INVENTORS
GERRIT HOWESTREYDT
JOHN D. LOGEMANN
KEES DELCOUR

BY Cushman, Darby & Cushman
ATTORNEYS
LIGHT NAPHTHA CONVERSION PROCESS

Gerrit Hovestreydt, Beck, Limburg, and Johan D. Logeman and Kees Delcourt, Gelsen, Netherlands, assignors to Stamicarbon N.V., Heerlen, Netherlands

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3 Claims

ABSTRACT OF THE DISCLOSURE

The recovery of hydrocarbon products from light naphtha oil is discussed, with review of various known processes. A new process is described for treating light naphtha oil to provide a liquid fraction with high aromatic content and a gaseous fraction rich in 2-4 carbon atom hydrocarbons. These fractions result from a process in which there is first a catalytic hydro-forming treatment of the oil, and thereafter there is a catalytic cracking step.

Summary of the invention

The present invention relates to a process for preparation of saturated aliphatic hydrocarbons containing 1-4 C atoms, in combination with aromatic hydrocarbons (benzene and its homologues), from light naphtha having a boiling range of 40 to 110-180°C.

Background of the invention

Various processes have been proposed for the preparation and removal of various hydrocarbon products from the thermal cracking products obtained from light naphtha oil. Light naphtha is a well known feedstock material which may be processed to provide products of valuable aromatic hydrocarbons in other processes. However, commercially suitable processes to obtain such valuable products have not really been developed for there are severe disadvantages in the various prior processes which have been used, rendering them unsuitable as a manufacturing method to produce the said aromatic hydrocarbons, etc.

It is, for instance, well known that the hydrocarbons present in light naphtha having a boiling range of 40 to 110-180°C, in particular those hydrocarbons containing from 5 to 7-9 carbon atoms, can, by thermal cracking at temperatures of 700-900°C, be principally converted into a major proportion of gaseous unsaturated hydrocarbons containing 2-4 C atoms, along with a minor amount of methane and hydrogen.

Depending on the composition of the starting material and on the process condition, such a cracking process converts, for instance, 20-25 percent of the naphtha into ethylene, 35-55 percent into methane, propylene, and unsaturated C4 hydrocarbons, and, in addition, 20-30 percent into liquid hydrocarbons. The latter fraction is the so-called "cracked naphtha", which in most cases has a higher aromatic content than the original naphtha (all figures referring to parts by weight).

The liquid hydrocarbons obtained in such a process have considerable value as fuel for petrol engines, due to their higher aromatic content.

However, this liquid fraction is not well suited as a starting material for the commercial recovery of pure aromatics as ultimate products, because of its relatively low aromatic content and the presence of unsaturated hydrocarbons.

Of the gaseous products obtained from the cracking process, ethylene and butadiene are the most valuable as starting materials for chemical synthesis processes. In general, the other gases will yield no more than their simple fuel value.

In another known process (see e.g., the British patent specification 935,681), the light naphtha feed material is first cracked by heating, whereby a large portion of it is converted into methane, ethylene, gaseous unsaturated 3-4 carbon hydrocarbons and an aromatic-containing liquid fraction ("cracked naphtha"). The latter fraction, after the gases are separated from it, is subjected to a catalytic treatment with hydrogen, carried out under pressure and under relative mild conditions of temperature, so as to convert the olefins content thereof into saturated alkanes.

The resulting naphtha is then suitable to use as a starting material for the extraction of aromatics therefrom, while subsequently, after the aromatics have been recovered, the remaining alkane-containing liquid is recycled to the thermal cracking step.

This process is complicated, however, and has the disadvantage that the aromatic content of the finally resulting cracked naphtha is still so low that the aromatics can only be effectively recovered by extraction, which is a costly method.

In still another known process (see e.g., U.S. Patent Specification No. 2,143,472) for the recovery of aromatics and olefins of low boiling point, the starting material is an oil distillate containing naphtha ethers. This material is subjected, in the vapor phase, to a catalytic treatment whereby the naphthenes are converted to aromatics, the reaction mixture being subsequently subjected to a non-catalytic cracking process in order that the paraffins having a higher boiling point than the aromatics and any remaining naphthenes as well, may be converted to olefins and paraffins of lower boiling point. The reaction mixture is thereafter separated, by rectification, into a tar fraction, a fraction of aromatics, fractions consisting of paraffins and olefins, and gaseous hydrocarbons.

To recover pure aromatics in this process, the aromatic fraction obtained must again be subjected to an extraction treatment, to effect a separation between the non-aromatics still present in the aromatic fraction—which do not dissolve in the extraction agent—and the aromatic proper—which form a solution with the extraction agent.

Object of the invention

The present invention provides as the principal object a process in which the light naphtha is so treated as to yield (1) a liquid fraction having a high aromatic content, this content being so high that the aromatics can be recovered from the fraction by a simple separation process such as rectification, which is much cheaper than extraction, and (2) a gaseous saturated hydrocarbon fraction containing for the greater part 2-4 carbon atoms. This gaseous hydrocarbons fraction is extraordinarily well suited for use as a starting material for the preparation of ethylene by thermal cracking, with by-product formation of only a small amount of less valuable material, such as propylene, in addition to the ethylene.

The process according to the invention has the added advantage of flexibility as regards the products to be recovered. That is, by change of the reaction conditions, the relative amount of the aromatics and gaseous hydrocarbons fractions may be singly altered, as desired.

GENERAL DESCRIPTION OF THE INVENTION

The effects referred to above are obtained, according to this invention, in that the starting material, light naphtha with a boiling range of 40 to 180°C, is subjected to a treatment with hydrogen at certain elevated temperature and pressure and in the presence of a dehydrogenation catalyst, so that the aromatics originally present in the naphtha are preserved, while also a considerable amount of additional aromatics and, simul-
3,455,813

3 taneously, some 1–4 C atom saturated hydrocarbons are formed. After separation of the resulting gaseous and liquid hydrocarbon fractions there is obtained a liquid fraction rich in aromatics (at least 70 percent by weight) and otherwise consisting mainly of saturated C₆ hydrocarbons.

The catalytic hydrogen reaction, under pressure, as provided and practiced according to this invention, essentially involves two reactions that are separately known in themselves.

Firstly, there is the so-called catalytic hydroforming treatment of the naphtha, which process increases the aromatic content of the oil. This occurs, for instance, by the dehydrogenation of the 6–8 C atom naphthenes content of the feed and by the isomerization of cyclic naphthenes with 5 C atoms in the ring to naphthenes with 6 C atoms in the ring, followed by dehydrogenation and by cyclization (with loss of hydrogen) of paraffin components to aromatics. Secondly, there is a catalytic cracking process taking place with hydrogenation of the higher paraffins to lower boiling saturated hydrocarbons with 1–4 C atoms.

The conditions under which the hydrogen treatment of the light naphtha takes place according to the invention are different from those under which the hydroforming of naphtha is generally performed, so that the final result is also different.

Thus, the object of the hydroforming process is the formation of aromatics, in particular toluene and xylene, and isomerization of the liquid hydrocarbons. The process thus gives rise to release of free hydrogen, but is so controlled that the amount of gaseous hydrocarbons formed is as small as possible.

In the hydrogen treatment according to the invention aromatics are also formed, but, in addition, a large proportion of the liquid non-aromatic hydrocarbons present in the starting material is converted into gaseous saturated 1–4 C atom hydrocarbon material, with no release of hydrogen. By contrast, the hydrogen treatment in general involves the consumption of a little hydrogen, e.g. 0–3 percent by weight, calculated to the amount of naphtha treated, depending on the composition of the original naphtha and the ratio between the aromatics and the gaseous products formed.

The more gas that is formed, the greater the hydrogen consumption will be.

In addition, if in the hydrogen treatment a higher temperature is applied, the ratio of benzene to its homologue in the resulting liquid containing aromatics can be influenced in favor of benzene.

The desired conversions are effected with the use of normal dehydrogenation catalysts, i.e. of such metal catalysts as Cr, Mo, Pt, Pd, or other noble metals, applied to a carrier.

Preferably very active platinum catalysts are used, with the platinum applied, in an amount of between 0.1 and 2 percent by weight, to a carrier material consisting mainly of alumina or silica or a mixture of alumina and silica.

The conditions of temperature and pressure, and the hydrogen-to-naphtha ratio in the hydrogen treatment, are so chosen that the aromatic content in the resulting liquid fraction will be at least 70 percent by weight, this fraction otherwise consisting mainly of saturated C₆ hydrocarbons. At the same time, half or more of the original starting material is converted into gaseous saturated C₆ hydrocarbons.

The pressures needed to achieve this end may vary, for instance, from about 15 to 90 atm., preferably from about 25 to 60 atm. The molar hydrogen-to-naphtha ratio may be from about 4 to 20, while final temperatures of, for instance, about 550 to 600 °C. can be used. The light naphtha may be passed over the catalyst at the rate of, say, about 0.5–10 volumes (liquid) per volume of catalyst and per hour.

At the start of the hydrogen treatment the temperature may be lower, as the formation of aromatics will proceed at temperatures of about 450 to 525 °C., but in order to effect the equally desirable conversion of the greater part of the paraffins that cannot be converted to aromatics to the desired gaseous saturated C₆–C₈ hydrocarbons, it is then necessary to raise the temperature by about 100–50 °C. towards the end of the hydrogen treatment. It will be advantageous, therefore, to carry out the hydrogen treatment in successive stages, each stage working with a different type of catalyst, if so desired, with a relatively low temperature and/or pressure being maintained in the first few stages, and a higher temperature and/or pressure in the final stages. The hydrogen treatment may be carried out with the catalyst mass present either as a fluid bed or as a fixed bed.

The process according to the invention has the advantage of yielding a liquid with a high content of valuable aromatics and doing away with the necessity of recovering these aromatics by extraction, since a simpler, less costly separation, viz. by rectification, will suffice.

A separation process of this kind, in which use is made of distillation, may be carried out, e.g. in a first stage, yielding a top product consisting of benzene and non-aromatic hydrocarbons and a bottom product, which in a following rectification can be separated into toluene as the top product and xylene contaminated with ethyl benzene as the bottom product.

The mixture obtained as the top product in the first rectification can be used for the recovery of pure benzene in a known way by subjecting the mixture to azeotropic distillation with, for instance, acetone as an auxiliary liquid.

In order to produce ethylene, the saturated gaseous hydrocarbons obtained in the hydrogen treatment are subjected to thermal cracking. Prior to the cracking proper, methane and hydrogen, which do not contribute to the formation of ethylene, can be separated from these gases.

The starting material used in the hydrogen treatment according to the invention need not be largely freed of sulphur compounds.

Light naphtha having a sulphur content of, say, 1000 p.p.m. may be processed as such. Although slightly less aromatics will then be formed, the amount of gaseous hydrocarbons that can be cracked to produce ethylene will be higher.

Description of the drawings

The processes according to the invention will be explained with reference to FIGURES I and II, which show process diagrams.

In the process according to FIGURE I, naphtha is supplied through conduit 1 to reactor R, in which the hydrogen treatment under pressure is effected.

The reaction mixture formed in, sent, through conduit 2, to a separator S₁, in which the gases are separated from the liquid fraction subsequent to cooling.

Through conduit 3 the liquid fraction is passed into a stripper column D₁, the top product from which consists of the still-dissolved gases, and the bottom liquid product is then passed to a following rectifying column D₂ through a conduit 4. In this column a separation is made between benzene and non-aromatic, mainly C₆ hydrocarbons—discharged through conduit 6—on the one hand, and the higher-boiling toluene xylene on the other hand. The toluene-xylene mixture is sent, through conduit 5, to a rectifying column D₃, the temperature forming off through conduit 7 is, toluene, and the bottom product, removed through conduit 8, the xylene, which always also contains some ethyl-benzene.

The mixture of benzene and paraffins removed as the top product from column D₂ can be separated in the usual way, by distillation, with e.g. acetone as an auxiliary liquid to recover pure benzene.

The gaseous mixture of hydrogen and saturated C₆–C₈ hydrocarbons to be discharged from separator S₂ is sent,
through conduit 9, to a separator S2, in which hydrogen is separated from the hydrocarbons by cooling. This hydrogen, restored to the proper pressure by compressor P, if necessary, is recycled to reactor R.

The hydrocarbons to be discharged from separator S2, and also the hydrocarbons recovered at the top product in distillation column D1, are passed, through conduits 10 and 11, respectively, to cracker K2, where the ethane, propane, and butane are subjected to a non-catalytic thermal cracking process in which ethylene is formed; the resulting reaction mixture is sent to a gas separator S3 through conduit 12.

The ethylene produced is discharged through conduit 13, the ethane not converted to ethylene is sent to ethane cracker K3 through conduit 14. The gas mixture obtained in this cracking is again sent to gas separator S3, through conduit 16. Through discharge conduits 15, of which only one is shown, residual gases (a mixture of, chiefly, methane, propylene, and propane) are removed from the system. If desired, these residual gases can be returned to a thermal cracker, either before or after they have been separated into their constituents.

The process according to FIGURE II differs from that according to FIGURE I in that hydrogen treatment is carried out in several reactors arranged in series, which are designated as R1 and R2, and in that the gaseous mixture of saturated C1-C4 hydrocarbons discharged from separator S2 and stripper D1 through conduit 11 is first sent to a gas separator S4 for the removal of methane, so that the load on the crackers will be lighter. The methane fraction, which always contains some components that can be cracked to produce ethylene, is then sent to gas separator S3 through conduit 18; the C2-C4 fraction to be discharged from separator S3 is fed to cracker K4 through conduit 17.

Reactor R1 may contain a catalyst more specifically suited for the formation of aromatics, for instance Pt on Al2O3, whether or not promoted by a small amount of a halogen (Cl, F), whereas reactor R2 may contain a catalyst more specifically adapted to the destructive hydrogenation of the paraffins, for instance Pt on Al2O3, promoted by a small amount of alkali or alkaline earth metals, or Pt on SiO2. It is also possible to raise the temperature in reactor R2 slightly above the level maintained in reactor R1, for instance 50°C above this level.

As the dehydrogenation reactions are endothermic, the reaction temperature or the temperature variation in reactor R1 can be controlled as desired by the supply of heat, whereas in reactor R2 generally cooling will have to be applied, to remove heat generated in the destructive hydrogenation of the paraffins and olefins.

The procedures represented in FIGURES I and II show only the principal operations. Of course, in practice use is made in the hydrogen treatment of several reactors, these being taken out of operation periodically in order to regenerate the catalyst which will have become inactive in the reactor, e.g., owing to the deposition of carbon.

Furthermore, in general it will be found necessary to apply hydrogen make-up, as in the hydrogen treatment hydrocarbon is consumed in an amount of 0–3 percent of the feed.

The following examples will give some idea of the results that can be achieved by means of the process according to the invention.

Example I

In apparatus as represented in FIGURE I a light naphtha feed material with a boiling range of 40–160°C was first led over a platinum-on-alumina catalyst (0.6 percent by weight of Pt, 0.66 percent by weight of Cl), at a space velocity of 1 litre of naphtha per litre of catalyst and per hour, together with a fivefold amount of hydrogen (calculated as grammolecules), at a temperature of 655°C and at 30 atm.

For every 100 grams of feed, this hydrogen treatment yielded 68 grams of gaseous C1-C4 hydrocarbons, viz.:

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>11</td>
</tr>
<tr>
<td>C2H6</td>
<td>20</td>
</tr>
<tr>
<td>C3H8</td>
<td>26</td>
</tr>
<tr>
<td>C4H10</td>
<td>11</td>
</tr>
</tbody>
</table>

which, together with steam, were fed to a thermal cracker K1 and were there cracked at a temperature of 800°C. The cracked reaction mixture was passed to the gas separator S3 from which 21.6 grams of ethane were sent, through conduit 14, to ethane cracker K3, to be again subjected to a cracking treatment, carried out at a temperature of 820°C.

Eventually, the gas separation yielded, per 100 grams of the original naphtha, 29.2 grams of ethylene, plus residual gases consisting of a hydrogen-methane fraction (23.9 grams), a propylene-propane fraction (11.5 grams), and a butylene-butane fraction (2.9 grams). The liquid fraction (34 grams) obtained in the hydrogen treatment, which had an aromatic content of 87.6 percent, can be separated into:

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>5.3</td>
</tr>
<tr>
<td>Toluene</td>
<td>13.1</td>
</tr>
<tr>
<td>Xylene and ethyl-benzene</td>
<td>11.4</td>
</tr>
<tr>
<td>Non-aromatic, mainly consisting of saturated C6 and a small amount of C6+ hydrocarbons</td>
<td>4.2</td>
</tr>
</tbody>
</table>

If the original naphtha was cracked direct, i.e., without having undergone the hydrogen treatment, this would have resulted in the production of:

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>23.5</td>
</tr>
<tr>
<td>Methane+hydrogen</td>
<td>15.5</td>
</tr>
<tr>
<td>Propylene+propane</td>
<td>18.5</td>
</tr>
<tr>
<td>C4 hydrocarbons</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Cracked naphtha with an aromatic content of 43 percent

Example II

In the same way as described in Example I a naphtha with a boiling range of 40–116°C was processed.

After the hydrogen treatment, every 100 grams of the original naphtha yielded 64 grams of gaseous C1-C4 hydrocarbons, viz.:

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>10</td>
</tr>
<tr>
<td>C2H6</td>
<td>19</td>
</tr>
<tr>
<td>C3H8</td>
<td>24</td>
</tr>
<tr>
<td>C4H10</td>
<td>11</td>
</tr>
</tbody>
</table>

After the thermal cracking these yielded 27.9 grams of ethylene, and residual gases consisting of a hydrogen-methane fraction (21.7 grams), a propylene-propane fraction (10.9), and a butylene-butane fraction (2.9 grams).

The liquid fraction (37 grams) obtained after the hydrogen treatment, which had an aromatic content of 89 percent, could be separated into:

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>9.3</td>
</tr>
<tr>
<td>Toluene</td>
<td>16.9</td>
</tr>
<tr>
<td>Xylene+ethyl-benzene</td>
<td>6.7</td>
</tr>
<tr>
<td>Non-aromatics, mainly consisting of C6 and for the remaining part of C6+ hydrocarbons</td>
<td>4.1</td>
</tr>
</tbody>
</table>

If this naphtha had been subjected direct to thermal cracking, without having undergone the hydrogen treatment, the resulting products would have been:

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>24.5</td>
</tr>
<tr>
<td>Methane+hydrogen</td>
<td>14</td>
</tr>
<tr>
<td>Propylene+propane</td>
<td>20.5</td>
</tr>
<tr>
<td>C4 hydrocarbons</td>
<td>12</td>
</tr>
</tbody>
</table>

Cracked naphtha with an aromatic content of 20 percent

| Grams | 23 |
What is claimed is:

1. A process for the simultaneous conversion of light naphtha oil feedstock having a boiling range of at least about 40° C. and up to a range between about 110–180° C. into a fraction composed of saturated aliphatic hydrocarbons containing from 1 to 4 carbon atoms and a fraction composed of monocyclic carbocyclic aromatic hydrocarbons consisting essentially of benzene and lower alkyl homologues thereof, which process comprises hydroforming and cracking said naphtha by subjecting said naphtha to a treatment in two stages with free hydrogen gas at an elevated temperature in the range of 450 to 600° C. and under an elevated pressure of between about 15 atm. and 60 atm., said first stage being carried out in the presence of a catalyst composed of from about 0.1 to about 2 percent by weight of platinum metal on a carrier of Al₂O₃ promoted by halogen, and the said second stage being carried out in the presence of a catalyst containing Pt on a carrier of Al₂O₃ promoted by alkali or alkaline earth metals, or Pt on a carrier of SiO₂ wherein the temperature at the end of said treatment is between about 550–600° C., while maintaining a molar ratio of hydrogen to naphtha at a value between about 4–20, and while passing said naphtha over the catalysts at the rate of about 0.5–10 liquid volumes per volume of catalyst per hour, such that at least about one-half of said naphtha is converted to gaseous saturated hydrocarbons containing from 1 to 4 carbon atoms, and the remaining part of said naphtha feedstock is converted substantially into a liquid reaction product having a content of said aromatic compounds of at least about 85 percent by weight, the remaining portions thereof consisting essentially of saturated hydrocarbons of five carbon atoms.

2. The process of claim 1 wherein the said liquid containing said aromatic compounds is subjected to a rectification procedure to recover the aromatic compounds therefrom.

3. The process of claim 1 wherein the said saturated gaseous hydrocarbon product is subjected to a thermal cracking process to form and recover ethylene therefrom.

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HERBERT LEVINE, Primary Examiner
U.S. Cl. X.R.
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