HYDROGENATION OF OIL PRODUCED BY NAPHTHA STEAM PYROLYSIS

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RESIDUAL PYROLYSIS OIL (RPO) PRODUCED AS A BY-PRODUCT OF NAPHTHA STEAM PYROLYSIS

Residual pyrolysis oil (RPO) produced as a by-product of naptha steam pyrolysis was hydrogenated (160-280°C; 60 bar, trickle-bed reactor with Co-Mo/γ-Al2O3) with the aim of suppressing the polymerization of the unsaturated compounds present in the oil (styrene, (–methylstyrene, 4-, 5- and 6-methyl-indene and others) which give a highly aromatic resin. The influence of temperature on the rate of hydrogenation was investigated at a constant liquid space velocity (LHSV) of 1 h⁻¹ and hydrogen/oil ratio of 600 Nm³/m³, while the influence of liquid space velocity (1-3 h⁻¹) was analyzed at 200°C and 60 bar at the same hydrogen/oil ratio. GC and GCE-MS analysis of the hydrogenated oil were carried out on the hydrogenated sample, as well as viscosity measurements, which showed that no polymerization occurred in the case of stabilized (hydrogenated) oil. The optimal hydrogenation temperature and LHSV values were 220°C and 1 h⁻¹, respectively. The result of the longterm hydrogenation test was used to study the kinetics of the catalyst deactivation process by determining the rate constants in the case of indene, 4-methyl-indene and 5- and 6-methyl-indene hydrogenation. Using the obtained rate constants, the conversion of the above compounds was mathematically simulated, showing satisfactory agreement with the experimentally observed values.

The physical characteristics of residual pyrolysis oil (RPO) are given elsewhere [1]. RPO can be used as a fuel, however better economical valorization can be realized by:

- the production of special chemicals, e.g. naphtalene;
- polymer swelling;
- wood protection;
- insecticide production;
- the preparation of coating materials;
- the production of highly aromatic lighter oil;
- the production of aromatic resins;
- coke production;
- the production of special additives for making industrial bitumen.

This work involves the analysis of RPO stabilization by hydrogenation with the goal of suppressing polymerization of the unsaturated compounds which are present in the oil (styrene, (–methylstyrene, 4-, 5- and 6-methyl-indene and others).

Hydrogenation leads to the formation of saturated double bonds in styrene and indene type compounds, but also under severe hydrogenation conditions to the unfavorable hydrogenation of aromatic compounds (naphtalene). The production of naphtalene and indene can be realized according to the following technological route:

RPO → Stabilization (Hydrogenation) → Distillation (Two Stage) → Indene, Naphthalene, Heavy Residue

The influence of temperature and the LHSV on the rate of hydrogenation was investigated under a constant pressure of 60 bar and a hydrogen to oil ratio of 600 Nm³/m³. The experiments were performed at 160, 200, 240 and 280°C with a LHSV of 1 h⁻¹, and at 200°C with a LHSV of 1, 1.5 and 3 h⁻¹. To study the behaviour of the catalyst during hydrogenation, a longterm hydrogenation test was performed which lasted 120h. During this experiment the temperature changed from 200 to 220°C. The conversion of indene, 4-methyl-indene and 5- and 6-methyl-indene, determined by GC analysis, was used to calculate the kinetic parameters of hydrogenation, as well as of catalyst deactivation and reactivation [2]. The kinetic data were used to perform a mathematical simulation of the so-called longterm deactivation test. GC analysis of the hydrogenated products was also used to follow the possible hydrogenation of the aromatic rings. The viscosity of the RPO was measured to see whether polymerization took place during the hydrogenation.

EXPERIMENTAL

The hydrogenation of RPO was performed in a trickle-bed reactor (5.8 cm i.d. and 520 cm length pipe), where 35 g of the catalyst (50 cm³) were diluted by using inactive alumina in the volumetric ratio 1:2 (catalyst/alumina). On both sides of the catalyst bed, a guard bed of inert alumina, 0.5 cm (below) and 1 cm (above the bed), was installed. A thermowell (2.2 cm i.d.) was placed in the center of the catalyst bed allowing precise catalyst temperature measurement during hydrogenation. The commercial catalyst (BASF MB-14, extrudate 1.3 mm) was sulfided in-situ using the RPO with CS₂ (22.5 gCS₂/1000 cm³ of residual oil, i.e. 2.2 % S in the oil) at 40 bar and 300°C (maximum), using the standard heating rate of 30-50 °C/h.

When experimental conditions were attained (pressure, temperature and flow rate of RPO), hydrogenation was carried out for at least 2-3 hours, when steady state conditions were established. The liquid product of the hydrotreated RPO was collected in regular time intervals (80 min) for detailed GC analysis.
Influence of temperature

The influence of temperature was analyzed at the beginning of hydrogenation when the catalyst showed its initial and highest activity. The experimental conditions were: 60 bar, LHSV=1 h⁻¹ (RP0=50 cm³/h and H₂=30 dm³/h). The hydrogenation was first analyzed at 160°C, and then, when the desired quantity of the hydrogenated product was collected, the hydrogenation temperature was raised to 200°C. This experimental procedure was repeated at 240 and 280°C.

The results of GC analysis indicated that the quality of hydrogenated RPO at 200°C has all the desired qualities (small quantity of unsaturated compounds, oil viscosity); however, hydrogenation performed at a higher temperature (>240°C) indicated some undesirable effects in the quality of the hydrogenated products such as large decreases of oil viscosity and the saturation of aromatic compounds (e.g. naphthalene). These results undoubtedly showed that the best effects of hydrogenation could be expected at 200–220°C.

Influence of LHSV

During RPO hydrogenation the following liquid hourly space velocities were analyzed: 1; 1.5 and 3 h⁻¹, always keeping the same hydrogen/oil ratio at the inlet of the reactor (H₂/oil=600 Ncm³/cm³), as well as pressure (60 bar) and temperature (200°C). The obtained results showed that LHSV=1 h⁻¹ gave the best results compared to other investigated liquid flow rates. Thus, all the investigations of the influence of temperature and LHSV on hydrogenation showed that the best results could be obtained if hydrotreatment were performed at 200–220°C, under 60 bar, LHSV=1 h⁻¹ and H₂/oil = 600 Ncm³/cm³.

Analysis of catalyst activity during 120 h (longterm test) reactor steady state operation

The longterm hydrogenation test was performed as follows. In situ re sulfidization of the catalyst was performed after study of the influences of temperature and LHSV was completed. The same procedure was applied for re sulfidization as for fresh catalyst. The first 40 hours of longterm hydrogenation were performed at 200°C, and then, to compensate for a small drop in the catalyst activity, the temperature in the reactor was increased to 210°C, and after an additional 5 hours of hydrogenation to 220°C. Namely, analysis of hydrogenation product indicated, that to obtain a product of constant quality, this hydrogenation temperature increase was necessary to suppress the negative influence of catalyst deactivation. The hydrogenation process was quite stable during the entire 120 h of operation, with minor changes of less than 3% in the key operating parameters (pressure 60 ±0.5 bar, temperature fluctuation 0.88% at 200°C and 0.97% at 220°C; LHSV=1–1.03 h⁻¹; hydrogen flow rate 29–31 Ndm³/h). Changes in the hydrogen flow rate were observed only when liquid product was withdrawn from the high pressure separator. However, such disturbances lasted only 1–2 min.

GC analysis of hydrogenation products

The liquid samples as well as samples of the gas phase collected during the hydro treatment tests were continuously analyzed enabling complete monitoring of the hydrogenation process.

The liquid samples were analysed by capillary gas chromatography using a Varian 3400 instrument equipped with a FID detector and a Spectrophysics System I computing integrator on a DB-5, 30 m glass capillary column with temperature programmed at 4°C/min from 60–300°C. Nitrogen was used as the carrier gas.

The gas analysis was always performed at the start of a test and after 5 hours of operation, and always when the liquid samples were withdrawn from the high pressure separator. A Shimadzu GC (model GC-9A) instrument equipped with FID and TCD was used for the gas analysis. The following columns and detectors were used for the detection of different gases and vapours: hydrogen, molecular sieve 5A (2m), TCD at 150°C, 50 ma; hydrocarbons, 20% squalene on Chromosorb PAV (4m), FID at 150°C. Gas analysis was performed on-line and the main components of the gas phase were hydrogen (more than 99%), but also smaller quantities of C1, C2, C3, n-C4 and i-C4 were detected (less than 1%).

The results of GC analysis of the gas phase during the hydrogenation of RPO are given in Table 1. The

| Table 1. GC analysis of the gas phase collected during the analysis of RPO hydrogenation at different temperatures and LHSV:

<table>
<thead>
<tr>
<th>HYDROGENATION TEMPERATURE, °C</th>
<th>C₂H₆ %vol.</th>
<th>CH₄ %vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>0.003</td>
<td>0.100</td>
</tr>
<tr>
<td>200</td>
<td>0.063</td>
<td>0.002</td>
</tr>
<tr>
<td>240</td>
<td>0.049</td>
<td>0.001</td>
</tr>
<tr>
<td>280</td>
<td>0.010</td>
<td>0.004</td>
</tr>
<tr>
<td>H₂/OIL, H⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.063</td>
<td>0.002</td>
</tr>
<tr>
<td>1.5</td>
<td>0.015</td>
<td>0.003</td>
</tr>
<tr>
<td>3</td>
<td>0.005</td>
<td>0.002</td>
</tr>
<tr>
<td>LHSV, 200°C, h⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 (200)</td>
<td>0.026</td>
<td>0.001</td>
</tr>
<tr>
<td>40 (200)</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>5 (210)</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>24 (220)</td>
<td>0.001</td>
<td>0.003</td>
</tr>
<tr>
<td>38 (220)</td>
<td>0.001</td>
<td>0.003</td>
</tr>
</tbody>
</table>
hydrogenation products were collected during the analysis of temperature and LHSV effects, and the results of GC-analysis of the liquid samples collected during these tests are presented in Table 2.

The viscosity of the liquid samples was determined at 20°C using a Vogel–Ossag viscosimeter.

RESULTS AND DISCUSSION

GC analysis of the gas phase showed the presence of small quantities of methane, ethane, propane, butane and isobutane, in addition to hydrogen, the content of which always amounted to over 99.7% vol. and mostly to over 99.9% vol. Methane and ethane are products of the hydrodealkylation of the methyl and ethyl, i.e. vinyl (via hydrogenation) substituted components of the RPO. The change of the content of methane and ethane in the gas phase depends on the hydrogenation temperature, LHSV and catalyst activity during the long-term hydrogenation test, as shown in Table 1. The quantity of methane decreases with increasing temperature. It is difficult to give a reasonable explanation for this phenomenon. The growth of the quantity of methane in the gas phase with increase of the residence time of the oil in the reactor, i.e. with decrease of LHSV value, is understandable, as there is more time for the hydrodealkylation to take place. During the stabilization period, which proceeds to the steady state, the methane content decreases to a constant value (0.001% in this particular case). The content of ethane, however, varied irregularly. As ethane present both, a product of the hydrodealkylation of an ethyl group, as well as of a vinyl group (via the hydrogenation of ethylene), and a vinyl group can polymerize and be regenerated through depolymerization, this irregularity could be understandable and could be caused by every disturbance of the process, for instance by taking samples from the liquid high pressure separator.

The results of GC analysis of the liquid products of RPO hydrogenation obtained during the study of the effects of temperature and LHSV are given in Table 2. Our experience showed that the total area percent values in Table 2, as well as in Table 3 should be multiplied by 0.65, to be converted to the appropriate weight percent. The results in Table 2 show that the temperature of 160°C was too low for the hydrogenation of double bonds to take place, i.e. the quantities of styrene, indene, 4-methyl-indene and 5- and 6-methyl-indene in the hydrogenated products practically did not change compared to their content in the original RPO. Increase of the viscosity from 15.8 to 20.0 mm²/s indicates, however, that polymerization took place to some extent, under that reaction condition. Hydrogenation at 200°C was very successful, as only traces of compounds with double bonds remained, the extent of polymerization (viscosity 19.6 mm²/s) was not greater than that at 160°C and no hydrogenation of the aromatic rings took place. Hydrogenation at 240°C was practically completed without hydrogenation of the aromatic rings and undesired polymerization did not take place or was compensated by desired

Table 2. GC analysis of the liquid products collected during hydrogenation tests of RPO

<table>
<thead>
<tr>
<th>SAMPLE NUMBER</th>
<th>TEMPERATURE, °C</th>
<th>LHSV, h⁻¹</th>
<th>VISCOSITY AT 20°C</th>
<th>COMPONENTS WITH GC RETENTION TIMES IN SECONDS, TOTAL AREA %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH₃, CH₂-CH₃</td>
<td>CH₂-CH₄, CH₂-CH₃, 1xCH₃, 4-CH₃, 5-6-CH₃, trans, cis</td>
</tr>
<tr>
<td>RPO</td>
<td>15.8</td>
<td>-</td>
<td>0.1, 0.8, 2.2, 2.6, 2.6, 4.7, 2.6, 32.5, 8.8, 6.1, 0.1, 0.9</td>
<td></td>
</tr>
<tr>
<td>1 160</td>
<td>20.0</td>
<td>0.4, 0.4, 2.6, 2.5, 1.5, 2.4, 5.9, 2.5, 29.9, 7.9, 5.7, 0.4, 0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 200</td>
<td>19.6</td>
<td>0.3, 4.2, 0.3, 2.3, 3.2, 2.2, 4.8, 2.7, 28.3, 8.6, 6.5, 0.7, 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 240</td>
<td>15.7</td>
<td>0.6, 0.4, 4.6, 0.1, 2.5, 4.0, 5.8, 24.0, 7.5, 5.6, 0.8, 1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 280</td>
<td>13.1</td>
<td>0.8, 0.1, 4.3, 2.5, 4.0, 5.8, 24.0, 7.5, 5.6, 0.8, 1.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| 1 200         | 0.3, 4.2, 0.3, 2.3, 3.2, 2.2, 24.0, 7.5, 5.6, 0.8, 1.4 |
| 2 200         | 0.3, 4.4, 0.7, 2.3, 0.9, 2.6, 2.5, 7.6, 5.3, 0.6, 1.0 |
| 3 200         | 0.2, 0.1, 3.0, 1.3, 1.7, 1.5, 2.1, 2.9, 2.3, 29.9, 8.4, 5.9, 0.5, 0.9 |
Table 3. Results of the GC analysis of the products of the longer term hydrogenation test

<table>
<thead>
<tr>
<th>SAMPLE NUMBER</th>
<th>TIME, h</th>
<th>TEMPERATURE, °C</th>
<th>VISCOSITY AT 100°C (cP)</th>
<th>COMPONENTS WITH GC RETENTION TIMES IN SECONDS, TOTAL AREA %, P=60 bar, LHSV=1 h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 RPO</td>
<td>15.8</td>
<td>-</td>
<td>0.1</td>
<td>CH₃, CH₂, CH₃                 CH₂-CH₂, CH₃, CH₃, 1CH₃, 1CH₃, 5,6-CH₃, 5,6-CH₃, trans, cis</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>0.1</td>
<td>0.1</td>
<td>0.8, 2.2, 0.6, 2.6, 9.7, 2.6, 32.5, 8.8, 6.1, 0.1, 0.9</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>0.5</td>
<td>1.0</td>
<td>1.1, 2.2, 0.9, 2.6, 2.5, 2.4, 28.9, 8.0, 6.0, 0.8</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0.2</td>
<td>0.1</td>
<td>0.8, 1.1, 2.6, 2.9, 2.5, 28.9, 8.0, 6.0, 0.8</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>0.1</td>
<td>1.0</td>
<td>1.1, 2.2, 0.9, 2.6, 2.5, 2.4, 28.9, 8.0, 6.0, 0.8</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>0.1</td>
<td>0.1</td>
<td>0.8, 1.1, 2.6, 2.9, 2.5, 28.9, 8.0, 6.0, 0.8</td>
</tr>
<tr>
<td>7</td>
<td>35</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>8</td>
<td>40</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>9</td>
<td>45</td>
<td>0.6</td>
<td>0.1</td>
<td>0.4, 0.9, 2.2, 2.5, 2.4, 3.4, 2.5, 2.5, 27.2, 8.1, 6.0, 0.9</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>0.6</td>
<td>0.1</td>
<td>0.4, 0.9, 2.2, 2.5, 2.4, 3.4, 2.5, 2.5, 27.2, 8.1, 6.0, 0.9</td>
</tr>
<tr>
<td>11</td>
<td>55</td>
<td>0.6</td>
<td>0.1</td>
<td>0.4, 0.9, 2.2, 2.5, 2.4, 3.4, 2.5, 2.5, 27.2, 8.1, 6.0, 0.9</td>
</tr>
<tr>
<td>12</td>
<td>60</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>13</td>
<td>65</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>14</td>
<td>70</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>15</td>
<td>75</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>16</td>
<td>80</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>17</td>
<td>85</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>18</td>
<td>90</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>19</td>
<td>95</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>21</td>
<td>105</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>22</td>
<td>110</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
<tr>
<td>23</td>
<td>115</td>
<td>0.1</td>
<td>0.8</td>
<td>0.8, 2.3, 2.3, 2.0, 25.2, 7.3, 5.3, 0.5, 0.8</td>
</tr>
</tbody>
</table>

Depolymerization. The temperature of 280°C was obviously too high as the undesired hydrogenation of aromatic rings took place (higher amounts of tetrahydroanthracene at the expense of napththalene). These results showed that the optimal effects of hydrogenation could be expected at about 220°C.

The experiments performed at 200°C also using different LHSV values showed a large influence of the liquid residence time in the reactor on the effect of hydrogenation. The LHSV values of 1.5 and especially of 3 h⁻¹ were too high, and the residence time of the oil in the reactor was too small in those cases to complete the

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hydrogenation process. Hence, the optimal temperature and LHSV values were 220°C and 1 h⁻¹, respectively, if the pressure was 60 bar and the H₂/Oil ratio amounted to 600 Ncm³/cm³.

The results of the longterm hydrogenation test are shown in Table 3. The experiment was initiated at 200°C, and after 40 hours steady-state operation, catalyst deactivation was detected. Namely, the content of indene, 4-methyl-indene and 5- and 6-methyl-indene gradually increased with hydrogenation time. That was the reason for the temperature increase, first to 210°C, however, without improvements in catalyst activity, which was the reason for further temperature increase to 220°C, when the initial catalyst activity according to GC analysis of the collected samples was re-established. A possible explanation for such an effect is that at 200°C covering of the catalyst surface by the polymerization products gradually suppresses the catalyst activity, while at higher temperatures depolymerization of the formed polymer is more favoured [4]. Moreover, a slightly higher temperature than 220°C is probably more promising, also taking into account the results of the liquid product viscosity.

The results of longterm hydrogenation test also enable analysis of the kinetics of RPO hydrogenation.

**Determination of the reaction rate constant of catalyst deactivation**

The results of the hydrogenation test during the longterm catalyst activity test at 200°C were analyzed assuming that a parallel mechanism of catalyst deactivation could be used for its determination:

\[ A \rightarrow R + P \]

where: P is polymer deposition on the catalyst surface. This type of deactivation is similar to deactivation caused by coke deposition in the process of the catalytic cracking of hydrocarbons. In this case the rate of deactivation could be expressed as [3]:

\[ \frac{da}{dt} = k_d \cdot C_A^a \cdot d^d \]  

(1)

where: a, catalyst activity; k_d, deactivation rate constant; C_A concentration of the compound which reacts with hydrogen and causes deactivation; n, d, empirical constants and exponents in the deactivation rate equation.

The mole balance of the compound denoted as A in the reactor, at the same time, could be defined by an equation taking into account that ideal plug flow exists when gas (hydrogen) and liquid (RPO) flow through the catalyst bed:

\[ (-\tau_A) \cdot dW = G_{AO} \cdot dX_A \]  

(2a)

or

\[ (-\tau_A) \cdot d(W/V_0) = (-\tau_A) \cdot dt = C_{AO} \cdot dX_A \]  

(2b)

where:

\[ (-\tau_A) = k \cdot a \cdot C_A^b \]  

(3)

In general, there are five kinetic constants: k, k_d, n, m and d which must be determined. To simplify the calculation procedure and the above constant determination, it is reasonable that, according to literature values, some of these constants are:

m = 1, first order reaction with respect to the unsaturated compounds;

n = 0, the rate of deactivation does not depend on the concentration of the unsaturated hydrocarbons, and

d = 1, which is valid for the parallel mechanism of deactivation without pore diffusion resistance for reactant A (unsaturated compounds).

The experimental data based on the above assumption and quite good results were obtained after applying the corresponding procedure for the determination of k and k_d.

The integral equation for a first order deactivation process defines activity as a function of time:

\[ a = a_0 \cdot \exp(-k_d t) \]  

(4)

By using equation (2), as well as the data of GC analysis regarding the content of indene (A), 4-methyl-indene and 4- and 6-methyl-indene (B and C, respectively), the deactivation rate constants were determined:

\[ k_{d,A} = 1.87 \text{ h}^{-1} \]  

(5a)

\[ k_{d,B} = 0.0175 \text{ h}^{-1} \]  

(5b)

\[ k_{d,A} = 0.0107 \text{ h}^{-1} \]  

(5c)

The above calculation were performed using the plot shown in Figure 1, assuming that under steady state conditions and oil plug flow, catalyst deactivation and hydrogenation proceed by the same first order reaction.

The obtained results showed that quite rapid catalyst deactivation occurred, and that, according to the first order deactivation model, the catalyst activity dropped to 20% of its initial value after the first 100 hours.

![Figure 1](image_url)

Figure 1. Dependence of ln(\(\text{ln}(\text{C}_{\text{O}}/\text{C})\)) on time used for the calculation of the catalyst deactivation reaction rate (k_d): i=A, indene; i=B, 4-methyl-indene; i=C, mixture of 5- and 6-methyl-indene.

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of hydrogenation. Increasing the temperature in the
reactor from 200 to 220°C resulted in the full reactivation
of the catalyst to its initial activity.

**Determination of the reaction rate constant for
indene and methyl-indene hydrogenation**

The following assumptions were used for this
calculation: hydrogenation is a first order reaction; the
effective wetting of catalyst particles for a trickle-bed
reactor indicates non-regularity of the liquid-solid phase
contact [3]:

\[-\ln (1 - X_i) = k_i (LHSV)^\alpha\]

(6)

where: \(X_i\) = conversion of compound \(i\); \(i = A\) (indene), \(B\) and \(C\) (4-methyl-indene and 5- and 6-methyl-indene),
respectively, while \(\alpha\) represents the experimentally
determined parameter which includes the catalyst
wetting effect. The influence of temperature on
hydrogenation was determined by using the values of
the reaction rate constants obtained by performing
hydrogenation with initially active catalyst \((a_0 = 1)\)
at different temperatures. The calculated values are
presented in Table 4.

**Table 4. Kinetic parameters \((A, E/R)\) and catalyst wetting
effect compound**

<table>
<thead>
<tr>
<th>Compound</th>
<th>(k = A\exp(-E/T))</th>
<th>(k) ((593 K))</th>
<th>(\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indene ((A))</td>
<td>4.32 \cdot 10^3</td>
<td>3660</td>
<td>-0.91</td>
</tr>
<tr>
<td>4-methyl-indene ((B))</td>
<td>8.43 \cdot 10^3</td>
<td>14950</td>
<td>-0.65</td>
</tr>
<tr>
<td>5- and 6-methyl-indene ((C))</td>
<td>1.09 \cdot 10^3</td>
<td>3420</td>
<td>-0.23</td>
</tr>
</tbody>
</table>

**Determination of the reaction rate constant when
hydrogenation temperature was increased from 200
to 220°C**

The results of the long-term run showed that slow
deactivation of the catalyst pellets influenced the
conversion degree of compounds A, B and C
measured at the reactor exit. Such an effect was
suppressed after 40 hours of continuous reactor
operation, when the temperature inside the reactor was
rised, at first to 210°C (for 5 hours) and then to 220°C for
a short period of time. This is the commonly used
method for stopping catalyst activity decrease, when at
constant molar flow rate of the reactant, the temperature
in the reactor is boosted to maintain a constant
conversion degree of the reacting compounds at the
reactor exit.

However, in the process of RPO hydrogenation a
slow increase of the conversion degree with time was
observed after the above explained procedure of
temperature increase from 200 to 220°C. The increase
of \(X_A\) conversion degree (as well as \(X_B\) and \(X_C\)) with
time was not expected if all the postulated mechanisms
(first order reaction and first order deactivation) were still
valid. Namely, if only increase of the reaction rate was
expressed, then starting from the integral equation of
the mole balance for a trickle-bed reactor:

\[-\ln (1 - X_i) = -\ln \left(\frac{C_{0i}}{C_{Ai}}\right) = k_{220} \cdot a \cdot (LHSV)^\alpha\]

(7)

one can expect, that for a constant concentration \(C_{0i}\),
at the exit of the reactor, the left-hand side of the mole
balance must be constant:

\[Z = k_{220} \cdot a \cdot (LHSV)^\alpha = k_0 e^{E/RT} \cdot a(t) \cdot (LHSV)^\alpha\]

(8)

However, during the long-term hydrogenation run,
the values of parameter \(Z\) at 220°C slowly increased
with time reaching higher and higher values in the
subsequent 75 hours of the hydrogenation test when
compared to the initial value when this run was started
(200°C, \(a_0 = 1\)). If the mechanism and rate of
deactivation (first order) were still valid \((a = a_0 e^{-k_A t})\),
as well as the influence of temperature on the reaction rate
constant \(k = k_0 e^{-E/RT}\) and if the hydrodynamic
conditions inside the reactor were unchanged \((LHSV; \alpha = \text{const})\),
then the effect of the increased conversion degree of unsaturated compounds \((A,\ \text{indene}; B,\ \text{4-methyl-indene};\) and \(C,\ 5-\) or 6-methyl-indene) could
probably be related a somewhat higher catalyst activity
at 220°C than expected. Such an increase of catalyst
activity is probably the result of depolymerization of
polymer deposits at the catalyst surface at 220°C
leading to more active sites on the catalyst surface,
which positively affect and increase the hydrogenation
rate.

In the case of the proposed mechanism of catalyst
deactivation (equation), depolymerization can be
expressed as a reversible reaction:

\[P \leftrightarrow nS\]

where:

\(P\) polymer covering the active cites of the catalyst
surface and plugging the pore mouth; \(S\), free surface of
catalyst (active cites). In the sense of the reaction
describing the catalyst deactivation mechanism, the
process of catalyst re-activation could be expressed by
the following equation:

\[-\frac{da}{dt} = k_d \cdot (1 - a)\]

(9)

where: the rate of catalyst re-activation and the increase of
the catalyst activity really depend on the potential, but
not useful catalyst activity expressed as term \((1-a)\) in
equation (9).

Solving equation (9) with the initial condition that at
the beginning of depolymerization at 220°C \((t = t_0)\), i.e.
when when the temperature in the reactor was
increased to 220°C, the catalyst activity has defined
values \((a_0 = a\ (t = t_0))\), one can obtain the change of
catalyst activity with time:
\[ a(t) = a' + (1 - e^{-k_j \cdot t}) \]  
(10a)
\[ a' = a_0 e^{-k_j \cdot t} \]  
(10b)

Such a relation and the experimental data from the longterm run at 220°C on the conversion degree for compounds A, B and C, can be used to determine the reaction rate constant of catalyst re-activation \( (k_d) \):

\[ \ln \left( \frac{C_i(t)}{C_i(0)} \right) = k_d \cdot t \]  
(11)

Or after arrangement, and taking logarithmic values of both sides of equation (11), the following linear function could be used for determining the catalyst re-activation rate constant:

\[ \ln \left( \frac{1 - Y}{1 - a^0} \right) = -k_d \cdot t \]

where:

\[ Y = \text{LHSV}^\alpha \cdot k_d^{-1} \cdot \ln \left( \frac{C_i(t)}{C_i(0)} \right) \]

The determined values of the re-activation constants for indene and methylindene are: \( k_{dA} = 0.011 \) h\(^{-1}\) and \( k_{dC} = 0.0083 \) h\(^{-1}\).

**Mathematical simulation of the longterm activity test**

Using the determined reaction rate constants \( (k_d) \) as well as the deactivation rate constant at 200°C \( (k_d) \) and reactivation rate constant at 220°C \( (k_d') \), the change in the conversion degree of the unsaturated compounds (indene and \( \alpha \)- and \( \beta \)-methylindene) were mathematically simulated and shown in Figures 2a, b and c. The simulation was made in two stages: the first one is the hydrogenation step at 200°C with a simultaneous deactivation process, and, the second one is hydrogenation at 220°C together with catalyst reactivation or degradation of polymer deposited on the catalyst active surfaces. The degree of conversion for specific compounds was calculated by using the following equations:

\[ X_i = 1 - \exp \left( -\frac{k_i(T) \cdot a(t)}{\text{LHSV}^\alpha} \right) \]  
(12)

the first stage of the longterm test:

\[ a(t) = e^{-k_d t} \]

\[ X_i = 1 - \exp \left( -\frac{k_i(T) \cdot a(t')}{\text{LHSV}^\alpha} \right) \]  
(13)

and, the second stage of the longterm test:

\[ a(t', t') = a(t') + (1 - e^{-k_d \cdot t'}) \]  
(14)

The obtained experimental results and mathematical simulation showed that the initial catalyst activity was practically restored to the value \( a_0 = 1 \) after about 100 hours of operation at 220°C. They also indicated that Co-Mo catalyst could successfully be applied for the hydrogenation of RPO at 220°C.

**CONCLUSION**

The goal of the hydrogenation was to saturate the double bonds of mainly styrene and indene type compounds, thus avoiding undesirable polymerization in the residual pyrolysis oil, without hydrogenation of the aromatic rings. These tasks were achieved by performing the hydrogenation of RPO at 220-240°C with Co-Mo catalyst (BASF MB-14). The performed
experiments showed that the catalyst was deactivated very rapidly at 200°C (an 80% decrease in the catalyst activity can be expected after 100 hours at this temperature) and the lowest temperature at which the initial catalyst activity was restored was 220°C. This could be explained by the assumption that at 200°C parallel to hydrogenation, polymerization occurred, giving products which covered the catalyst surface. At 220°C and higher temperatures depolymerization prevailed over polymerization, thus restoring the initial catalyst activity. Deactivation of the catalyst, as well as the kinetics of hydrogenation were analysed by following the conversions of indene, 4-methyl-indene and 5- and 6-methyl-indene (considered as a single component), as the most representative components of the RPO which could polymerize. Hence, the hydrogenation of 4-methyl-indene, with the relatively lowest k and α values should be considered as the process which determines the overall rate of RPO hydrogenation.

REFERENCES


IZVOD

HIDROGENOVANJE PIROLITIČKOG ULJA NASTALOG U PROCESU PIROLIZE PRIMARNOG BENZINA – ODREĐIVANJE AKTIVNOSTI KATALIZATORA

(Naučni rad)

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Ispitivano je hidrogenovanje pirolitičkog ulja koje nastaje pri proizvodnji etilena (piroliza primarnog benzina, prinos 0,2 t/t). Ovo ulje ključa u intervalu temperature 180–280°C a ima gustinu 1,05 g/cm³ i sadrži u najvećoj meri nefalen i njegove supstituisane derivate ali i druga jedinjenja stienske, odnosno indenske strukture. Hidrogenovanjem se može spreći pojava polimerizacije pristih neazidihen jedinjenja u ovom ulju kao što su stiren, α-metilstiren, 4-, 5- i 6- metil–inden pri čemu nastaju smole sa pretežno aromatskim strukturom. Pre nego što se pristupi izdvajanju nefalen sa pirolitičkog ulja, u cilju sprečavanja njegove polimerizacije neophodno je ovo ulje stabilizirati hidrogenovanjem. Ovo se postiže uz pomoć CO–Mo katalizatora na relativno niskim pritisicima i temperaturema (60 bar; 200–280°C).

U ovom radu ispitivan je uticaj temperature i prostorne brzine na brzinu hidrogenovanja sa ciljem da se utvrdi osnovni kinetički i hidrodinamički parametri pri korišćenju protočnog reaktora sa nepokretnim slojem katalizatora. Hidrogenovanje je u prvoj fazi ispitivan pri konstantnoj prostornoj uljulja (LHSV = 1 h⁻¹) i odnosu vodonik/uljulja (600 Nm³/m³) prateći efekte na temperaturema od 160 do 280°C. Zatim je za izabranu temperature (200°C) i isti odnos vodonik/uljulja ispitivan uticaj prostorne brzine (1, 1,5 i 3 h⁻¹). Gasna hromatografija, GC–MS analiza i određivanje viskoziteta ulja su iskorišćeni za identifikaciju sastava pirolitičkog ulja i njegove promene tokom hidrogenovanja. Relativna stabilnost viskoziteta hidrogenovanog pirolitičkog ulja uključuje u kojoj meri je ulja stabilizisana i spriječene neželjene reakcije polimerizacije neazidihen aromatskih jedinjenja.

Key words: Pyrolytic oil • Hydrogenation • Catalyst activity • Deactivation • Re-activation • Mechanism • Kinetics.

Ključne reči: pirolitičko ulje • hidrogenovanje • aktivnost katalizatora • deaktivacija • reaktivacija • mehanizam • kinetika.