

## **PROCESS TO MANUFACTURE LOW SULFUR FUELS**

### **FIELD OF THE INVENTION**

[0001] The instant invention relates to a process for upgrading of hydrocarbon mixtures boiling within the naphtha range. More particularly, the instant invention relates to a process to produce high octane, low sulfur naphtha products through the simultaneous skeletal isomerization of feed olefins and selective hydrotreating.

### **BACKGROUND OF THE INVENTION**

[0002] Liquid hydrocarbon streams that boil within the naphtha range, i.e. below 232°C, and produced from the Fluidized Catalytic Cracking Unit ("FCC") are typically used as blending components for motor gasolines. Environmentally driven regulatory pressure concerning motor gasoline sulfur levels is expected to result in the widespread production of less than 50 wppm sulfur mogas by the year 2004. Levels below 10 wppm are being considered for later years in some regions of the world, and this will require deep desulfurization of naphthas in order to conform to emission restrictions that are becoming more stringent. The majority, i.e., 90% or more, of sulfur contaminants present in motor gasolines are typically present in naphtha boiling range hydrocarbon streams. However, the naphtha boiling range streams are also rich in olefins, which boost octane, a desirable quality in motor gasolines.

[0003] Thus, many processes have been developed to produce low sulfur products from naphtha boiling range streams while attempting to minimize olefin loss, such as, for example, hydrodesulfurization processes. However, these processes also typically hydrogenate feed olefins to some degree, thus reducing the

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octane number of the product. Therefore, processes have been developed that recover octane lost during desulfurization. Non-limiting examples of these processes can be found in United States Patent Numbers 5,298,150; 5,320,742; 5,326,462; 5,318,690; 5,360,532; 5,500,108; 5,510,016; and 5,554,274, which are all incorporated herein by reference. In these processes, in order to obtain desirable hydrodesulfurization with a reduced octane loss, it is necessary to operate in two steps. The first step is a hydrodesulfurization step, and a second step recovers octane lost during hydrodesulfurization.

**[0004]** Other processes have also been developed that seek to minimize octane lost during hydrodesulfurization. For example, selective hydrodesulfurization is used to remove organically bound sulfur while minimizing hydrogenation of olefins and octane reduction by various techniques, such as the use of selective catalysts and/or process conditions. For example, one selective hydrodesulfurization process, referred to as SCANfining, has been developed by ExxonMobil Research & Engineering Company 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. Although selective hydrodesulfurization processes have been developed to avoid significant olefin saturation and loss of octane, such processes have a tendency to liberate H<sub>2</sub>S a portion of which may react with retained olefins to form mercaptan sulfur by reversion.

**[0005]** Thus, there still exists a need in the art for a process to reduce the sulfur content in naphtha boiling range hydrocarbon streams while minimizing octane loss and mercaptan reversion.

**SUMMARY OF THE INVENTION**

[0006] The instant invention is directed at a process for producing low sulfur naphtha products through simultaneous skeletal olefin isomerization and selective desulfurization. The process comprises:

- a) contacting a naphtha boiling range feedstream containing organically bound sulfur and olefins in a reaction zone, operated under effective hydrotreating conditions and in the presence of hydrogen-containing treat gas, with a supported catalyst comprising at least one medium pore zeolite selected from ZSM-23, ZSM-12, ZSM-22, ZSM-57, and ZSM-48, 0.1 to 27 wt.% of at least one Group VIII metal oxide, and 1 to 45 wt.% of at least one Group VI metal oxide to produce a desulfurized product.

**BRIEF DESCRIPTION OF THE FIGURES**

[0007] Figure 1 compares results obtained from the Examples herein at constant bromine number reduction.

[0008] Figure 2 compares product iso-olefin to n-olefin ratios of products resulting from the Examples herein.

[0009] Figure 3 compares product iso-paraffin to n-paraffin ratios of products resulting from the Examples herein.

**DETAILED DESCRIPTION OF THE INSTANT INVENTION**

[0010] It should be noted that the terms "hydrotreating" and "hydrodesulfurization" are sometimes used interchangeably herein, and the prefixes "i-" and "n" are meant to refer to "iso-" and "normal", respectively.

[0011] In the hydrotreating of naphtha boiling range feedstreams, olefins are typically saturated in the hydrotreating zone resulting in a decrease in octane number of the desulfurized product. However, the present invention reduces the decrease in octane of the desulfurized product through the use of a novel process involving contacting a naphtha boiling range feedstream in a reaction zone operated under effective hydrotreating conditions. This reaction zone contains a supported catalyst comprising at least one medium pore zeolite, 0.1 to 27 wt.% of at least one Group VIII metal oxide, and 1 to 45 wt.% of at least one Group VI metal oxide supported on a suitable substrate.

[0012] The desulfurized product thus obtained has a higher iso-paraffin to n-paraffin ratio, and thus a higher octane than a desulfurized naphtha treated by a selective or non-selective hydrotreating process only, i.e., without an octane recovery step. The higher octane of the desulfurized product results from the unexpected finding by the inventors hereof that by operating the reaction zone under conditions effective for encouraging the skeletal isomerization of n-olefins to iso-olefins results in a desulfurized naphtha product having a higher octane number than a desulfurized product resulting from a selective hydrodesulfurization process only. The inventors hereof have found that the degree of skeletal isomerization of n-olefins to iso-olefins benefits the final product because the saturation of iso-olefins to iso-paraffins that occurs in the reaction zone herein provides for less octane loss in the final product when compared to the saturation of n-olefins to n-

paraffins. It should be noted that iso-paraffins typically have a much higher octane than their corresponding n-paraffin. Further, the rate of saturation of iso-olefins is typically slower than that of n-olefins. Therefore, by increasing the ratio of iso-olefins to n-olefins present in the reaction zone effluent, the resulting desulfurized naphtha product exiting the reaction zone also typically has a higher iso-olefin to n-olefin ratio as well as a higher olefin content, and thus a higher octane than a desulfurized naphtha treated by a selective or non-selective hydrotreating process only.

**[0013]** In the hydroprocessing of naphtha boiling range hydrocarbon feedstreams, it is typically highly desirable to remove sulfur-containing compounds from the naphtha boiling range feedstreams with as little olefin saturation as possible. It is also highly desirable to convert as much of the organic sulfur species of the naphtha to hydrogen sulfide with as little mercaptan reversion as possible. By mercaptan reversion we mean the reaction of hydrogen sulfide with olefins during the hydrotreating to form undesirable alkylmercaptans. The inventors hereof have unexpectedly found that through the use of the presently claimed invention, high levels of sulfur can be removed from an olefinic naphtha stream without excessive olefin saturation or mercaptan reversion taking place.

**[0014]** Feedstreams suitable for use in the present invention include naphtha boiling range refinery streams that typically boil in the range of 50°F (10°C) to 450°F (232°C) containing both olefins and sulfur containing compounds. Thus, the term "naphtha boiling range feedstream" as used herein includes those streams having an olefin content of at least 5 wt.%. Non-limiting examples of naphtha boiling range feedstreams that can be treated by the present invention 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 as long as the blend has an olefin content of at least 5 wt.%, based on the total weight of the naphtha feedstream.

**[0015]** Cracked naphtha refinery streams generally 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. The olefin-containing naphtha feedstream can contain an overall olefins concentration ranging as high as 70 wt.%, more typically as high as 60 wt.%, and most typically from 5 wt.% to 40 wt.%. The olefin-containing naphtha feedstream can also have a diene concentration up to 15 wt.%, but more typically less than 5 wt.% based on the total weight of the feedstock. The sulfur content of the naphtha feedstream will generally range from 50 wppm to 7000 wppm, more typically from 100 wppm to 5000 wppm, and most typically from 100 to 3000 wppm. The sulfur will usually be present as organically bound sulfur. That is, as 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, tetrahydrothiophene, benzothiophene and their higher homologs and analogs. Feedstreams suitable for use herein can also contain nitrogen contaminants that are typically present in a range from 5 wppm to 500 wppm.

**[0016]** The feedstreams used herein are typically preheated prior to entering the reaction zone herein and final heating is typically targeted to the effective hydrotreating temperatures. If the naphtha boiling range feedstream is preheated, it can be reacted with the hydrogen-containing treat gas stream prior to, during, and/or after preheating. At least a portion of the hydrogen-containing treat gas can

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also be added at an intermediate location in the reaction zone. Hydrogen-containing treat gasses suitable for use in the presently disclosed process can be comprised of substantially pure hydrogen or can be mixtures of other components typically found in refinery hydrogen streams. It is preferred that the hydrogen-containing treat gas stream contains little, more preferably no, hydrogen sulfide. The hydrogen-containing treat gas purity should be at least 50% by volume hydrogen, preferably at least 75% by volume hydrogen, and more preferably at least 90% by volume hydrogen for best results. It is most preferred that the hydrogen-containing stream be substantially pure hydrogen.

[0017] In the reaction zone, the above-described naphtha boiling range feedstream is contacted with a catalyst comprising at least one medium pore zeolite. Zeolites are porous crystalline materials, and medium pore zeolites as used herein can be any zeolite described as a medium pore zeolite in Atlas of Zeolite Structure Types, W.M. Maier and D.H. Olson, Butterworths. Typically, medium pore zeolites are defined as those having a pore size of 5 to 7 Angstroms, such that the zeolite freely sorbs molecules such as n-hexane, 3-methylpentane, benzene and p-xylene. Another common classification used for medium pore zeolites involves the Constraint Index test which is described in United States Patent Number 4,016,218, which is hereby incorporated by reference. Medium pore zeolites typically have a Constraint Index of 1 to 12, based on the zeolite alone without modifiers and prior to treatment to adjust the diffusivity of the catalyst. Preferred medium pore zeolites for use herein are selected from ZSM-23, ZSM-12, ZSM-22, ZSM-57, and ZSM-48, with ZSM-48 being the most preferred.

[0018] Another means of describing zeolites is alpha value or number. Alpha value, or alpha number, is a measure of zeolite acidic functionality and is more

fully described together with details of its measurement in United States Patent Number 4,016,218, J. Catalysis, 6, pages 278-287 (1966) and J. Catalysis, 61, pages 390-396 (1980), which are all incorporated herein by reference. Generally the alpha value reflects the relative activity with respect to a high activity silica-alumina cracking catalyst. To determine the alpha value as used herein, n-hexane conversion is determined at 800°F. Conversion is varied by variation in space velocity such that a conversion level of 10 to 60 percent of n-hexane is obtained and converted to a rate constant per unit volume of zeolite and compared with that of the silica-alumina catalyst, which is normalized to a reference activity of 1000°F. Catalytic activity is expressed as a multiple of this standard, i.e. the silica-alumina standard. The silica-alumina reference catalyst contains 10 wt.%  $\text{Al}_2\text{O}_3$  and the remainder is  $\text{SiO}_2$ . Therefore, as the alpha value of a zeolite catalyst decreases, the tendency towards non-selective cracking also decreases. Zeolites suitable for use herein have an alpha value of up to 20, preferably between 0.1 and 20, more preferably 1 to 19, and most preferably between 10 and 20.

**[0019]** The medium pore zeolites used herein are typically combined with a suitable porous binder or matrix material. Non-limiting examples of such materials include active and inactive materials such as clays, silica, and/or metal oxides such as alumina. Non-limiting examples of naturally occurring clays that can be composited include clays from the montmorillonite and kaolin families including the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia, and Florida clays. Others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite may also be used. The clays can be used in the raw state as originally mixed or subjected to calcination, acid treatment, or chemical modification prior to being combined with the medium pore zeolite.

**[0020]** It is preferred that the porous matrix or binder material comprises silica, alumina, or a kaolin clay. It is more preferred that the binder material comprise alumina. In this embodiment the alumina is present in a ratio of less than 15 parts zeolite to one part binder, preferably less than 10, more preferably less than 5, and most preferably 2.

**[0021]** The catalysts used herein also comprises 0.1 to 27 wt.% of at least one Group VIII metal oxide and 1 to 45 wt.% of at least one Group VI metal oxide. The at least one Group VIII metal oxide concentration of the catalysts used herein is preferably 0.1 to 10 wt.%, more preferably 1 to 8 wt.%, and most preferably 1 to 5 wt.%, and the at least one Group VIII metal oxide concentration of the catalysts used herein is preferably 1 to 30 wt.%, more preferably 1 to 20 wt.%, and most preferably 2 to 10 wt.%. Preferred Group VIII metal oxides are those selected from Fe, Co and Ni, more preferably Co and/or Ni, and most preferably Co. Preferred Group VI metal oxides are those selected from Mo and W, more preferably Mo. The at least one Group VIII metal oxide and the at least one Group VI metal oxide can be incorporated onto the above-described supported medium pore zeolite by any means known to be effective at doing so. Non-limiting examples of suitable incorporation means include incipient wetness, ion exchange, mechanical mixing of metal oxide precursor(s) with zeolite and binder, or a combination thereof.

**[0022]** The reaction zone used herein can be comprised of one or more fixed bed reactors or reaction zones each of which can comprise one or more catalyst beds of the same or different catalyst. Thus, it is within the scope of the instant invention that catalysts comprising different zeolites, different Group VIII and Group VI metal oxides, and mixtures thereof be used in the same reaction vessel. Although other types of catalyst beds can be used, non-limiting examples of suitable bed

types include fluidized beds, ebullating beds, slurry beds, and moving beds. Preferred are fixed catalyst beds. Interstage cooling or heating between reactors or reaction zones, or between catalyst beds in the same reactor, can be employed since some olefin saturation can 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, conventional 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.

**[0023]** As stated above, the above-defined naphtha boiling range feedstream containing organically bound sulfur and olefins is contacted with the supported catalyst described herein in a reaction zone operated under effective hydrotreating conditions. By effective hydrotreating conditions, it is meant those conditions that provide for the skeletal isomerization of at least 20 wt.% of the n-olefins present in the feedstream to iso-olefins, preferably at least 40 wt.%, more preferably at least 50 wt.%. By skeletal isomerization, it is meant the reorientation of the molecular structure of the normal olefins (n-olefins) with a preference for branched chain iso-olefins over straight. Thus, skeletal isomerization, as used herein, refers to the conversion of a normal olefin to a branched olefin or to the rearranging or moving of branch carbon groups, which are attached to the straight chain olefin molecule, to a different carbon atom, and non-skeletal isomerization can be described as the rearranging of the position of the double bond within the straight chain or branched olefin molecule.

**[0024]** By effective hydrotreating conditions, it is also meant those conditions chosen that will achieve a resulting desulfurized naphtha product having less than

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100 wppm sulfur, preferably less than 50 wppm sulfur, more preferably less than 30 wppm sulfur. Typical effective hydrotreating conditions will be those that include temperatures ranging from 150°C to 425°C, preferably 200°C to 370°C, more preferably 230°C to 350°C. Typical weight hourly space velocities ("WHSV") range from 0.1 to 20hr<sup>-1</sup>, preferably from 0.5 to 5hr<sup>-1</sup>. Any effective pressure can be utilized, and pressures typically range from 4 to 70 atmospheres, preferably 10 to 40 atmospheres. In a most preferred embodiment, the effective hydrotreating conditions are selective hydrotreating conditions configured to achieve a sulfur level and degree of skeletal isomerization within the above-defined ranges, most preferably the conditions are selected such that the desulfurized naphtha product has a sulfur level sufficiently low to meet current regulatory standards in place at that time. By selective hydrotreating conditions, it is meant conditions such as those contained in U.S. Patent Nos. 5,985,136; 6,013,598; and 6,126,814, all of which have already been incorporated by reference herein, which disclose various aspects of SCANfining, a process developed by the ExxonMobil Research and Engineering Company in which olefinic naphthas are selectively desulfurized with little loss in octane.

**[0025]** As previously stated, the desulfurized product thus obtained will typically have a higher iso-paraffin to n-paraffin ratio, and thus a higher octane than a desulfurized naphtha treated by a selective or non-selective hydrotreating process. Typical iso-paraffin to n-paraffin ratios in the desulfurized product resulting from the present process are greater than 1, preferably 2, more preferably 3. Thus, compared to selective hydrodesulfurization catalyst systems, the processing of the naphtha boiling range feedstream over the present catalyst system results in a desulfurized naphtha product with a higher octane at constant olefin saturation even

when both catalyst systems maintain similar desulfurization/olefin saturation selectivity.

**[0026]** In one embodiment of the instant invention, the nitrogen content of the naphtha boiling range feedstreams is reduced in a feed pre-treatment step because catalytic treatments are impeded by nitrogen-containing compounds present in the feedstream. Thus, one embodiment of the instant invention involves treating the naphtha boiling range feedstream with an acidic material to reduce the nitrogen content of the feedstreams. Non-limiting examples of suitable acidic materials include sulfuric acid, Amberlyst, alumina, spent sulfuric acid obtained from an alkylation unit, and any other material known to be effective at reducing the nitrogen concentration of a naphtha boiling range feedstream. Preferred acidic materials are Amberlyst and alumina. In the feed pretreatment step, the naphtha boiling range feedstream can be contacted with the acidic material under conditions effective for removing at least a portion of the nitrogen-containing compounds present in the naphtha boiling range feedstream. By at least a portion, it is meant at least 10 wt.% of the nitrogen-containing compounds present in the feedstream. Preferably, at least that amount of nitrogen-containing compounds that will result in a first reaction zone effluent containing less than 50 wppm total nitrogen, based on the first reaction zone effluent. More preferably the first reaction zone effluent contains less than 25 wppm total nitrogen, most preferably less than 10 wppm nitrogen, and in an ideally suitable case, less than 5 wppm total nitrogen. Thus, by "conditions effective for removal of at least a portion of the nitrogen-containing compounds", it is meant those conditions under which the first reaction zone effluent will have the above described total nitrogen concentrations, i.e., 10 wt.% removal, etc. It should be noted that if sulfuric acid or spent sulfuric acid obtained from an alkylation unit is used, the acid concentration should be adjusted by adding

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a diluent before either is contacted with the naphtha boiling range feedstream to avoid polymerizing olefins.

[0027] The above description is directed to several embodiments of the present invention. Those skilled in the art will recognize that other embodiments that are equally effective could be devised for carrying out the spirit of this invention.

[0028] The following examples will illustrate the effectiveness of the present invention, but is not meant to limit the present invention in any fashion.

## **EXAMPLES**

### **EXAMPLE 1 - CATALYST PREPARATION**

[0029] A base ZSM-48 catalyst comprising 65% ZSM-48 / 35% Alumina was used to prepare a catalyst as contemplated herein. The properties of the base catalyst are given in Table 1 below.

[0030] 100 grams of the base catalyst was charged to a rotary cone for impregnation with Mo. The Mo solution used for impregnation was prepared by dissolving 22.6 grams of ammonium heptamolybdate in a quantity of water sufficient to completely wet it. The Mo solution was sprayed onto the base catalyst and the resulting catalyst was dried at 250°F for 12 hours. The Mo containing base catalyst was calcined in a tube furnace for 3 hours at 1000°F using an air circulation rate of 5 vol. air/vol. catalyst.

[0031] The Mo impregnated catalyst was again charged to the rotary cone for impregnation with Co. The Co solution used for impregnation was prepared by

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dissolving 18.3 grams of cobalt nitrate in a quantity of water sufficient to wet the entire cobalt nitrate solid. The Co solution was sprayed onto the base catalyst and the resulting catalyst was dried at 250°F for 12 hours. The Co/Mo containing base catalyst was calcined in a tube furnace for 3 hours at 1000°F using an air circulation rate of 5 vol. air/vol. catalyst.

[0032] The finished catalyst contained 2.59 wt.% Co and 9.51 wt.% Mo.

**TABLE 1**

**BASE CATALYST PROPERTIES**

|                      |                       |
|----------------------|-----------------------|
| Alpha                | 20                    |
| Surface Area         | 224 m <sup>2</sup> /g |
| Density              | 0.66 g/cc             |
| Water sorption       | 8.8 wt.%              |
| Hexane sorption      | 8 wt.%                |
| Cyclohexane sorption | 9 wt.%                |

**EXAMPLE 2**

[0033] An FCC naphtha was treated at ambient conditions and liquid hourly space velocities ("LHSV") of 2-3 hr<sup>-1</sup> with Amberlyst-15 to reduce the nitrogen content of the feed to 3wppm. The feed having the properties described in Table 2 below was then contacted with the catalyst described in Example 1 above. The contacting conditions included various temperatures within the range of 480-650°F, i.e. 480, 482, 400, 518, 525, 536, 552, 624, 649°F, hydrogen treat rates of 2000scf/bbl of 100% pure hydrogen, pressures of 250psig, and LHSV of 2hr<sup>-1</sup>. The results of this experiment are described in the Figures below.

**EXAMPLE 3 - COMPARATIVE (I)**

[0034] An FCC naphtha was treated at ambient conditions and liquid hourly space velocities ("LHSV") of 2-3 hr<sup>-1</sup> with Amberlyst-15 to reduce the nitrogen content of the feed to 1wppm. The feed having the properties described in Table 2 below was then contacted with a commercial hydrotreating catalyst having 1.2 wt.% CoO and 4.2 wt.% MoO. The contacting conditions were selected from those known in the art to be "selective" and included various temperatures within the range of 450-600°F, i.e. 480, 503, 421, 537, and 557°F hydrogen treat rates of 2000scf/bbl of 100% pure hydrogen, pressures of 250psig and LHSV of 4hr<sup>-1</sup>. The results of this experiment are described in the Figures below. The concentration of mercaptans produced in this Example was also compared to the concentration of mercaptans produced in Example 2 at 525°F. These results are contained in Table 3 below.

**EXAMPLE 4 - COMPARATIVE (II)**

[0035] An FCC naphtha feed having the properties described in Table 2 below was contacted with a commercial hydrotreating catalyst having 1.2 wt.% CoO and 4.2 wt.% MoO. The contacting conditions included a temperature of 525°F, hydrogen treat rates of 3000scf/bbl of 100% pure hydrogen, pressures of 170psig and LHSV of 2.3hr<sup>-1</sup>. The results of this experiment are described in the Figures below. The concentration of mercaptans produced in this Example was also compared to the concentration of mercaptans produced in Example 2 at 525°F. These results are contained in Table 3 below.

**TABLE 2****FEED PROPERTIES**

|                                | Example 2 | Example 3 | Example 4 |
|--------------------------------|-----------|-----------|-----------|
| API Gravity                    | 56.6      | 56.7      | 57.1      |
| Total S, wppm                  | 711       | 603       | 735       |
| Nitrogen, wppm                 | 3         | 1         | 48        |
| Bromine Number                 | 69.8      | 70.2      | 71        |
| Hydrogen                       | 13.27     | 13.29     | 13.23     |
| Road Octane Number("RON")      | 92.2      | 92.5      | 93.5      |
| Paraffins (wt.%)               |           |           |           |
| n-Paraffins                    | 3         | 3.22      | 3.02      |
| iso-Paraffins                  | 21.91     | 23.22     | 22.08     |
| Total Paraffins                | 24.91     | 26.43     | 25.11     |
| Naphthenes                     | 8.42      | 8.37      | 9.28      |
| Aromatics                      | 28.44     | 29.69     | 25.19     |
| Olefins (wt.%)                 |           |           |           |
| n-Olefins                      | 12.6      | 11.95     | 12.83     |
| iso-Olefins                    | 17.68     | 17.35     | 17.01     |
| Other olefins                  | 7.91      | 6.2       | 10.61     |
| Total olefins                  | 37.97     | 35.5      | 40.43     |
| Distillation (°F) (ASTM D2887) |           |           |           |
| 5%                             | 95        | 90        | 85        |
| 10%                            | 109       | 107       | 105       |
| 50%                            | 230       | 228       | 222       |
| 90%                            | 350       | 346       | 341       |
| 95%                            | 373       | 371       | 365       |

**TABLE 3**

|           | Feed S,<br>wppm | Treat<br>Gas<br>scf/bbl | Total<br>Pressure,<br>psig | iso to<br>n-olefin<br>ratio | Product S,<br>wppm | Mercaptan/<br>Bromine Number<br>Ratio |
|-----------|-----------------|-------------------------|----------------------------|-----------------------------|--------------------|---------------------------------------|
| Example 2 | 711             | 2000                    | 250                        | 2.9                         | 30                 | 0.24                                  |
| Example 3 | 603             | 2000                    | 250                        | 1.5                         | 100                | 0.41                                  |
| Example 4 | 735             | 3000                    | 170                        | N/A                         | 30                 | 0.63                                  |

[0036] As described above, mercaptans are generally formed by the reversion reaction of olefins with hydrogen sulfide. Thermodynamics for model compounds show that mercaptan reversion equilibrium for branched olefins, i.e. iso-olefins, is lower than that for normal olefins. Consequently, the isomerization of n-olefins to iso-olefins can give a lower mercaptan concentration at constant bromine number. This benefit is readily illustrated by comparing mercaptan/bromine number ratios at constant temperature. Thus, by comparing the mercaptan/bromine number ratios of the products produced at 525°F in Examples 2, 3, and 4, the results contained in Table 3 show that the catalyst used in Example 2 above produced less mercaptans than the catalysts used in Examples 3 and 4. It should be noted that the mercaptan/bromine number ratio is sensitive to the equilibrium constant for feeds with similar sulfur concentrations subjected to catalysis with similar treat gas rates, which is a function of the ratio of iso to n-paraffins.

[0037] Figure 1 shows that at constant bromine number reduction, the octane loss was much lower for Example 1 than for the comparative Examples. The reduction in bromine number was measured according to ASTM 1159.

**[0038]** Figure 2 shows that at constant bromine number, the catalyst of Example 1 provided a higher iso-olefin to n-olefin ratio than the catalysts of the comparative Examples. Higher branched olefin concentrations, i.e. iso-olefins, results in higher octane at constant bromine number since octane numbers for branched olefins are typically higher than those for normal olefins.

**[0039]** Figure 3 shows that the catalysts of the catalyst of Example 1, one contemplated by the instant invention produced a product having a higher iso-paraffin to n-paraffin ratio. A higher iso-paraffin to n-paraffin ratio in a product will result in a product having a higher octane than a product with a lower ratio.

**CLAIMS:**

1. A process for producing low sulfur naphtha products from an olefin and sulfur containing naphtha boiling range feedstream comprising:
  - a) contacting a naphtha boiling range feedstream containing organically bound sulfur and olefins in a reaction zone, operated under effective hydrotreating conditions and in the presence of hydrogen-containing treat gas, with a supported catalyst comprising at least one medium pore zeolite selected from ZSM-23, ZSM-12, ZSM-22, ZSM-57, and ZSM-48, 0.1 to 27 wt.% of at least one Group VIII metal oxide, and 1 to 45 wt.% of at least one Group VI metal oxide to produce a desulfurized product.
2. The process according to claim 1 wherein said naphtha boiling range feedstream boils in the range of 50°F (10°C) to 450°F (232°C), an olefin content of at least 5 wt.%, and a sulfur content of 50 to 7000 wppm sulfur.
3. The process according to any preceding claim wherein said naphtha boiling range feedstream is selected from fluid catalytic cracking unit naphtha (FCC catalytic naphtha or cat naphtha), steam cracked naphtha, coker naphtha, blends of olefinic naphthas with non-olefinic naphthas wherein the blend has an olefin content of at least 5 wt.%, based on the total weight of the naphtha boiling range feedstream.
4. The process according to any preceding claim wherein said naphtha boiling range feedstream has a nitrogen content of 5 wppm to 500 wppm nitrogen.

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5. The process according to any preceding claim wherein said reaction zone comprises one or more catalyst beds selected from fluidized beds, ebullating beds, slurry beds, fixed beds, and moving beds wherein each of said one or more catalyst beds contains a catalyst suitable for the reaction zone in which the catalyst bed is located.
6. The process according to any preceding claim wherein said process further comprises interstage cooling between catalyst beds in said reaction zone.
7. The process according to any preceding claim wherein said medium pore size zeolite has an alpha value of up to 20.
8. The process according to any preceding claim wherein said medium pore size zeolite is selected from ZSM-23 and ZSM-48.
9. The process according to any preceding claim wherein said catalyst comprises 0.1 to 10 wt.% of a Group VIII metal oxide and 1 to 30 wt.% of a Group VI metal oxide. 1 to 45 wt.% of at least one Group VI metal oxide.
10. The process according to any preceding claim wherein said effective hydrotreating conditions are selected to cause skeletal isomerization of at least 20 wt.% of the n-olefins present in said naphtha boiling range feedstream.
11. The process according to any preceding claim wherein said support is a suitable binder or matrix material selected from clays, silica, and metal oxides.

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12. The process according to any preceding claim wherein said effective hydrotreating conditions are selected in such a manner that said desulfurized naphtha product has less than 100 wppm sulfur.
13. The process according to any preceding claim wherein said effective hydrotreating conditions are selective hydrotreating conditions.
14. The process according to any preceding claim wherein said desulfurized naphtha product has a higher concentration of iso-paraffins than n-paraffins.
15. The process according to any preceding claim wherein said process further comprises a feed pretreatment step wherein said feed pretreatment step comprises:
  - a) contacting the naphtha boiling range feedstream containing organically bound sulfur, nitrogen-containing compounds, and olefins in a reaction zone, operated under conditions effective at removing at least a portion of said nitrogen-containing compounds, with an acidic material to produce a first reaction zone effluent having a reduced amount of nitrogen-containing compounds.
16. The process according to any preceding claim wherein said acidic material is selected from Amberlyst, alumina, sulfuric acid, spent sulfuric acid obtained from an alkylation unit, and any other acidic material known to be effective at removing nitrogen compounds from a naphtha boiling range hydrocarbon stream.