td>
<td>0.7091</td>
</tr>
<tr>
<td>Non-aromatics (NA)</td>
<td>0.2909</td>
</tr>
</tbody>
</table>

Table 1 Composition of Feed Reformate for Process Calculation
i.e., gas oil and permeate, $D_4$, ideally by DT4 as follows:

\[ x_{D4, GO} = 0 \]  
\[ x_{S, GO} = 1 \]

Common sizes were employed for the distillators DT1 and DT2. The flow rate ratio of the solvent relative to the stream introduced to the permeator was also the same as in the previous study.

### 3.2.2. Method

The process calculation was carried out as follows: DT1, DT2, and MX6 were calculated by a commercial process simulator (Chemstations, Inc., ChemCAD III); the equations for PT3, DT4, and DV5 were solved by a program written in FORTRAN77 with the result of $D_2$ from the first calculation; and, to satisfy the results of this second calculation, DT4 was calculated by the simulator.

In the calculation of the permeator, $P_i$ in Eq. (1) was estimated by the previous empirical correlation of the emulsion phase mass transfer coefficient in the packed column permeator\(^5\). The following equations were substituted for the specifications of Eqs. (7) and (8) in the calculation of DT4 by the simulator:

\[ x_{D4, GO} = 0.0001 \]  
\[ x_{S, GO} = 0.9999 \]  
\[ x_{D4, GO} = 0 \]  
\[ x_{S, GO} = 1 \]  
\[ x_{D4, GO} = 0 \]  
\[ x_{S, GO} = 1 \]

The activity coefficients in the liquid phase were calculated by the UNIFAC Method for the distillators. The distillation stages were assumed to be adiabatic and ideal. The physical properties of the gas oil were substituted by those of hexadecane (C\(_{16}\)H\(_{34}\)) and the permeation of the gas oil through the liquid membrane was therefore neglected.

The heat energies required for the reboilers of the distillators per unit mass of the feed reformate were selected as approximate values of the energy requirements for the separation, $q_s$. The sum of these $q_s$ was the energy requirement for the whole process, $q_o$.

### 4. Results and Discussion

#### 4.1. Operation Conditions and Sizes of Equipment

Table 3 shows the reflux ratios, the height of the permeator and the size of the solvent recovery distillator, DT4. The low-benzene reformate of the same specifications used in the previous study (Eqs. (4) and (5)) could be obtained by distillators of practical sizes as shown in Table 1 and reflux ratios. The height of the permeator, $Z_3$, was half of that in the previous process. Although the reflux ratio for the permeator, $r_3$, was also smaller, this remained at an impractical value. It is necessary to find better specifications and conditions to reduce this value. The number of distillation stages of DT4 was smaller than the previous result.

#### 4.2. Streams

The main results of the streams in the process are given in Table 4. The total aromatics content in the low-benzene reformate, $x_{M6,A}$, was higher (0.8218) than that of the original reformate ($x_{F,A} = 0.7091$), in contrast to the previous process ($x_{R3,A} = 0.6236 < x_{F,A}$). The modification of the process allowed removal of only benzene from the aromatics in the reformate favorably. The octane number of the low-benzene reformate is thus higher than that of the original reformate. The flow rate of the stream to the permeator, the benzene and non-aromatics removed from the reformate, $D_2$, was naturally smaller than that in the previous process where the original reformate, $F$, was fed directly to the permeator. In other words, the modified process on the whole can treat a larger amount of the reformate than the previous process with an equivalent size of permeator and flow rate of the solvent. Content of aromatics other than benzene in $D_3$ was naturally smaller than that in the previous process where the original reformate, $F$, was fed directly to the permeator. In other words, the modified process on the whole can treat a larger amount of the reformate than the previous process with an equivalent size of permeator and flow rate of the solvent. Content of aromatics other than benzene in $D_3$ was very low. Consequently, the flow rate of the extract, $E_3$, which was led to the solvent recovery distillator, was smaller (about a quarter). The mass fraction of benzene in the product, $x_{E3,B}$, was about 0.86 and considerably higher than that in the previous process, $x_{W7,B} = 0.295$. The benzene yield defined by Eq. (3), $Y_B$, was almost the same (0.98) as in the previous process (0.99).
4.3. Energy Requirement

The energy requirements, \( q_k \), \( q_t \), are summarized in Table 5. Solvent recovery absorbed the major part of the energy requirement for the whole process, as in the previous process. The energy required for solvent recovery was smaller than the previous process, mainly because the flow rate of the extract, \( E_3 \), was smaller. The energy requirement for the modified process was therefore lower than that for the previous process.

4.4. Low-benzene Motor Gasoline

Table 6 shows rough estimates of the benzene and aromatics contents in the motor gasoline. The aromatics content increased, namely, the octane number was improved, although the benzene content was lowered to a fifth of that in the original motor gasoline, and was much lower than that in low-benzene motor gasoline in Japan.

5. Conclusion

The benzene removal process based on an emulsion liquid membrane and distillation could be improved to remove only benzene among aromatics in the reformate and to purify the benzene more efficiently. Further improvement of the process is expected by adjustment and optimization of specifications and conditions.

Nomenclatures

- \( a \): specific interfacial area between emulsion and solvent in permeator \([\text{m}^{-1}]\)
- \( D \): inner diameter of permeator \([\text{m}]\)
- \( D_k \): flow rate of distillate from distillator \( k \) \([\text{kg-h}^{-1}]\)
- \( E \): flow rate of extract phase in permeator \([\text{kg-h}^{-1}]\)
- \( E_3 \): flow rate of extract from permeator \([\text{kg-h}^{-1}]\)
- \( F \): flow rate of feed reformate \([\text{kg-h}^{-1}]\)
- \( n_k \): number of distillation stages of distillator \( k \) \([-]\)
- \( n_{kA} \): feed stage of distillator \( k \) \([-]\)
- \( P_f \): flow rate of permeate from stream divider \([\text{kg-h}^{-1}]\)
- \( q_k \): energy requirement for distillator \( k \) \([\text{kJ}-(\text{kg-F})^{-1}]\)
- \( q_t \): energy requirement for whole process \([\text{kJ}-(\text{kg-F})^{-1}]\)
- \( R_5 \): flow rate of reflux from permeator \([\text{kg-h}^{-1}]\)
- \( R_k \): flow rate of raffinate from permeator \([\text{kg-h}^{-1}]\)
- \( S \): flow rate of solvent (gas oil) \([\text{kg-h}^{-1}]\)
- \( W_b \): flow rate of bottom product from distillator \( k \) \([\text{kg-h}^{-1}]\)
- \( x_i \): mass fraction of component \( i \) in stream \( l \) \([-]\)
- \( Z_k \): height of permeator \([\text{m}]\)
- \( z \): distance from top of permeator \([\text{m}]\)

Subscripts

- \( 1, 2, 4, 7 \): distillator DT1, DT2, DT4, or DT7

Previous results in parentheses\(^3\).

Table 5 Energy Requirements for Separation

| Distillator 1 (DT1), \( q_i \) | \([\text{kJ}-(\text{kg-F})^{-1}]\) | 220 |
| Distillator 2 (DT2), \( q_i \) | \([\text{kJ}-(\text{kg-F})^{-1}]\) | 340 |
| Distillator 4 (DT4), \( q_i \) | \([\text{kJ}-(\text{kg-F})^{-1}]\) | 1840 (6880) |
| Distillator 7 (DT7, enrichment of aromatics) | \([\text{kJ}-(\text{kg-F})^{-1}]\) | 56.7 |
| Whole process, \( q_t \) | \([\text{kJ}-(\text{kg-F})^{-1}]\) | 2400 (6940) |

Previous results in parentheses\(^3\).

Table 6 Compositions of Low-benzene Motor Gasoline

<table>
<thead>
<tr>
<th>Volume fraction ([-])</th>
<th>Benzene</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordinary motor gasoline</td>
<td>0.023</td>
<td>0.29</td>
</tr>
<tr>
<td>Low-benzene motor gasoline in Japan</td>
<td>0.0045 (0.0045)</td>
<td>0.33 (0.26)</td>
</tr>
</tbody>
</table>

Previous results in parentheses\(^3\).
2MBt: 2-methylbutane
2MPt: 2-methylpentane
3: permeator (PT3)
3MPt: 3-methylpentane
5: stream divider (DV5)
6: stream mixer (MX6)
A: aromatics
B: benzene
Dk, E, E3, F, P5, Rk, S, Wk: stream Dk, E, E3, F, P5, Rk, S, or Wk
EB: ethylbenzene
Hp: heptane
Hx: hexane
i: component i
NA: non-aromatics
Pt: pentane
T: toluene
TMB: trimethylbenzene
X: xylene

References
1) Li, N. N., AICHe J., 17, (2), 459 (1971).

要 旨
自動車ガソリン中のベンゼン含有量低減のための乳化液膜および蒸留からなるプロセスの改良
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既に報告した、改質ガソリンから有害ベンゼンを除去するプロセスを改良した。本プロセスにおいては、改質ガソリンから蒸留によりベンゼンおよびこれと沸点の近接する非芳香族成分を除去し、乳化液膜を通じて除去したベンゼンと非芳香族成分を蒸留分離装置により分離するものとしました。プロセス計算には既製の Merchandizing透過装置における移動係数の関係式を用いた。実用的な段数および運転条件の蒸留塔により、流量とベンゼンの質量分率について既報と同様の低ベンゼン改質ガソリンが得られた。既報のプロセスの場合は異なり、原料改質ガソリンに比較して低ベンゼン改質ガソリン中の非芳香族含有量は大きく、オクタン値は向上した。ベンゼンの収率は既報のプロセスの場合と同程度であり、ベンゼン製品中のベンゼンの濃度は著しく増加した。プロセス全体で処理可能な改質ガソリンの流量は増加する結果となった。溶媒回収において蒸留段数および所要熱エネルギーの双方を減少した。プロセス全体における所要熱エネルギーに対して溶媒回収に必要なエネルギーの占める割合が最も大きく、したがってプロセス全体の所要熱エネルギーは減少した。

Keywords
Motor gasoline, Benzene content decrease, Reformate, Emulsion liquid membrane, Distillation, Process improvement

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