PROCESS FOR HYDROGENATING AROMATIC COMPOUNDS CONTAINING SULFUR IMPURITIES

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Attorney, Agent, or Firm—Millen, Raptes & White

ABSTRACT
Process for hydrogenating aromatic compounds containing sulfur impurities by contacting the same, at a temperature in the range of from 200° to 450°C and under a pressure of from 10 to 200 Kg/cm², in a first step, with a catalyst containing a desulfurizing element selected from the oxides and/or sulfides of molybdenum, tungsten, nickel and cobalt, and an iron oxide, deposited on an alumina carrier used in an amount of 0.25 to 4 times the iron oxide amount, and in a second step, with a metal hydrogenation catalyst.

14 Claims, No Drawings
1 PROCESS FOR HYDROGENATING AROMATIC COMPOUNDS CONTAINING SULFUR IMPURITIES

This invention concerns a process for hydrogenating aromatic compounds, particularly such aromatic compounds as benzene, alkylbenzenes, polycyclic aromatic hydrocarbons and their alkyl derivatives, alone or diluted in various petroleum cuts, in the presence of a composite catalyst system which has in particular the advantage of permitting the treatment of materials having high sulfur compound contents and of providing a product which is not only de aromatized but also desulfurized.

An important application of this invention consists of hydrogenating aromatic compounds present in certain petroleum cuts such as white spirit, commonly used in various industries such as those of paint, rubber, solvents for use in agriculture etc.

Another application, which is not less important, is the hydrogenation of the aromatic hydrocarbons present in the kerosene cuts, used as fuel, in view of improving their "smoke point"; this empirical index is in fact proportional to the ratio of hydrogen to carbon in the considered hydrocarbon or cut. This ratio H/C is directly responsible for the combustion heat which is higher as the ratio H/C is greater, i.e. when the aromatic hydrocarbons have been more completely hydrogenated. This quality is specially required for such fuels as jet-fuels which have an always increasing demand (consumption in France of 850 000 metric tons in 1965, 1,500,000 metric tons in 1970, about 2,700,000 metric tons expected for 1975), the specification of such fuels with respect to the maximum content of aromatic compounds being liable to become more severe as the result of the increased use of supersonic transport.

The processes for hydrogenating aromatic hydrocarbons, as already known, may be classified into two categories which both have a certain number of disadvantages.

In the first category are the processes performed in a single stage, using catalysts comprising metals of the iron group (iron, cobalt, nickel) of the periodic classification of elements, associated with metals of group VI A. In these processes, the catalysts are active in the sulfured state. The catalysts used in this category of processes, perform simultaneously the hydrodesulfurization of the feed charge and a certain hydrogenation of the aromatic compounds. However, in spite of the use of high hydrogen pressure and of high temperature (350°C and 60 Kg/cm² by way of example), the final contents of aromatic hydrocarbons are generally high (3 to 5% by volume as a minimum) and do not permit the production of sufficiently de aromatized solvents. Moreover, in this type of process a certain amount of hydrocracking is always observed and requires subsequent fractionations which increase the cost of the process.

The second category of processes performed in two stages, makes use of catalysts comprising metals of group VIII acting in the metal state after reduction.

The catalysts generally used are either based on nickel, or on noble metals such, for example, as platinum. The catalysts are particularly sensitive to the presence of sulfur compounds and/or hydrogen sulfide. It is accordingly necessary to desulfurize the charges and to remove H₂S before the hydrogenation step so that a charge whose sulfur content is generally smaller than 50 ppm (parts per million of parts) is contacted by the hydrogenation catalyst.

The removal of H₂S between the two stages, makes the process more complex. In the case of a flow sheet with a single hydrogen circuit, it is necessary to provide a device for washing the recycle gas; when it is desired to omit said washing of the gas, it is necessary in such a case, to have two independent recycle circuits. In both cases the process is complex and results in a high operating cost.

Some processes carried out with catalysts based on platinum are considered as adapted to the treatment of charges containing up to 300 ppm of sulfur. But, under these conditions, the content of residual aromatic hydrocarbons becomes quickly too high for making it possible to use the resulting product as solvent and, in addition, it becomes necessary to operate at higher temperatures in order to compensate for the loss of activity of the catalyst. Such a high temperature treatment is thermodynamically unfavourable and is detrimental to the yield of the operation and to the cost of the process, since it produces, as the processes of the first category, a certain amount of hydrocracking.

The process of the invention avoids these disadvantages.

As a matter of fact, it makes it possible to process petroleum cuts containing up to 1000 ppm of sulfur while producing cuts substantially entirely free of aromatics and containing substantially no sulfur (generally less than 1 ppm) with a yield by weight close to 100%.

The process consists of treating, in the presence of hydrogen, at a temperature of from 200° to 450°C, preferably from 250° to 350°C, under a pressure of from 10 to 200 Kg/cm², preferably from 20 to 70 Kg/cm², at least one aromatic hydrocarbon in a reaction system comprising in successive order: first of all a hydrodesulfurization catalyst adapted to retain the hydrogen sulfide formed during the hydrodesulfurization reaction and then a hydrogenation catalyst, without intermediary fractionation. The treated material may consist for example of benzene, alkylbenzenes, particularly toluene, xylenes, ethylbenzene, aromatic and alkyloromatic polynuclear hydrocarbons, separately or in admixture with one another, or diluted in petroleum cuts such as white spirit or kerosene, these hydrocarbon mixtures and/or cuts containing optionally up to 1000 ppm by weight of sulfur, and for example 1 to 1000 ppm.

The treated feedstocks generally have boiling points within the range of from 50° to 350°C and may be obtained by straight run distillation of petroleum or by any other operation of refining and/or transformation of petroleum cuts. They may contain for example from 1 to substantially 100% of aromatic hydrocarbons.

The catalyst used according to this invention for simultaneously removing the sulfur compounds from the feedstock and retain the hydrogen sulfide formed during the dehydrodesulfurization reaction, comprises essentially:

a. at least one element active for hydrodesulfurization as known in the art, for example molybdenum and/or tungsten, with or without nickel and/or cobalt, and preferably cobalt-molybdenum, nickel-molybdenum, cobalt-tungsten, nickel-tungsten etc... particularly in the form of oxides or sulfides;

b. alumina;
c. iron oxide or a material containing iron oxide, the ratio by weight of Al₂O₃ to Fe₂O₃ in the catalyst being from 0.25 to 4 and preferably from 0.65 to 1.8.

Among the materials containing iron oxide there can be used an iron ore such as hematite, bauxite or preferably the so-called "red mud" material, consisting of the residue obtained in the manufacture of alumina, whose composition is substantially as follows:

<table>
<thead>
<tr>
<th>Element</th>
<th>Calculated as</th>
<th>Weight Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe₂O₃</td>
<td>30 to 60% of dry weight</td>
</tr>
<tr>
<td>Ti</td>
<td>TiO₂</td>
<td>1 to 10</td>
</tr>
<tr>
<td>Si</td>
<td>SiO₂</td>
<td>5 to 20</td>
</tr>
<tr>
<td>Na</td>
<td>Na₂CO₃</td>
<td>5 to 15</td>
</tr>
<tr>
<td>Al</td>
<td>Al₂O₃</td>
<td>5 to 30</td>
</tr>
<tr>
<td>Mn</td>
<td>MnO₂, P₂O₅, V₂O₅</td>
<td>0 to 5 (for example CaO)</td>
</tr>
<tr>
<td>Misc</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The separation of the red mud is described for example in Kirk and Othmer Encyclopedia of Chemical technology, second edition, Vol 1 (1963) pages 937-941:


In the Bayer process for manufacturing alumina, bauxite is dissolved in a soda lye: the obtained sodium aluminate solution is separated from an insoluble residue, called red mud. The red mud is then washed with water for extracting soda and sodium aluminate from there.

As iron source there can be used an iron salt, for example a nitrate, acetate, carbonate, sulfate or chloride, although this is less preferable.

The proportion of active elements, molybdenum, tungsten, cobalt and/or nickel oxides and/or sulfides in the catalyst, is generally from 2 to 40%, expressed by weight of the corresponding metal. A preferred catalyst contains from 5 to 35% by weight of molybdenum and/or tungsten and from 1 to 10% by weight of nickel and/or cobalt calculated as metal. The catalyst has a specific surface generally from 50 to 400 m²/g, preferably from 100 to 300 m²/g.

In some cases, the material containing iron oxide also contains alumina; it is the case of the red muds; however, these red mudds generally do not permit, by themselves, to obtain a catalyst having the required specific surface, unless a certain proportion of conventional alumina such as, for example, an alumina gel, is added thereto.

The so-composed catalyst is particularly interesting since it performs the hydrodesulfurization reaction over a relatively long period without formation of hydrogen sulfide in the gaseous and/or liquid effluents, in contrast to the use of conventional hydrodesulfurization catalysts, such as Co-Mo, Ni-Mo or Ni-W supported on alumina, for example. This catalyst is also very interesting in that it is easily regenerated by a mere treatment with steam, so that its use results in an economical and really continuous process.

The compounds of metals which are precursors of species active for hydrodesulfurization may be introduced into the catalyst either by mixing with the mixture alumina + iron oxide or red muds or by impregnating of the mixture alumina+iron oxide or red muds preliminarily brought to the desired shape, for example by extrusion. For manufacturing the catalyst carrier, there will advantageously be used ratios of Al₂O₃ to red muds, from 9 to 0.11 by weight and preferably from 2.3 to 0.43 these values being not limitative.

Another technique consists of mixing, as homogeneously as possible, the particles, extrudates for example, of a conventional hydrodesulfurization catalyst with particles, e.g. extrudates, of iron oxide and/or red muds.

As hydrogenation catalysts, there can be used all those which are generally known as such, i.e. the metals of group VIII of the periodic classification of elements such as Ni, Co, Pt, Rh, Ru, Pd etc. incorporated to or deposited on any carrier such for example as alumina, silica, alumina-silica etc. These metals may be used alone or in association in the form of mixtures and/or alloys with one another or with an element from groups VI A or VII A such for example as: W, Mo, Re, Ru, Os, Mt. The content of metal from group VIII is generally from 0.1 to 1.5% by weight of the catalyst.

The molybdenum, tungsten, nickel, cobalt or noble metal compounds which can be used for manufacturing the abovementioned catalysts need not to be listed here, since they are well-known in the art.

The two catalysts in the process of the invention may be used in different manners.

According to a first manner, the two catalysts may be arranged in successive beds, in a single reactor, the first bed consisting of the absorbing hydrodesulfurizing catalyst and the second bed of the hydrogenation catalyst.

According to a second manner of operation, the two catalysts are placed in two successive reactors which are traversed in successive order by the totality of the reactants.

In another alternative embodiment of the process, which is generally preferred, the absorbing hydrodesulfurizing catalyst is placed in two reactors branched in parallel and used alternatively, one being in regeneration, while the other is in operation, the hydrogenation catalyst being placed in a third reactor following the hydrodesulfurization reactor in operation.

An important feature of the process described in the present invention, is that, irrespective of the retained flow sheet and of the use of a single reactor or successive reactors, there is still obtained an integrated system which does not require any intermediate treatment of the effluents (such as for example cooling, separation, gas expansion...). Moreover, the operating conditions are such that practically no hydrocracking occurs and therefore, it is unnecessary to provide for a fractionation system of the liquid product.

As far as the regeneration of the absorbing hydrodesulfurizing catalyst is concerned, it may be easily carried out by passing steam through the catalyst bed, for example at a temperature from 100° to 600°C and preferably from 350° to 450°C, these values being not limitative. This treatment may be applied only to the absorbing-hydrodesulfurizing catalyst or to both catalysts used according to the invention. The steam may be either pure or diluted with inert gas; for example gas produced by the combustion of hydrocarbons may be convenient. A steam content of at least 10% in the regeneration gas is preferred.

This regeneration is appropriate as soon as there is observed the presence of a noticeable proportion of free H₂S in the effluent issuing from the first catalyst zone. During the regeneration, H₂S is liberated from the catalyst. The regeneration may be discontinued as
soon as H₂S is no longer liberated in a noticeable amount.

The regeneration period is generally from 10 minutes to 48 hours according to the selected steam flow rate. This regeneration is advantageously followed by a scavenging with hydrogen so as to expel the residual hydrogen sulfide.

The usual conditions of p.p.h., i.e. of the hourly flow rate of feedstock by weight with respect to the catalyst weight, may be advantageously as follows:

On the absorbing hydrodesulfurizing catalyst, the p.p.h. will be advantageously from 0.2 to 10 and preferably from 0.5 to 5; the optimal p.p.h. depends on the sulfur content of the feedstock and of the ratio alumina/iron oxide of the catalyst; for example, for feedstock containing from 300 to 600 ppm of sulfur, treated over a catalyst having a ratio alumina/red muds of 1, the p.p.h. values may be chosen in the range of from 0.5 to 2.

The selected p.p.h. over the hydrogenation catalyst depends on the desired aromatic hydrocarbons content of the hydrogenated product; it will generally be in the range of from 1 to 20 and preferably from 5 to 15.

These usual values of the p.p.h. are given by way of mere illustration, it being understood that, in some particular cases, satisfactory results are obtained by using p.p.h. values outside the above-defined ranges.

The following examples illustrate the invention, but are not to be considered as limiting the scope thereof.

EXAMPLE 1

In this example, three catalysts are prepared. The first catalyst is a hydrodesulfurization catalyst containing cobalt oxide and molybdenum oxide in a proportion of 4.7% by weight of CoO and 13.6% by weight of MoO₃ admixed with an alumina gel. The incorporation of the metal oxides is carried out in a conventional manner, for example by mixing, in the presence of a small amount of water, the alumina gel with the desired proportion of cobalt nitrate and ammonium paramolybdate; the resulting paste is extruded and then calcined in air at about 550°C so as to obtain the corresponding oxides of cobalt and molybdenum. Another equivalent method for incorporating the metal oxides consists of impregnating the alumina, preliminarily brought to the desired shape, by means of aqueous solutions of catalyst metals and then calcining as above in air at about 550°C.

The second catalyst is a hydrogenation catalyst containing 0.3% by weight of platinum deposited on an alumina carrier. The deposit of platinum is carried out in a conventional manner by impregnating the carrier with an aqueous solution of hexachloroplatinic acid and then drying and calcining at about 550°C.

The third catalyst is an absorbing hydrodesulphurization catalyst containing 4.7% by weight of cobalt oxide and 13.6% by weight of molybdenum oxide introduced by mixing cobalt nitrate and ammonium molybdate with an alumina-red mud mixture having a ratio alumina/red mud equal to 0.67, i.e. containing 40% by weight of alumina and 60% by weight of red muds; the resulting product being extruded and calcined at 550°C as above indicated. The composition of the red muds used for manufacturing this catalyst is as follows:

<table>
<thead>
<tr>
<th>Element</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>46.40</td>
</tr>
<tr>
<td>TiO₂</td>
<td>4.80</td>
</tr>
<tr>
<td>SiO₂</td>
<td>13.20</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>10.15</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17.57</td>
</tr>
<tr>
<td>Ratio</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td></td>
<td>1.8 b.w.</td>
</tr>
<tr>
<td>MnO</td>
<td>0.49</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.09</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.39</td>
</tr>
<tr>
<td>H₂O</td>
<td>93.09</td>
</tr>
<tr>
<td>miscelle-</td>
<td>93.09</td>
</tr>
<tr>
<td>aneous</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The characterizing features of the various solid catalysts used in this example can be summarized as follows:

Hydrodesulfurization catalyst (HDS.CATA.)
Shape: extrudates having a 1.5 mm diameter
Filling density: 0.69 g/cc
Total pore volume: 0.545 cc/g
Specific surface: 324 m²/g (B.E.T. method)

Hydrogenation catalyst (H.CATA.)
Shape: extrudates of a 1.5 mm diameter
Filling density: 0.61 g/cc
Total pore volume: 0.7 cc/g
Specific surface: 214 m²/h (B.E.T. method)

Absorbing hydrodesulfurizing catalyst (A.H.DS.CATA.)
Shape: extrudates of 1.5 mm diameter
Filling density: 0.73 g/cc
Total pore volume: 0.546 cc/g
Specific surface: 188 m²/g (B.E.T. method)

The feedstock subjected to hydrogenation consists of a petroleum cut from straight run distillation, of the white spirit type, having the following characteristics:
ASTM distillation range: 152-195°C Specific gravity at 15°C: 0.792
Aromatic content: 17.5% by volume
Sulfur content (as present in sulfur compounds): 410 ppm by weight

The desired final product is a solvent which does not contain more than 3% by volume of aromatic compounds.

The following three tests have been carried out:
1. In a first test the white-spirit is hydrogenated over the hydrogenation catalyst containing platinum (H.CATA.) in the following conditions:
   Temperature: 300°C
   Total pressure: 45 Kg/cm²
   p.p.h.: 4
   H₂/Feed stock: 1.5 moles/mole
2. In the second test the same white-spirit is hydrogenated in a reactor containing two successive beds of catalyst: the first bed is formed from the hydrodesulfurization catalyst (HDS. CATA.) and the second bed from the platinum hydrogenation catalyst (H. CATA.).
The conditions of pressure, temperature and ratio H₂/feedstock are the same as for the first test: for each of the two catalysts, taken separately, the p.p.h. is equal to 4.

3. In the third test, the same white-spirit is still hydrogenated in a reactor containing a first bed of absorbing dehydrodesulfurizing catalyst (A.HDS.CATA.) followed with a second bed of platinum hydrogenation catalyst (H. CATA.).

The conditions of pressure, temperature and ratio H₂/feedstock are the same as in the preceding tests 1 and 2; the respective p.p.h. values being:

A.HDS.CATA. p.p.h. = 1.35
H. CATA. p.p.h. = 8

As shown in the following table I, the device although operating with a p.p.h. value of 8 over a platinum hydrogenation catalyst gives better results than the device of test 2 with a p.p.h. value of 4 (8/2) over the hydrogenation catalyst.

The results of these three tests are summarized in Table I in which the percent by volume of the residual aromatics is given as a function of the operation time of the catalyst system.

From the above table I it is apparent that only test No. 3 carried out according to this invention with the new catalysts results in the production, over a long period, of a product having the desired specifications (% by volume of aromatics <3). Moreover, the product is obtained during the whole test period with a yield by weight close to 100% and with a sulfur content lower than 0.3 ppm by weight.

EXAMPLE 2

The catalytic system of test no. 3 as reported in example 1 has been in operation for 220 hours and after stoppage of the fluid injections (hydrogen and feedstock) and of the scavenging with hydrogen, is treated with a steam of steam at 400°C for 24 hours, and for 15 hours by means of a hydrogen stream at 400°C, in order to remove the totality of the hydrogen sulfide contained in the system.

A test in every respect identical to test No. 3 of Example 1, is then carried out with the “regenerated” catalyst system; the obtained results are reported in the following table II:

The characterizing features of this kerosene are the following:

- d₅₀ : 0.821
- Sulfur content ppm by weight: 329 (in the form of sulfur compounds)
- Aromatics: 19% by volume (AFNOR MO 7 024)
- Smoke point: 18 mm (AFNOR MO7 028)
- ASTM distillation:
  - Initial point: 164°C
  - 50% distilled point: 204.5°C
  - Final point: 244.5°C

It is desired to obtain a product having a smoke point higher than 23 mm, which corresponds approximatively to an aromatic hydrocarbon content smaller than 10% by volume.

The device used for carrying out this test is the following:

The hydrodesulfurization catalyst also acting as H₂S absorbent is placed into two parallel reactors, one of which is in a regeneration phase while the other is in operation; the hydrogenation reactor is placed at the outlet of the operating hydrodesulfurization reactor without using any intermediary fractionation device. The catalysts A.HDS.CATA. and

50

8

TABLE II

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>% by volume of aromatics in the product</th>
<th>Yields % b.w.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.5</td>
<td>99.5</td>
</tr>
<tr>
<td>20</td>
<td>0.5</td>
<td>100.5</td>
</tr>
<tr>
<td>40</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>60</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>80</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>100</td>
<td>0.6</td>
<td>100</td>
</tr>
<tr>
<td>150</td>
<td>1.5</td>
<td>100</td>
</tr>
<tr>
<td>200</td>
<td>2.4</td>
<td>100</td>
</tr>
<tr>
<td>220</td>
<td>4.7</td>
<td>99</td>
</tr>
</tbody>
</table>

The sulfur content of the product in this test has also been always lower than 0.3 ppm.

This example makes it apparent that the system of the invention is regenerable.

EXAMPLE 3

In this example the feedstock subjected to the treatment is kerosene and it is intended to improve its smoke point; for this purpose there is carried out a partial hydrogenation of the aromatic hydrocarbons contained therein.

TABLE I

<table>
<thead>
<tr>
<th>Test number</th>
<th>Catalytic system</th>
<th>% by volume of aromatics in the final product after (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 20 40 60 80 100 150 200 220</td>
</tr>
<tr>
<td>1</td>
<td>CATA. H</td>
<td>1.1 2.5 5.4</td>
</tr>
<tr>
<td>2</td>
<td>CATA. HDS</td>
<td>1.5 2.4 4.9</td>
</tr>
<tr>
<td>3</td>
<td>CATA. H</td>
<td>&lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5</td>
</tr>
<tr>
<td>4</td>
<td>CATA. H</td>
<td>&lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5</td>
</tr>
<tr>
<td>5</td>
<td>CATA. H</td>
<td>&lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5 &lt;0.5</td>
</tr>
</tbody>
</table>

The characterizing features of this kerosene are the following:

- d₅₀ : 0.821
- Sulfur content ppm by weight: 329 (in the form of sulfur compounds)
- Aromatics: 19% by volume (AFNOR MO 7 024)
- Smoke point: 18 mm (AFNOR MO7 028)
- ASTM distillation:
  - Initial point: 164°C
  - 50% distilled point: 204.5°C
  - Final point: 244.5°C

It is desired to obtain a product having a smoke point higher than 23 mm, which corresponds approximatively to an aromatic hydrocarbon content smaller than 10% by volume.

The device used for carrying out this test is the following:

The hydrodesulfurization catalyst also acting as H₂S absorbent is placed into two parallel reactors, one of which is in a regeneration phase while the other is in operation; the hydrogenation reactor is placed at the outlet of the operating hydrodesulfurization reactor without using any intermediary fractionation device. The catalysts A.HDS.CATA. and
H.CATA. are identical to those described in example 1. The conditions of pressure, temperature and ratio of the hydrogen to the feedstock are the same for both operating reactors:

<table>
<thead>
<tr>
<th>Total pressure: 55 Kg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature: 300°C</td>
</tr>
<tr>
<td>H₂/Feedstock: 1.5 in moles/mole.</td>
</tr>
</tbody>
</table>

The p.p.h. values for the operating reactors are:

A. H.D.S.CATA.: 1.35 (for 1 reactor in operation and the other in regeneration).

H.CATA.: 8

The results obtained are given in table III below:

**TABLE III**

<table>
<thead>
<tr>
<th>Operating time in hours</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>220</th>
<th>240</th>
<th>260</th>
<th>280</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smoke point in mm</td>
<td>&gt;30</td>
<td>30</td>
<td>29</td>
<td>28.5</td>
<td>27</td>
<td>26</td>
<td>24.5</td>
<td>23.5</td>
<td>23</td>
</tr>
<tr>
<td>% by volume of residual aromatics yields % b.w.</td>
<td>-0.5</td>
<td>0.5</td>
<td>1.7</td>
<td>2.2</td>
<td>4.1</td>
<td>5.8</td>
<td>8.2</td>
<td>10.3</td>
<td>11</td>
</tr>
</tbody>
</table>

After 300 hours of continuous operation, the limit of the desired smoke point (23 mm) is reached, the first reactor containing the absorbing hydrodesulfurizing catalyst is then put in regeneration under a steam as indicated in Example 2, while the second reactor containing the absorbing hydrodesulfurizing catalyst is put in operation until the smoke point limit is reached.

**EXAMPLE 4**

The test carried out in this example is similar to test No. 3 of example 1 and makes use of an absorbing hydrodesulfurizing agent, nickel and molybdenum instead of cobalt and molybdenum.

The catalyst is prepared as described in example 1, starting from nickel nitrate and ammonium molybdate, and it contains 4.7% by weight of nickel oxide and 13.6% by weight of molybdenum oxide and a carrier of alumina and red muds with a ratio of the alumina to the red muds equal to 0.67 by weight.

The hydrogenation catalyst is the same as in the third test of example 1. The operating conditions are in any respect identical to those of test No. 3 of example 1. The obtained results are given in the following table:

<table>
<thead>
<tr>
<th>% by volume of aromatic hydrocarbons in the product after hours</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>80</th>
<th>180</th>
<th>200</th>
<th>210</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1.6</td>
<td>2.9</td>
<td>4.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As in the test No. 3 of Example 1 there is obtained a product having the desired specifications over a long period, with a yield by weight close to 100% and a sulfur content lower than 0.5 ppm by weight.

**EXAMPLE 5**

There is carried out again a test identical to test No. 3 of example 1, but using an absorbing hydrodesulfurizing catalyst based on nickel-tungsten.

The catalyst prepared as described in example 1, from nickel nitrate and ammonium tungstate, contains 4.7% by weight of nickel oxide and 21.8% by weight of tungsten oxide on a carrier of alumina and red muds with a ratio of the alumina to the red muds of 0.67 by weight.

As in example 4, the operating conditions and the hydrogenation catalyst are unchanged.

The following results have been obtained:

A mixture of hydrogen with at least one aromatic compound containing sulfur impurity is contacted, at a temperature of from 200° to 450°C, under a pressure of from 10 to 200 kg/cm² in successive order with:

a. at least one desulfurizing element selected from the oxides and/or sulfides of molybdenum, tungsten, nickel and cobalt;

b. alumina and,
c. iron oxide, the ratio by weight of Al₂O₃ to Fe₂O₃ in this catalyst being from 0.25 to 4; and.

A group VIII metal hydrogenation catalyst.

2. A process according to claim 1, in which the desulfurizing element, calculated as metal, forms from 2 to 40% by weight of the catalyst A.

3. A process according to claim 1, in which the desulfurizing element is present in the form of a sulfide.

4. A process according to claim 1, in which the iron oxide is present in the form of red mud, which is a residue of the alumina manufacture.

5. A process according to claim 4, in which the red mud contains, by weight, from 30 to 60% of iron, expressed as Fe₂O₃ from 1 to 10% of titanium, expressed as TiO₂ from 5 to 20% of silicon, expressed as SiO₂ from 5 to 15% of sodium, expressed as Na₂CO₃ and from 5 to 30% of aluminum, expressed as Al₂O₃.

6. A process according to claim 1 in which the ratio of Al₂O₃ to Fe₂O₃ in the catalyst (A) is from 0.65 to 1.8 by weight.

7. A process according to claim 1 in which the specific surface of the catalyst (A) is from 50 to 400 m²/g.

8. A process according to claim 1, in which the specific surface of the catalyst (A) is from 100 to 300 m²/g.

9. A process according to claim 1, in which the catalyst contains from 5 to 35% by weight of molybdenum and/or tungsten oxide or sulfide and from 1 to 10% by weight of nickel and/or cobalt oxide or sulfide, expressed as metal.

10. A process according to claim 1, in which the metal is platinum.

11. A process according to claim 1, in which the temperature is from 250° to 350°C and the pressure from 20 to 70 kg/cm².

12. A process according to claim 1, in which the treated feedstock is a hydrocarbon fraction containing from 1 to 100% by weight of aromatic hydrocarbons and from 1 to 1000 ppm by weight of sulfur.

13. A process according to claim 1, further comprising regenerating the catalyst by passing steam through the catalysts A and B at a temperature from 100° to 600°C and thereafter employing the regenerated cata-
A process according to claim 1 further comprising regenerating the catalyst (A) by passing steam at a temperature of from 100° to 600°C therethrough and thereafter employing the regenerated catalyst in the hydrogenation step.

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