Pure Aromatic Hydrocarbons from Petroleum Fractions by Dehydrogenation-Hydrogenolysis Combination Process*  
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Summary: Catalytic dehydrogenation of ethylcyclohexane, thermal hydrogenolysis of ethylbenzene and ethylcyclohexane, and the combination process comprising successive operations of dehydrogenation and hydrogenolysis for ethylcyclohexane, kerosene and gas oil have been studied using a conventional flow apparatus. Dehydrogenation has been carried out over a commercial chromia-alumina catalyst at temperatures ranging from 485 to 565°C under an atmospheric pressure, while hydrogenolysis at temperatures from 710 to 760°C also under an atmospheric pressure.

Main products in the dehydrogenation of ethylcyclohexane are hydrogen, ethylbenzene, xylenes, benzene, and toluene. Those in the hydrogenolysis of ethylbenzene are benzene, toluene, and styrene. The hydrogenolysis of ethylcyclohexane results in a production of gases containing an appreciable amount of ethylene. Product distributions in the combination process for ethylcyclohexane are compatible with those found in the separate studies of the individual component reactions. Thus liquids produced are very high in aromatic content, while gases are rich in olefin content.

The combination process has been further examined for kerosene and gas oil. It has been found that the liquids obtained from these higher hydrocarbons consisted of benzene, naphthalene and their alkyl derivatives but neither paraffins nor olefins whose boiling points are higher than that of benzene were present. Sufficiently pure components of aromatic hydrocarbons are obtainable from the liquid products by a conventional distillation. An additional advantage in the combination process is the production of gases of high ethylene content. A model plant of the combination process is presented for the separation of benzene, toluene and xylenes.

Introduction

Aromatic hydrocarbons have generally been separated from petroleum fractions by means of physical processes such as extraction and adsorption. Commercial units based on these methods are currently applied to naphtha reformates as well as for bottom fractions from the naphtha cracking process. The shortcoming of such physical methods, when applied in an industrial scale, becomes apparent if one considers the production of a large amount of raffinates which are of low market value. The separation usually involves further complication by the hydrogenation process required for feedstocks.

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are rich in olefin content. A flow diagram of a model plant will also be presented.

**Experimental**

**Apparatus and procedures**

Illustrated in Fig. 1 and Fig. 2 are the flow diagrams of the apparatus employed. The apparatus shown in Fig. 1 was used to study each of the component reactions of ethylcyclohexane and ethylbenzene. Ethylcyclohexane, or ethylbenzene, was stored in a saturator bottle which was fitted in a methanol vapor jacket. The reactant vapor was introduced into a reactor with a stream of hydrogen carrier gas passing through the saturator. Partial pressure of the reactant vapor was thus determined by the boiling temperature of methanol. The reactor, made of a quartz tubing of 400 mm in length and 20 mm inside diameter, was placed in a

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**Fig. 1** Flow diagram of the apparatus for the catalytic dehydrogenation and thermal hydrogenolysis, respectively

**Fig. 2** Flow diagram of the apparatus for the combined reaction, catalytic dehydrogenation-thermal hydrogenolysis

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vertical position. It was uniformly heated by an electric furnace provided with a controlling instrument. Reaction temperature was measured to within ±1°C by a chromel-alumel thermocouple in a sheath installed along the longitudinal axis at the center of the reactor. The reactor was filled with chromia-alumina catalyst of approximately 12.5ml bulk volume in the case the catalytic dehydrogenation, whereas in the case of the thermal hydrogenolysis, the catalyst bed was replaced by quartz chips. The voidage was 50.5% in the latter case leaving an effective reactor volume of approximately 37ml. Condensable components of the products were collected in a trap immersed in a Dry Ice-methanol bath. While non-condensable components were led into a conventional gas holder maintained at an atmospheric pressure. The analyses of both liquid and gaseous products were carried out by a gas-liquid chromatography.

Carbonaceous materials deposited on the catalyst were burnt after the end of each run by passing a stream of air through the reactor for two hours at temperatures above 400°C. The regeneration temperature was maintained below 700°C by controlling the flow rate of air.

The apparatus illustrated in Fig. 2 was used for the combination process. The construction of the reactor was similar to that described above. In this instance, however, the reactor was divided into two parts, i.e. the upper part being packed with chromia-alumina catalyst for the catalytic dehydrogenation and the lower part being packed with quartz chips for the thermal hydrogenolysis. Bulk volume of the catalyst zone was 12.5ml, while the free volume at the thermal reaction zone was 11.3ml. The procedures were otherwise the same as those described for the component reactions.

Materials

Ethylcyclohexane was prepared by the hydrogenation of ethylbenzene over platinum catalyst at approximately 200°C in an autoclave. It was then treated by acid and alkali, and was thoroughly washed with water. The purity of the prepared ethylcyclohexane was 99.9% as analyzed by a gas-liquid chromatography. Commercially available ethylbenzene of GR grade was used without further purification. Some physical properties of kerosene and gas oil used as charged stocks are listed in Table I. Cylinder hydrogen of 99.9% purity was used after passing over Deoxo catalyst and drying agent.

Catalyst of 4~8 mesh containing 7 mole% chromia supported on alumina was supplied from Nikki Chemicals Co., Ltd.

Results and Discussion

**Catalytic dehydrogenation of ethylcyclohexane**

Illustrated in Fig. 3 are the distributions of liquid products in the catalytic dehydrogenation of ethylcyclohexane at four different temperatures varying from 485 to 565°C at a fixed LHSV of 0.27 ml/hr. Conversion of ethylcyclohexane was 41.4 mole% at 485°C, and was increased almost linearly with reaction temperature to reach as high as 95.4% at 565°C. Main liquid products in the decreasing order were ethylbenzene, xylenes, benzene and toluene. Smaller amounts of cyclopentane, methylcyclopentane, methylcyclohexane and paraffin and olefin hydrocarbons from C4's to C6's were also present in the liquid products. In a
A typical run carried out at 515°C in which 68.6% of charged ethylcyclohexane was consumed, aromatic content of the liquid products was 61.5%. The main reaction must therefore be the dehydrogenation of aliphatic ring to form aromatic nucleus. In conformity with the above, more than two moles of hydrogen was produced for each mole of ethylcyclohexane consumed. The amount of hydrogen accounted for approximately 95% of the total gases produced. Appreciable isomerization and dealkylation were also assumed to take place simultaneously to explain the formation of benzene, toluene and xylenes. In addition to hydrogen, very small amounts of methane, ethane, ethylene, propane and propylene were identified in the gaseous products. These low molecular hydrocarbons were probably produced by dealkylation and hydrogenolysis.

Illustrated in Fig. 4 are the distributions of liquid products at 560°C at four different LHSV's varying from 0.70 to 0.10 ml/hr. Conversion of ethylcyclohexane was 35.9% at LHSV of 0.70 ml/hr, while it was increased to 97.6% when LHSV was decreased to 0.10 ml/hr. The formation of aromatic hydrocarbons became more pronounced upon raising reaction temperature and decreasing LHSV. It can be seen in Fig. 3 and Fig. 4, however, reactions other than the simple dehydrogenation become manifest under these severe conditions.

**Thermal hydrogenolysis of ethylbenzene**

Illustrated in Fig. 5 are the distributions of liquid products in the thermal hydrogenolysis of ethylbenzene at contact times varying from 1.9 to 11.7 sec. Conversion of ethylbenzene under the given conditions was between 96.1 and 99.7%. The liquid products were mainly composed of benzene with very small amounts of toluene and styrene. The yield of benzene was increased with contact time. The main reaction was undoubtedly the detachment of ethyl group. Maxima amounts of styrene and hydrogen were observed at an extremely short contact time, and the latter was estimated to be in the range of 0.5~1.0 sec, in our recent studies. This suggests that the thermal dehydrogenation of ethylbenzene occurred at an earlier stage of the reaction. Thus the thermal reaction of ethylbenzene is complicated due to the two reactions taking place simultaneously.

Illustrated in Fig. 6 are the distributions of gaseous products. Traces of propane and propylene were also identified besides those indicated in Fig. 6.

**Thermal hydrogenolysis of ethylcyclohexane**

Illustrated in Fig. 7 are the distributions of gaseous products in the thermal hydrogenolysis of ethylcyclohexane at contact
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Fig. 6 Variation of the gaseous products distribution with contact time in the thermal hydrogenolysis of ethylcyclohexane at 740°C and \( a = 10.2 \)

\( a \): the mole ratio of hydrogen to feed

Times varying from 2.1 to 11.2 sec. Conversion of ethylcyclohexane under the given conditions was between 93.0 and 99.6%. Main products were methane, ethane, ethylene and propylene. The yields of methane and ethylene were increased with increasing contact time. The formation of the latter declined, however, after contact times exceeded approximately 8 sec. Olefin content of the gases produced was 40~50%, of which 70~82% consisted of ethylene. Small amounts of propane, C\(_4\)-hydrocarbons, and higher boiling materials were also produced.

Liquid products, corresponding to about 10% of charged ethylcyclohexane, were mainly composed of benzene and toluene. Also included in the heavy fractions were xylenes, ethylbenzene, styrene, cyclopentane, methylcyclopentane, methylethylcyclohexane and traces of many other unidentified components. The aromatic content of the liquid products was more than 70%.

Dehydrogenation-hydrogenolysis combination process for ethylcyclohexane

In the preceding paragraphs, general features for each of the component reactions of ethylcyclohexane and ethylbenzene have been described. These observations can be used to predict possible product distributions resulting from the combination process for ethylcyclohexane. Thus ethylcyclohexane will be dehydrogenated and to some extent the dehydrogenated products will be further isomerized at the catalytic dehydrogenation zone of the reactor to produce mainly ethylbenzene and xylenes. In the subsequent thermal hydrogenolysis zone ethylbenzene, and xylenes will be converted to benzene, toluene and styrene in the presence of an excess hydrogen, while unreacted ethylcyclohexane will be the source of gases containing

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a considerable amount of ethylene. One of the advantages of the proposed combination process, as compared with the successive operation of the two separate component reactions, exists in the fact that it directly utilizes, in the second zone of the reactor, the large amount of hydrogen evolved in the preceding reactor zone. It thus produces, in a simple one-step operation, liquids and gases of favorable compositions.

Illustrated in Fig. 8 and Fig. 9 are respectively the distributions of liquid and gaseous products in the combination process for ethylcyclohexane. Runs were carried out at four different temperatures of the catalytic dehydrogenation zone varying from 510 to 580°C for a mixture consisting of four parts of hydrogen for each part of ethylcyclohexane at a fixed temperature of the thermal hydrogenolysis zone of 710°C and at a fixed LHSV of 0.37 ml/hr. Complete conversion of ethylcyclohexane was attained under the conditions studied. Liquid products were mainly composed of benzene, toluene, styrene, ethylbenzene and xylenes. The amount of benzene increased with the temperature of the dehydrogenation zone. With an exception of methylocyclopentane, neither paraffins nor olefins were detected in the boiling range higher than benzene. The amount of methylcyclopentane was limited to 0.06~0.14% of the liquid products. In addition to the above, minute amounts of C3- and C4-hydrocarbons were also present. The yields of methane and ethane tend to become higher at lower dehydrogenation temperatures.

Illustrated in Fig. 10 are the distributions of the liquid products observed at a fixed temperature of the catalytic dehydrogenation of 560°C, while temperature of the hydrogenolysis was varied between 710 and 760°C. A mixture of four parts of hydrogen for each part of ethylcyclohexane was fed into the reactor at a fixed LHSV of 0.37 ml/hr. The latter corresponds to a contact time of about 1 sec in the hydrogenolysis zone. Conversion was again complete under the conditions studied. Liquid products were similar to those indicated in Fig. 9.

The results of the combination process are in every respects compatible with the product distributions expected from the independent studies of the component reactions. Pure aromatic hydrocarbons can readily be separated from the liquid products by a simple fractional distillation. Gaseous products, on the other hand, can be used as an excellent source of olefins.

Combination process for kerosene and gas oil

The combination process was applied for kerosene and gas oil to examine versatility of the proposed scheme. Listed in Table II are the results obtained for runs carried out in the stream of hydrogen at an atmospheric pressure.
Table II Experimental Data of the Combination Process for Kerosene and Gas Oil

<table>
<thead>
<tr>
<th></th>
<th>Kerosene</th>
<th>Gas Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic dehydrogenation temp. (°C)</td>
<td>560</td>
<td>540</td>
</tr>
<tr>
<td>Thermal hydrogenolysis temp. (°C)</td>
<td>760</td>
<td>760</td>
</tr>
<tr>
<td>LHSV (ml/hr)</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>Feed (g)</td>
<td>1.82</td>
<td>1.90</td>
</tr>
<tr>
<td>Hydrogen introduced (ml)</td>
<td>450</td>
<td>415</td>
</tr>
<tr>
<td>Liquid products (g)</td>
<td>0.92</td>
<td>0.95</td>
</tr>
<tr>
<td>Concentrations of liquid products (mole %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₇-C₁₀ paraffins, cyclopentane</td>
<td>1.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>16.5</td>
<td>12.3</td>
</tr>
<tr>
<td>Toluene</td>
<td>23.2</td>
<td>19.4</td>
</tr>
<tr>
<td>m,p-Xylene, ethylbenzene</td>
<td>10.8</td>
<td>8.5</td>
</tr>
<tr>
<td>o-Xylene, styrene</td>
<td>9.8</td>
<td>8.9</td>
</tr>
<tr>
<td>C₆-C₁₀ aromatics</td>
<td>9.8</td>
<td>10.1</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>15.7</td>
<td>17.1</td>
</tr>
<tr>
<td>Methylnaphthalene</td>
<td>8.7</td>
<td>16.1</td>
</tr>
<tr>
<td>C₁₇-aromatics</td>
<td>4.1</td>
<td>7.0</td>
</tr>
<tr>
<td>Yields of gaseous products (wt %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.1</td>
<td>4.7</td>
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<tr>
<td>Methane</td>
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<tr>
<td>Ethane</td>
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<tr>
<td>Ethylene</td>
<td>13.6</td>
<td>9.8</td>
</tr>
<tr>
<td>Propane</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Propylene</td>
<td>2.0</td>
<td>1.7</td>
</tr>
<tr>
<td>C₁₁'s</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Total</td>
<td>38.5</td>
<td>31.4</td>
</tr>
</tbody>
</table>

It should be noted that, contrary to the observations made for the reactions of ethylcyclohexane, a considerable amount of naphthalene ring was formed in the reactions of kerosene and gas oil. According to our unpublished data, however, naphthalene ring was readily formed when the combination process was applied for n-decane, n-dodecane and diisopropylcyclohexane. The formation of naphthalene ring may be accounted for by similar reactions, since the pressure. Recoveries of liquid products were approximately 50% in weight for both kerosene and gas oil. Principal components of the liquid products were benzene, toluene, ethylbenzene, xylenes, naphthalene and methylnaphthalene. Included in the liquid were small amounts of many other unidentified higher aromatic hydrocarbons mentioned above, approximately twenty-six components of lower hydrocarbons such as cyclopentane, cyclopentadiene, isoprene, butadiene were also detected. Distinguished features of the product distributions are the absence of higher hydrocarbons other than aromatics as well as the extremely small amounts of those components such as cyclohexane, methylcyclopentane, dimethylpentane, n-heptane and methylcyclohexane whose boiling points are in the proximity of that of benzene. Principal components of the gaseous products were hydrogen, methane and ethylene, which were accompanied by limited quantities of C₆- and C₇-hydrocarbons.

Fig. 11 Flow diagram of commercial apparatus suggested
components, such as mentioned above, are present in both kerosene and gas oil. Such reactions, in fact, may offer an attractive route for naphthalene from petroleum fractions.

**Model plant of the combination process**

A typical flow diagram of a model plant, as illustrated in Fig. 11, can be drawn as a result of the observations made for the combination process. Charging stock is fed into a catalytic dehydrogenation section of the reactor equipped with a regeneration device for catalysts, and the dehydrogenated oil is then introduced into a thermal hydrogenolysis section. Products are quenched and separated into gases and liquids. An absorption oil is then applied for the liquids containing aromatic hydrocarbons, and are subsequently separated for benzene, toluene, and xylenes by a series of fractionators. Bottom fraction contains higher aromatics such as naphthalene. Recycle lines are also provided in the diagram. Although it is by no means necessary, the clay treating can be applied before the fractional distillation to remove diolefins whose presence is known to interfere with the subsequent operations. Our preliminary test of a conventional laboratory distillation preceded by the clay treating of the liquid products confirms the separation of as pure aromatic components as those obtained by the Udex process.

While only chromia-alumina catalyst was cited in the present study, other commercial catalysts such as those used for Platforming and Hydroforming processes can be equally employed. The catalytic dehydrogenation section illustrated in Fig. 11 may therefore be replaced by a platforming tower. Although in the present communication studies were confined to atmospheric pressure, the same objective can be achieved at pressures up to about 10 atmospheres.

**Acknowledgment**

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**References**