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(54) Title: THE PRODUCTION OF LOW SULFUR NAPHTHA STREAMS VIA SWEETENING AND FRACTIONATION COMBINED WITH THIOPHENE ALKYLATION

(57) Abstract: Naphtha streams, preferably cracked naphtha streams containing both olefinic compounds and mercaptans, are first treated to convert at least a portion of the mercaptans to disulfides followed by thiophene alkylation. This results in a sufficient change in boiling range to allow for separation of at least a portion of the alkylated sulfur species and disulfides from the light naphtha. This results in a low sulfur light naphtha stream with little loss in octane number.



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**THE PRODUCTION OF LOW SULFUR NAPHTHA
STREAMS VIA SWEETENING AND FRACTIONATION
COMBINED WITH THIOPHENE ALKYLATION**

FIELD OF THE INVENTION

[0001] Naphtha streams, such as cracked naphtha streams containing both olefinic compounds and mercaptans, are first treated to convert at least a portion of the mercaptans to disulfides followed by thiophene alkylation. This results in a sufficient change in boiling range to allow for separation of at least a portion of the alkylated sulfur species and disulfides from the light naphtha. This results in a low sulfur light naphtha stream with little loss in octane number.

BACKGROUND OF THE INVENTION

[0002] Cracked naphthas obtained from thermal and catalytic cracking processes form a major part of the gasoline product pool in the United States. Not only do both thermal cracking and fluidized catalytic cracking provide a significant part of the gasoline pool, they also provide a large proportion of the sulfur that appears in the gasoline pool. Sulfur in catalytically cracked liquid products is typically in the form of organic sulfur compounds and is an undesirable impurity that is converted to undesirable sulfur oxides when these products are utilized as a fuel. In addition, sulfur impurities can deactivate many of the catalysts that have been developed for catalytic converters that are used on automobiles to catalyze the conversion of harmful engine exhaust emissions to gases that are less objectionable. Accordingly, it is desirable to reduce the sulfur content of products from catalytic cracking, such as gasoline, to the lowest possible levels.

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[0003] The sulfur-containing impurities of straight run gasolines, which are separated from crude oil, are typically different from those found in gasolines resulting from a cracking process. The former contain mostly mercaptans and sulfides, whereas the latter are rich in thiophene, benzothiophene and derivatives of thiophene and benzothiophene that are harder to remove than mercaptans and sulfides.

[0004] Non-mercaptan sulfur is generally removed from cracked naphtha by hydrodesulfurization. Hydrodesulfurization involves treatment of a sulfur-containing stream with a hydrodesulfurization catalyst in the presence of hydrogen resulting in the conversion of the sulfur in the sulfur-containing compounds to hydrogen sulfide, which can be separated and converted to elemental sulfur. Unfortunately, hydrodesulfurization can be expensive as it requires a source of hydrogen, high pressure process equipment, hydrodesulfurization catalysts, and a sulfur recovery plant for conversion of the resulting hydrogen sulfide to elemental sulfur. In addition, hydrodesulfurization can result in the undesired destruction of olefins in the feedstock by converting them to saturated hydrocarbons through hydrogenation. This saturation of olefins by hydrogenation is undesirable because it results in the consumption of expensive hydrogen, and also because the olefins are valuable as high octane components of gasoline. As an example, a cracked naphtha (a gasoline boiling range stream) from a fluid catalytic cracking process has a relatively high octane number as a result of relatively high olefin content. Hydrodesulfurizing such a stream causes a reduction in the olefin content in addition to the desired desulfurization, resulting in a reduction in the octane number. Typically, the greater the degree of desulfurization, the greater the degree of olefin saturation and the greater the reduction in octane number.

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[0005] It is known that thiophene, and its derivatives, can be alkylated by reaction with olefinic hydrocarbons in the presence of a catalyst, typically an acid catalyst, to form higher boiling alkylated products that can then be separated from the naphtha boiling range stream by distillation. See for example U.S. Patent Nos. 2,448,221; 2,921,081; and 2,563,087; all of which are incorporated herein by reference. U.S. Patent No. 5,599,441, which is also incorporated herein by reference, discloses a process for removing thiophenic sulfur compounds from a cracked naphtha by: (1) contacting the cracked naphtha with an acid catalyst at alkylation conditions to alkylate the thiophenic compounds with the indigenous olefins of the cracked naphtha stream as an alkylating agent; (2) removing an effluent stream from the alkylation zone; and (3) separating the alkylated thiophenic compounds from the alkylation zone effluent stream by fractional distillation.

[0006] U.S. Patent No. 6,059,962, which is also incorporated herein by reference, discloses a multiple stage process for removing sulfur from a naphtha feedstock wherein the feedstock is first subjected to thiophene alkylation followed by a first fractionation step to produce a lower boiling lower sulfur fraction and a higher boiling high sulfur fraction. The higher boiling fraction is subjected to a second alkylation step and another fractionation step to produce another lower boiling fraction having an even more reduced sulfur level and another higher boiling fraction that contains a higher sulfur level.

[0007] While there are thiophene alkylation processes for reducing the level of sulfur in naphtha boiling range streams, some of which have met with a degree of commercial success, there still remains a need for improved sulfur conversion processes capable of reducing the level of sulfur, particularly thiophenic sulfur, in cracked naphthas without substantially reducing the octane number.

SUMMARY OF THE INVENTION

[0008] In an embodiment, there is provided a process for the removal of sulfur from cracked naphtha feedstocks containing mercaptan sulfur, thiophenic sulfur, and olefins, which process comprises:

(a) converting at least a portion of the mercaptan sulfur under mercaptan conversion conditions to their corresponding disulfides, thereby resulting in a disulfide-containing naphtha product stream;

(b) conducting said disulfide-containing naphtha product stream to a thiophene alkylation zone wherein it is contacted with a catalytically effective amount of an acid catalyst under thiophene alkylation conditions, thereby alkylating at least a portion of the thiophenes with at least a portion of the olefins in said cracked naphtha feedstock, and producing a product stream containing alkylated thiophenes;

(c) separating from the product stream from step (b) above at least a lower boiling stream having a final boiling point equal to or less than about 250°F and at least one higher boiling stream.

[0009] In a selected embodiment, the fractionation step produces a lower boiling range stream having a final boiling point of equal to or less than about 250°F (121°C), an intermediate boiling stream boiling in the range of about 250°F to about 350°F (177°C), and a higher boiling stream having an initial boiling point of at least about 350°F.

[0010] In another related embodiment, both the intermediate boiling product stream and the higher boiling product streams are subjected to hydrodesulfurization in the presence of a hydrodesulfurization catalyst and hydrogen at hydrodesulfurization conditions.

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[0011] In another related embodiment, the intermediate boiling product stream is subjected to selective hydrodesulfurization wherein sulfur is removed with hydrogenation of olefins kept to a minimum.

[0012] In yet another related embodiment, the product stream from hydrodesulfurizing the intermediate boiling product stream is subjected to reforming at reforming conditions in the presence of a Pt-containing reforming catalyst.

DETAILED DESCRIPTION OF THE INVENTION

[0013] In an embodiment, the invention relates to a sulfur removal process. A feedstock is conducted to the process, and a product containing alkylated thiophenes is conducted away from the process. Suitable feedstocks include olefinic, naphtha-boiling range, refinery streams containing sulfur in the form of both mercaptans and thiophenes. Such streams typically boil in the naphtha boiling range, i.e., about 50°F to about 450°F, and contain not only paraffins, naphthenes and aromatics, but also unsaturates, such as open-chain and cyclic olefins, dienes and cyclic hydrocarbons with olefinic side-chains. In an embodiment, the feedstock is an olefinic naphtha stream having an olefin content of at least about 5 wt.%. Non-limiting examples of olefinic naphtha streams include fluid catalytic cracking unit naphtha (FCC catalytic naphtha or cat naphtha), steam cracked naphtha, and coker naphtha. Also included are blends of olefinic naphthas with non-olefinic naphthas, provided the blend has an olefin content of at least about 5 wt.%.

[0014] The olefinic streams can contain an overall olefins concentration ranging as high as about 60 wt.%, more typically as high as about 50 wt.%, and most typically from about 5 wt.% to about 40 wt.%. The olefinic naphtha stream

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can also have a diene concentration up to about 15 wt.%, but more typically less than about 5 wt.% based on the total weight of the stream. When the olefinic naphtha is obtained from a catalytic cracking process, the sulfur content of such cracked naphtha streams will depend on the sulfur content of the feed to the catalytic cracker ("FCC" unit) as well as on the boiling range of the selected fraction used as the feed in the sulfur removal process. For example, lighter fractions will tend to have lower sulfur contents than the higher boiling fractions. Typically, the sulfur content will exceed 50 ppmw, more typically in excess of 100 ppmw, and in most cases in excess of about 500 ppmw, based on the weight of the feedstock. For the fractions that have 95 percent points over about 380°F (193°C), the sulfur content may exceed about 1,000 ppmw and may be as high as 4,000 or 5,000 ppmw or even higher. Since much of the nitrogen compounds in the FCC unit's feed are removed from the FCC process as catalyst coke, the nitrogen content of the FCC unit's cracked naphtha product is not as characteristic of the FCC feed as is the sulfur content. Accordingly, feedstock nitrogen content is generally not greater than about 20 ppmw, based on the weight of the FCC unit's cracked naphtha product, although higher nitrogen levels typically up to about 200 ppmw may be found in certain higher boiling feeds with 95 percent points in excess of about 380°F (193°C). The nitrogen level will, however, usually not be greater than 250 or 300 ppmw.

[0015] The sulfur present in the feed to the sulfur removal process will typically be present as organically-bound sulfur. That is, the sulfur will be in the form of sulfur compounds such as simple aliphatic, naphthenic, and aromatic mercaptans, sulfides, di- and polysulfides and the like. Other organically bound sulfur compounds include the class of heterocyclic sulfur compounds such as thiophene and its higher homologs and analogs. Such cyclic sulfur compounds

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are typically substantially more difficult to remove, and are often referred to as "hard" sulfur compounds.

[0016] The sulfur removal process can be practiced by first conducting the feedstock to a mercaptan removal zone, where at least a portion of feedstock mercaptan sulfur is converted to non-mercaptan species ("sweetening"), removed from the feedstock ("extraction"), or both. In mercaptan extraction, mercaptan sulfur is removed from the feedstock and conducted away from the process. This can be accomplished conventionally, for example, by contacting the feedstock with an aqueous, alkali metal hydroxide treatment solution capable of removing oil-soluble mercaptans from the feedstock and converting them into water-soluble mercaptides in the aqueous phase. The mercaptides can be catalytically converted to water-insoluble disulfides, separated from the aqueous phase, and then conducted away from the process. In sweetening, the oil-soluble disulfides formed from mercaptan conversion remain in (or are returned to) the feedstock.

[0017] In an embodiment, mercaptans are converted by sweetening, which will now be described in more detail. Conventional sweetening technology can be used in the practice of the present invention. Among the mercaptan oxidation processes that may be used are the copper chloride oxidation process, Mercapfining, chelate sweetening, MEROX™ (available from UOP, Des Plaines, Illinois), and caustic processes such as MERICAT™ (available from Merichem, Houston, Texas). In a caustic sweetening process, such as MEROX or MERICAT, a hydrocarbon stream, such as a mercaptan-containing naphtha stream, is contacted with an alkaline reagent (aqueous caustic solution) and an oxidizing agent (such as air) in the presence of an oxidation catalyst to convert mercaptans to their corresponding disulfides. In the copper chloride sweetening

process, mercaptans are converted by oxidation with cupric chloride, which is regenerated with air that is introduced with the feed in the oxidation step.

[0018] In caustic extraction processes such as MERICAT and MEROX, feedstock mercaptans are extracted into an aqueous alkali metal hydroxide phase and converted into a corresponding mercaptide. The mercaptides are converted into the corresponding disulfides by a catalytically effective amount of an oxidization catalyst (such as sulfonated cobalt phthalocyanine) in the presence of an oxidizing agent like air under catalytic mercaptide oxidation conditions. The disulfide product is poorly soluble in water, but generally soluble in oil. Accordingly, the disulfides can be returned to the feedstock to the sulfur removal process for removal by, e.g., hydrotreating. Alternatively, the disulfides can be separated and conducted away from the process.

[0019] Preferred alkaline reagents are caustic solutions such as sodium hydroxide, potassium hydroxide, and ammonium hydroxide. Sodium hydroxide is most preferred based on its cost and availability, and is normally used in concentrations from about 1% to about 5% by weight in aqueous solution. The preferred oxidizing agent is oxygen gas, and, for convenience, air can be used by dissolving an effective amount in the liquid mixture comprising feedstock and alkaline reagent. By an effective amount of air is meant that sufficient oxygen is contained therein to oxidize from about 50% to about 300% of any sulfides and mercaptans present in the liquid mixture. Sulfides result from the reaction between the alkaline reagent and trace hydrogen sulfide gas dissolved in the hydrocarbon feedstock. For example, if aqueous sodium hydroxide solution is used as the alkaline reagent, the presence of hydrogen sulfide in the hydrocarbon will yield sodium sulfide. Sulfide reaction products of hydrogen sulfide and any of the aforementioned alkaline reagents are readily oxidized, under the oxidizing

conditions of the process of the present invention, to thiosulfates. Thus, sodium sulfide is converted under the mercaptan oxidation conditions to sodium thiosulfate.

[0020] In general, as the mercaptan sulfur level in petroleum hydrocarbon feedstock increases, the amount of oxygen required for sweetening also increases. Consequently, the pressure necessary to dissolve the oxygen, injected into the liquid reaction mixture as air, increases as well. Absolute reaction pressure can vary from about atmospheric pressure to about 30 atmospheres. Oxidizing conditions can also include a temperature from about 30°C to about 100°C and a catalyst liquid hourly space velocity from about 0.1 hr⁻¹ to about 10 hr⁻¹. As mentioned, the sweetening process is carried out in the presence of a catalytically effective amount of an oxidation catalyst.

[0021] Suitable oxidation catalyst compositions preferably comprise a metal phthalocyanine or sulfonated derivative thereof (e.g., cobalt phthalocyanine or cobalt phthalocyanine disulfonate) supported on a solid carrier (e.g., activated carbon) which is essentially inert in the mercaptan oxidation reaction environment. Types of catalysts are disclosed, for example, in U.S. Pat. No. 2,988,500 and various improvements upon these formulations are also well known. The mercaptide oxidation process employs a fixed bed of catalyst particles preferably essentially spherical in shape, although other catalyst shapes are possible. The use of an appropriate oxidation catalyst under oxidation conditions described above will yield a treated (or sweetened) hydrocarbon having preferably less than 1 ppm by weight of sulfur as mercaptan sulfur.

[0022] Although the mercaptan removal step has been described in terms of a caustic extraction process, it is not limited to such processes. So long as the

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mercaptans are converted to higher boiling disulfides that, upon fractionation, appear in a higher boiling fraction, they can be subjected to hydrogenative removal together with the thiophene and other forms of sulfur present in the higher boiling portion of the cracked feed.

[0023] Mercaptan oxidation processes are described in Modern Petroleum Technology, G. D. Hobson (Ed.), Applied Science Publishers Ltd., 1973, ISBN 085334 487 6, as well as in Petroleum Processing Handbook, Bland and Davidson (Ed.), McGraw-Hill, New York 1967, pages 3-125 to 3-130. The MEROX process is described in Oil and Gas Journal 63, No. 1, pp. 90-93 (January 1965). Reference is made to these works for a description of these processes which may be used for converting the lower boiling sulfur components of the front end to higher boiling materials in the back end of the cracked feed.

[0024] At least a portion of the effluent from the mercaptan removal or conversion step is sent to a thiophene alkylation step wherein the thiophenes are alkylated with olefins in the effluent under catalytic alkylation conditions in the presence of a catalytically effective amount of an acid alkylation catalyst. The removal of a substantial amount, for example about 90 wt.% or more, of the mercaptans enables the use of thiophene alkylation catalysts that are more selective for alkylating thiophenes instead of a conventional alkylation catalyst that is typically selective for alkylating both mercaptans and thiophenes. Heterogeneous acid catalysts containing either Bronsted acid sites or Lewis acid sites are useful for the thiophene alkylation step of the present invention. Typical Lewis acids include those derived from AlCl_3 , FeCl_3 , SbCl_3 , BF_3 , ZnCl_2 , TiCl_4 and P_2O_5 ; but particularly, Lewis acids such as AlCl_3 /silica, AlCl_2 /silica, and BF_3 /silica are useful for the process of the invention. Typical Bronsted acids include HF, H_2SO_4 , metasilicates, silica-alumina, sulfonic acid resins, and the

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like. Well-known methods of maintaining or recovering catalyst activity, such as promoter co-feed or hydrogenative or oxidative regeneration, may also be employed.

[0025] Other catalysts useful in the thiophene alkylation step of the present invention include the crystalline aluminosilicate zeolites having a silica to alumina ratio of at least 12, and constraint index of about 1 to 12. Representative of the ZSM-5 type zeolites are ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, MCM-22, MCM-36, MCM-49, MCM-49 and ZSM-48. By ZSM-5 type, we mean those zeolites isostructural to ZSM-5. ZSM-5 is disclosed and claimed in U.S. Pat. No. 3,702,886 and U.S. Pat. No. Reissue. 29,948; ZSM-11 is disclosed and claimed in U.S. Pat. No. 3,709,979. All of these patents are incorporated herein by reference.

[0026] The larger pore zeolites which are useful as thiophene alkylation catalysts, i.e., those zeolites having a Constraint Index of no greater than about 2, are conventional. Representative of these zeolites are zeolite Beta, TEA mordenite, faujasites, USY and ZSM-12.

[0027] Zeolite Beta is described in U.S. Reissue Pat. No. 28,341 (of original U.S. Pat. No. 3,308,069), to which reference is made for details of this catalyst, and which is incorporated herein by reference.

[0028] Zeolite ZSM-12 is described in U.S. Pat. No. 3,832,449, to which reference is made for the details of this catalyst, and which incorporated herein by reference.

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[0029] The method by which Constraint Index is determined is described fully in U.S. Pat. No. 4,016,218, to which reference is made for details of the method, and which is incorporated herein by reference.

[0030] The preferred catalysts for use in the present invention are members of the MCM-22 group which includes MCM-22, MCM-36, MCM-49 and MCM-56. MCM-22 is described in U.S. Pat. No. 4,954,325. MCM-36 is described in U.S. Pat. No. 5,250,277 and MCM-36 (bound) is described in U.S. Pat. No. 5,292,698. MCM-49 is described in U.S. Pat. No. 5,236,575 and MCM-56 is described in U.S. Pat. No. 5,362,697, all of which are incorporated herein by reference.

[0031] In an embodiment, the sulfur level in a cracked naphtha is reduced while minimizing volume and octane number loss. Olefins, either present in cracked naphthas or added to virgin naphtha, are used to convert sulfur species to higher molecular weight compounds thereby concentrating the sulfur in the "back-end" of the naphtha, i.e., the higher region of the naphtha boiling range. Upon fractionation, this redistribution of the sulfur in the naphtha leads to a relatively sulfur-free light naphtha and a sulfur-rich heavy naphtha which may be desulfurized by hydrotreating including selective hydrotreating. Conversion of the sulfur in the heavy portion naphtha reduces the amount of naphtha that must be hydrodesulfurized which, in the case of cracked naphthas, leads to lower hydrogen consumption and greater octane-barrels. As used herein, the light portion of the naphtha boils in the range of about 50°F to about 250°F. The heavy portion of the naphtha boils in the range of about 250°F to about 450°F. The portion of naphtha boiling between about 250°F and 350°F is often referred to as an "intermediate" naphtha.

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[0032] The thiophenes are alkylated by contacting them with a suitable acidic alkylation catalyst, as defined above, at temperatures from about 40°C to about 370°C, preferably from about 150°C to about 200°C, and pressures from about atmospheric pressure to about 7000 kPa.

[0033] Various reactor configurations can be employed to carry out the alkylation step. Non-limiting examples of suitable reactor configurations include a down-flow, liquid phase, fixed bed process; an up-flow, fixed bed, trickle phase process; an ebulating, fluidized bed process; or a transport, fluidized bed process. All of these different process schemes are conventional, and the choice of the particular mode of operation is a matter of discretion, although the fixed bed arrangements are preferred for simplicity of operation.

[0034] The effluent from the thiophene alkylation step is conducted to a fractionation unit wherein a lower boiling stream having an average upper boiling point of less than or equal to 250°F is produced and at least two different higher boiling point fractions, each having an average boiling point in excess of about 250°F. It is preferred that the effluent from the thiophene alkylation step be fractionated to produce: a lower boiling fraction having a final boiling point equal to or less than about 250°F; an intermediate boiling range fraction boiling in the range of greater than about 250°F and less than about 350°F, and a higher boiling range fraction having an initial boiling point in excess of about 350°F.

[0035] Both the intermediate and higher boiling range fractions can be further processed by, e.g., a hydrodesulfurization or reforming step. In an embodiment, at least one of these streams (usually the intermediate stream) is hydrodesulfurized, preferably selectively hydrodesulfurized. In selective

hydrodesulfurization, sulfur is removed under conditions that limit the amount of undesirable olefin saturation.

[0036] Hydrodesulfurization (or "HDS") involves the removal of organically-bound feed sulfur by conversion to hydrogen sulfide. HDS is typically achieved by reacting hydrogen and the feed's sulfur in the presence of a non-noble metal sulfided catalyst, especially those of Co/Mo and Ni/Mo. The catalyst can be a supported catalyst. Conventional non-selective HDS uses relatively severe temperatures and pressures in order to meet product quality specifications, or to supply a desulfurized stream to a subsequent sulfur sensitive process.

[0037] Hydrodesulfurization of cracked naphthas using conventional naphtha desulfurization catalysts under conventional startup procedures and under conventional conditions required for sulfur removal, typically leads to a significant loss of olefins through hydrogenation. This results in a lower grade fuel product that needs additional refining, such as isomerization, blending, etc. to produce higher octane fuels. Such additional refining, of course, adds significantly to production costs.

[0038] Although conventional non-selective hydrodesulfurization can be used for treating the intermediate and higher boiling fractions, it is preferred to use selective hydrodesulfurization. In selective hydrodesulfurization, organically-bound sulfur is removed while minimizing hydrogenation of olefins and octane reduction by various techniques, such as selective catalysts and/or process conditions. For example, a process referred to as SCANfining has been developed by Exxon Mobil Corporation in which olefinic naphthas are selectively desulfurized with little loss in octane. U.S. Patent Nos. 5,985,136; 6,013,598; and

6,126,814, all of which are incorporated by reference herein, disclose various aspects of SCANfining.

[0039] Selective hydrodesulfurization conditions suitable for use in the practice of the present invention will vary as a function of the concentration and types of sulfur of the feedstock. Generally, hydrodesulfurization conditions include: temperatures from about 230°C to about 370°C, preferably from about 260°C to about 355°C; pressures from about 150 to 800 psig, preferably from about 200 to 500 psig; hydrogen feed rates of about 1000 to 5000 standard cubic feet per barrel (scf/b), preferably from about 1000 to 2500 scf/b; hydrogen purity from about 20 to 100 vol.%, preferably from about 65 to 100 vol.%; and liquid hourly space velocities of about 0.5 hr⁻¹ to about 15 hr⁻¹, preferably from about 0.5 hr⁻¹ to about 10 hr⁻¹, more preferably from about 1 hr⁻¹ to about 5 hr⁻¹. Reaction pressures and hydrogen feed rates below these ranges can result in higher catalyst deactivation rates.

[0040] The reaction zone can be comprised of one or more fixed bed reactors each of which can comprise one or more catalyst beds. Interstage cooling between fixed bed reactors, or between catalyst beds in the same reactor, can be employed since some olefin saturation will take place, and olefin saturation and the desulfurization reaction are generally exothermic. A portion of the heat generated during hydrodesulfurization can be recovered. Where this heat recovery option is not available, cooling may be performed through cooling utilities such as cooling water or air, or through use of a hydrogen quench stream. In this manner, optimum reaction temperatures can be more easily maintained.

[0041] In an embodiment, a selective hydrodesulfurization catalyst is used which comprises: (a) a MoO₃ concentration of about 1 to 10 wt.%, preferably

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about 2 to 8 wt.%, and more preferably about 4 to 6 wt.%, based on the total weight of the catalyst; (b) a CoO concentration of about 0.1 to 5 wt.%, preferably about 0.5 to 4 wt.%, and more preferably about 1 to 3 wt.%, also based on the total weight of the catalyst; (c) a Co/Mo atomic ratio of about 0.1 to about 1.0, preferably from about 0.20 to about 0.80, more preferably from about 0.25 to about 0.72; (d) a median pore diameter of about 60 Å to about 200 Å, preferably from about 75 Å to about 175 Å, and more preferably from about 80 Å to about 150 Å; (e) a MoO₃ surface concentration of about 0.5×10^{-4} to about 3×10^{-4} g. MoO₃/m², preferably about 0.75×10^{-4} to about 2.5×10^{-4} , more preferably from about 1×10^{-4} to about 2×10^{-4} ; and (f) an average particle size diameter of less than 2.0 mm, preferably less than about 1.6 mm, more preferably less than about 1.4 mm, and most preferably as small as practical for a commercial hydrodesulfurization process unit. The most preferred catalysts will also have a high degree of metal sulfide edge plane area as measured by the Oxygen Chemisorption Test described in "Structure and Properties of Molybdenum Sulfide: Correlation of O₂ Chemisorption with Hydrodesulfurization Activity," S. J. Tauster et al., Journal of Catalysis 63, pp 515-519 (1980), which is incorporated herein by reference. The Oxygen Chemisorption Test involves edge-plane area measurements made wherein pulses of oxygen are added to a carrier gas stream and thus rapidly traverse the catalyst bed. For example, the oxygen chemisorption will be from about 800 to 2,800, preferably from about 1,000 to 2,200, and more preferably from about 1,200 to 2,000 μmol oxygen/gram MoO₃. The terms hydrotreating and hydrodesulfurization are sometimes used interchangeably in this document.

[0042] When the hydrodesulfurization catalyst is a supported catalyst, any suitable inorganic oxide support material may be used. Non-limiting examples of

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suitable support materials include: alumina, silica, titania, calcium oxide, strontium oxide, barium oxide, carbons, zirconia, diatomaceous earth, lanthanide oxides including cerium oxide, lanthanum oxide, neodymium oxide, yttrium oxide, and praeodymium oxide; chromia, thorium oxide, urania, niobia, tantalum, tin oxide, zinc oxide, and aluminum phosphate. Preferred are alumina, silica, and silica-alumina. More preferred is alumina. For the catalysts with a high degree of metal sulfide edge plane area of the present invention, magnesia can also be used. It is to be understood that the support material can contain small amount of contaminants, such as Fe, sulfates, silica, and various metal oxides that can be present during the preparation of the support material. These contaminants are present in the raw materials used to prepare the support and will preferably be present in amounts less than about 1 wt.%, based on the total weight of the support. It is more preferred that the support material be substantially free of such contaminants. It is an embodiment, about 0 to 5 wt.%, preferably from about 0.5 to 4 wt.%, and more preferably from about 1 to 3 wt.%, of an additive is present in the support. The additive is selected from the group consisting of phosphorus and metals or metal oxides from Group IA (alkali metals) of the Periodic Table of the Elements.

CLAIMS:

1. A multi-step process for the removal of sulfur from cracked naphtha feedstocks containing mercaptan sulfur, thiophenic sulfur, and olefins, which process comprises:

(a) converting at least a portion of the mercaptan sulfur under mercaptan conversion conditions to their corresponding disulfides in a mercaptan conversion zone, thereby resulting in a disulfide-containing naphtha product stream;

(b) conducting said disulfide-containing naphtha product stream to a thiophene alkylation zone wherein said product stream is contacted with a catalytically effective amount of an acid catalyst under thiophene alkylation conditions, thereby resulting in the alkylation of at least a portion of the thiophenes with at least a portion of the olefins in said cracked naphtha feedstock, and producing a product stream containing alkylated thiophenes;

(c) separating from the product stream from step (b) above into at least a lower boiling stream having a final boiling point equal to or less than about 250°F and at least one higher boiling stream.

2. The process of claim 1 wherein the mercaptan conversion zone is operated by contacting the cracked naphtha feedstock with an aqueous caustic solution in the presence of an oxidizing agent and an oxidation catalyst.

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3. The process of claim 2 wherein the caustic solution is selected from the group consisting of a sodium hydroxide solution, a potassium hydroxide solution, and an ammonium hydroxide solution.

4. The process of claim 3 wherein the caustic solution is a sodium hydroxide solution.

5. The process of claim 2 wherein the oxidizing catalyst is selected from the group consisting of metal phthalocyanines and sulfonated derivatives thereof.

6. The process of claim 5 wherein the oxidizing catalyst is selected from cobalt phthalocyanine and cobalt phthalocyanine disulfonate.

7. The process of claim 1 wherein the acid catalyst is selected from the group consisting of AlCl_3 /silica, AlCl_2 /silica, and BF_3 /silica.

8. The process of claim 1 wherein the acid catalyst is selected from the crystalline aluminosilicate zeolites having a silica to alumina ratio of at least 12 and a constraint index of about 1 to 12.

9. The process of claim 8 wherein the acid catalyst is selected from the crystalline aluminosilicate zeolites having a silica to alumina ratio of at least 12 and a constraint index of no greater than about 2.

10. The process of claim 8 wherein the acid catalyst is selected from the group consisting of ZSM-5 type zeolites, zeolite Beta, and MCM-22 type zeolites.

11. The process of claim 1 wherein the separating step produces a lower boiling stream having a final boiling point equal to or less than about 250°F (121°C), an intermediate boiling stream boiling in the range of about 250°F to

about 350°F (177°C), and a higher boiling stream having an initial boiling point of at least about 350°F.

12. The process of claim 1 wherein both the intermediate boiling product stream and the higher boiling range product streams are subjected to hydrodesulfurization in the presence of a hydrodesulfurization catalyst and hydrogen at hydrodesulfurization conditions.

13. The process of claim 1 wherein the intermediate boiling product stream is subjected to selective hydrodesulfurization wherein sulfur is removed with hydrogenation of olefins kept to a minimum.

14. The process of claim 1 wherein the product stream from hydrodesulfurizing the intermediate boiling product stream is subjected to reforming at reforming conditions in the presence of a Pt-containing reforming catalyst.

15. A multi-step process for the removal of sulfur from cracked naphtha feedstocks containing mercaptan sulfur, thiophenic sulfur, and olefins, which process comprises:

(a) conducting said cracked naphtha feedstock to a mercaptan oxidation zone which is operated under conditions wherein the cracked naphtha feedstock is contacted with an aqueous caustic solution in the presence of an oxidizing agent and an oxidation catalyst, thereby converting at least a portion of the mercaptans to their corresponding disulfides;

(b) conducting the product stream of step a) above to a thiophene alkylation zone wherein said product stream is contacted with an acid catalyst under thiophene alkylation conditions, thereby resulting in the alkylation of at

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least a portion of the thiophenes with at least a portion of the olefins in said cracked naphtha feedstock, and producing a product stream containing alkylated thiophenes;

(c) fractionating the product stream from step b) above to produce a lower boiling stream having a final boiling point equal to or less than about 250°F (121°C), an intermediate boiling stream boiling in the range of about 250°F to about 350°F (177°C), and a higher boiling stream having an initial boiling point of at least about 350°F.

16. The process of claim 15 wherein the caustic solution is selected from the group consisting of a sodium hydroxide solution, a potassium hydroxide solution, and an ammonium hydroxide solution.

17. The process of claim 16 wherein the caustic solution is a sodium hydroxide solution.

18. The process of claim 15 wherein the oxidizing catalyst is selected from the group consisting of metal phthalocyanines and sulfonated derivatives thereof.

19. The process of claim 18 wherein the oxidizing catalyst is selected from cobalt phthalocyanine and cobalt phthalocyanine disulfonate.

20. The process of claim 15 wherein the acid catalyst is selected from the group consisting of AlCl_3 /silica, AlCl_2 /silica, and BF_3 /silica.

21. The process of claim 15 wherein the acid catalyst is selected from the crystalline aluminosilicate zeolites having a silica to alumina ratio of at least 12 and a constraint index of about 1 to 12.

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22. The process of claim 21 wherein the acid catalyst is selected from the crystalline aluminosilicate zeolites having a silica to alumina ratio of at least 12 and a constraint index of no greater than about 2.

23. The process of claim 21 wherein the acid catalyst is selected from the group consisting of ZSM-5 type zeolites, zeolite Beta, and MCM-22 type zeolites.

24. The process of claim 15 wherein both the intermediate boiling product stream and the higher boiling product streams are subjected to hydrodesulfurization in the presence of a hydrodesulfurization catalyst and hydrogen at hydrodesulfurization conditions.

25. The process of claim 15 wherein the intermediate boiling product stream is subjected to selective hydrodesulfurization wherein sulfur is removed with hydrogenation of olefins kept to a minimum.

26. The process of claim 15 wherein the product stream from hydrodesulfurizing the intermediate product stream is subjected to reforming at reforming conditions in the presence of a Pt-containing reforming catalyst.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/24832

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C10G 29/00, 29/20

US CL : 208/238, 208R, 237

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/238, 208R, 237

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,059,962 A (ALEXANDER et al), 09 May 2000 (09.05.2000), columns 1-4.	1-26
A	US 6,024,865 A (ALEXANDER et al) 15 February 2000 (15.02.2000), columns 1-4.	1-26
A	US 5,599,441 A (COLLINS et al) 04 February 1997 (04.02.1997), columns 1-4.	1-26
A, P	US 6,736,963 B2 (PRADHAN et al) 18 May 2004 (18.05.2004), columns 1-4.	1-26

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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document member of the same patent family

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07 December 2004 (07.12.2004)

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