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DESULFURIZATION OF HYDROCARBON OILS

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This invention relates to desulfurization of hydrocarbon oils.

Hydrocarbon oils, such as for example those obtained by fractional distillation of petroleum, often are contaminated with sulfur containing impurities. For many purposes it is desirable that such impurities should be removed. For example desulfurization of the hydrocarbon feedstock is a necessary step in the manufacture of methanol from a mixture of carbon monoxide and hydrogen produced by steam reforming of a straight-run naphtha. In this process it is essential that the naphtha should be substantially free from sulfur, because if the sulfur content of the naphtha is greater than about 5 p.p.m. the catalyst used in the steam reforming process deteriorates rapidly under normal commercial conditions.

Several desulfurization processes are at present known which make a big decrease in the sulfur content of hydrocarbon oils. For example the sulfur content of a straight-run naphtha may be decreased from 200–1000 p.p.m. to 20–100 p.p.m. by treatment with sulfuric acid. The degree of desulfurization depends on the amount of acid used and on the thoroughness with which the acid and the hydrocarbon are mixed. Alternatively partial desulfurization may be achieved by hydrodesulfurization. For example we have found that the sulfur content of a straight-run naphtha of boiling range up to 165° C. may be decreased from 357 p.p.m. to 10–26 p.p.m. by passing the vapor mixed with an equimolecular volume of hydrogen at 50 atmospheres' pressure over a catalyst comprising cobalt molybdate on alumina at 380° C. A similar degree of desulfurization may be achieved by passing the vapor, with or without hydrogen, over a contact material comprising zinc oxide, manganese oxide or iron oxide at 350° C. to 450° C.

No known desulfurization process is capable of achieving in one stage a decrease to less than 5 p.p.m. of the sulfur content of straight-run naphthas commonly available. However, we have found that the problem of economically achieving this degree of desulfurization is solved by using a process comprising a novel combination of desulfurization stages as hereinafter specified.

According to the present invention, therefore, there is provided a process for desulfurization of a hydrocarbon oil which is substantially free from ethylenically or acetylenically unsaturated compounds, which process comprises three stages, of which the first stage comprises treating the hydrocarbon oil with sulfuric acid under conditions as hereinafter specified, and/or vaporizing it and then passing the vapor thus produced over a contact material comprising zinc oxide, manganese oxide or iron oxide (preferably zinc oxide) at a temperature between 350° C. and 450° C. and at a pressure between 1 and 50 atmospheres, the second stage comprises passing the vaporized hydrocarbon, together with hydrogen, at a temperature between 350° C. and 450° C. and at a pressure between 1 and 50 atmospheres, over a hydrodesulfurization catalyst, and the third stage comprises contacting the product from the second stage with a hydrogen sulfide absorbing material.

As stated above the first stage of the process comprises one or both of two specified desulfurization steps. However, it is preferred that the first stage include both of these steps—i.e. treating the hydrocarbon oil with sulfuric acid, then vaporizing it and passing the vapor thus produced over a contact material comprising zinc oxide, manganese oxide or iron oxide (preferably zinc oxide) under conditions as hereinbefore specified.

The sulfuric acid treatment may conveniently be effected at or below room temperature. The temperature of the oil and acid mixture should not be allowed to rise above about 40° C. A convenient concentration of sulfuric acid is 90 to 98% by weight.

The oil and acid mixture remaining after the sulfuric acid treatment stage may conveniently be separated electrostatically.

After electrostatic separation from the acid, the hydrocarbon oil is preferably washed with an aqueous alkali, for example sodium hydroxide, to remove any remaining sulfuric acid, electrostatically separated from the alkali, and finally washed with water.

The separated acid may be recycled to the vessel in which the hydrocarbon oil and acid are mixed.

In the second stage of the process the temperature is preferably within the range 380° C. to 400° C., and the pressure is preferably between 4 and 20 atmospheres.

Particularly suitable hydrodesulfurization catalysts are palladium, platinum or cobalt molybdate, supported on alumina. So-called cobalt molybdate catalysts are well known and comprise the oxides of cobalt and molybdenum either as such or in combined form.

Any suitable material which is capable of absorbing hydrogen sulfide may be used in the third stage of the process. However, the absorbing material preferably comprises zinc oxide, manganese oxide or iron oxide (zinc oxide being preferred). These substances have the advantage that they will effectively absorb hydrogen sulfide from the hot hydrocarbon vapor, which therefore does not have to be cooled first.

The treatment with a contact material comprising zinc oxide, manganese oxide or iron oxide which may comprise at least part of the first stage of the process, and the second and third stages of the process may conveniently be effected in one operation by passing the hydrocarbon vapor, mixed with hydrogen, through a sandwich consisting of a bed of hydrodesulfurization catalyst between two beds each of which comprises zinc oxide, manganese oxide or iron oxide.

The process of the present invention is particularly suitable for desulfurization of a straight-run naphtha, by which is meant a mixture of paraffinic, naphthenic and aromatic hydrocarbons obtained by fractional distillation of petroleum and having a boiling range of about 10° C. to about 200° C. The process is not suitable for desulfurization of hydrocarbons containing substantial amounts of ethylenically or acetylenically unsaturated compounds, such as for example hydrocarbons obtained as a result of a thermal cracking process.

When a straight-run naphtha is desulfurized according to the present invention, in the second stage of the process the naphtha is mixed with hydrogen preferably in a 1:1 molar ratio.

We have found that in order to reduce the sulfur content of a straight-run naphtha from 500–2000 p.p.m. to 2–5 p.p.m. or less, which is highly desirable if the naphtha is to be used in a steam reforming process for the production of methanol synthesis gas, it is important that most of the sulfur should be removed before the hydrodesulfurization stage. In the process of the present invention sulfur is removed in the first stage of the process. In the second step which it is preferred to include in the first stage of the process the bed of zinc oxide or its equivalent removes substantially the entire remaining amount of those types of sulfur containing impurities which that material is capable of removing, i.e. mercap-

tans, sulfides and disulfides. It is believed that these impurities are either absorbed as such or hydrogenated to hydrogen sulfide which is then absorbed. Thus the amount of sulfur remaining is very small. The hydrodesulfurization catalyst catalyses the hydrogenation of organic sulfur compounds, such as for example thiophenes and thiophanes, to hydrogen sulfide, which is absorbed by the final bed of zinc oxide or its equivalent. The ratio of hydrogen to hydrogen sulfide in contact with the hydrodesulfurization catalyst is very high. Consequently it is impossible for any detectable amount of organic sulfur compounds to exist in equilibrium with hydrogen and the hydrogen sulfide formed in the hydrodesulfurization reaction, and a very high degree of sulfur removed can be obtained.

The mixture of hot desulfurized naphtha vapor and hydrogen, which is produced by the preferred process of the present invention, may be mixed with steam and used as the feed in a steam reforming process for production of methanol synthesis gas. This of course is only one use of the invention, which finds a wide application to industrial processes where hydrocarbon oils need to be desulfurized to a high degree.

The following examples are illustrative of the process of the present invention.

Example 1

A Venezuelan straight-run naphtha of specific gravity 0.746 and boiling range 103° C. to 164° C. containing 250 p.p.m. of sulfur was passed through a bed of zinc oxide at 400° C. at a liquid hourly space velocity of 0.75. The sulfur content of the product was 56 p.p.m. This partially purified material, mixed with an equimolar volume of hydrogen, was then passed through a catalyst comprising 0.3% platinum on alumina at 385° C., and then through a bed of zinc oxide in the form of ⅛ inch pills at 385° C. to 390° C. The liquid hourly space velocities through these beds were respectively 1.1 and 0.75. The sulfur content of the product was less than 1 p.p.m.

Example 2

A straight-run naphtha of specific gravity 0.72 approximately and boiling range 55° C. to 166° C. containing 357 p.p.m. of sulfur was treated with 2% by weight of 98% sulfuric acid in a vibrating plate mixer, and the sulfur content was thereby decreased to 46 p.p.m. This partially purified material was then vaporized and passed, together with an equimolecular volume of hydrogen, through beds of cobalt molybdate on alumina and pills of zinc oxide, under the following conditions:

Temperature, °C.	380
Pressure, lbs./in.²	45
Liquid hourly space velocity over cobalt molybdate catalyst	0.9
Liquid hourly space velocity over zinc oxide pills	1.2

The sulfur content of the product after the seven days run of the experiment was 1–3 p.p.m.

Example 3

A straight-run Kuwait naphtha of specific gravity 0.725 and boiling range 55°C. to 166°C. containing 250 p.p.m. of sulfur was treated with 2% by weight of 96% sulfuric acid in a paddle type mixer, washed with 10% caustic soda, and finally washed with water. This treatment decreased the sulfur content to 20 p.p.m.

The naphtha was then vaporized, mixed with an equimolecular volume of hydrogen and preheated to 400° C. under a total pressure of 16 atmospheres. The mixture of naphtha and hydrogen was then passed successively through a bed of zinc oxide pills, a bed of cobalt molybdate pellets, and finally a second bed of zinc oxide pills. The liquid hourly space velocities through these beds were respectively 2.4, 1.0 and 2.4. The total sulfur content of the naphtha after this treatment was 3–5 p.p.m.

We claim:

1. A process for desulfurization of straight-run petroleum naphtha which is substantially free from ethylenically and acetylenicaly unsaturated compounds comprising
   (1) contacting said oil with sulfuric acid,
   (2) separating the acid from the oil,
   (3) vaporizing said oil,
   (4) passing the vapors of said oil in contact with a material selected from the group consisting of zinc oxide, manganese oxide and iron oxide at a temperature between 350° C. and 450° C. and a pressure of between 1 and 50 atmospheres,
   (5) contacting the resulting gas together with hydrogen with a hydrodesulfurization catalyst at a temperature of 350–450° C. and a pressure between 1 and 50 atmospheres and then
   (6) contacting the resulting product, while vaporized, with a material selected from the group consisting of zinc oxide, manganese oxide and iron oxide to remove hydrogen sulfide,

   whereby the sulfur content of the hydrocarbon material is reduced to at most 5 parts per million.

2. A process for desulfurization of a straight run petroleum naphtha which is substantially free from ethylenically and acetylenically unsaturated compounds comprising
   (1) treating said oil with sulfuric acid,
   (2) separating the oil from the acid,
   (3) vaporizing the oil separated from said acid,
   (4) contacting the vapors together with hydrogen with a hydrodesulfurization catalyst at a temperature of between 350° C. and 450° C. and a pressure of between 1 and 50 atmospheres and then
   (5) contacting the resulting product, while vaporized, with a material selected from the group consisting of zinc oxide, manganese oxide and iron oxide to remove hydrogen sulfide,

   whereby the sulfur content of said oil is reduced to at most 5 parts per million.

3. A process according to claim 2 in which the sulphuric acid is of 90% to 98% concentration by weight.

4. A process according to claim 2 in which the naphtha and acid mixture remaining after the sulphuric acid treatment stage is separated electrostatically.

5. A process according to claim 4 in which the separated naphtha is washed with aqueous alkali, electrostatically separated from the said alkali, and then washed with water.

6. A process according to claim 2 in which the hydrodesulfurization catalyst is an alumina supported catalyst selected from the group consisting of palladium, platinum and cobalt molybdate.

7. A process according to claim 1 in which the naphtha is mixed with hydrogen in a 1:1 molar ratio while in contact with a hydrodesulfurization catalyst.

8. A process according to claim 2 in which sulfuric acid separated from the naphtha after treatment thereof is recycled and combined with crude hydrocarbon oil for acid treatment of the oil.

9. A process according to claim 2 in which the naphtha is contacted with said hydrodesulfurization catalyst at a temperature within the range of 380° C. to 400° C.

10. A process according to claim 2 in which the naphtha is contacted with said hydrodesulfurization catalyst at a pressure between 4 and 20 atmospheres.

11. A process for desulfurization of a straight run petroleum naphtha which is substantially free from ethylenically and acetylenically unsaturated compounds comprising
   (1) vaporizing said oil,
   (2) passing the vapors of said naphtha in contact with a material selected from the group consisting of zinc oxide, manganese oxide and iron oxide at a tempera-

ture between 350° C. and 450° C. and a pressure of between 1 and 50 atmospheres,

(3) passing the vaporized hydrocarbon and hydrogen over a hydrodesulfurization catalyst at a temperature between 350° C. and 450° C. and a pressure of between 1 and 50 atmospheres and

(4) then contacting the resulting product, while vaporized, with a material selected from the group consisting of zinc oxide, manganese oxide and iron oxide to remove hydrogen sulfide,

whereby the sulfur content of the hydrocarbon material is reduced to at most 5 parts per million.

12. A process for desulfurization as set forth in claim 11 in which the oil is passed through a sandwich consisting of a bed of hydrodesulfurization catalyst between two beds each of which comprises material selected from the group consisting of zinc oxide, manganese oxide and iron oxide.

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