PROCESS FOR REMOVING CARBONYL COMPOUNDS FROM HYDROCARBONS

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Field of Search..... 208/289, 48 A; 260/677 A, 260/679, 681.5; 210/21

ABSTRACT

Liquid hydrocarbons and mixtures thereof containing carbonyl compounds as impurities are purified by a liquid-liquid extraction with an aqueous solution of a hydrazinium compound. The carbonyl free hydrocarbon phase is then separated from the aqueous phase.

6 Claims, 2 Drawing Figures
PROCESS FOR REMOVING CARBONYL COMPOUNDS FROM HYDROCARBONS

This invention relates to a process for separating carbonyl compounds from hydrocarbons or hydrocarbon mixtures by treating the hydrocarbons or hydrocarbon mixtures in the liquid-liquid, two-phase system with an aqueous solution of a hydrazinium compound and subsequently separating the carbonyl-free hydrocarbon phase from the aqueous phase.

The steam cracking of light petroils is accompanied by secondary reactions which are evidently attributable to the chemical mixture also contains carbonyl compounds, especially aldehydes and ketones (hereinafter referred to as carbonyl compounds such as ethanol, propanol, acetone and others which, because of their boiling point, enter the C6- or C8-fraction during separation of the cracking gases. The carbonyl content depends on whether the light petrol is cracked at lower or high temperatures. Normally the content varies within the range of from a few hundred to more than 1,000 ppm, based on the hydrocarbons. Furthermore, carbonyl compounds can be fore in hydrocarbons as derivatives of compounds which are formed autoxidation of unsaturated hydrocarbons.

Experience has shown that the carbonyl compounds have an inhibiting effect during the further processing of otherwise pure hydrocarbons. Even quantities as small as 100 ppm have an extremely adverse effect upon stereo-specific polymerisation, especially in case where organometallic catalysts are used. In the hydrogeneration of diolefins or diolefin-containing mixtures, an increased carbonyl content contributes towards polymer formation and deposition and hence towards deactivation of the catalyst.

The carbonyl compounds cannot be separated off by distillation because it is particularly the carbonyls of low molecular weight, such as ethanol, propanal and acetone, which form azeotropes with numerous hydrocarbons, for example ethanol with 1,3-butadiene or acetone with isoprene, cyclopentadiene and piperylene, cf. "Azeotropic Data", ACS Monograph No. 6 Washington 1952.

Accordingly we have sought to find a process by which the carbonyl compounds could be removed in simple and economic manner from hydrocarbons or hydrocarbon mixtures of the kind formed for example during the working up of cracking gases.

SUMMARY

We have now found that liquid hydrocarbons or hydrocarbon mixtures containing carbonyl compounds as impurities in quantities of up to about 5,000 ppm can be purified in a simple and economic manner by subjecting the hydrocarbon or the hydrocarbon mixture to a liquid-liquid extraction with an aqueous solution of a hydrazinium compound and separating the purified hydrocarbon phase from the aqueous phase.

DESCRIPTION OF THE DRAWING

The present invention will be more fully understood from the accompanying drawing wherein:

FIG. 1 is a diagrammatic view of apparatus suitable for carrying out the process of the invention continuously; and

FIG. 2 is a graph of four curves showing residual carbonyl content as described in Examples 2-5 herein.

DESCRIPTION

By the process of the invention, carbonyl impurities can be removed from any hydrocarbon or hydrocarbon mixture which forms two liquid phases with the aqueous hydrazinium compound solution under the conditions according to the invention, for example from saturated and unsaturated hydrocarbons, from the C6- and C8-fraction which accumulate during the cracking of light petroils, such as butadiene, butene pentanes, pentenes, isomethanes, isoprene, piperylene, cyclopentadiene or from mixtures of these compounds.

Hydrazinium compounds suitable for use in the process according to the invention include compounds of the general formula N,H,X (wherein X is a monovalent anion) which are soluble in water. Specific examples of such hydrazinium compounds are hydrazinium sulphate, hydrazinium chloride and preferably hydrazinium hydroxide (hydrazine hydrate). The hydrazinium compounds are used in an aqueous solution.

The molar ratio of the hydrazinium compound to the carbonyls should preferably amount to at least 1 : 1, but more preferably to within the range 3 : 1 to 10 : 1. The hydrazinium compounds are dissolved in water to form a 0.5 to 10 percent by weight solution and preferably a 1 to 5 % by weight solution.

The extraction temperatures can be varied within a relatively wide range, the lower limit being determined by the freezing point of the washing solution. The upper limit to the temperature range is imposed solely by the requirement that two liquid phases should exist alongside one another. In other words the temperature range rises with increased pressure. In general, however, the reaction is carried out at a temperature in the range of from 5°C to 50°C under pressure of from 0.5 to 5 bars, and preferably at a temperature of from 10°C to 30°C under normal pressure.

In the process according to the invention, a single wash with a hydrazine hydrate solution is sufficient to reduce the carbonyl content from up to several thousand ppm to considerably below 100 ppm, based on the hydrocarbon or the hydrocarbon mixture. In some cases, a simple subsequent wash with water is required to remove traces of hydrazinium compound dissolved in the hydrocarbons to below the detection limit.

The process according to the invention can be used for purifying hydrocarbons by intensively contacting in a container a bath of the hydrocarbon or hydrocarbon mixture to be purified with the washing solution and, thereafter, optionally washing the hydrocarbon phase with water to remove traces of dissolved hydrazinium compound following phase separation.

In a preferred embodiment, the process is carried out continuously. In this case, any type of conventional mixer-separators can be used for intermixing the two liquid phases and for subsequently separating them again. Following their separation, the hydrocarbons purified by the process according to the invention are washed with water and then further processed. In a simple embodiment, washing with water can take the form of, for example, a countercurrent wash. The continuous procedure enables the hydrazinium compound in the washing solution to be maintained in the required concentration to remove the carbonyl compounds by
removing part of the washing solution and introducing fresh solution.

One continuous embodiment of the process is explained in detail with reference to FIG. 1:

The hydrocarbon or the hydrocarbon mixture to be treated by the process according to the invention is passed via pipe 1 and a pump 2 and combined with an aqueous solution of a hydrazinium compound from a pipe 3 and pump 4. The combined streams are carried through a feed pipe 5 into a mixing pump 7 arranged in the lower part of the mixing apparatus 6. Under the effect of the mixing pump, the intensively mixed liquid streams from the feed pipe 5 and the upper part of the mixing apparatus are guided into the lateral pipe 11 of the mixing apparatus 6. The mixed phase flows through the lateral pipe through a packed layer into the upper part of the mixing apparatus. From there, the part of the mixed phase flows through a pipe 8 into a settling chamber 9, whilst the rest of the mixed phase is drawn downwards into the mixing pump 7 back to the mixing zone.

The upper part of the settling chamber 9 is filled with a packing to promote phase separation. The purified hydrocarbon phase separated off is optionally washed by being delivered via a pipe 10 in countercurrent to a stream of water. The lower part of the settling chamber 9 acts as a reservoir for the recycled aqueous solution of the hydrazinium compound. This solution is again delivered to the mixing apparatus through a pipe 3 and can be replaced at any point by removing a fraction and introducing fresh solution.

The process according to the invention has a number of advantages. For example, it enables reaction conditions such as temperature and pressure, under which the washing is carried out to be adapted to particular requirements. The starting material can be directly subjected to the process according to the invention in the liquid phase in an economically favourable manner. Another advantage is that the process of the invention functions without any loss of hydrocarbons because the hydrocarbons themselves do not react or are not prompted to react, for example to polymerise, with the substances of the washing solution.

The process according to the invention is illustrated by the following Examples:

**EXAMPLE 1**

Three-hundred ml of a hydrocarbon mixture of which substantially 90% by weight consisted of cis- and trans-1,3-pentadiene and substantially 10 percent by weight of other C₂-paraffins, olefins, diolefins and acetylenes, was treated with aqueous hydrazinium hydroxide solution in accordance with Table 1 in a vessel mounted on a vibration machine. The hydrocarbon mixture had an initial carbonyl content of 2,100 ppm. The residual contents of carbonyl compounds in the hydrocarbon batches treated and the level of reduction (content of carbonyl compounds in the starting material/carbonyl compounds in the purified mixture), are shown in Table 1. The contents of carbonyl compounds were determined with hydroxylamine hydrochloride in accordance with an ASTM method, and are based on ethanol.

**TABLE 1**

<table>
<thead>
<tr>
<th>Washing solution</th>
<th>concentration of aqueous solution of NH₂OH</th>
<th>vibration time min.</th>
<th>residual content of carbonyl compounds ppm</th>
<th>reduction level</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%</td>
<td>300</td>
<td>15</td>
<td>132</td>
<td>15.9</td>
</tr>
<tr>
<td>1%</td>
<td>300</td>
<td>15</td>
<td>46</td>
<td>45.7</td>
</tr>
<tr>
<td>2%</td>
<td>300</td>
<td>15</td>
<td>42</td>
<td>50.0</td>
</tr>
<tr>
<td>5%</td>
<td>300</td>
<td>18</td>
<td>116.7</td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>300</td>
<td>10</td>
<td>60</td>
<td>35.0</td>
</tr>
<tr>
<td>5%</td>
<td>300</td>
<td>5</td>
<td>70</td>
<td>30.6</td>
</tr>
<tr>
<td>5%</td>
<td>300</td>
<td>2</td>
<td>114</td>
<td>18.4</td>
</tr>
<tr>
<td>5%</td>
<td>200</td>
<td>15</td>
<td>75</td>
<td>28.0</td>
</tr>
<tr>
<td>5%</td>
<td>100</td>
<td>15</td>
<td>119</td>
<td>17.7</td>
</tr>
</tbody>
</table>

**EXAMPLE 2**

In an apparatus of the kind shown in FIG. 1, 1,000 ml/h of a hydrocarbon mixture with the same composition as described in Example 1 (carbonyl content 2,100 ppm) were continuously combined through pipe 1 and pump 2 with 330 ml/h of an aqueous 5 percent hydrazinium hydroxide solution from pump 4 and pipe 5. The combined streams were delivered through pipe 5 into the mixing apparatus 6 and intensively admixed at substantially 2,000 rpm by means of a mixing pump 7. The temperature was 20°C and the reaction took place at normal pressure. The mixed phase was delivered from the upper part of the mixing apparatus through the pipe 8 into a settling chamber 9, the lower part of which acted as a reservoir for the washing solution. The clear hydrocarbon phase was run off from the upper part of the settling chamber through pipe 10 and subjected to a countercurrent wash. The hydrazinium hydroxide solution (1,300 ml in the system) was recycled. FIG. 2, curve 1 shows the residual carbonyl content in the hydrocarbon mixture. The hydrazinium compound content of the purified hydrocarbon phase was below the detection limit of 1 ppm.

**EXAMPLE 3**

As in Example 2, 500 ml/h of a hydrocarbon mixture with the same composition as in Example 1 (2,100 ppm of carbonyl compounds) were treated with 425 ml/h of a 2 percent aqueous hydrazinium hydroxide solution. The reaction conditions were the same as in Example 2. The residual carbonyl contents in the purified product are shown in FIG. 2, curve 2.

**EXAMPLE 4**

One thousand ml/h of the same hydrocarbon mixture as in Example 1, except that it had a carbonyl compound content of only 181 ppm, were treated as in Example 2 with 330 ml/h of a 2 percent aqueous solution of hydrazinium hydroxide. FIG. 2 curve 3 shows the residual carbonyl content in the purified hydrocarbon mixture.

**EXAMPLE 5**

One thousand ml/h of a C₂-hydrocarbon fraction of the kind obtained during the cracking of light petrol which consisted of (in percent by weight) 30.9 percent
of paraffins, 30.1 percent of olefins, 38.2 percent of di-
olefins and 0.7 percent of acetylenes, and which con-
tained 1,242 ppm of carbonyl compounds was treated
as in Example 2 with 330 ml/h of a 2 percent aqueous
hydradzinum hydride solution under normal pressure
at a temperature of 20° C. Thereafter, the purified C_5-
fractrons had a carbonyl content of only 50 – 60 ppm
(see FIG. 2, curve 4).

EXAMPLE 6

As in Example 2, 500 ml/h of 99.9 percent n-hexane
which was contaminated by 1,200 ppm of acetone,
were combined and treated with 425 ml/h of a 5 per-
cent aqueous solution of hydrazinium hydride. It was
not possible to detect any more acetone in the purified
n-hexane by the method of detection described in Ex-
ample 1.

EXAMPLE 7

The process according to the invention was carried
out in a continuous countercurrent extraction installa-
tion (rotating-plates system with an effective extraction
zone of 3 metres) at a rotational speed of 520 r.p.m.
150 kg/h of a crude cyclopentene fraction consisting of
95 percent of cyclopentene, 3.2 percent of cyclopen-
tane, 1.8 percent of C_5- hydrocarbons and 423 ppm of
carbonyl compounds, were guided in countercurrent to
30 kg/h of a 4 percent aqueous solution of hydrazinium
hydride. Extraction was carried out at room tempera-
ture and normal pressure, the washing solution being
dispersed in the hydrocarbon phase. The purified crude
cyclopentene thus obtained has a residual carbonyl
content of 18 ppm.

EXAMPLE 8

Seven hundred ml of a C_5-hydrocarbon fraction of
the kind obtained during the cracking of light petrol, of
which 4.9 percent consisted of iso- and n-butenes, 55.5
percent of iso- and n-butenes, 38.9 percent of 1,3-
butadiene, 0.7 percent of acetylenes and C_5-allene, and
which had a carbonyl content of 88 ppm, was bubbled
upwards through 175 ml of a 0.85 percent aqueous hy-
drazinium hydride washing solution in a 300 ml ca-
pacity pressure vessel, at a rate of 2,500 ml/h. To
5 improve distribution, the hydrocarbon mixture was forced
through a glass frit at the base of the pressure vessel.
Extraction took place at 20° C under a pressure of 4 bars.
The clear hydrocarbon phase was run off from the
upper part of the pressure vessel and washed with wa-
ter. The residual carbonyl content in the purified C_5-
hydrocarbon fraction, which was determined by the
method described in Example 1, was below the detection
limit of 1 ppm.

What is claimed is:

1. Process for purifying liquid hydrocarbons contain-
ing aldehydes and ketones as impurities in quantities of
up to about 5,000 ppm, which comprises extracting
said hydrocarbons with an aqueous solution of a hydra-
zinium compound having the formula N_xH_2X, wherein
X is a monovalent anion, and separating the purified
hydrocarbon phase.

2. Process of claim 1 wherein the hydrazinium com-
pound is selected from the group of hydrazinium sulphate,
hydrazinium chloride and hydrazine hydrate.

3. Process of claim 1 wherein from 0.5 to 10 percent
by weight aqueous solution of the hydrazinium com-
pound is used.

4. Process of claim 1 wherein the molar ratio of the
hydrazinium compound to the carbonyl impurities is
within the range of 3:1 to 10:1.

5. Process of claim 1 wherein the extraction is carried
out at a temperature in the range of 5° to 50° C.

6. Process of claim 1 wherein the extraction is carried
out at a pressure of from 0.5 to 5 bars.

* * * * *
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,793,187 Dated February 19, 1974

Inventor(s) Hans-Dieter Marx et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 14, after "chemical" insert:

--addition of water to hydrocarbons. Thus, the cracking--

Column 1, line 16, after "compounds" close parenthesis;

Column 1, line 21, "lower" should read --low--;

Column 1, line 24, "formed" should read --formed--;

Column 1, line 32, "case" should read --cases--;

Column 1, line 36, "formation" should read --formation--;

Column 2, line 25, "TO" should read --to--;

Signed and sealed this 19th day of November 1974.

(SEAL)
Attest:

McCoy M. Gibson Jr. C. Marshall Dann
Attesting Officer Commissioner of Patents