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2,996,447

CATALYTIC REFORMING OF PETROLEUM HYDROCARBONS


7 Claims. (Cl. 208—66)

This invention relates to the catalytic reforming of petroleum hydrocarbons to give products of increased octane number suitable for use in motor gasoline.

In the well-known catalytic reforming process, a naphtha fraction is contacted at elevated temperature and pressure and in the presence of hydrogen with a dehydrogenation catalyst to produce a gasoline fraction of increased octane number. Catalysts that are used commercially include molybdenum oxide on alumina and catalysts consisting essentially of platinum on alumina without or with combined halogen. A catalytic reforming process using a platinum on alumina type catalyst will hereinafter be referred to as platinum reforming and the products as platinum reformates.

The feedstock to the platinum reforming process is usually a heavy naphtha, having a boiling range for example of 90 to 175° C., and by operating under conditions to give a product having an octane number of 90 to 100 Research (clear), it is possible to achieve long catalyst life without regeneration. The volatility of the product, however, is in all cases below 45% volume recovered at 100° C. and although a product of increased volatility may be obtained by processing a feedstock with a lower final boiling point, more severe operation conditions are required with a consequent reduction in catalyst life.

The principal object of the present invention is to enable a high octane number product of increased volatility to be obtained from a heavy naphtha.

In accordance with the present invention, a heavy naphtha is subjected to platinum reforming under conditions such that regeneration of the catalyst in situ is not required (i.e. a catalyst life of at least 40 barrels of feedstock processed per lb. of catalyst), the platinum reformate is fractionated to obtain a light fraction and a heavy fraction, the heavy fraction is subjected to catalytic hydrocracking at a temperature of 900 to 1100° F., a pressure of 200 to 750 p.s.i.g., a space velocity of the liquid feedstock of 0.5 to 5 v.v./hr and a molar hydrogen/hydrocarbon ratio of 0.5 to 15, and the liquid product of the hydrocracking operation is blended with said light fraction to give a product having an increased volatility by comparison with the platinum reformate. The preferred molar hydrogen/hydrocarbon ratio for the catalytic hydrocracking is from 4 to 10.

The term heavy naphtha means a naphtha having an ASTM final boiling point between 150° C. and 200° C. and, preferably, an ASTM initial boiling point within the range 70° C. to 100° C.

The platinum reforming stage is preferably operated to give a reformate having an octane number Research (clear) of 90 to 100. Any convenient platinum reforming process which does not require in situ regeneration of the catalyst may be used. The process conditions will normally fall within the following ranges:

- Catalyst: 0.1-10% platinum on alumina with or without 0.1 to 8% of halogen, particularly fluoride and/or chlorine.
- Temperature: 600-1200° F., preferably 900-1000° F.
- Pressure: 20,000-30,000 p.s.i.g., preferably 200-700 p.s.i.g.
- Space velocity: 0.5-10 v.v./hr., preferably 1-3 v.v./hr.
- Molar hydrogen/hydrocarbon ratio: 0.5-15, preferably 6-10.

The platinum reformate is preferably fractionated so that the cut-point between the light and heavy fractions is between 80° C. and 120° C. It has been found that the higher the cut-point, the lower the volatility of the final blended product. The final blended product preferably has a volatility of from 40 to 60% volume recovered at 100° C. and an octane number Research (clear) of at least 90.

The present invention besides increasing the volatility of a heavy naphtha has the further advantage that it improves the octane number distribution by increasing the octane number of the lower boiling portion of the product.

Various catalysts may be used in the hydrocracking stage including known reforming catalysts, for example, platinum on alumina, with or without combined halogen, the oxides of cobalt and molybdenum (as such, or in combined form, or both) on alumina, and molybdenum oxide on alumina. The preferred compositions of the above-mentioned catalysts are as follows, all percentages being by weight of total catalyst stable at 1020° F.

- 0.1-10% platinum on alumina with or without 0.1-8% of halogen, particularly fluoride and/or chlorine.
- 1.5-5% cobalt oxide and 5-25% molybdenum oxide on alumina.
- 5-25% molybdenum oxide on alumina.

The following experiments illustrate the results that may be obtained by the process according to the invention.

EXAMPLE 1

A 90 to 175° C. ASTM naphtha was subjected to platinum reforming to give a reformate having an octane number of 93.0 Research (clear) and a volatility of 35.5% recovered to 100° C. The reforming conditions were: 925° F., 500 p.s.i.g., 1 v.v./hr., 10:1 hydrogen/hydrocarbon mol ratio and a catalyst of 0.7% platinum, 0.45% fluoride and 0.3% chlorine, the balance being alumina. This product was fractionated into a fraction boiling below 100° C. and a fraction boiling above 100° C. The high boiling fraction was subjected to hydrocracking at a temperature of 1000° F., a pressure of 500 p.s.i.g., a space velocity of 2 v.v./hr., and a hydrogen to hydrocarbon ratio of 5:1, using hydrogen obtained in the platinum reforming process. Separate hydrocracking operations were carried out using catalysts consisting of 0.56% platinum and 0.65% chlorine on et al., 2.5% cobalt oxide and 14.9% molybdenum oxide on alumina, and 15.9% molybdenum oxide on alumina, all percentages being by weight of total catalyst stable at 1020° F. The product from the hydrocracking operation was then blended with the fraction...
of the platinum reformate boiling below 100° C. and the following results were obtained:

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield percent wt. on naphtha feedstock</th>
<th>Octane No. Res. Clear</th>
<th>Volatility, percent vol. recovered at 100° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum on alumina</td>
<td>71.0</td>
<td>60.0</td>
<td>48.8</td>
</tr>
<tr>
<td>Cobalt and molybdenum oxides on alumina</td>
<td>66.6</td>
<td>59.0</td>
<td>50.1</td>
</tr>
<tr>
<td>Molybdenum oxide on alumina</td>
<td>67.8</td>
<td>58.1</td>
<td>52.4</td>
</tr>
</tbody>
</table>

EXAMPLE 2

A 90–175° C. ASTM naphtha was subjected to reforming over a catalyst consisting of 0.56% platinum and 0.65% chlorine on eta-alumina to give a yield of 70.2% wt. of a product having a Research octane (clear) of 99.2 and a volatility of 34.0% vol. recovered at 100° C. The reforming conditions were 980° F., 450 p.s.i.g., 1.5 v./v./hr., and 10:1 hydrogen/hydrocarbon mol ratio. The product was fractionated at 100° C. to give light and heavy fractions as follows:

Table 2

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling range, ° F. (ASTM Dist.)</th>
<th>Yield on feed to splitter, percent wt.</th>
<th>O.N. Res. Clear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light platinum reformate</td>
<td>49–46</td>
<td>31.5</td>
<td>76.3</td>
</tr>
<tr>
<td>Heavy platinum reformate</td>
<td>111–204</td>
<td>66.5</td>
<td>107.8</td>
</tr>
</tbody>
</table>

The heavy platinum reformate was subjected to hydrocracking under various conditions and the product blended with the light platinum reformate. The following results were obtained:

Table 3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pressure, p.s.i.g.</th>
<th>Temp., ° F.</th>
<th>Space Velocity, v./v./hr.</th>
<th>Blend of second stage reformate with light reformate</th>
<th>Yield on feed to splitter, percent wt.</th>
<th>O.N. Res. Clear</th>
<th>Volatility, percent vol. recovered at 100° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum on eta-alumina</td>
<td>500</td>
<td>1,000</td>
<td>2</td>
<td></td>
<td>62.1</td>
<td>95.1</td>
<td>43.2</td>
</tr>
<tr>
<td>Cobalt and molybdenum oxides on</td>
<td>500</td>
<td>975</td>
<td>2</td>
<td></td>
<td>62.8</td>
<td>97.7</td>
<td>43.9</td>
</tr>
<tr>
<td>eta-alumina</td>
<td>500</td>
<td>1,000</td>
<td>2</td>
<td></td>
<td>63.2</td>
<td>96.8</td>
<td>45.0</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>975</td>
<td>2</td>
<td></td>
<td>58.1</td>
<td>97.3</td>
<td>47.8</td>
</tr>
</tbody>
</table>

The compositions of the catalysts used were the same as in Example 1.

EXAMPLE 3

A 90–175° C. ASTM naphtha was subjected to reforming over a catalyst consisting of 0.56% platinum and 0.65% chlorine on eta-alumina to give a yield of 71.6% wt. of a product having a Research octane number (clear) of 98.0 and a volatility of 34.6% vol. recovered at 100° C. The reforming conditions were 975° F., 450 p.s.i.g., 1.5 v./v./hr., and 9:1 hydrogen/hydrocarbon mol ratio. The product was divided into two portions which were fractionated at cut-points of 88° C. and 115° C. respectively. Inspection data on the fractions were as follows:

Table 4

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Yield on feed to splitter, percent wt.</th>
<th>O.N. Res. Clear</th>
<th>Yield on feed to splitter, percent wt.</th>
<th>O.N. Res. Clear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light platinum reformate</td>
<td>26.8</td>
<td>78.2</td>
<td>62.1</td>
<td>95.1</td>
</tr>
<tr>
<td>Heavy platinum reformate</td>
<td>26.8</td>
<td>78.2</td>
<td>62.1</td>
<td>95.1</td>
</tr>
</tbody>
</table>

The product was fractionated using a cut-point of 100° C. to give fractions as follows:

Table 6

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Yield on feed to splitter, percent wt.</th>
<th>O.N. Res. Clear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light platinum reformate</td>
<td>37–82</td>
<td>36.4</td>
</tr>
<tr>
<td>Heavy platinum reformate</td>
<td>109–205</td>
<td>64.6</td>
</tr>
</tbody>
</table>

The heavy platinum reformate was subjected to hydrocracking under the conditions set out in Example 3 and 4.

Each of the heavy platinum reformates was subjected to hydrocracking under the following conditions:

Temperature: 975° F.
Pressure: 500 p.s.i.g.
Space velocity: 2.0 v./v./hr.
Hydrogen/hydrocarbon: 5:1
Benzol mol ratio:

Table 5

<table>
<thead>
<tr>
<th>Cut-point</th>
<th>Yield percent wt. on naphtha feedstock</th>
<th>Octane No. Res. Clear</th>
<th>Volatility, percent vol. recovered at 100° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>88° C.</td>
<td>63.2</td>
<td>96.6</td>
<td>48.2</td>
</tr>
<tr>
<td>115° C.</td>
<td>64.5</td>
<td>99.9</td>
<td>46.3</td>
</tr>
</tbody>
</table>

It will be seen that by increasing the cut-point from 88 to 115° C. a 5% increase in volatility and 2.3% increase in yield is obtained at the expense of a loss of octane number of 1.7 units.

EXAMPLE 4

A 75–160° C. ASTM naphtha was subjected to reforming over a catalyst consisting of 0.57% platinum and 0.81% chlorine on eta-alumina to give a yield of 71.2% wt. of a product having a Research octane number (clear) of 98.9 and a volatility of 42.0% recovered at 100° C.
the product blended with the light platinum reformate. The following results were obtained.

Table 7

<table>
<thead>
<tr>
<th>Yield</th>
<th>Octane No.</th>
<th>Volatility, percent vol. recovered at 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.2</td>
<td>99.0</td>
<td>43.0</td>
</tr>
</tbody>
</table>

This final product was again fractionated at a cutpoint of 100°C and the Research octane numbers (clear) of the light and heavy fractions determined. They compared with the Research octane numbers (clear) of the light and heavy platinum reformates as follows:

Light platinum reformate, 76.0—
Heavy fraction of product, 82.0—
Heavy fraction, 110.0—
Heavy fraction of product, 108.0—

Thus the hydrocracking of the heavy platinum reformate has improved the octane number distribution by increasing the octane number of the fraction boiling below 100°C.

We claim:

1. A process for treating a heavy naphtha to produce a product for use in motor gasoline having a volatility of from 40 to 60% volume recovered at 100°C and an octane number of Research (clear) of at least 90, comprising subjecting the naphtha to platinum reforming under conditions including a temperature within the range 600–1200°F, a pressure within the range 50–1000 p.s.i.g., a space velocity within the range 0.5–10 v./v./hr, and a molar hydrogen/hydrocarbon ratio within the range 0.5–15, such that the catalyst life is at least 40 barrels of feedstock per lb. of catalyst, fractionating the platinum reformate with a cut-point of from 80 to 120°C. to obtain a light fraction and a heavy fraction, catalytically hydrocracking the heavy fraction at a temperature of 900–1100°F, a pressure of 200–750 p.s.i.g., a space velocity of 0.5–5 v./v./hr, and a molar hydrogen/hydrocarbon ratio of from 0.5 to 15, and blending the hydrocracked heavy fraction with the light fraction to give said product.

2. A process according to claim 1 wherein the molar hydrogen/hydrocarbon ratio for the catalytic hydrocracking is from 4 to 10.

3. A process according to claim 1 wherein the platinum reformate has an octane number Research (clear) of from 90 to 100.

4. A process as claimed in claim 1 wherein the catalyst for the hydrocracking consists essentially of 0.1–10% platinum on alumina.

5. A process as claimed in claim 1 wherein the catalyst for the hydrocracking consists essentially of 0.1–10% wt. of platinum, and 0.1–8% wt. of halogen on alumina.

6. A process as claimed in claim 1 wherein the catalyst for the hydrocracking comprises 1.5 to 5% wt. of cobalt oxide and 5 to 25% wt. of molybdenum oxide on alumina.

7. A process as claimed in claim 1 wherein the catalyst for the hydrocracking comprises 5 to 25% wt. of molybdenum oxide on alumina.

References Cited in the file of this patent

UNITED STATES PATENTS

2,361,138 Voorhies Oct. 24, 1944
2,573,829 Kasel Oct. 30, 1951
2,698,829 Haensel Jan. 4, 1955
2,731,396 Harding et al. Jan. 14, 1956
2,758,062 Arundale et al. Aug. 7, 1956
2,780,661 Hemminger et al. Feb. 5, 1957
2,889,263 Hemminger et al. June 2, 1959
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,996,447

Frederick William Bertram Porter et al.

August 15, 1961

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 19, after "octane" insert -- number --;
column 6, line 32, for "2,573,829" read -- 2,573,149 --; same
column 6, line 34, for "Jan. 14, 1956" read -- Jan. 17, 1956 --.

Signed and sealed this 16th day of January 1962.

(SEAL)
Attest:

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Attesting Officer

DAVID L. LADD
Commissioner of Patents