

- 1 -

**DESULFURIZING ORGANOSULFUR
HETEROCYCLES IN DIESEL WITH SUPPORTED SODIUM**

FIELD OF THE INVENTION

[0001] The invention relates to desulfurizing refractory organosulfur heterocycle compounds in a hydrocarbon liquid using a solid reagent comprising supported free sodium. More particularly the invention comprises desulfurizing a hydrocarbon liquid, such as a diesel fraction which contains refractory organosulfur heterocycles, by contacting it with a solid reagent comprising supported sodium having a free sodium content.

BACKGROUND OF THE INVENTION

[0002] There is an increasing need for reduced sulfur levels in petroleum and chemical streams due to increasingly stricter environmental requirements. This is especially so for middle distillate fuels such as diesel fuel, jet fuel, kerosene, heavy furnace oils and the like, whose combustion products are released into the environment. In hydrocarbon streams derived from petroleum refining and chemical processing, sulfur is present in the form of organosulfur compounds and is typically removed by a process known as hydrodesulfurization. In this process, the stream is contacted with hydrogen, in the presence of a suitable catalyst, to convert the sulfur in the organosulfur compounds to H_2S . The H_2S is then separated from the sulfur-reduced stream. Simple, sulfur-bearing organic compounds, such as aliphatic, naphthenic, and aromatic mercaptans, sulfides, di- and polysulfides and the like, are relatively

- 2 -

easy to hydrodesulfurize and the sulfur in these types of compounds, being relatively easy to remove, is therefore referred to as "labile sulfur". It is much more difficult to remove sulfur from more refractory sulfur compounds, such as derivatives of dibenzothiophene, especially those mono- and di-substituted and condensed ring dibenzothiophenes that exhibit steric hindrance, and sulfur in these compounds is referred to as refractory sulfur. These highly refractory sulfur heterocycles are present in the higher boiling [e.g., 500°F to 800°F (260°C to 427°C)] fractions of middle distillate streams and resist hydrodesulfurization, as a consequence of the steric inhibition precluding the requisite catalyst-substrate interaction.

[0003] Removing sulfur from these refractory sulfur heterocycles can be achieved under relatively severe hydrodesulfurization process conditions, but this requires high temperatures and pressures, is expensive, and can result in product loss due to cracking and degradation. As a consequence, processes have been developed to remove these refractory sulfur heterocycles from streams that have previously been substantially desulfurized, and typically by conventional hydrodesulfurization. For example, U.S. patents 6,193,877 and 6,245,221 relate to hydrodesulfurizing such sulfur-reduced streams, which still contain refractory sulfur heterocycles, in the presence of an H₂S sorbent and a catalyst comprising noble metal or nickel on a particulate support. U.S. patent 6,251,262 discloses the use of three separate stages and catalysts to remove them, to produce product having .005 wt.% (≤ 50 wppm) or less sulfur. This is still too high for many specifications. U.S. patent 6,210,564 discloses the use of sodium metal to remove sulfur from petroleum-derived feeds, but this requires special handling and forms sludge, which must be separated from the treated oil. The literature

- 3 -

discloses the use of free and supported sodium for removing thiophene from naphtha, but doesn't address or suggest that this would be effective for the higher boiling, refractory sulfur heterocycles found in higher boiling streams. Examples are found in (i) B. M. Vanderbilt, "Desulfurization and Refining of Naphthas by Metallic Sodium," *Ind. & Eng. Chem.*, v. 49, n. 4, April, 1957 and (ii) Gerlock, et. al. in "Reaction of Thiophene with Sodium on Alumina. A Method for Desulfurization of Volatile Fuels," *Ind. Eng. Chem. Fundam.*, v. 17, n. 1, 1978. There is a need for a process that can remove sulfur from these refractory sulfur heterocycles and particularly from middle distillate streams, without resorting to expensive catalysts, difficult processes employing multiple catalytic stages and catalysts, and severe hydrodesulfurization conditions.

SUMMARY OF THE INVENTION

[0004] A process has now been found for removing refractory sulfur from a hydrocarbon stream, such as a petroleum and a chemical hydrocarbon stream, which comprises contacting the stream with a sodium reagent comprising free sodium on a particulate solid support (hereinafter "sodium reagent"). By free sodium is meant sodium that is supported on, but not chemically bound to, the support material and which will react with water or moisture. The preparation of a sodium reagent useful in the process of the invention can be achieved by simply impregnating the support with sodium, in an amount sufficient for the supported sodium to have a free-sodium content, as is explained in detail below. The free sodium will react with most sulfur and not just refractory sulfur, and is therefore preferably used after the hydrocarbon stream has first been treated to remove sulfur from more labile sulfur compounds in the stream. The more labile

- 4 -

sulfur is removed from a sulfur-bearing hydrocarbon stream by any suitable means, but typically and preferably by hydrodesulfurization for petroleum and chemical hydrocarbon streams. By "labile sulfur" is meant sulfur in relatively simple sulfur-containing organic compounds, such as aliphatic, naphthenic, and aromatic mercaptans, sulfides, di- and polysulfides and the like, which do not exhibit steric hindrance. By refractory sulfur is meant sulfur in organic heterocycle sulfur compounds (refractory sulfur heterocycles), such as derivatives of dibenzothiophene, especially mono- and di-substituted, and condensed ring dibenzothiophenes, which exhibit steric hindrance.

[0005] Thus, in one embodiment the invention comprises a process for removing sulfur from a sulfur-bearing hydrocarbon stream containing both labile and refractory sulfur, which comprises contacting it with hydrogen in the presence of a hydrodesulfurizing catalyst, at reaction conditions effective to remove labile sulfur, but not refractory sulfur, to produce a sulfur-reduced stream, followed by contacting the sulfur-reduced stream with a sodium reagent to remove at least a portion of the refractory sulfur, to further reduce its sulfur content. By removing labile sulfur is meant that at least a portion, and preferably at least most or all the sulfur in the labile sulfur compounds, is removed. By not removing refractory sulfur means not removing more than 10 wt.%.

[0006] As is known, hydrodesulfurization converts sulfur in sulfur-bearing organic compounds to H_2S . H_2S that is not removed from the sulfur-reduced stream will react with the free sodium of the reagent and, if present in sufficient amounts, may consume the free sodium before it can remove the

- 5 -

refractory sulfur. Therefore H_2S is preferably removed from the sulfur-reduced stream before it is contacted with the reagent. In another embodiment, the invention comprises removing refractory sulfur remaining in a hydrocarbon stream that has previously been hydrosulfurized to remove at least a portion and preferably most or all of the labile sulfur, by contacting it with the sodium reagent to further reduce its sulfur content.

[0007] In the case of a middle distillate stream, conventional hydrosulfurizing may reduce its sulfur content down to between 40 to 100 wppm. Contacting the hydrosulfurized, sulfur-reduced stream with the solid reagent will further reduce its sulfur content. The process of the invention makes it possible to reduce the sulfur content down to a level of less than 10 wppm by using the sequential steps of (i) hydrosulfurizing to produce a sulfur-reduced stream and H_2S , (ii) separating the H_2S from the stream and then (iii) contacting the H_2S reduced stream with the sodium reagent. This enables deeper desulfurization using existing conventional hydrosulfurization equipment, process conditions and catalysts. Thus, another embodiment of the invention comprises a process for removing sulfur from a sulfur-bearing, middle distillate hydrocarbon stream containing both labile and refractory sulfur, which comprises reacting it with hydrogen in the presence of a hydrosulfurizing catalyst, at reaction conditions effective to remove labile sulfur to produce a sulfur-reduced stream, followed by contacting the sulfur-reduced stream with a sodium reagent to remove at least a portion of the refractory sulfur, to further reduce its sulfur content down to a level of less than 10 wppm.

- 6 -

DETAILED DESCRIPTION

[0008] Hydrodesulfurization is a process in which the sulfur content of a sulfur-bearing hydrocarbon stream is reduced by contacting it with hydrogen or a hydrogen-containing treat gas, in the presence of one or more suitable hydrodesulfurization catalysts active for the removal of sulfur, at reaction conditions effective for the hydrogen to react with sulfur-bearing organic compounds present in the stream, and remove the sulfur as H₂S. As is known, during hydrodesulfurization other heteroatoms such as nitrogen and oxygen are removed, along with saturation of at least some aromatics and other unsaturates. Hydrodesulfurization catalysts are well known and include, for example, catalysts comprising one or more Group VIII metal catalytic components, typically non-noble metals such as Fe, Co and Ni, and more typically Co and/or Ni, and one or more Group VI metal catalytic components, typically Mo and W, with Mo being most often used, on a high surface area support material, such as alumina. The Groups referred to herein refer to Groups as found in the Periodic Table of the Elements copyrighted in 1968 by the Sargent-Welch Scientific Company. Other suitable hydrodesulfurization catalysts include zeolitic catalysts, as well as noble metal catalysts, wherein the noble metal is selected from Pd and Pt. However, conventional hydrodesulfurization typically employs the less expensive non-noble metal catalysts. Typical non-noble metal hydrodesulfurization catalysts include, for example, Ni/Mo on alumina, Co/Mo on alumina, Co/Ni/Mo on alumina, and the like. Hydrodesulfurization conditions typically include temperatures in the range of from 530°F to 750°F (277°C to 400°C), preferably 600°F to 725°F (316°C to 385°C), and most preferably 600°F to 700°F (316°C to 371°C), at a

- 7 -

total pressure in the range of to 2000 psi (715 to 11436 kPa), a hydrogen treat gas rate in the range of 300 to 3000 SCF/B (53 to 534 S m³ of H₂/m³ of oil), and a feed space velocity of 0.1 to 2.0 LHSV. By "hydrogen treat gas" is meant either pure hydrogen or a hydrogen-containing gas stream containing hydrogen in an amount at least sufficient for the intended reaction, plus other gas or gasses (e.g., nitrogen and light hydrocarbons such as methane) which will not adversely interfere with or affect either the reaction or the product.

[0009] The sodium reagent useful in the process of the invention is a composite of a sodium component comprising both supported and free sodium (free sodium is sometimes referred to as active sodium), and a support component. As set forth above, preparation of the reagent may be achieved by simple impregnation of a support component, such as alumina, carbon, silica and the like, with molten metallic sodium under vacuum or an inert atmosphere. The Gerlock, et. al., and Vanderbilt articles referred to above give preparation techniques for preparing a supported sodium reagent having free sodium. It is preferred to protect the supported sodium reagent from exposure to water. The free sodium content, which may range from 1 to 20 wt.% of the total weight of the composite of sodium and support components, may be determined by measuring the volume of hydrogen released upon reaction of the reagent with 2-methoxyethanol, which is also disclosed in Gerlock, et. al., the disclosure of which is incorporated herein by reference. Another method that may be used to determine the free or active sodium content, is to react a measured amount of the reagent and H₂O, measure the amount of evolved hydrogen (by Gas Chromatography, for example) and then calculate the amount of free or reactive sodium based on the amount of hydrogen released. Contacting a hydrocarbon

- 8 -

stream containing refractory sulfur with the sodium reagent may be achieved at temperatures ranging from 212°F to 752°F (100°C to 400°C), preferably from 482°F to 662°F (250°C to 350°C) and pressures ranging from below atmospheric to 400 psig (2859 kPa). The reagent may be present in a guard bed through which a hydrodesulfurized stream, separated from the H₂S produced by the hydrodesulfurization reaction, but still containing refractory sulfur, is passed to remove the refractory sulfur. This permits lower sulfur levels to be achieved using conventional hydrodesulfurization conditions and catalysts. The sulfur in so-called labile or easy sulfur compounds can be removed without using severe process conditions.

[0010] The prior art teaches that substantially more severe conditions are needed to remove sulfur from the so-called "hard" or refractory sulfur compounds referred to herein as refractory sulfur heterocycles during hydrodesulfurization, which are typically present in middle distillate fractions derived from one or more naturally-occurring hydrocarbon sources, such as petroleum, bitumen, shale oil and the like, as derivatives of dibenzothiophene, especially those mono- and di-substituted and condensed ring dibenzothiophenes, which exhibit steric hindrance or inhibition. Steric hindrance tends to make the requisite catalyst-substrate interaction with the sulfur atom in the molecule difficult and thereby substantially reduces the sulfur removal reaction kinetics. It retards inter- or intramolecular interactions as a result of the spatial structure of the molecule preventing access to the sulfur atom. Illustrative, but non-limiting, examples of such refractory sulfur heterocycles include 1-, 2- and 3-methyldibenzothiophenes,

- 9 -

4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. The effect of steric hindrance on relative reaction kinetics of sulfur removal can be seen in an article by D. D. Whitehurst, et. al., titled "Present State of the Art and Future Challenges in the Hydrodesulfurization of Polyaromatic Sulfur Compounds," in *Advances in Catalysis*, v. 47, p. 345-471, 1998. In this article, the relative reaction rates of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene relative to dibenzothiophene are given as 0.3 and 0.1, respectively.

[0011] These highly refractory sulfur heterocycles are present in the higher boiling, e.g., from 600°F to 850°F (316°C to 454°C) and more typically from 650°F to 850°F (343°C to 454°C) fractions of petroleum and other mineral-derived middle distillate streams, and resist hydrodesulfurization as a consequence of their steric hindrance. Feed streams suitable for being treated by the present invention are those petroleum based feeds or streams which contain condensed ring sulfur heterocyclic compounds, as well as other ring compounds, including multi-ring aromatic and naphthenic compounds. They are also found in similar boiling range fractions derived from some chemical processes and those obtained or derived from tar sand bitumen, shale oil and other naturally occurring, mineral types of hydrocarbon sources. However, the invention is not intended to be limited to just these feeds and feed sources. As set forth above, in a broad sense, the invention is useful for removing refractory sulfur from a hydrocarbon stream, and this could be any hydrocarbon stream that will not, of itself, react with the sodium reagent.

[0012] Non-limiting examples of such feeds include diesel fuels, jet fuels, heating oils, and lubes. The feeds may also include feeds derived from synthetic

- 10 -

processes, such as the Fischer-Tropsch process, which have been blended with feeds from naturally-occurring feeds. Such feeds typically have a boiling range from 240°F to 1112°F (116°C to 600°C), preferably from 347°F to 752°F (175°C to 400°C). The invention is particularly useful with middle distillate feeds typically boiling in the range of from 240°F to 850°F (116°C to 454°C) and, at the option of the practitioner, the higher boiling heavy diesel fractions [e.g., from 600°F to 850°F (316°C to 454°C)] of middle distillate feeds that contain the refractory sulfur. In the process of the invention, it is preferred that the feed first be hydrodesulfurized to reduce its sulfur content to less than 150 wppm sulfur, preferably less than 100 wppm, more preferably less than 50 wppm, and still more preferably less than 40 wppm sulfur, before it is contacted with the sodium reagent. The contacting with the sodium reagent may take place in the presence or absence of hydrogen. The invention will be further understood with reference to the examples below.

EXAMPLES

Example 1

[0014] Diethyldibenzothiophene, a highly sterically hindered, refractory sulfur heterocycle, in an amount of 0.579 g was dissolved in sufficient hexadecane to achieve a concentration of 1000 wppm. This solution was added to 0.56 g of a sodium reagent comprising solid, supported sodium on alumina, under dry argon. The amount of Na (sodium metal) on the alumina comprised 12% of the total weight of the composite, with 2 wt.% of the total weight of the composite free or active Na. The mixture was then heated to 392°F (200°C) at

- 11 -

atmospheric pressure under argon. Samples of the solution were removed after 21, 25 and 45 hours, and analyzed for hexadecane and diethyldibenzothiophene by gas chromatography. The amount of diethyldibenzothiophene removed was 32, 42 and 93 wt.%, respectively. The reaction stoichiometry was calculated to be 5:1 atoms of sodium per atom of sulfur, which was close to the theoretical of 4:1. This demonstrates that the sodium reagent removed the sulfur from the diethyldibenzothiophene.

Example 2

[0015] A diesel feed comprising a hydrocarbon fraction boiling in the diesel fuel range of from 300°F to 800°F (149°C to 427°C) is obtained by fractionating a petroleum crude oil. It contains 15000 wppm (1.5 wt.%) sulfur in the form of aliphatic, naphthenic, and aromatic mercaptans, sulfides, di- and polysulfides and sterically hindered refractory sulfur heterocycles. This stream is hydrodesulfurized by contacting it with a hydrodesulfurization catalyst, comprising cobalt and molybdenum supported on an alumina support, in the presence of hydrogen, at reaction conditions of 650°F (343°C), a hydrogen treat gas rate of 1500 SCF/B (267 S m³ of H₂/m³ of oil), an LHSV of 0.5, and a hydrogen pressure of 325 psi (2324 kPa). This removes most of the sulfur as H₂S and reduces the sulfur content down to 55 wppm sulfur, most of which is in the form of one or more refractory sulfur heterocycles. The H₂S is separated from the feed by flashing and/or stripping. The stripped and/or flashed feed is then contacted with a sodium reagent comprising sodium supported on alumina. The sodium reagent is in the form of a fixed bed of reagent mixed with alumina and is in a guard bed downstream of the stripper. The amount of sodium is 12 wt.%

- 12 -

of the reagent, with 2.4 wt.% of the reagent being free or active sodium.

Contacting is conducted at a temperature of 600°F (316°C) and a pressure of 300 psig (2170 kPa). This further reduces the sulfur content of the diesel feed down to less than 10 wppm sulfur.

- 13 -

CLAIMS:

1. A process for removing refractory sulfur from a hydrocarbon stream containing refractory sulfur, which process comprises contacting said stream with a sodium reagent comprising a sodium component having free sodium, supported on a particulate solid support component.
2. A process according to claim 1 wherein said free sodium is present in an amount of from 1 to 20 wt.% of said sodium reagent.
3. A process according to any preceding claim wherein said sodium reagent also contains sodium bound to said support component and said hydrocarbon stream is derived from a naturally-occurring hydrocarbon source.
4. A process according to any preceding claim wherein said hydrocarbon stream comprises a middle distillate fuel fraction that has ben hydrodesulfurized to remove more labile sulfur before it is contacted with said sodium reagent.
5. A process according to any preceding claim wherein said hydrocarbon stream comprises a fraction boiling in the diesel fuel range.
6. A process for removing sulfur from a sulfur-bearing hydrocarbon stream containing both labile and refractory sulfur, which process comprises contacting said stream with hydrogen in the presence of a hydrodesulfurization catalyst, at reaction conditions effective to remove labile

- 14 -

sulfur, to produce a sulfur-reduced stream, followed by contacting said sulfur-reduced stream with a sodium reagent, comprising free sodium on a solid support component, to remove at least a portion of said refractory sulfur, to further reduce its sulfur content and produce a hydrocarbon stream having a low sulfur content.

7. A process according to claim 6 wherein at least most of said labile sulfur is removed by said hydrodesulfurization.
8. A process according to either of claims 6 or 7 wherein not more than 10 wt.% of said refractory sulfur is removed by said hydrodesulfurization.
9. A process according to any of claims 6-8 wherein said hydrocarbon stream comprises a middle distillate fuel stream and has less than 10 wppm sulfur.
10. A process according to any of claims 6-9 wherein said hydrocarbon stream comprises a diesel fuel fraction.