The invention relates to a selective desulphurisation method for thiophene derivatives contained in the hydrocarbons emitted from the distillation of crude oil, refined or not, consisting in oxidising the atoms of thiophene sulphur in sulphone in the presence of an oxidising agent and separating the sulphonated compounds from said hydrocarbons. This inventive method comprises at least one first stage involving the oxidation/absorption by heterogeneous catalysis of the sulphurous compounds in an organic environment, at a temperature of at least 40°C, at atmospheric pressure in the presence of an organic oxidiser from the family of peroxides and peracids, in the presence of a catalyst having a specific surface area greater than 100 m²/g and a porosity varying from 0.2 to 4 ml/g, and a second stage wherein the used catalyst is regenerated.
FIG. 3.1

Amount of residual sulfur (ppm)

TIME (h)

FIG. 3.2

Amount of residual sulfur (ppm)

TIME (h)
The present invention concerns a process and a device for desulfurizing hydrocarbons, and particularly, for desulfurizing fuel bases for gasolines, kerosenes, and gasolines. In particular, it concerns the desulfurization of fuel bases containing dibenzothiophenic compounds.

The presence of sulfur in fuels constitutes what is considered today to be a major problem for the environment. Indeed, through combustion, sulfur is converted to various sulfur oxides that can be transformed into acids, thus contributing to the formation of acid rain.

In general, refineries use catalytic hydrodesulfurization processes to reduce the sulfur content in fuels. Thus, gasolines derived directly from distillation are hydrorefined at 300° and 400° C under pressure of hydrogen varying between 30 and 100 bars (30 to 100 10^5 Pa), in the presence of a catalyst on a fixed bed and composed of sulfides of metals of groups VIIb and VIII deposited on alumina oxide, for example cobalt and molybdenum sulfides or nickel and molybdenum sulfides. Because of the operating conditions and the consumption of hydrogen, these processes can be costly both in investment and in operation, particularly if fuels with very low sulfur content are to be produced. Consequently, in order to desulfurize a fuel initially containing 1% sulfur by weight until it has a concentration of sulfur of between 0.05 and 0.005% by weight, the size of the reactor can be multiplied by four and the quantity of hydrogen needed for the reaction must be increased by about 20%. It is particularly difficult to eliminate traces of sulfur by such processes, especially if the sulfur belongs to refractory molecules such as alkyl dibenzothiophene in position 4, or 4 and 6.

In some countries like Sweden, the United States, particularly in California, and others, the total sulfur content of gasolines is already limited to 0.005% by weight. This limitation could become generalized in time within the OECD countries. For Europe, this goal of 0.005% by weight of total sulfur could be achieved in 2005.

Unlike gasolines, gasolines are not only distilled directly from crude oil, these gasolines being then slightly sulfurous, but can also be obtained by several processes such as reforming of naphthas, isomerization of light naphthas, alkylation of butane or propane producing isooctane, methoxylation of isobutene, and the catalytic cracking of distillates under vacuum or atmospheric residue. In particular, catalytic cracking provides between 20% and 60% by weight of final gasoline. However, these gasolines contain up to 0.1% by weight of sulfur. It is common, therefore, to desulfurize gasolines produced by catalytic cracking using processes similar to those described for the hydrodesulfurization of gasolines, for which the operating conditions of hydrogen pressure, space velocity, and temperature are more stringent. These processes, although costly, do not enable total sulfur content in cracked gasoline of between 0.005% and 0.03% by weight to be obtained by conventional means. Although refiners, in order to reduce this sulfur content, have thought that including additives in the cracking catalyst would break down the sulfurous compounds formed during the process, particularly mercaptans and sulfides, these additives have only a limited or even no effect on the benzothiophenic derivatives, even when the mercaptans and the sulfides have been eliminated before cracking.

In the case of gasolines from catalytic cracking that generate sulfur in gasolines, hydridesulfurization is not only ineffective with respect to thiophenic compounds, but it is also destructive with respect to the octane index of the gasoline. Indeed, during the hydrodesulfurization reaction, there is a partial hydrogenation of the olefins contained in these cracked gasolines, their disappearance resulting in a decrease in the octane index of the gasoline and thus a deterioration in the quality of the gasoline. To compensate for this loss, it is possible to introduce other components to improve this index or to reprocess the gasoline itself to increase this index. The inclusion of an additive or the reprocessing to improve the quality of the gasoline affects the production cost that much more, and it is therefore advantageous to have a processing method that enables the direct elimination of the refractory sulfur compounds, such as benzothiophenic derivatives, by limiting the use of hydrogen.


Processes using molybdenum- and tungsten-based metallic catalysts in the presence of hydrogen peroxide in aqueous solution (heterogeneous catalysis) take place at temperatures of more than 60° C., and there is excessive consumption of hydrogen peroxide, a part of this oxidant being broken down by the catalyst used. The peroxides used, very powerful oxidants, obtained by reaction of hydrogen peroxide and a carboxylic acid such as formic acid or acetic acid, are generally less effective than hydrogen peroxide and less selective with respect to sulfurous compounds and in particular can oxidize olefins.

Other oxide sulfurization processes in organic medium have been proposed. They consist of placing in contact powdered metallic oxides, or of forming metallic compounds having peroxy groups in aqueous or organic solutions with the hydrocarbons containing these refractory sulfurous compounds, whether or not in the presence of organic or aqueous peroxides which are introduced with an alcohol type solvent or in the water (see U.S. Patent No. 3,816,301, U.S. Patent No. 4,956,578, U.S. Patent No. 5,598,224).

Another process, described in U.S. Patent No. 3,945,914, consists of producing a desulfurized hydrocarbonated material in three processing steps. The first step consists of at least partially oxidizing the sulfurous compound by placing them in contact with peroxides in the presence of
metallic catalysts containing metals from the group including titanium, zirconium, molybdenum, tungsten, vanadium, tantalum, chromium, and their mixtures, in liquid or solid form possibly supported, although the supports are not essential for the reaction. The second step consists of placing the hydrocarbonated material containing the oxidized compounds in contact with another metallic component, metallic oxide or peroxide (metals from the group including nickel, molybdenum, cobalt, tungsten, iron, zinc, vanadium, copper, manganese, mercury, and their mixtures), at a temperature varying from 250° C. to 730° C., under hydrogen pressure. The third step consists of recovering the desulfurized hydrocarbonated material.

[0012] In all these methods and processes, the derivatives of thiophene in their sulfonated and/or sulfonic form are transformed. However, for some of these compounds, even when working at high temperature, the reaction is relatively slow and total conversion is not achieved in less than one hour, except by using very strong concentrations of oxidant, often far greater than the quantities necessary for the oxidation of the sulfurous derivatives. In other cases, it is possible to work in several steps, but they are costly in time and in monitoring the unit.

[0013] The present invention, therefore, proposes a process for desulfurizing hydrocarbons, particularly those used as bases for fuels containing thiophenic derivatives, without reducing the index of the octane number or of the cetane number, sometimes even increasing these indices. In particular, it concerns the treatment of hydrotreated gasolines, kerosenes, and catalytic cracked gasolines with high concentrations of refractory thiophenic derivatives in hydrogenations.

[0014] Furthermore, the invention proposes such a process that makes it possible to reach oxidation levels that are identical if not greater than the known processes, while limiting the reaction and separation times of the oxidized sulfurous compounds from the desulfurized hydrocarbons.

[0015] An object of the present invention is therefore a process for selectively desulfurizing the thiophenic compounds contained in the hydrocarbons produced from the distillation of crude oil, refined or not, consisting of oxidizing the thiophenic sulfur atoms into sulfones in the presence of an oxidizing agent and a catalyst, and of separating the obtained sulfonated compounds from said hydrocarbons, this process being characterized in that it comprises at least a first step of oxidation/adsorption by heterogeneous catalysis of the sulfurous compounds, in an organic medium, at a temperature of at least 40° C., in the presence of an organic oxidizer from the family of peroxides and peracids and in the presence of a catalyst having a specific surface area greater than 100 m²/g and a porosity varying from 0.2 to 4 ml/g, and a second step of regeneration of the used catalyst, the regeneration step always following the oxidation/adsorption step.

[0016] Within the scope of the present invention, derivatives of thiophene are understood as being benzothiophenic, polybenzothiophenic compounds and their alkyl derivatives, among which are the alkylidibenzothiophenes, particularly refractory to the conversion processes usually used by refiners.

[0017] The process of the invention has the advantage, on the one hand, of ensuring the oxidation at atmospheric pressure of all of the sulfur contained in the hydrocarbons, and more selectively a conversion of the thiophenic derivatives into sulfohnes, this by means of a simple industrial process, and on the other hand, of simultaneously adsorbing these sulfoxide compounds on the catalyst. In fact, the separation of the hydrocarbons from most of the formed sulfoxides is immediate, with the latter ending up in solid form deposited on the catalyst or deposited in a form that can be filtered by known means, in the treated hydrocarbons. This catalyst, on which these sulfoxide compounds have been absorbed, constitutes the “used catalyst.” The sulfoxides that may have been dissolved in the treated hydrocarbons can be extracted. Moreover, this oxidation/adsorption has no effect on the olefins, which in catalytic cracked gasolines does not change the octane index, or the concentration of unsulfurous aromatic compounds. In addition, the oxidation process according to the invention improves the cetane number of the gasolines.

[0018] Without being limited by a theory, it has become clear that the greater the specific surface area of the catalyst, the longer it remains active.

[0019] Furthermore, because compounds of the sulfone and sulfoxide type have a strongly polar nature, they are kept on the surface of the catalyst, probably at the catalyst’s Lewis acid sites. In addition, the larger the size of the pores, the less the catalyst’s pore risk becoming quickly clogged and the greater the longevity of the catalyst during the oxidation cycle. For the present invention, it is to select the catalyst that has the best compromise of specific surface area and pore size to obtain sufficient activity, for as long as possible, to be the most effective for oxidation/adsorption.

[0020] When the process is continuously implemented intermittently, the oxidation/adsorption and regeneration steps can be performed in the same reactor or simultaneously in reactors arranged in parallel and operating alternatively for one or the other of the fixed bed steps, or in at least two moving-bed reactors connected to each other by the catalytic bed, one being used for oxidation/adsorption and the other for regeneration.

[0021] With a fixed bed, the first reactor containing a fixed catalyst bed receives the flow of hydrocarbons and oxidizing agent and the second receives, for the regeneration of the catalyst, liquid effluents, such as a washing solvent, or oxidizing gaseous effluents like air or air/N₂ mixture, the temperature of the catalytic bed being increased. These reactors change function when the effectiveness of the catalyst in the oxidation/adsorption reactor is no longer sufficient in oxidation and/or adsorption.

[0022] With a moving-bed, the hydrocarbons are brought into the first reactor where the oxidation takes place, the catalyst being pushed progressively toward the second reactor, the regeneration being performed before being returned to the oxidation/adsorption reactor. The moving-bed reactors, well known particularly in the area of reforming, can be used in this device. In this form of embodiment, a third reactor is used, placed between the first two reactors and making it possible to eliminate the hydrocarbons from the used catalyst before washing it or burning off the trapped sulfoxide and sulfoxide compounds.

[0023] The catalysts used according to the present invention are selected among the supports from the group con-
sisting of silicas, aluminum oxides, zirconias, amorphous or crystalline aluminosilicates, alumino phosphates, mesoporous siliceous and silicoaluminate solids, activated carbon and clays, these supports being used alone or in mixture. In the catalysts of the invention, these supports can be used advantageously as supports of metals of the group consisting of titanium, zirconium, vanadium, chromium, molybdenum, iron, manganese, cerium, and tungsten; these metals in oxide form can be introduced into the matrix of the support or deposited on the surface of the support. In fact, a synergistic effect has been noted of the metal with the support, that is, an unexpected increase of activity of the catalyst with respect to the oxidation of the thiophenic compounds, and at the same time, an increased trapping of the sulfone and sulfoxide compounds in the pores of the catalyst, without any of them being subsequently desorbed.

[0024] In the process according to the invention, the catalyst contains from 0 to 30% by weight of metal in oxide form on at least one support. Preferably, the catalyst contains from 0 to 20% metal in oxide form.

[0025] Among the supports composed of refractory oxides, gamma-aluminum oxides, silicon oxides, silicic mesoporous solids, and silicoaluminates are preferred.

[0026] Among the supported catalysts, catalysts containing tungsten or titanium in oxide form are preferred, deposited on a support or introduced into the matrix, this support being selected from among the silicon oxides, aluminum oxides and aluminosilicates, alone or in mixture.

[0027] In a preferred form of implementation of the process, the total oxidizer/sulfur mol ratio contained in the hydrocarbons is between 2 and 20, and preferably between 2 and 6.

[0028] According to the invention, the oxidizers are selected from among the compounds with the general formula \( R_1 \text{OOR}_2 \), in which \( R_1 \) and \( R_2 \) are identical or different, selected from among hydrogen, linear or branched alkyg groups having from 1 to 30 carbon atoms and aryl or alkylaryl groups the aryl motif of which can be replaced by alkyl groups, while \( R_1 \) and \( R_2 \) cannot be hydrogen simultaneously.

[0029] In a preferred embodiment, the oxidizer of the formula \( R_1 \text{OOR}_2 \) is selected from the group consisting of tert-butyl hydroperoxide and di-tert-butyl peroxide.

[0030] Other oxidizers of the invention, the peracids of formula \( R_1 \text{COOOH} \), are selected so that \( R_1 \) is hydrogen or a linear or branched alkyl group having from 1 to 30 carbon atoms. They are preferably selected from the group consisting of peracetic acid, perfomic acid, and perbenzoic acid.

[0031] In the process of the invention, the catalyst regeneration step consists of eliminating the formed deposits by washing or combustion.

[0032] For the washing, a solvent is used, preferably polar, from the group consisting of water, linear or branched alkanols having from 1 to 30 carbon atoms, alone or in mixture with water, alkynitriles having from 1 to 6 carbon atoms. Water, acetonitrile, methanol, and their mixtures are preferred.

[0033] By combustion, the catalyst is brought up to a temperature of no more than 800° C., preferably a temperature equal to or less than 650° C., under a pressure varying from 10⁵ Pa to 10⁶ Pa, preferably from 10⁵ Pa to 2 x 10⁶ Pa, in the presence of an oxidizing gas. Oxidizing gas is understood as being pure oxygen and all mixtures of gas containing oxygen, particularly mixtures of oxygen and nitrogen and air itself. The quantity of oxygen in the nitrogen is adjusted in order to limit the formation of water vapor, since too great a quantity of water vapor has the side effect of modifying the structure of the pores of the catalyst by decreasing their volume, specifically when it contains crystalline aluminosilicates such as zeolites or aluminophosphates as support. Moreover, this adjustment makes it possible to control the temperature variations related to the exothermicity of the combustion.

[0034] A second object of the invention is a device for implementing the process defined above, this device comprising at least a first reactor containing an oxidation catalyst and having feed pipes for the hydrocarbons and the oxidizer and an outlet pipe for the desulfurized hydrocarbons, and possibly a second reactor having feed pipes for solvent or oxidizing gas of the catalyst, in order to regenerate it, and an outlet pipe for the combustion gases. Oxidizing gas is understood here as oxygen/air, air/nitrogen, and oxygen/nitrogen mixtures.

[0035] When the device includes two reactors, the reactors can operate with a fixed bed or a moving bed.

[0036] A third object of the invention is the application of the process defined above to the specific finish treatment of gasolines produced from catalytic cracking, or the treatment of gasolines having been previously hydro treated and kerosenes, for better economy of the process.

[0037] The invention will now be described in more detail, with reference to the appended drawings in which:

[0038] FIG. 1 is a diagram of a device with two reactors operating alternatively for oxidizing and for regenerating the catalyst;

[0039] FIG. 2 is a diagram of a device having two moving-bed reactors, the first corresponding to the oxidation step, the second to the catalyst regeneration step, a pipe for return of the regenerated catalyst being added to the system;

[0040] FIGS. 3-1 and 3-2 show graphs illustrating the total sulfur content, as a function of time, of the hydrocarbons treated according to the invention in the Example III below.

[0041] The device of FIG. 1 has two reactors 1 and 2 charged with a catalyst arranged as fixed-bed. When the reactor 1 is operating in oxidation and the reactor 2 operates in regeneration, the pipe 3 takes the sulfurous hydrocarbon load, into which the oxidizer has been introduced by the pipe 4, the three-way valve 6a and the pipe 8a. The flow of desulfurized hydrocarbons leaves the reactor 1 by the pipe 9a and reaches the desulfurized hydrocarbon outlet pipe 10a via the three-way valve 7a.

[0042] At the same time, the pipe 5 takes to the reactor 2 either an appropriate solvent or an oxidizing gas, via the three-way valve 6b and the pipe 8b. When the reactor operates in combustion, the temperature of the catalytic bed is held at 500° C. The solvent containing the sulfones recovered on the catalyst or the combustion gases, primarily
SO₂, CO, and CO₂, are evacuated via the pipe 9bia the three-way valve 7b and the pipe 11b in the pipe 11a.

[0043] When the regeneration of the catalyst is done and the activity of the catalyst of reactor 1 becomes insufficient, the function of the two reactors is exchanged. Thus, the hydrocarbons/oxidizer mixture passes through the pipe 3a and the valve 6b to enter the reactor 2. The desulfurized hydrocarbons are removed by the pipe 9b and are taken to the outlet pipe 10a via the valve 7b and the pipe 10b.

[0044] At the same time, the solvent or the oxidizing gas arriving by the pipe 5 is sent to the reactor 1 by the pipe 3a, the valve 5a and the pipe 8a. The solvent or the oxidation gases are taken back to the outlet pipe 11a via the pipe 9a and the valve 7a.

[0045] The valves 6a, 6b, 7a, and 7b can be exchanged according to a common procedure, in order to allow the circulation of the proposed flows.

[0046] A filter can be placed advantageously on one of the pipes 9a or 9b, on 11a or 11b, to recover the solid sulfones formed during oxidation and remaining in suspension in the hydrocarbons. Sulfur traps equipped with absorbents such as silica or activated alumina can be advantageously added to these same pipes, downstream from these filters, to trap sulfones that are still dissolved in the treated hydrocarbons.

[0047] The device of FIG. 2 includes two reactors 20a and 20b, arranged in series, each containing a moving-bed catalyst, the reactor 20a operating in oxidation mode and the reactor 20b in regenerative mode, and a propulsion device 30 to allow the catalyst from the reactor 20b to return to the reactor 20a.

[0048] The hydrocarbons are taken by the pipe 4a into the reactor 20a, after having been deposed by the oxidizer via the pipe 5a. For example, the reactor 20a can be selected from among funnel-shaped reactors, the moving bed of the cataly being moved by gravity toward the lower part of the reactor. In this way, while the desulfurized hydrocarbons are removed by the pipe 60, the catalyst is forced by gravity into the reactor 20b through the pipe 70. The solvent or combustion gas is introduced via the channel 80 in the reactor 20b. In order to effect regeneration by combustion, the temperature is increased to and held at 500°C. The sulfone-containing solvent or the combustion gases are removed by the pipe 10a.

[0049] Since these moving-beds generally operate intermittently, the catalyst not being moved continuously, it is beneficial to place on the reactor 20b a solvent or nitrogen purge to eliminate the hydrocarbons before purging, and/or eliminate the combustion gases by stripping the nitrogen.

[0050] When it leaves the reactor 20b, the regenerated catalyst is taken via the pipe 110 to the device 30. This device can be a pressurized gas propulsion device or a worm gear. It takes the regenerated catalyst back to the reactor 20a via the pipe 120.

[0051] In some special forms of embodiment of these moving reactors, the reactors 20a and 20b can be part of the same unit having two separate stages.

EXAMPLE 1

[0053] The present example describes the effectiveness of the process, according to the invention, with respect to the elimination of the derivatives of the dibenzothiophene present in the partially desulfurized bases for fuels.

[0054] The samples of catalyst used are of two types, the catalysts formed from a single support and those to which are combined one or more metals deposited by impregnation. Table 1 below provides the specific surface area and porosity characteristics of each of them.

```
<table>
<thead>
<tr>
<th>Catalyst sample</th>
<th>Type of support</th>
<th>Specific surface area (m²/g)</th>
<th>Pore size (Angeles)</th>
<th>Metal oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>SiO₂</td>
<td>160</td>
<td>252</td>
<td></td>
</tr>
<tr>
<td>C₂</td>
<td>SiO₂</td>
<td>140</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>C₃</td>
<td>Al₂O₃ gamma</td>
<td>245</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>C₄ Beta zeolite</td>
<td></td>
<td>470</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>C₅ Mesoporous</td>
<td></td>
<td>1000</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>C₆ Mesoporous</td>
<td></td>
<td>830</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>C₇ Al₂O₃ γ</td>
<td></td>
<td>210</td>
<td>95</td>
<td></td>
</tr>
</tbody>
</table>
```

[0055] The catalysts C₂, C₃, and C₄ were obtained by wet impregnation with a metallic salt, respectively ammonium metatungstate and ammonium hexamolybdate, in a concentration of 140 mg of metal per gram of support, then dried and finally calcinated at a temperature of 500°C.

[0056] The catalyst C₄ was obtained by treating a beta zeolite with commercially available titanium according to the procedure described in patent EP 0,842,114.

[0057] To test the oxidation activity of these catalysts as a function of time, 20 ml of catalyst is introduced into a 150 ml micropliot. A charge of average distillates after hydrotreatment, containing 212 ppm of residual sulfur remaining from hydrotreatment, doped with 1,800 ppm of tert-butyl hydroperoxide (tBHP), is circulated over the catalyst at an hourly space velocity (HSV) of 1 h⁻¹, under atmospheric pressure at a temperature of 70°C. Samples are taken regularly during oxidation to measure the activity of the catalyst over time. A representative sample called T₁, corresponding to the use of a catalyst alone without peroxide, is also monitored.

[0058] In Table II below, the results are given of the effectiveness of these catalysts over time.

```
<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst</th>
<th>Total sulfur (ppm) after different periods of operation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2 hrs</td>
</tr>
<tr>
<td>T₁</td>
<td>C₁</td>
<td>121</td>
</tr>
<tr>
<td>X₁</td>
<td>C₂</td>
<td>49</td>
</tr>
<tr>
<td>X₂</td>
<td>C₃</td>
<td>28</td>
</tr>
<tr>
<td>X₃</td>
<td>C₄</td>
<td>30</td>
</tr>
<tr>
<td>X₄</td>
<td>C₅</td>
<td>18</td>
</tr>
<tr>
<td>X₅</td>
<td>C₆</td>
<td>35</td>
</tr>
<tr>
<td>X₆</td>
<td>C₇</td>
<td>23</td>
</tr>
<tr>
<td>X₇</td>
<td>C₈</td>
<td>34</td>
</tr>
</tbody>
</table>
```

[0059] After two hours of operation, these results confirm that, apart from the effect due to the nature of the catalyst,
the greater the catalyst pore size and specific surface area, the lower the sulfur content of the treated hydrocarbons. Moreover, it is verified that the activity of the catalyst increases when it is comprised of a metal oxide with support. However, after 24 hours, irrespective of the catalyst, a slight increase is observed of the sulfur content of the desulfurized hydrocarbons, which may correspond to the beginning of clogging of the catalyst’s pores, the sulfones and sulfoxides being attached thereto.

[0060] By this process, it is clear that the choice of a catalyst for the process of the invention is the result of a compromise between the nature of the catalyst, its specific surface area, and the size of the pores thereof.

EXAMPLE II

[0061] In this Example, the effectiveness of the catalyst is measured as a function of the oxidation of the compounds.

[0062] The same process as in Example I is used, with catalysts C1-Cn, and the formation is monitored of sulfones and sulfoxides with reference to the dibenzothiophene compounds, particularly the benzothiophene (BT), dibenzothiophene (DBT) and the 4,6 dimethyl dibenzothiophene (DMBT), by gas chromatography equipped with a sulfur specific detector (SIEVERS process).

[0063] Table III below shows the results obtained.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Oxidizer concentration (eq%)</th>
<th>% Sulfone oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BT</td>
<td>DBT</td>
</tr>
<tr>
<td>C1</td>
<td>3</td>
<td>80</td>
</tr>
<tr>
<td>C2</td>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>C3</td>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>C4</td>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>C5</td>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>C6</td>
<td>3</td>
<td>90</td>
</tr>
</tbody>
</table>

[0064] These results show that there is a conversion of at least 80% of the refractory thiophenic derivatives into sulfones, with catalysts composed of a single support, and of more than 90% with catalysts composed of supports and at least a metal in the form of metal oxide inserted into the matrix of the support or deposited on the support.

EXAMPLE III

[0065] The present example seeks to show, at the same time as the oxidation, the effect as a function of time of the adsorption of the sulfone and sulfoxide compounds on the oxidation/adsorption and regeneration sequences, and the effectiveness with reference to the oxidation/adsorption.

[0066] This was done with the C2 catalyst under the operating conditions described in Example I on a middle distillate containing 44 ppm of sulfur after hydrotreatment, and in the presence of 600 ppm of tBP.

[0067] The results of the oxidation/adsorption are given in FIG. 3-1, when the catalyst is fresh. After two days, the total concentration of sulfur in the hydrocarbons increases substantially again to the initial value, in the absence of the treatment, according to the invention.

[0068] The results of FIG. 3-2 correspond to monitoring the sulfur content of these same hydrocarbons when this same catalyst C2, regenerated by combustion, is used. The results obtained on a fresh catalyst are nearly identical to those obtained on the same regenerated catalyst.

[0069] These two graphs show the importance of the process of the invention that proposes an alternative operation of the same catalyst for oxidation/adsorption or for regeneration, the oxidation/adsorption time naturally being adapted to the content in sulfur.

1. Process for selectively desulfurizing the thiophenic derivatives contained in the hydrocarbons produced from the distillation of crude oil, refined or not, consisting of oxidizing the thiophenic sulfur atoms into sulfones in the presence of an oxidizing agent, and of separating the sulfonated compounds from said hydrocarbons, this process being characterized in that it includes at least a first step of oxidation/adsorption by heterogeneous catalysis of the sulfur compounds, in organic medium, at a temperature of at least 40°C, in the presence of an organic oxidizer from the family of peroxides and peracids and in the presence of a catalyst having a specific surface area greater than 100 m²/g and a porosity varying from 0.2 to 4 m³/g, and a second step of regeneration of the used catalyst, the regeneration step always following the oxidation/adsorption step.

2. Process according to claim 1, characterized in that the oxidation/adsorption and regeneration steps are carried out successively in the same reactor on the same catalyst.

3. Process according to claim 1, characterized in that the oxidation/adsorption and regeneration steps are carried out simultaneously in reactors (1, 2) arranged in parallel and operating alternately for one and other steps.

4. Process according to claim 1, characterized in that the oxidation/adsorption and regeneration steps are carried out in two moving-bed reactors (20a, 20b) connected to each other by the catalytic bed, one being used for the oxidation, the other for the regeneration.

5. Process according to claim 1, characterized in that the oxidizing agent is selected from the group consisting of organic peroxides, organic hydroperoxides, and peracids.

6. Process according to claim 1, characterized in that the catalyst includes a support selected from the group consisting of silicas, aluminas, zirconias, amorphous or crystalline aluminosilicates, aluminophosphates, mesoporous solids, activated carbon, clays, and their mixtures.

7. Process according to claim 6, characterized in that the catalyst contains at least a metal selected from the group consisting of titanium, zirconium, vanadium, chromium, molybdenum, iron, manganese and tungsten, this metal being introduced into the matrix of the support or deposited in oxide form on the support.

8. Process according to claim 1, characterized in that the catalyst contains from 0 to 30% by weight of metal in oxide form.

9. Process according to claim 1, characterized in that the catalyst is comprised of at least a support selected from gamma-alumina, silica and silicate mesoporous solids and silicoaluminates.

10. Process according to claim 9, characterized in that the supported catalyst is selected from catalysts containing tungsten on a support selected from silicas and aluminum oxides, alone or in mixture.
11. Process according to claim 1, characterized in that the oxidizer/total sulfur mol ratio in the hydrocarbons varies from 2 to 20.

12. Process according to claim 1, characterized in that the oxidizer is a compound with the general formula R₃OOR₂, in which R₁ and R₂ are selected identical or different from the group consisting of the hydrogen atom and the alkyl groups, linear or branched, having from 1 to 30 carbon atoms, while R₃ cannot be hydrogen simultaneously.

13. Process according to claim 12, characterized in that the oxidizer is selected from the group consisting of tert-butyl hydroperoxide and di-tert butyl peroxide.

14. Process according to claim 1, characterized in that the oxidizer is a peracid of formula R₃COOOH, in which R₃ is hydrogen or a linear or branched alkyl group having from 1 to 30 carbon atoms.

15. Process according to claim 14, characterized in that the oxidizer is selected from the group consisting of peracetic acid, performic acid, and perbenzoic acid.

16. Process according to claim 1, characterized in that the catalyst regeneration step consists of eliminating the formed deposits by washing or combustion.

17. Process according to claim 1, wherein the hydrocarbons produced from the distillation of crude oil are selected from the group consisting of hydrotreated gas oils, kerosenes, and gasolines.

18. Process according to claim 11, characterized in that the catalyst contains from 0 to 20% by weight of metal in the oxide form.

19. Process according to claim 11, characterized in that the oxidizer/total sulfur mol ratio in the hydrocarbons varies from 2 to 6.

20. Process according to claim 17, wherein the hydrocarbons produced from the distillation of crude oil are gasolines produced from catalytic cracking.

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