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(73) Proprietor: **BP Corporation North America Inc.
Warrenville, IL 60555 (US)**

(72) Inventors:
• **MCDANIEL, Stacey
Riverside, IL 60546 (US)**

• **BURNETT, Ptoshia, A.
Wilmington, Delaware 19802 (US)**

(74) Representative: **Hamer, Christopher K. et al
Mathys & Squire
120 Holborn
London EC1N 2SQ (GB)**

(56) References cited:
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Description**Field of the Invention**

[0001] This invention relates to a process for removing sulfur-containing impurities from olefin-containing hydrocarbon mixtures. More particularly, the process involves converting the feedstock to an intermediate product of reduced bromine number, separating the intermediate product into fractions of different boiling point, and subjecting the high boiling fraction to hydrosulfurization, and the intermediate boiling fraction to selective hydrotreating.

Background of the Invention

[0002] The fluidized catalytic cracking process is one of the major refining processes which is currently employed in the conversion of petroleum to desirable fuels such as gasoline and diesel fuel. In this process, a high molecular weight hydrocarbon feedstock is converted to lower molecular weight products through contact with hot, finely-divided, solid catalyst particles in a fluidized or dispersed state. Suitable hydrocarbon feedstocks typically boil within the range from about 205° C to about 650° C, and they are usually contacted with the catalyst at temperatures in the range from about 450° C to about 650° C. Suitable feedstocks include various mineral oil fractions such as light gas oils, heavy gas oils, wide-cut gas oils, vacuum gas oils, kerosenes, decanted oils, residual fractions, reduced crude oils and cycle oils which are derived from any of these as well as fractions derived from shale oils, tar sands processing, and coal liquefaction. Products from a fluidized catalytic cracking process are typically based on boiling point and include light naphtha (boiling between about 10° C and about 221° C), heavy naphtha (boiling between about 10° C and about 249° C), kerosene (boiling between about 180° C and about 300° C), light cycle oil (boiling between about 221° C and about 345° C), and heavy cycle oil (boiling at temperatures higher than about 345° C).

[0003] Naphtha from a catalytic cracking process comprises a complex blend of hydrocarbons which includes paraffins (also known as alkanes), cycloparaffins (also known as cycloalkanes or naphthenes), olefins (as used herein, the term olefin includes all acyclic and cyclic hydrocarbons which contain at least one double bond and are not aromatic), and aromatic compounds. Such a material typically contains a relatively high olefin content and includes significant amounts of sulfur-containing aromatic compounds, such as thiophenic and benzothiophenic compounds, as impurities. For example, a light naphtha from the fluidized catalytic cracking of a petroleum derived gas oil can contain up to about 60 wt. % of olefins and up to about 0.7 wt. % of sulfur wherein most of the sulfur will be in the form of thiophenic and benzothiophenic compounds. However, a typical naphtha from the catalytic cracking process will usually contain from about 5 wt. % to about 40 wt. % olefins and from about 0.07 wt. % to about 0.5 wt. % sulfur.

[0004] Not only does the fluidized catalytic cracking process provide a significant part of the gasoline pool in the United States, it also provides a large proportion of the sulfur that appears in this pool. The sulfur in the liquid products from this process is in the form of organic sulfur compounds and is an undesirable impurity which is converted to sulfur oxides when these products are utilized as a fuel. The sulfur oxides are objectionable air pollutants. In addition, they can deactivate many of the catalysts that have been developed for the catalytic converters which are used on automobiles to catalyze the conversion of harmful engine exhaust emissions to gases which are less objectionable. Accordingly, it is desirable to reduce the sulfur content of catalytic cracking products to the lowest possible levels.

[0005] Low sulfur products are conventionally obtained from the catalytic cracking process by hydrotreating either the feedstock to the process or the products from the process. The hydrotreating process involves treatment of the feedstock with hydrogen in the presence of a catalyst and results in the conversion of the sulfur in the sulfur-containing impurities to hydrogen sulfide, which can be separated and converted to elemental sulfur. The hydrotreating process can result in the destruction of olefins in the feedstock by converting them to saturated hydrocarbons through hydrogenation. This destruction of olefins by hydrogenation is usually undesirable because: (1) it results in the consumption of expensive hydrogen, and (2) the olefins are usually valuable as high octane components of gasoline. As an example, a typical naphtha of gasoline boiling range from a catalytic cracking process has a relatively high octane number as a result of a large olefin content. Hydrotreating such a material causes a reduction in the olefin content in addition to the desired desulfurization, and the octane number of the hydrotreated product decreases as the degree or severity of the desulfurization increases.

[0006] U.S. Patent No. 5,865,988 (Collins et al.) is directed to a two step process for the production of low sulfur gasoline from an olefinic, cracked, sulfur-containing naphtha. The process involves: (a) passing the naphtha over a shape selective acidic catalyst, such as ZSM-5 zeolite, to selectively crack low octane paraffins and to convert some of the olefins and naphthenes to aromatics and aromatic side chains; and (2) hydrosulfurizing the resulting product over a hydrotreating catalyst in the presence of hydrogen. It is disclosed that the initial treatment with the shape selective acidic catalyst removes the olefins which would otherwise be saturated in the hydrosulfurization step.

[0007] International Patent Application No. WO 98/30655 (Huff et al.), published under the Patent Cooperation Treaty, discloses a process for the production of a product of reduced sulfur content from a feedstock wherein the feedstock

is comprised of a mixture of hydrocarbons and contains organic sulfur compounds as unwanted impurities. This process involves converting at least a portion of the sulfur-containing impurities to sulfur-containing products of a higher boiling point by treatment with an alkylating agent in the presence of an acid catalyst and removing at least a portion of these higher boiling products by fractionation on the basis of boiling point.

[0008] U.S. Patent Nos. 5,298,150 (Fletcher et al.); 5,346,609 (Fletcher et al.); 5,391,288 (Collins et al.); and 5,409,596 (Fletcher et al.) are all directed to a two step process for the preparation of a low sulfur gasoline wherein a naphtha feedstock is subjected to hydrosulfurization followed by treatment with a shape selective catalyst to restore the octane which is lost during the hydrosulfurization step.

[0009] U.S. Patent No. 5,171,916 (Le et al.) is directed to a process for upgrading a light cycle oil by: (1) alkylating the heteroatom containing aromatics of the cycle oil with an aliphatic hydrocarbon having at least one olefinic double bond through the use of a crystalline metallosilicate catalyst; and (2) separating the high boiling alkylation product by fractional distillation. It is disclosed that the unconverted light cycle oil has a reduced sulfur and nitrogen content, and the high boiling alkylation product is useful as a synthetic alkylated aromatic functional fluid base stock.

[0010] U.S. Patent No. 5,599,441 (Collins et al.) discloses a process for removing thiophenic sulfur compounds from a cracked naphtha by: (1) contacting the naphtha with an acid catalyst in an alkylation zone to alkylate the thiophenic compounds using the olefins present in the naphtha 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. It is also disclosed that the sulfur-rich high boiling fraction from the fractional distillation may be desulfurized using conventional hydrotreating or other desulfurization processes.

[0011] U.S. Patent No. 5,863,419 (Huff, Jr. et al.) discloses a catalytic distillation process for the production of a product of reduced sulfur content from a feedstock wherein the feedstock is comprised of a mixture of hydrocarbons which contains organic sulfur compounds as unwanted impurities. The process involves carrying out the following process steps simultaneously within a distillation column reactor: (1) converting at least a portion of the sulfur-containing impurities to sulfur-containing products of a higher boiling point by treatment with an alkylating agent in the presence of an acid catalyst; and (2) removing at least a portion of these higher boiling products by fractional distillation. It is also disclosed that the sulfur-rich high boiling fraction can be efficiently hydrotreated at relatively low cost because of its reduced volume relative to that of the original feedstock.

[0012] More recently, U.S. Patent No. 6,024,865 in the name of Bruce D. Alexander, George A. Huff, Vivek R. Pradhan, William J. Reagan and Roger H. Cayton disclosed a product of reduced sulfur content which is produced from a feedstock which is comprised of a mixture of hydrocarbons and includes sulfur-containing aromatic compounds as unwanted impurities. The process involves separating the feedstock by fractional distillation into a lower boiling fraction which contains the more volatile sulfur-containing aromatic impurities and at least one higher boiling fraction which contains the less volatile sulfur-containing aromatic impurities. Each fraction is then separately subjected to reaction conditions which are effective to convert at least a portion of its content of sulfur-containing aromatic impurities to higher boiling sulfur-containing products by alkylation with an alkylating agent in the presence of an acidic catalyst. The higher boiling sulfur-containing products are removed by fractional distillation. It is also stated that alkylation can be achieved in stages with the proviso that the conditions of alkylation are less severe in the initial alkylation stage than in a secondary stage, e.g., through the use of a lower temperature in the first stage as opposed to a higher temperature in a secondary stage.

[0013] U.S. Patent No. 6,059,962 in the name of Bruce D. Alexander, George A. Huff, Vivek R. Pradhan, William J. Reagan and Roger H. Clayton disclosed a product of reduced sulfur content wherein the product is produced in a multiple stage process from a feedstock which is comprised of a mixture of hydrocarbons and includes sulfur-containing aromatic compounds as unwanted impurities. The first stage involves: (1) subjecting the feedstock to alkylation conditions which are effective to convert a portion of the impurities to higher boiling sulfur-containing products, and (2) separating the resulting products by fractional distillation into a lower boiling fraction and a higher boiling fraction. The lower boiling fraction is comprised of hydrocarbons and is of reduced sulfur content relative to the feedstock. The higher boiling fraction is comprised of hydrocarbons and contains unconverted sulfur-containing aromatic impurities and also the higher boiling sulfur-containing products. Each subsequent stage involves: (1) subjecting the higher boiling fraction from the preceding stage to alkylation conditions which are effective to convert at least a portion of its content of sulfur-containing aromatic compounds to higher boiling sulfur-containing products, and (2) separating the resulting products by fractional distillation into a lower boiling hydrocarbon fraction and a higher boiling fraction which contains higher boiling sulfur-containing alkylation products. The total hydrocarbon product of reduced sulfur content from the process is comprised of the lower boiling fractions from various stages.

[0014] Another approach to reducing the sulfur-containing organic impurities content of a feedstock comprised of a normally liquid mixture of hydrocarbons which includes olefins is disclosed in International Publication Number WO 01/53432, A1. This approach involves (a) contacting the feedstock with an olefin-modification catalyst in an olefin-modification reaction zone under conditions which are effective to produce a product having a bromine number which is lower than that of the feedstock; (b) fractionating the product from the olefin-modification reaction zone to produce:

(i) a first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is in the range from about 135° C to about 221° C; and (ii) a second fraction which is higher boiling than the first fraction and comprises sulfur-containing organic impurities; and (c) contacting the first fraction with a hydrodesulfurization catalyst in the presence of hydrogen in a hydrodesulfurization reaction zone under conditions which are effective to convert at least a portion of the sulfur in the sulfur-containing impurities of the first fraction to hydrogen sulfide.

[0015] It has now been discovered that the sulfur-containing organic impurities while undergoing reaction in the olefin-modification zone form refractive sulfur compounds. The formation of these refractive compounds is undesirable because they can only be treated by conventional hydrodesulfurization means which results in undesirable concomitant octane loss. These refractive sulfur compounds cannot be removed via a selective hydrotreating process. It has further been discovered that these refractive sulfur compounds concentrate in the fraction of the olefin-modification reaction zone product having a boiling range above about 200° C. The removal of these compounds can only be achieved through conventional hydrodesulfurization that results in the saturation of olefins and the loss of octane. Trace amounts of olefin-modification catalyst are also leached off of the catalyst in the olefin modification reaction zone and pass into the olefin-modification zone product. There is a potential for these compounds or components containing the leached olefin-modification catalyst to cause both catalyst deactivation and pressure drop in any downstream units such as downstream hydrotreaters. Additionally it has been discovered that these compounds like the refractive sulfur compounds tend to concentrate in the 200° C plus boiling range fraction.

[0016] By utilizing the process of the present invention the problems associated with refractive sulfur compounds and compounds or components containing leached olefin-modification catalyst can be ameliorated by fractionating the product from the olefin-modification zone into at least three fractions. The advantage of splitting the olefin-modification zone product into at least three fractions is that the refractive compounds and leached catalyst containing compounds or components can be recovered in a relatively small volume stream of the highest boiling fraction of the olefin modification zone product. The remainder of the olefin-modification zone product is split into at least two fractions wherein the lowest boiling fraction is relatively desulfurized and can be passed directly to the gasoline pool, and the intermediate boiling fraction can be passed to a selective hydrotreating zone, wherein the octane number is retained while the sulfur-containing organic impurities are converted to hydrogen sulfide. Although not preferred alternatively, the intermediate fraction can be passed to a conventional hydrotreater and subsequently to a reformer to upgrade the octane of this fraction. In accordance with the process of the invention the bulk of the olefin-modification zone effluent, e.g. 90 vol. % to 98 vol. %, can be split into two fractions containing a paucity of refractive sulfur and leached olefin modification catalyst and not be subjected to an octane reducing hydrodesulfurization step.

[0017] The highest boiling fraction, ideally, can be routed to a conventional diesel or naphtha hydrotreater or back to the fluidized catalytic cracking unit for removal of both the refractive and non-refractive sulfur compounds. The leached olefin-modification compounds or components can be removed with activated aluminum via conventional means known to those skilled in the art prior to being passed to the hydrotreater.

Summary of the Invention

[0018] Hydrocarbon liquids which boil at standard pressure over either a broad or a narrow range of temperatures within the range from about 10° C to about 345° C are referred to herein as "hydrocarbon liquids." Such liquids are frequently encountered in the refining of petroleum and also in the refining of products from coal liquefaction and the processing of oil shale or tar sands, and these liquids are typically comprised of a complex mixture of hydrocarbons, and these mixtures can include paraffins, cycloparaffins, olefins and aromatics. For example, light naphtha, heavy naphtha, gasoline, kerosene and light cycle oil are all hydrocarbon liquids.

[0019] Hydrocarbon liquids which are encountered in a refinery frequently contain undesirable sulfur-containing impurities which must be at least partially removed. Hydrotreating procedures are effective and are commonly used for removing sulfur-containing impurities from hydrocarbon liquids. Unfortunately, conventional hydrotreating processes are usually unsatisfactory for use with highly olefinic hydrocarbon liquids because such processes result in significant conversion of the olefins to paraffins which are usually of lower octane. In addition, the hydrogenation of the olefins results in the consumption of expensive hydrogen.

[0020] in accordance with International Publication Number WO 01/53432, A1 organic sulfur compounds can be removed from hydrocarbon liquids by a multiple step process which comprises (a) contacting the feedstock with an olefin-modification reaction zone under conditions which are effective to produce a product having a bromine number which is lower than that of the feedstock; (b) fractionating the product into two fractions: namely a first fraction having a distillation endpoint of 135 C to 221 C and a higher boiling fraction; and (c) carrying out a hydrodesulfurization reaction with the lower boiling fraction.

[0021] Unfortunately such a process results in undesirable octane loss because the first fraction is subjected to conventional hydrotreating which serves to reduce octane via olefin saturation. Additionally such a process does not address or present a solution to the problems associated with converting refractive sulfur compounds to hydrogen

sulfide while retaining octane. Further, such a process does not address the difficulties presented downstream of the olefin-modification zone by the leached catalyst compounds or components such as increased pressure drop and catalyst deactivation in downstream units.

[0022] Accordingly, there is a need for a process which can achieve a substantially complete removal of sulfur-containing impurities from olefin-containing hydrocarbon liquids which: (1) is relatively inexpensive to carry out, (2) results in little if any octane loss; and (3) addresses the problems associated with refractive sulfur compounds and leached catalyst compounds or components. For example, there is a need for such a process which can be used to remove sulfur-containing impurities from hydrocarbon liquids, such as products from a fluidized catalytic cracking process, which are highly olefinic and contain relatively large amounts of sulfur-containing organic materials such as mercaptans, thiophenic compounds, and benzothiophenic compounds as unwanted impurities.

[0023] It has now been discovered that such an improved process involves modifying the olefin content of the feedstock over an olefin-modification catalyst in an olefin-modification step, fractionating the products from the olefin-modification step into at least three fractions on the basis of boiling point, selectively hydrotreating the intermediate boiling fraction, and hydrodesulfurizing the highest boiling of the resulting fractions. The olefin-modification step results in a reduction of the olefinic unsaturation of the feedstock, as measured by bromine number. As a consequence of the olefin-modification step, a sulfur-lean product is obtained from the subsequent selective hydrotreating step which has little loss of octane relative to that of the feedstock to the olefin-modification step. In addition, the reduction of olefinic unsaturation in the olefin-modification step results in a corresponding reduction of hydrogen consumption in the respective selective hydrotreating and hydrodesulfurization steps since there is a reduced number of olefinic double bonds to consume hydrogen in hydrogenation reactions.

[0024] One embodiment of the invention is a process for producing a product of reduced sulfur content from a feedstock, wherein said feedstock contains sulfur-containing organic impurities and is comprised of a normally liquid mixture of hydrocarbons which includes olefins, said process comprising:

- (a) contacting the feedstock with an olefin-modification catalyst in an olefin-modification reaction zone under conditions which are effective to produce a product having a bromine number which is lower than that of the feedstock;
- (b) fractionating the product from said olefin-modification reaction zone to produce:

- (i) a first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 140° C;
- (ii) a second fraction which is higher boiling than the first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 240° C; and
- (iii) a third fraction which is higher boiling than the second fraction and comprises sulfur-containing organic impurities and refractive sulfur compounds;

(c) contacting the second fraction with a selective hydrotreating catalyst in the presence of hydrogen in a selective hydrotreating reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur-containing impurities of the second fraction to hydrogen sulfide; and

(d) contacting the third fraction with a hydrodesulfurization catalyst in the presence of hydrogen in a hydrodesulfurization reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur-containing impurities of the third fraction to hydrogen sulfide.

[0025] Another embodiment of the invention is a process for producing products of reduced sulfur content from a feedstock, wherein said feedstock contains sulfur-containing organic impurities and is comprised of a normally liquid mixture of hydrocarbons which includes olefins, said process comprising:

- (a) contacting the feedstock with an olefin-modification catalyst in an olefin-modification reaction zone under conditions which are effective to produce a product which has a lower bromine number than that of the feedstock, wherein said olefin-modification catalyst is an acid catalyst;

- (b) fractionating the product from said olefin-modification reaction zone to produce:

- (i) a first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 120° C;
- (ii) a second fraction which is higher boiling than the first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 200° C; and;
- (iii) a third fraction which is higher boiling than the second fraction and comprises sulfur-containing organic impurities and refractive sulfur compounds;

(c) contacting the second fraction with a selective hydrotreating catalyst in the presence of hydrogen in a selective hydrotreating reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur-containing impurities of the second fraction to hydrogen sulfide; and

(d) contacting the third fraction with a hydrodesulfurization catalyst in the presence of hydrogen in a hydrodesulfurization reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur-containing impurities of the third fraction to hydrogen sulfide.

[0026] In another embodiment although not preferred, the second fraction can be passed to a hydrodesulfurization zone followed by a reforming zone to increase the octane number of the fraction which was reduced in the hydrodesulfurization zone.

[0027] An object of the invention is to provide an improved process for the removal of sulfur-containing impurities from a hydrocarbon liquid which contains a significant olefin content.

[0028] Another object of the invention is to provide an improved method for the efficient removal of sulfur-containing impurities from an olefinic cracked naphtha.

[0029] A further object of the invention is to provide an improved method for desulfurizing an olefinic cracked naphtha which yields a product of substantially unchanged octane.

[0030] Yet another object of the invention is to provide an improved method for handling problems associated with refractive sulfur compounds and leached catalyst compounds or components in a process for removing sulfur-containing impurities in a hydrocarbon liquid.

Brief Description of the Drawing

[0031] The drawing is a schematic representation of an embodiment of the invention.

Detailed Description of the Invention

[0032] A process for the production of a product of reduced sulfur content from an olefin-containing distillate hydrocarbon liquid which contains sulfur-containing impurities has been discovered. The process can be used to produce a product which is substantially free of sulfur-containing impurities, has a reduced olefin content, and has an octane which is similar to that of the feedstock.

[0033] The invention involves contacting the feedstock with an olefin-modification catalyst in a reaction zone under conditions which are effective to produce an intermediate product which has a reduced amount of olefinic unsaturation relative to that of the feedstock as measured by bromine number. The intermediate product is then separated into at least three fractions of different volatility. The fraction of highest volatility (i.e., the lowest boiling fraction) is relatively free of sulfur-containing organic impurities i.e. generally below 20 parts per million by weight sulfur and therefore can be passed directly to the gasoline pool. The second fraction or intermediate boiling range fraction, is contacted with a selective hydrotreating catalyst in the presence of hydrogen under conditions effective to convert at least a portion of its sulfur-containing organic impurities to hydrogen sulfide. The hydrogen sulfide can be easily removed by conventional methods to provide a product of substantially reduced sulfur content relative to the feedstocks. The third fraction or highest boiling fraction is contacted with a hydrodesulfurization catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of the sulfur-containing organic impurities and refractive sulfur compounds to hydrogen sulfide. The hydrogen sulfide can be easily removed by conventional methods to provide a product of substantially reduced sulfur content relative to the feedstocks.

[0034] Aromatic sulfur-containing impurities in the feedstock, such as thiophenic and benzothiophenic compounds, undergo conversion, at least in part, within the olefin-modification reaction zone to higher boiling sulfur-containing products some of which can be characterized as refractive sulfur compounds as further defined hereinafter. This conversion is believed to be a result of alkylation of the aromatic sulfur-containing impurities by olefins which is catalyzed by the olefin-modification catalyst. Upon fractionation of the effluent from the olefin-modification reaction zone, most of these high boiling sulfur-containing materials including the refractive sulfur compounds appear in the third boiling fraction or highest boiling fraction, and the first or lowest boiling fraction and the intermediate boiling fraction have a reduced sulfur content relative to that of the feedstock to the olefin-modification zone.

[0035] In a highly preferred embodiment, the second fraction is contacted with a selective hydrotreating catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of the fraction's sulfur-containing impurities to hydrogen sulfide. This can be accomplished by utilizing one of the selective hydrotreating processes that are presently being licensed such as the SCANfining process licensed by ExxonMobil Research and Engineering Company and the PRIME-G+ process licensed by IFP North America Inc. or by operating a conventional hydrotreating process at selective hydrotreating conditions that are relatively less severe such that the desulfurization

occurs while limiting olefin saturation. Such selective hydrotreating processes are also disclosed in U.S. Patent No. 6,007,704 (Chapus et al.), U.S. Patent No. 5,821,397 (Joly et al.), and U.S. Patent No. 6,255,548 (Didillon et al.)

[0036] The third fraction is contacted with a hydrodesulfurization catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of its sulfur-containing impurities including refractive sulfur compounds to hydrogen sulfide. A large portion of the sulfur-containing impurities of the higher boiling fraction or fractions will frequently be comprised of aromatic sulfur-containing compounds, such as thiophenic and benzothiophenic compounds and refractive sulfur compounds, which are more difficult to remove by hydrodesulfurization than mercaptans and thiophenic compounds. Accordingly, a preferred embodiment of the invention will comprise the use of more vigorous hydrodesulfurization conditions.

[0037] Feedstocks which can be used in the practice of this invention are comprised of normally liquid hydrocarbon mixtures which contain olefins and boil over a range of temperatures within the range from about 10° C to about 345° C as measured by the ASTM D 2887 - 97a procedure (which can be found in the 1999 Annual Book of ASTM Standards, Section 5, Petroleum Products, Lubricants, and Fossil Fuels, Vol. 05.02, page 200, and said procedure is hereby incorporated herein by reference in its entirety) or by conventional alternative procedures. In addition, suitable feedstocks will preferably include a mixture of hydrocarbons which boils in the gasoline range. If desired, such feedstocks can also contain significant amounts of lower volatility hydrocarbon components which have a higher boiling point than said high volatility fraction. The feedstock will be comprised of a normally liquid mixture of hydrocarbons which desirably has a distillation endpoint which is about 345° C or lower, and is preferably about 249° C or lower. Preferably, the feedstock will have an initial boiling point which is below about 79° C and a distillation endpoint which is not greater than about 345° C. Suitable feedstocks include any of the various complex mixtures of hydrocarbons which are conventionally encountered in the refining of petroleum, such as natural gas liquids, naphthas, light gas oils, heavy gas oils, and wide-cut gas oils, as well as hydrocarbon fractions which are derived from coal liquefaction and the processing of oil shale or tar sands. Preferred feedstocks are comprised of olefin-containing hydrocarbon mixtures which are derived from the catalytic cracking or the coking of hydrocarbon feedstocks.

[0038] Catalytic cracking products are highly preferred as a source of feedstock hydrocarbons for use in the subject invention. Materials of this type include liquids which boil below about 345° C, such as light naphtha, heavy naphtha and light cycle oil. However, it will also be appreciated that the entire output of volatile products from a catalytic cracking process can be utilized as a source of feedstock hydrocarbons for use in the practice of this invention. Catalytic cracking products are a desirable source of feedstock hydrocarbons because they typically have a relatively high olefin content and they usually contain substantial amounts of organic sulfur compounds as impurities. For example, a light naphtha from the fluidized catalytic cracking of a petroleum derived gas oil can contain up to about 60 wt. % of olefins and up to about 0.7 wt. % of sulfur wherein most of the sulfur will be in the form of thiophenic and benzothiophenic compounds. In addition, the sulfur-containing impurities will usually include mercaptans and organic sulfides. A preferred feedstock for use in the practice of this invention will be comprised of catalytic cracking products and will contain at least 1 wt. % of olefins. A preferred feedstock will be comprised of hydrocarbons from a catalytic cracking process and will contain at least 10 wt. % of olefins. A highly preferred feedstock will be comprised of hydrocarbons from a catalytic cracking process and will contain at least about 15 wt. % or 20 wt. % of olefins.

[0039] In one embodiment of the invention, the feedstock for the invention will be comprised of a mixture of low molecular weight olefins with hydrocarbons from a catalytic cracking process. For example, a feedstock can be prepared by adding olefins which contain from 3 to 5 carbon atoms to a naphtha from a catalytic cracking process.

[0040] In another embodiment of the invention, the feedstock for the invention will be comprised of a mixture of a naphtha from a catalytic cracking process with a source of volatile aromatic compounds, such as benzene and toluene. For example, a feedstock can be prepared by mixing a light reformat with a naphtha from a catalytic cracking process. A typical light reformat will contain from about 0 to about 2 vol. % olefins, from about 20 to about 45 vol. % aromatics, and will have distillation properties such that the 10% distillation point ("T10") is no greater than about 160° F (71° C), the 50% distillation point ("T50") is no greater than about 200° F. (93° C), and the 90% distillation point ("T90") is no greater than about 250° F. (121° C.). It will be understood that these distillation points refer to a distillation point obtained by the ASTM D 86-97 procedure (which can be found in the 1999 Annual Book of ASTM Standards, Section 5, Petroleum Products, Lubricants, and Fossil Fuels, Vol. 05.01, page 16, and said procedure is hereby incorporated herein by reference in its entirety) or by conventional alternative procedures. A typical light reformat will contain from about 5 to about 15 vol. % of benzene.

[0041] Another embodiment of the invention involves the use of a feedstock which is comprised of a mixture of: (1) hydrocarbons from a catalytic cracking process; (2) a source of volatile aromatic compounds; and (3) a source of olefins which contain from 3 to 5 carbon atoms.

[0042] Suitable feedstocks for the invention will contain at least 1 wt. % of olefins, preferably at least 10 wt. % of olefins, and more preferably at least about 15 wt. % or 20 wt. % of olefins. If desired, the feedstock can have an olefin content of 50 wt. % or more. In addition, suitable feedstocks can contain from about 0.005 wt. % up to about 2.0 wt. % of sulfur in the form of organic sulfur compounds. However, typical feedstocks will generally contain from about 0.05

wt. % up to about 0.7 wt. % sulfur in the form of organic sulfur compounds.

[0043] Feedstocks which are useful in the practice of this invention, such as naphtha from a catalytic cracking process, will occasionally contain nitrogen-containing organic compounds as impurities in addition to the sulfur-containing impurities. Many of the typical nitrogen-containing impurities are organic bases and, in some instances, can cause a relatively rapid deactivation of the olefin-modification catalyst of the subject invention. In the event that such deactivation is observed, it can be prevented by removal of the basic nitrogen-containing impurities before they can contact the olefin-modification catalyst. Accordingly, when the feedstock contains basic nitrogen-containing impurities, a preferred embodiment of the invention comprises removing these basic nitrogen-containing impurities from the feedstock before it is contacted with the olefin-modification catalyst. In another embodiment of the invention, a feedstock is used which is substantially free of basic nitrogen-containing impurities (for example, such a feedstock will contain less than about 50 ppm by weight of basic nitrogen). A highly desirable feedstock is comprised of a treated naphtha which is prepared by removing basic nitrogen-containing impurities from a naphtha produced by a catalytic cracking process.

[0044] Basic nitrogen-containing impurities can be removed from the feedstock or from a material that is to be used as a feedstock component by any conventional method. Such methods typically involve treatment with an acidic material, and conventional methods include procedures such as washing with an aqueous solution of an acid or passing the material through a guard bed. In addition, a combination of such procedures can be used. Guard beds can be comprised of materials which include but are not limited to A-zeolite, Y-zeolite, L-zeolite, mordenite, fluorided alumina, fresh cracking catalyst, equilibrium cracking catalyst and acidic polymeric resins. If a guard bed technique is employed, it is often desirable to use two guard beds in such a manner that one guard bed can be regenerated while the other is in service. If a cracking catalyst is utilized to remove basic nitrogen-containing impurities, such a material can be regenerated in the regenerator of a catalytic cracking unit when it has become deactivated with respect to its ability to remove such impurities. If an acid wash is used to remove basic nitrogen-containing compounds, the treatment will be carried out with an aqueous solution of a suitable acid. Suitable acids for such use include but are not limited to hydrochloric acid, sulfuric acid and acetic acid. The concentration of acid in the aqueous solution is not critical, but is conveniently chosen to be in the range from about 0.1 wt. % to about 30 wt. %. For example, a 5 wt. % solution of sulfuric acid in water can be used to remove basic nitrogen containing impurities from a heavy naphtha produced by a catalytic cracking process.

[0045] The process of this invention is highly effective in removing sulfur-containing organic impurities of all types from the feedstock. Such impurities will typically include aromatic, sulfur-containing, organic compounds which include all aromatic organic compounds which contain at least one sulfur atom. Such materials include thiophenic and benzothiophenic compounds, and examples of such materials include but are not limited to thiophene, 2-methylthiophene, 3-methylthiophene, 2,3-dimethylthiophene, 2,5-dimethylthiophene, 2-ethylthiophene, 3-ethylthiophene, benzothiophene, 2-methylbenzothiophene, 2,3-dimethylbenzothiophene, and 3-ethylbenzothiophene. Other typical sulfur-containing impurities include mercaptans and organic sulfides and disulfides.

[0046] The olefin-modification catalyst of the invention can be comprised of any material which is capable of catalyzing the oligomerization of olefins. Desirably, the olefin-modification catalyst will be comprised of a material which is also capable of catalyzing the alkylation of aromatic organic compounds by olefins. Conventional alkylation catalysts are highly suitable for use as the olefin-modification catalyst of this invention because they typically have the ability to catalyze both olefin oligomerization and the alkylation of aromatic organic compounds by olefins. Although liquid acids, such as sulfuric acid can be used, solid acidic catalysts are particularly desirable, and such solid acidic catalysts include liquid acids which are supported on a solid substrate. The solid catalysts are generally preferred over liquid catalysts because of the ease with which the feed can be contacted with such a material. For example, the feed can simply be passed through one or more fixed beds of solid particulate catalyst at a suitable temperature. Alternatively, the feed can be passed through an ebulated bed of solid particulate catalyst.

[0047] Olefin-modification catalysts which are suitable for use in the practice of the invention can be comprised of materials such as acidic polymeric resins, supported acids, and acidic inorganic oxides. Suitable acidic polymeric resins include the polymeric sulfonic acid resins which are well-known in the art and are commercially available. Amberlyst® 35, a product produced by Rohm and Haas Co., is a typical example of such a material.

[0048] Supported acids which are useful as olefin-modification catalysts include but are not limited to Brønsted acids (examples include phosphoric acid, sulfuric acid, boric acid, HF, fluorosulfonic acid, trifluoromethanesulfonic acid, and dihydroxyfluoroboric acid) and Lewis acids (examples include BF_3 , BCl_3 , AlCl_3 , AlBr_3 , FeCl_2 , FeCl_3 , ZnCl_2 , SbF_5 , SbCl_5 and combinations of AlCl_3 and HCl) which are supported on solids such as silica, alumina, silica-aluminas, zirconium oxide or clays. When supported liquid acids are employed, the supported catalysts are typically prepared by combining the desired liquid acid with the desired support and drying. Supported catalysts which are prepared by combining a phosphoric acid with a support are highly preferred and are referred to herein as solid phosphoric acid catalysts. These catalysts are preferred because they are both highly effective and low in cost. U.S. Patent No. 2,921,081 (Zimmerschied et al.), which is incorporated herein by reference in its entirety, discloses the preparation of solid phosphoric acid catalysts by combining a zirconium compound selected from the group consisting of zirconium oxide and the halides

of zirconium with an acid selected from the group consisting of orthophosphoric acid, pyrophosphoric acid and triphosphoric acid. U.S. Patent No. 2,120,702 (Ipatieff et al.), which is incorporated herein by reference in its entirety, discloses the preparation of solid phosphoric acid catalysts by combining a phosphoric acid with a siliceous material. Finally, British Patent No. 863,539, which is incorporated herein by reference in its entirety, also discloses the preparation of a solid phosphoric acid catalyst by depositing a phosphoric acid on a solid siliceous material such as diatomaceous earth or kieselguhr.

[0049] With respect to a solid phosphoric acid that is prepared by depositing a phosphoric acid on kieselguhr, it is believed that the catalyst contains: (1) one or more free phosphoric acids (such as orthophosphoric acid, pyrophosphoric acid and triphosphoric acid) supported on kieselguhr; and (2) silicon phosphates which are derived from the chemical reaction of the acid or acids with the kieselguhr. While the anhydrous silicon phosphates are believed to be inactive as an olefin-modification catalyst, it is also believed that they can be hydrolyzed to yield a mixture of orthophosphoric and polyphosphoric acids which is active as an olefin-modification catalyst. The precise composition of this mixture will depend upon the amount of water to which the catalyst is exposed. In order to maintain a solid phosphoric acid alkylation catalyst at a satisfactory level of activity when it is used as an olefin-modification catalyst with a substantially anhydrous feedstock, it is conventional practice to add a small amount of an alcohol, such as isopropyl alcohol, to the feedstock to maintain the catalyst at a satisfactory level of hydration. It is believed that the alcohol undergoes dehydration upon contact with the catalyst, and that the resulting water then acts to hydrate the catalyst. If the catalyst contains too little water, it tends to have a very high acidity which can lead to rapid deactivation as a consequence of coking and, in addition, the catalyst will not possess a good physical integrity. Further hydration of the catalyst serves to reduce its acidity and reduces its tendency toward rapid deactivation through coke formation. However, excessive hydration of such a catalyst can cause the catalyst to soften, physically agglomerate, and create high pressure drops in fixed bed reactors. Accordingly, there is an optimum level of hydration for a solid phosphoric acid catalyst, and this level of hydration will be a function of the reaction conditions. Although the invention is not to be so limited, with solid phosphoric acid catalysts, we have found that a water concentration in the feedstock which is in the range from about 50 to about 1,000 ppm by weight will generally maintain a satisfactory level of catalyst hydration. If desired, this water can be provided in the form of an alcohol such as isopropyl alcohol which is believed to undergo dehydration upon contact with the catalyst.

[0050] Acidic inorganic oxides which are useful as olefin-modification catalysts include but are not limited to aluminas, silica-aluminas, natural and synthetic pillared clays, and natural and synthetic zeolites such as faujasites, mordenites, L, omega, X, Y, beta, and ZSM zeolites. Highly suitable zeolites include beta, Y, ZSM-3, ZSM-4, ZSM-5, ZSM-18, and ZSM-20. If desired, the zeolites can be incorporated into an inorganic oxide matrix material such as a silica-alumina.

[0051] Olefin-modification catalysts can comprise mixtures of different materials, such as a Lewis acid (examples include BF_3 , BCl_3 , SbF_5 and AlCl_3), a nonzeolitic solid inorganic oxide (such as silica, alumina and silica-alumina), and a large-pore crystalline molecular sieve (examples include zeolites, pillared clays and aluminophosphates).

[0052] In the event that a solid olefin-modification catalyst is used, it will desirably be in a physical form which will permit a rapid and effective contacting with feed in the olefin-modification reaction zone. Although the invention is not to be so limited, it is preferred that a solid catalyst be in particulate form wherein the largest dimension of the particles has an average value which is in the range from about 0.1 mm to about 2 cm. For example, substantially spherical beads of catalyst can be used which have an average diameter from about 0.1 mm to about 2 cm. Alternatively, the catalyst can be used in the form of rods which have a diameter in the range from about 0.1 mm to about 1 cm and a length in the range from about 0.2 mm to about 2 cm.

[0053] In the practice of the invention, the feedstock is contacted with an olefin-modification catalyst in an olefin-modification reaction zone under conditions which are effective to produce a product having a bromine number which is lower than that of the feedstock without causing any significant cracking of any paraffins in the feedstock. It will be understood that the "bromine number" referred to herein is preferably determined by the ASTM D 1159-98 procedure, which can be found in the 1999 Annual Book of ASTM Standards, Section 5, Petroleum Products, Lubricants, and Fossil Fuels, Vol. 05.01, page 407, and said procedure is hereby incorporated herein by reference in its entirety. However, other conventional analytical procedures for the determination of bromine number can also be used. The bromine number of the product from the olefin-modification reaction zone will desirably be no greater than 80% that of the feedstock to said reaction zone, preferably no greater than 70% that of said feedstock, and more preferably no greater than 65% that of said feedstock.

[0054] The reaction zone can consist of one or more fixed bed reactors containing the same or different catalysts. A fixed reactor can also comprise a plurality of catalyst beds. The plurality of catalyst beds in a single fixed bed reactor can also comprise the same or different catalysts.

[0055] The conditions utilized in the olefin-modification reaction zone are also preferably selected so that at least a portion of the olefins in the feedstock is converted to products which are of a suitable volatility to be useful as components of fuels, such as gasoline and diesel fuels.

[0056] Although the invention is not to be so limited, it is believed that the olefins in the feedstock to the olefin-

modification reaction zone are at least partially consumed in a variety of chemical reactions upon contact of the feedstock with the olefin-modification catalyst in said zone. And it is believed that the specific chemical reactions will depend upon the composition of the feedstock. These chemical processes are believed to include olefin polymerization and the alkylation of aromatic compounds by olefins.

[0057] The condensation reaction of an olefin or a mixture of olefins over an olefin-modification catalyst to form higher molecular weight products is referred to herein as a polymerization process, and the products can be either low molecular weight oligomers or high molecular weight polymers. Oligomers are formed by the condensation of 2, 3 or 4 olefin molecules with each other, while polymers are formed by the condensation of 5 or more olefin molecules with each other. As used herein, the term "polymerization" is used to broadly refer to a process for the formation of oligomers and/or polymers. Olefin polymerization results in a consumption of olefinic unsaturation. For example, the simple condensation of two molecules of propene results in the formation of a six carbon olefin which has only a single olefinic double bond (2 double bonds in the starting materials have been replaced by 1 double bond in the product). Similarly, the simple condensation of three molecules of propene results in the formation of a nine carbon olefin which has only a single olefinic double bond (3 double bonds in the starting materials have been replaced by 1 double bond in the product).

[0058] Although olefin polymerization is a simple model for understanding the reduction in bromine number that occurs in the olefin-modification reaction zone, it is believed that other processes are also important. For example, the initial products of simple olefin condensation can undergo isomerization in the presence of the olefin-modification catalyst to yield highly branched monounsaturated olefins. In addition, polymerization reactions may occur to yield polymers which subsequently undergo fragmentation in the presence of the olefin-modification catalyst to yield highly branched products which are of a lower molecular weight than the initial polymerization product. Although the invention is not to be so limited, it is believed that the following transformations occur within the olefin-modification reaction zone: (1) olefins in the feedstock which are of low molecular weight are converted to olefins of higher molecular weight which are both highly branched and within the gasoline boiling range; and (2) unbranched or modestly branched olefins in the feedstock are isomerized to highly branched olefins which are within the gasoline boiling range.

[0059] The alkylation of aromatic compounds is also an important chemical process which can occur in the olefin-modification reaction zone and acts to reduce the bromine number of the feedstock. The alkylation of an aromatic organic compound by an olefin, which contains a single double bond, results in the destruction of the double bond of the olefin and results in the substitution of an alkyl group for a hydrogen atom on the aromatic ring system of the substrate. This destruction of the olefinic double bond of the olefin contributes to the formation of a product in the olefin-modification reaction zone which has a reduced bromine number relative to that of the feedstock. However, aromatic organic compounds vary widely in their reactivity as alkylation substrates. For example, the relative reactivities of some representative aromatic compounds toward alkylation by 1-heptene at 204° C over a solid phosphoric acid catalyst are set forth in Table I, wherein each rate constant was derived from the slope of the line obtained by plotting experimental data in the form of $\ln(1-x)$ as a function of time where x is the substrate concentration.

[0060] As used herein, the term "sulfur-containing aromatic compound" and "sulfur-containing aromatic impurity" refer to any aromatic organic compound which contains at least one sulfur atom in its aromatic ring system. Such materials include thiophenic and benzothiophenic compounds.

[0061] Sulfur-containing aromatic compounds are usually alkylated more rapidly than aromatic hydrocarbons. Accordingly, the sulfur-containing aromatic impurities can, to a limited degree, be selectively alkylated in the olefin-modification reaction zone. However, if desired, the reaction conditions in the reaction zone can be selected so that significant alkylation of aromatic hydrocarbons does take place. This embodiment of the invention can be very useful if the feedstock contains volatile aromatic hydrocarbons, such as benzene, and it is desired to destroy such material by conversion to higher molecular weight alkylation products. This embodiment is particularly useful when the feedstock contains significant amounts of low molecular weight olefins, such as olefins which contain from 3 to 5 carbon atoms. The products from mono- or dialkylation of benzene with such low molecular weight olefins will contain from 9 to 16 carbon atoms and, accordingly, will be of sufficient volatility to be useful as components of gasoline or diesel fuels.

TABLE I.

Alkylation Rate Constants for Various Aromatic Substrates upon Reaction with 1-Heptene at 204° C over a Solid Phosphoric Acid Catalyst.

Compound	Rate Constant, min ⁻¹
Thiophene	0.077
2-Methylthiophene	0.046
2,5-Dimethylthiophene	0.004
Benzothiophene	0.008

TABLE I. (continued)

Alkylation Rate Constants for Various Aromatic Substrates upon Reaction with 1-Heptene at 204° C over a Solid Phosphoric Acid Catalyst.	
Compound	Rate Constant, min ⁻¹
Benzene	0.001
Toluene	0.002

[0062] The alkylation of sulfur-containing aromatic impurities in the feedstock to the olefin-modification reaction zone results in the formation of higher boiling sulfur-containing products. Accordingly, such materials can be removed by fractionation of the reaction zone effluent on the basis of boiling point. As a very crude approximation, each carbon atom in the side chain of a monoalkylated thiophene adds about 25° C to the 84° C boiling point of thiophene. As an example, 2-octylthiophene has a boiling point of 259° C, which corresponds to a boiling point increase of 23° C over that of thiophene for each carbon atom in the eight carbon alkyl group. Accordingly, monoalkylation of thiophene with a C₇ to C₁₅ olefin in the olefin-modification reaction zone will usually yield a sulfur-containing alkylation product which has a high enough boiling point to be easily removed by fractional distillation as a component of a high boiling fraction which has an initial boiling point of about 210° C.

[0063] The alkylation of a sulfur-containing aromatic compound by an olefin is illustrated by the mono-alkylation of thiophene with propene to yield either 2-isopropylthiophene or 3-isopropylthiophene. The higher molecular weight of such an alkylation product is reflected by a higher boiling point relative to that of the starting material. In one embodiment of the invention, reaction conditions in the olefin-modification reaction zone are selected so that a major portion of any sulfur-containing aromatic impurities in the feedstock are converted to higher boiling sulfur-containing products.

[0064] Mercaptans are a class of organic sulfur-containing compounds which frequently appear in significant quantity as impurities in the hydrocarbon liquids which are conventionally encountered in the refining of petroleum. For example, straight run gasolines, which are prepared by simple distillation of crude oil, will frequently contain significant amounts of mercaptans and sulfides as impurities. In addition, benzothiophenic compounds and some multisubstituted thiophenes, such as certain 2,5-dialkylthiophenes, will also be relatively unreactive under the conditions employed in the olefin-modification reaction zone. Accordingly, a large proportion of the mercaptans in the feedstock and significant amounts of certain relatively unreactive sulfur-containing aromatic compounds can survive the reaction conditions in the olefin-modification reaction zone.

[0065] In the practice of this invention, the feedstock is contacted with the olefin-modification catalyst within the olefin-modification reaction zone at a temperature and for a period of time which are effective to result in the desired reduction of the feedstock's olefinic unsaturation as measured by bromine number. The contacting temperature will be desirably in excess of about 50° C, preferably in excess of 100° C and more preferably in excess of 125° C. The contacting will generally be carried out at a temperature in the range from about 50° C to about 350° C, preferably from about 100° C to about 350° C, and more preferably from about 125° C to about 250° C. It will be appreciated, of course, that the optimum temperature will be a function of the olefin-modification catalyst used, the olefin concentration in the feedstock, the type of olefins present in the feedstock, and the type of aromatic compounds in the feedstock that are to be alkylated.

[0066] The feedstock can be contacted with the olefin-modification catalyst in the olefin-modification reaction zone at any suitable pressure. However, pressures in the range from about 0.01 to about 200 atmospheres are desirable, and a pressure in the range from about 1 to about 100 atmospheres is preferred. When the feedstock is simply allowed to flow through a catalyst bed, it is generally preferred to use a pressure at which the feed will be a liquid.

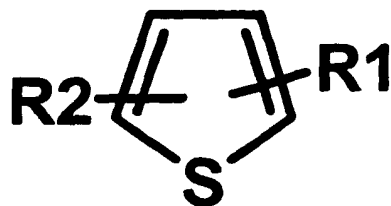
[0067] In a highly preferred embodiment of the invention, the conditions utilized in the olefin-modification reaction zone are selected so that no significant cracking of paraffins in the feedstock takes place. For example, desirably less than 10% of the paraffins in the feedstock will be cracked, preferably less than 5% of the paraffins will be cracked, and more preferably less than 1% of the paraffins will be cracked. It is believed that any significant cracking of paraffins will result in the formation of undesirable by-products, for example, the formation of low molecular weight compounds which results in gasoline volume loss.

[0068] In the practice of the invention, the effluent from the olefin-modification reaction zone is fractionated on the basis of volatility into at least three fractions.

[0069] The distillation initial boiling point of the highest boiling third fraction is desirably greater than about 200° C.

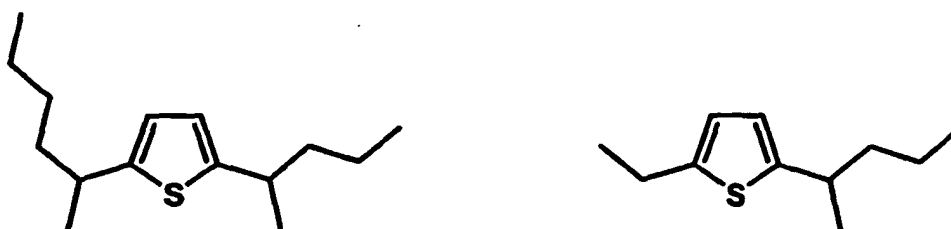
[0070] This fraction will contain a concentration of various compounds that can cause rapid catalyst deactivation in downstream selective and conventional hydrotreaters. Specifically, in the olefin-modification reaction zone, refractive sulfur species are created. These refractive sulfur compounds concentrate in the 200° C plus fraction of the olefin-modification zone product. The removal of these compounds can only be accomplished via conventional hydrotreating or hydrodesulfurization which also detrimentally results in the saturation of olefins causing octane loss.

[0071] It is believed these refractive sulfur compounds have the following structure:



[0072] Where R2 and R1 must have two or more carbons, e.g. C₂H₅, C₃H₇ etc. and one chain must have more than five carbons, e.g. C₅H₁₁, C₆H₁₃, etc.

[0073] Thus examples of refractive sulfur compounds are:



[0074] It is believed refractive sulfur is a thiophene containing seven or more alkyl carbons.

[0075] Additionally, trace amounts of the olefin-modification catalyst can be leached off in the olefin-modification zone and enter the olefin-modification zone product. This leached catalyst can cause catalyst deactivation and/or pressure drop difficulties in any downstream selective hydrotreater or hydrodesulfurization reactor. This leached catalyst tends to concentrate in the 200° C plus boiling fraction.

[0076] Other undesirable compounds that concentrate in the 200° C plus boiling range fraction include nitrogen-containing compounds and dienes.

[0077] The advantage of the process of the invention is that these compounds can be recovered in the relative small volume of the 200° C plus fraction. The volume of this fraction can range from 2 volume percent to 10 volume percent of the olefin-modification zone product. Preferably, this volume percent can range from 2 volume percent to 6 volume percent.

[0078] Thus the bulk, e.g., 90-98 volume percent, of the olefin-modification product, can be split into two fractions. The 140° C minus, or more preferably the 120° C minus boiling range first or lowest boiling fraction can be routed directly to gasoline. The lowest boiling range first fraction is typically sulfur free such that it contains less than about 50 parts per million by weight sulfur and preferably less than 30 parts per million by weight sulfur and most preferably less than 20 parts per million by weight, and can therefore be directly used as blending stock for gasoline.

[0079] The intermediate fraction or second boiling fraction, preferably has a distillation end point of less than about 240 °C and most preferably less than about 200 °C. The intermediate or second boiling fraction is passed to a selective hydrotreating zone that removes sulfur compounds while retaining the octane.

[0080] The highest boiling fraction, which has a boiling range higher than the intermediate fraction, from fractionation of the product from the olefin-modification reaction zone is contacted with a hydrodesulfurization catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of the sulfur in its sulfur-containing organic impurities including the refractive sulfur compounds to hydrogen sulfide. In a highly preferred embodiment, at least a portion of the higher boiling fraction or fractions are also contacted with a hydrodesulfurization catalyst in the presence of hydrogen under conditions which are effective to convert at least a portion of the sulfur in its sulfur-containing organic impurities to hydrogen sulfide. Alternatively the highest boiling fraction can be recycled to the fluidized catalytic cracking unit.

[0081] The hydrodesulfurization catalyst can be any conventional catalyst, for example, a catalyst comprised of a Group VI and/or a Group VIII metal which is supported on a suitable substrate. The Group VI metal is typically molybdenum or tungsten, and the Group VIII metal is typically nickel or cobalt. Typical combinations include nickel with molybdenum and cobalt with molybdenum. Suitable catalyst supports include, but are not limited to, alumina, silica, titania, calcium oxide, magnesia, strontium oxide, barium oxide, carbon, zirconia, diatomaceous earth, and lanthanide

oxides. Preferred catalyst supports are porous and include alumina, silica, and silica-alumina.

[0082] The particle size and shape of the hydrodesulfurization catalyst will typically be determined by the manner in which the reactants are contacted with the catalyst. For example, the catalyst can be used as a fixed bed catalyst or as an ebulating bed catalyst.

[0083] The hydrodesulfurization reaction conditions used in the practice of this invention are conventional in character. For example, the pressures can range from about 15 to about 1500 psi (about 1.02 to about 102.1 atmospheres); the temperature can range from about 50° C to about 450° C, and the liquid hourly space velocity can range from about 0.5 to about 15 LHSV. The ratio of hydrogen to hydrocarbon feed in the hydrodesulfurization reaction zone will typically range from about 200 to about 5000 standard cubic feet per barrel. The extent of hydrodesulfurization will be a function of the hydrodesulfurization catalyst and reaction conditions selected and also the precise nature of the sulfur-containing organic impurities in the feed to the hydrodesulfurization reaction zone. However, the hydrodesulfurization process conditions will be desirably selected so that at least about 50% of the sulfur content of the sulfur-containing organic impurities is converted to hydrogen sulfide, and preferably so that the conversion to hydrogen sulfide is at least about 75% or more.

[0084] After removal of hydrogen sulfide, the product from hydrodesulfurization of the highest boiling fraction from the olefin-modification reaction zone will have a sulfur content which is desirably less than 50 ppm by weight, preferably less than 30 ppm by weight, and more preferably less than 10 ppm by weight. The octane of this hydrodesulfurization product will be desirably at least 90% that of the feedstock to the olefin-modification reaction zone, preferably at least 95% that of said feedstock, and more preferably at least 97% that of said feedstock. Unless otherwise specified, the term octane as used herein refers to an (R+M)/2 octane, which is the sum of a material's research octane and motor octane divided by 2.

[0085] The intermediate boiling second fractionation product of the effluent from the olefin-modification reaction zone is contacted with a selective hydrotreating catalyst in the presence of hydrogen under conditions which are effective to selectively convert at least a portion of the sulfur in its sulfur-containing organic impurities to hydrogen sulfide with minimum hydrogenation of olefins.

[0086] One such selective hydrotreating process called SCANfining™ is licensed by ExxonMobil Research and Engineering Company. The SCANfining Process is a catalytic desulfurization process that utilizes a catalyst designated as RT 225 to selectively remove sulfur from fluidized catalytic cracking naphtha with minimum hydrogenation of olefins, hereby preserving octane. Yet another selective hydrotreating process is called PRIME-G+™ and is licensed by IFP North America, Inc. This process enables over 98% desulfurization of FCC naphtha while maximizing octane barrel by limiting olefin saturation. Another method for effecting the selective hydrotreating process in accordance with the process of the present invention is to contact the intermediate boiling second fraction with conventional hydrotreating catalyst at selective hydrotreating zone conditions which are generally less severe or milder than conventional hydrotreating conditions. The selective hydrotreating zone conditions include a temperature in the range of from about 100° C to about 300° C, a pressure range from about 300 psig to about 600 psig, and a liquid hourly space velocity in the range of about 3 to about 10. The ratio of hydrogen to hydrocarbon feed in the selective hydrotreating zone will range from about 700 to about 2000 standard cubic feet per barrel of feed.

[0087] After the carrying out the selective hydrotreating step and removing hydrogen sulfide, the intermediate boiling fraction will have a sulfur content which is desirably less than about 50 ppm by weight, preferably less than 30 ppm by weight, and more preferably less than 10 by weight. The octane of this intermediate fraction selective hydrotreating process will desirably be at least 95 percent of that of the feedstock to the olefin-modification zone, preferably at least 97 percent and most preferably 98 percent of that of the subject feedstock.

[0088] One embodiment of the invention is schematically illustrated in the drawing. With reference to the drawing, total catalytic naphtha from a fluidized catalytic cracking process is passed through line 1 into pretreatment vessel 2. The naphtha feedstock is comprised of mixture hydrocarbons which include olefins, paraffins, naphthenes, and aromatics, and the olefin content is in the range from about 10 wt. % to about 60 wt. %. In addition, the naphtha feedstock contains from about 0.2 wt. % to about 0.5 wt. % sulfur in the form of sulfur-containing organic impurities, which include thiophene, thiophene derivatives, benzothiophene and benzothiophene derivatives, mercaptans, sulfides and disulfides. The feedstock also contains from about 5 to about 200 ppm by weight of basic nitrogen containing impurities.

[0089] The basic nitrogen containing impurities are removed from the feedstock in pretreatment vessel 2 through contact with an acidic material, such as an aqueous solution of sulfuric acid, under mild contacting conditions which do not cause any significant chemical modification of the hydrocarbon components of the feedstock.

[0090] Effluent from pretreatment vessel 2 is passed through line 3 and is introduced into olefin-modification reactor 4, which contains an olefin-modification catalyst. The feed to reactor 4 passes through the reactor where it contacts the olefin-modification catalyst under reaction conditions which are effective to produce a product having a bromine number which is lower than that of the feed from line 3. In addition, a substantial portion of the thiophenic and benzothiophenic impurities are converted to higher boiling sulfur-containing material including refractive sulfur compounds through alkylation by the olefins in the feed.

[0091] The products from olefin-modification reactor **4** are discharged through line **5** and are passed to distillation column **6** where these products are fractionally distilled. A high boiling fraction, which comprises a hydrocarbon mixture which contains alkylated sulfur-containing impurities including refractive sulfur compounds and leached catalyst compounds or components, is withdrawn from distillation column **6** through line **7**. An intermediate boiling fraction, which is of reduced sulfur content relative to the sulfur content of the original heavy naphtha feedstock and has a distillation endpoint less than about 240 °C, is withdrawn from distillation column **6** through line **8**. The lowest boiling fraction is withdrawn from distillation column **6** through line **9**.

[0092] The highest boiling third fraction from distillation column **6** is passed through line **7** and is introduced into hydrodesulfurization reactor **11**, and hydrogen is introduced into reactor **11** through line **10**. This third fraction is contacted with a hydrodesulfurization catalyst within reactor **11** in the presence of hydrogen under conditions which are effective to convert at least a portion of the sulfur in the sulfur-containing impurities of the feed from line **7** to hydrogen sulfide. A product is withdrawn from reactor **11** through line **12** which, after removal of hydrogen sulfide, has a reduced sulfur content relative to that of the feed from line **7**. The sulfur content of this product will, typically, be less than about 30 ppm by weight.

[0093] The intermediate boiling fraction from distillation column **6** is passed through line **8** and is introduced into selective hydrotreating reactor **14**, and hydrogen is introduced into reactor **14** through line **13**. The intermediate fraction is contacted with a selective hydrotreating catalyst within reactor **14** in the presence of hydrogen under conditions which are effective to convert at least a portion of the sulfur in the sulfur-containing impurities of the feed from line **8** to hydrogen sulfide. A product is withdrawn from reactor **14** through line **15** which, after removal of hydrogen sulfide, has a reduced sulfur content relative to both the heavy naphtha feedstock to the process and the feed from line **8**. The sulfur content of this product will, typically, be less than about 30 ppm by weight.

[0094] The lowest boiling first fraction is withdrawn from the distillation column **6** through line **9**. The sulfur content of this fraction will typically be 10 ppm by weight.

[0095] The following examples are intended only to illustrate the invention and is not to be construed as imposing limitations on the invention.

Example 1

[0096] A naphtha feedstock having the following analysis was contacted in an olefin-modification zone in accordance with the present invention.

Table 11

S, ppm	580
Basic N, ppm	less than 5
Total N, ppm	10
Mercaptan S, ppm	53
RVP, psia	7.41
RON	92.4
MON	79.8
R+M/2	86.1
ASTM D86 Distillation	
IBP °C	102.7
FBP °C	269.9
Peak Group Information, ppm Thiophene	117.55
C1 Thiophene	253.58
C2 + Thiophenes	128.6

[0097] The olefin-modification zone consisted of two stages of fixed bed of solid phosphoric acid (obtained from Sud Chemie and sold under the name C84-5-01) and was operated at a temperature of 172° C in the first stage and 122° C in the second stage, a pressure of 500 psig and a liquid hourly space velocity of 1.5 LHSV.

[0098] The resulting olefin-modification reaction zone product was fractionally distilled into three fractions in accordance with the process of the invention and two fractions for comparative purposes.

[0099] Distillations of the olefin-modification zone products were carried out on a Fischer 800 Bench-scale semi-automatic distillation unit in accordance with the ASTM D2892 method.

[0100] The sample was heated in a three-liter flask with magnetic stirrer, under a Nitrogen bleed.

[0101] Fractionation took place in a column of 18mm diameter packed with 4mm Pro-pak gauze packing to give an

efficiency of 15 theoretical plates.

[0102] The vapor was liquefied on a condenser chilled to -20°C, and the distillate taken-off at a ratio of 20:4 via a timed reflux divider into a chilled receiver.

[0103] The temperature cut point was determined by measuring the vapor temperature with a resistance thermometer and associated electronic meter.

[0104] The unit had the capacity to distil under vacuum, but in this case samples were distilled at atmospheric pressure, with temperatures corrected to 760mm.

[0105] Distillation products were purged with nitrogen and stored under refrigeration prior to further testing.

[0106] The following Table III shows the relative amounts olefin-modification catalyst ("phosphorous"), total sulfur in comparative boiling range fractions: 100°C-, and 100°C+ and the three boiling range fractions in accordance with the present invention: 100°C-, 100°C to 200°C, and 200°C+.

Table III

Two Cut Splitter vs. Three Cut Splitter Product Contaminants							
	Total Sulfur (ppm)	Normal Sulfur (ppm)	Refractive Sulfur (ppm)	Phosphorous (ppm)	Nitrogen (ppm)	Bromine No.	Yields Wt%
Feed	580	580	0	<0.2	10	84.9	100
Two Cut Splitter							
OVHD:	10.6	10.6	0	<0.2	<0.3	62.3	49.9
(IBP/100° C)							
Bottoms:	1140	440	700	13.6	7.1	83.8	50.1
(100° C +)							
Three Cut Splitter							
OVHD:	158	155	3	<0.2	<0.3	62.3	49.9
(IBP/ 100°C)							
Sidedraw:	359	352	7	<0.2	0.5	64.8	39.1
(100°C/ 200°C)							
Bottoms:	3970	651	3319	61.1	33	117	11
(200°C)							

[0107] As can be observed from the above table the phosphorus and refractive sulfur is preferentially concentrated in the highest boiling range fraction when the olefin modification zone effluent is split into three fractions in accordance with the present invention. This highest boiling range is of relatively small volume, i.e., 11 % wt. % yield and therefore permits a much smaller fraction of the olefin modification zone product to be treated by the octane reducing, hydrosulfurization process. Note in the comparative bottoms fraction, the yield is 50.1 wt. % which means that one half of the olefin-modification stream effluent would have to be hydrotreated nonselectively to remove refractive sulfur resulting in undesirable octane loss for one-half of the stream versus 11 % of the stream in accordance with the process of the invention.

Example 2

[0108] A naphtha feedstock having the following analysis was contacted in an olefin-modification zone in accordance with the present invention.

Table IV

S, ppm	450
Basic N, ppm	less than 5
Total N, ppm	13
Mercaptan S, ppm	4
RVP	11.12
RON	94.4
MON	80.1
R+M/2	87.3
ASTM D86 Distillation	
IBP °C	87.6
FBP °C	255.8
Peak Group Information, ppm Thiophene	156.43
C1 Thiophenes	179.91
C2 + Thiophenes	37.4

[0109] The above feedstock was contacted in an olefin modification zone comprising fixed bed of solid phosphoric acid (obtained from Sud Chemie and sold under the name C84-5-01). The olefin-modification zone was operated at a temperature of 193° C, a pressure of 250 psig and a liquid hourly space velocity of 1.5.

[0110] The reaction zone product was fractionated into three fractions in accordance with the present invention and two fractions for comparative purposes in a unit having the following characteristics:

pot volume	- 1500 gallons
column height	34'6"
column diameter	12" with structured packing
number of theoretical plates	33

[0111] With respect to the three fractions, the product was atmospherically distilled to a head temperature of 100° C. The take-off ratios were 33 percent until head temperature equaled 80° C, 14 percent until head temperature equaled 90° C, 8 percent until head temperature equaled 100° C. The system was then set for total reflux return. The receiver containing the IBP-100° C fraction was cut. The system was then pulled under vacuum to 55 mmHG and take-off initiated. The take-off ratios were between 5 percent and 8 percent during the 100-200° C cut. The system was shutdown when the head temperature reached 106° C at 55 mmHG. The 100-200° C fraction, pot fraction 200-FBP and vacuum trap fraction were cut.

[0112] The comparative two fraction splitting was carried out in an analogous way resulting in a IBP to 100° C fraction and a 100° C + fraction.

[0113] The following table shows the sulfur distribution in the respective three fractions prepared in accordance with the present invention. It should be noted that the fractionation that was carried out was less than ideal, because the IBP -100° C fraction shows the presence of C3 + thiophenes which would ordinarily not be present in this fraction.

Table V

Sulfur Distribution Per Fraction			
Components	IBP - 100° C	100 °C - 200 °C	200°C +
H ₂ S	0	0	0
Mercaptans+1 Coeluting Unknown	17.81	0	0
Sulfides	3.17	6.33	0
Disulfides	0.72	0	0
Sulfoxides/Sulfones	0	0	0
Thiophene	11.16	0	0

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Table V (continued)

Sulfur Distribution Per Fraction			
Components	IBP - 100°C	100 °C - 200 °C	200°C +
Tetrahydrothiophene & Me-Thiophene	1.45	20.08	0
C1 Thiophene	6.59	31.38	0
C2 Thiophene	2.58	66.14	0
C3 + C4 Thiophenes	2.33	75.02	0.63
C5 Thiophene	3.72	179.93	12.39
C6 Thiophene	5.24	35.74	919.06
C7 Thiophene	3.77	2.18	412.21
C8 + C9 Thiophene	2	0.25	410.2
C10 Thiophene	2.19	0	549.25
C11 Thiophene	1.34	0	477.88
C12 Thiophene	0.74	0	743.41
Unknowns	1.62	3.44	0

[0114] The comparative 100° C + fraction was subjected to conventional hydrotreating at the following conditions:

318° C
450 psig
3 LHSV

[0115] The side-cut or 100° C to 200° C fraction obtained in accordance with the present invention was subjected to a hydrotreating step at selective hydrotreating conditions including:

307° C
450 psig
3 LHSV

[0116] The hydrotreating unit was a fixed bed, downflow hydrotreating pilot plant configured for once-through processing of naphtha or distillate feeds at hydrogen pressures up to 2000 psig, hydrogen flows to 5 scfh, liquid feed rates to 600 cc/hr and temperatures to 800 deg. F. The reactor was approximately .96" id x 18" long and can hold up to a 120 cc of catalyst charge and is heated by a salt bath. The internal catalyst bed temperature was monitored by a programmable traversing single point thermocouple. An LDC ConstaMetric 3200 precision metering pump pumps the feed in and hydrogen flow into the unit through a Brooks mass flow meter. The combined liquid and gas flows were passed through the downflow reactor and are separated in a Strahman sight gage glass. The offgas pressure is controlled via a Rosemount pressure transmitter and Badger control valve where the offgas flow goes through a caustic scrubber and is measured downstream at atmospheric pressure via an Alexander Wright wet test meter. The liquid product in the separator had a level control via Rosemount differential transmitter and a Badger control valve. The product was cooled via a tube in tube heat exchanger and collected in a refrigerator through an automated valve manifold, sequenced by computer control into one of three product receivers. The computer control/data collection was done via Analog Devices uMac 6000 and automated safeguard shutdowns were controlled via a Siemens Simatic T1505 PLC.

[0117] Table VI below shows the octane retention afforded by the invention while effecting deep desulfurization. Note that the sulfur level in the combined overhead "OVHD" and intermediate fraction "Sidedraw" would have been significantly lower had the fractionation been carried out ideally. Specifically, the combined first and second fractions ("OVHD" and "Sidedraw") show an octane loss of 87.3 to 84.5 with a desulfurization of down to 50 ppm, wt, while the comparative process only desulfurizes to 60 ppmw for a similar octane loss. The results would have been more significant had the fractionation been more ideal. Further, in order to achieve the product sulfur in the comparative combined fraction, the hydrodesulfurization conditions would have to be substantially more severe and would be:

332 °C
450 psig
1.5 LHSV

[0118] These more severe conditions would result in further octane loss on 33.1 % of the stream.

Table VI

Two Cut Splitter vs. Three Cut Splitter Octane Retention			
	Sulfur (ppm)	Octane	Wt.% Yields
Feed	450	87.3	100
Two Cut Splitter			
OVHD: (IBP/100 °C)	69	86.1	66.9
Bottoms: (100 °C +)	70	82.4	33.1
Combined Product	69	84.9	100
Three Cut Splitter			
OVHD: (IBP/100 °C)	69	86.1	66.9
Sidedraw: (100 °C/200 °C)	15	80	24.6
Bottoms: (200 °C)			8.5
OVHD/SD Combined Product	50	84.5	91.5

Claims

1. A process for producing a product of reduced sulfur content from a feedstock, wherein said feedstock contains sulfur-containing organic impurities and is comprised of a normally liquid mixture of hydrocarbons which includes olefins, said process comprising:

(a) contacting the feedstock with an olefin-modification catalyst in at least one olefin-modification reaction zone under conditions which are effective to produce a product having a bromine number which is lower than that of the feedstock and wherein the product contains refractive sulfur compounds;

(b) fractionating the product from said olefin-modification reaction zone to produce:

(i) a first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which less than about 140° C;

(ii) a second fraction which is higher boiling than the first fraction which comprises sulfur-containing organic impurities and has a distillation endpoint which is less than about 240° C; and

(iii) a third fraction which is higher boiling than the second fraction and comprises sulfur-containing organic impurities and refractive sulfur compounds;

(c) contacting said second fraction with a selective hydrotreating catalyst in the presence of hydrogen in a selective hydrotreating reaction zone under conditions which are effective to convert at least a portion of the sulfur containing impurities in the second fraction to hydrogen sulfide; and

(d) contacting said third fraction with a hydrodesulfurization catalyst in the presence of hydrogen in a hydrodesulfurization reaction zone under conditions which are effective to convert at least a portion of the sulfur in said sulfur-containing impurities of the third fraction to hydrogen sulfide.

2. The process of claim 1 wherein the feedstock contains paraffins and wherein the conditions in said olefin-modification reaction zone are effective to produce a product having a bromine number which is lower than that of the feedstock and less than 10% of the paraffins in the feedstock are cracked.

3. The process of claim 1 which additionally comprises removing hydrogen sulfide from the effluent of said selective hydrotreating reaction zone to yield a desulfurized product which contains less than about 50 parts per million by weight of sulfur.

4. The process of claim 3 wherein the octane of the desulfurized product is at least 95% that of the feedstock to the olefin-modification reaction zone.
- 5 5. The process of claim 1 wherein the feedstock contains from about 0.05 wt. % to about 0.7 wt. % of sulfur in the form of organic sulfur compounds.
6. The process of claim 1 which additionally comprises removing hydrogen sulfide from the effluent of said hydrodesulfurization reaction zone to yield a desulfurized product which contains less than about 50 parts per million by weight sulfur.
- 10 7. The process of claim 6 wherein the octane of the desulfurized product is at least 90% that of the feedstock to the olefin-modification reaction zone.
- 15 8. The process of claim 1 wherein said feedstock contains basic nitrogen-containing impurities and said process additionally comprises removing said basic nitrogen-containing impurities from the feedstock before it is contacted with the olefin-modification catalyst.
9. The process of claim 8 wherein said feedstock is comprised of hydrocarbons from a catalytic cracking process.
- 20 10. The process of claim 1 wherein said feedstock is substantially free of basic nitrogen-containing impurities.
11. The process of claim 1 wherein said feedstock is comprised of a mixture of hydrocarbons which boils in the gasoline range.
- 25 12. The process of claim 1 wherein the feedstock is comprised of a treated naphtha which is prepared by removing basic nitrogen-containing impurities from a naphtha produced by a catalytic cracking process.
13. The process of claim 1 wherein the third fraction ranges from 2 to 10 vol % of the product from the olefin-modification reaction zone.
- 30 14. The process of claim 1 wherein the feedstock has an initial boiling point which is below about 79° C and distillation endpoint which is not greater than about 345° C.
- 35 15. The process of claim 1 wherein said olefin-modification catalyst is selected from the group consisting of all solid acid catalysts; and wherein
 - (i) said first fraction which comprises sulfur-containing organic impurities has a distillation endpoint which is less than about 120° C;
 - (ii) said second fraction which is higher boiling than the first fraction which comprises sulfur-containing organic impurities has a distillation endpoint which is less than about 200° C; and
 - (iii) said third fraction which is higher boiling than the second fraction comprises sulfur-containing organic impurities and refractive sulfur compounds;
- 40 16. The process of claim 15 which additionally comprises removing hydrogen sulfide from the effluent of said selective hydrotreating reaction zone to yield a desulfurized product having an octane which is at least 98% that of the feedstock to the olefin-modification reaction zone.
- 45 17. The process of claim 15 which additionally comprises removing hydrogen sulfide from the effluent of said hydrodesulfurization reaction zone to yield a desulfurized product having an octane which is at least 97% that of the feedstock to the olefin-modification reaction zone.
- 50 18. The process of claim 15 wherein said feedstock is comprised of hydrocarbons from a catalytic cracking process.
- 55 19. The process of claim 15 wherein the feedstock is comprised of a treated naphtha which is prepared by removing basic nitrogen-containing impurities from a naphtha produced by a catalytic cracking process.

Patentansprüche

1. Ein Verfahren zur Herstellung eines Produkts mit verringertem Schwefelgehalt aus einem Einsatzmaterial, wobei das Einsatzmaterial schwefelhaltige organische Verunreinigungen enthält und eine normalerweise flüssige Mischung von Kohlenwasserstoffen umfasst, die Olefine einschließt, wobei das Verfahren Folgendes umfasst:

(a) In-Kontakt-Bringen des Einsatzmaterials mit einem Olefinmodifikationskatalysator in zumindest einer Olefinmodifikationsreaktionszone unter Bedingungen, die wirksam sind, um ein Produkt mit einer Bromzahl herzustellen, die geringer als die des Einsatzmaterials, und wobei das Produkt refraktive Schwefelverbindungen enthält;

(b) Fraktionieren des Produkts aus der Olefinmodifikationsreaktionszone zur Herstellung:

(i) einer ersten Fraktion, die schwefelhaltige organische Verunreinigungen umfasst und einen Destillationsendpunkt aufweist, der geringer als ungefähr 140 °C ist;

(ii) einer zweiten Fraktion, die höher siedet als die erste Fraktion, welche schwefelhaltige organische Verunreinigungen umfasst und einen Destillationsendpunkt aufweist, der geringer als ungefähr 240 °C ist; und

(iii) einer dritten Fraktion, die höher siedet als die zweite Fraktion und schwefelhaltige organische Verunreinigungen und refraktive Schwefelverbindungen umfasst;

(c) In-Kontakt-Bringen der zweiten Fraktion mit einem selektiven Hydrotreatingkatalysator in der Gegenwart von Wasserstoff in einer selektiven Hydrotreatingreaktionszone unter Bedingungen, die wirksam sind, um zumindest einen Teil der schwefelhaltigen Verunreinigungen in der zweiten Fraktion zu Schwefelwasserstoff umzuwandeln; und

(d) In-Kontakt-Bringen der dritten Fraktion mit einem Hydroentschwefelungskatalysator in der Gegenwart von Wasserstoff in einer Hydroentschwefelungsreaktionszone unter Bedingungen, die wirksam sind, um zumindest einen Teil des Schwefels in den schwefelhaltigen Verunreinigungen der dritten Fraktion zu Schwefelwasserstoff umzuwandeln.

2. Das Verfahren nach Anspruch 1, wobei das Einsatzmaterial Paraffine enthält und wobei die Bedingungen in der Olefinmodifikationsreaktionszone wirksam sind, um ein Produkt mit einer Bromzahl herzustellen, die geringer als die des Einsatzmaterials ist, und wobei weniger als 10 % der Paraffine in dem Einsatzmaterial gekrackt werden.

3. Das Verfahren nach Anspruch 1, das zusätzlich ein Entfernen von Schwefelwasserstoff aus dem Ausfluss der selektiven Hydrotreatingreaktionszone umfasst, um ein entschwefeltes Produkt zu ergeben, das gewichtsbezogen weniger als ungefähr 50 ppm an Schwefel enthält.

4. Das Verfahren nach Anspruch 3, bei dem das Octan des entschwefelten Produkts mindestens 95 % von dem des Einsatzmaterials zu der Olefinmodifikationsreaktionszone beträgt.

5. Das Verfahren nach Anspruch 1, bei dem das Einsatzmaterial von ungefähr 0,05 Gew.-% bis ungefähr 0,7 Gew.-% an Schwefel in der Form von organischen Schwefelverbindungen enthält.

6. Das Verfahren nach Anspruch 1, das zusätzlich ein Entfernen von Schwefelwasserstoff aus dem Ausfluss der Hydroentschwefelungsreaktionszone umfasst, um ein entschwefeltes Produkt zu ergeben, das gewichtsbezogen weniger als ungefähr 50 ppm an Schwefel enthält.

7. Das Verfahren nach Anspruch 6, bei dem das Octan des entschwefelten Produkts mindestens 90 % von dem des Einsatzmaterials zu der Olefinmodifikationsreaktionszone beträgt.

8. Das Verfahren nach Anspruch 1, bei dem das Einsatzmaterial Verunreinigungen, die basischen Stickstoff enthalten, enthält und das Verfahren zusätzlich ein Entfernen der Verunreinigungen, die basischen Stickstoff enthalten, aus dem Einsatzmaterial umfasst, bevor es mit dem Olefinmodifikationskatalysator in Kontakt gebracht wird.

9. Das Verfahren nach Anspruch 8, bei dem das Einsatzmaterial Kohlenwasserstoffe aus einem katalytischen Crackverfahren umfasst.

10. Das Verfahren nach Anspruch 1, bei dem das Einsatzmaterial im Wesentlichen frei von Verunreinigungen, die

basischen Stickstoff enthalten, ist.

11. Das Verfahren nach Anspruch 1, bei dem das Einsatzmaterial eine Mischung aus Kohlenwasserstoffen umfasst, die im Benzinbereich siedet.

12. Das Verfahren nach Anspruch 1, bei dem das Einsatzmaterial behandeltes Naphtha umfasst, welches hergestellt wird durch Entfernen von Verunreinigungen, die basischen Stickstoff enthalten, aus einem Naphtha, das durch ein katalytisches Crackverfahren hergestellt wird.

13. Das Verfahren nach Anspruch 1, bei dem die dritte Fraktion von 2 bis 10 Vol.-% des Produkts aus der Olefinmodifikationsreaktionszone reicht.

14. Das Verfahren nach Anspruch 1, bei dem das Einsatzmaterial einen Anfangssiedepunkt aufweist, der unterhalb von ungefähr 79 °C liegt, und einen Destillationsendpunkt aufweist, der nicht größer ist als ungefähr 345 °C.

15. Das Verfahren nach Anspruch 1, bei dem der Olefinmodifikationskatalysator aus der Gruppe ausgewählt ist, die aus allen festen Säurekatalysatoren besteht, und bei dem

(i) die erste Fraktion, welche schwefelhaltige organische Verunreinigungen umfasst, einen Destillationsendpunkt aufweist, der geringer als ungefähr 120 °C ist;

(ii) die zweite Fraktion, welche höher siedet als die erste Fraktion, welche schwefelhaltige organische Verunreinigungen umfasst, einen Destillationsendpunkt aufweist, der geringer als ungefähr 200 °C ist; und

(iii) die dritte Fraktion, welche höher siedet als die zweite Fraktion, schwefelhaltige organische Verunreinigungen und refraktive Schwefelverbindungen umfasst.

16. Das Verfahren nach Anspruch 15, das zusätzlich ein Entfernen von Schwefelwasserstoff aus dem Ausfluss der selektiven Hydrotreatingreaktionszone umfasst, um ein entschwefeltes Produkt zu ergeben, das ein Octan aufweist, welches mindestens 98 % von dem des Einsatzmaterials zu der Olefinmodifikationsreaktionszone ist.

17. Das Verfahren nach Anspruch 15, das zusätzlich ein Entfernen von Schwefelwasserstoff aus dem Ausfluss der Hydroentschwefelungsreaktionszone umfasst, um ein entschwefeltes Produkt zu ergeben, das ein Octan aufweist, welches mindestens 97 % von dem des Einsatzmaterials zu der Olefinmodifikationsreaktionszone ist.

18. Das Verfahren nach Anspruch 15, bei dem das Einsatzmaterial Kohlenwasserstoffe aus einem katalytischen Crackverfahren umfasst.

19. Das Verfahren nach Anspruch 15, bei dem das Einsatzmaterial ein behandeltes Naphtha umfasst, das hergestellt wird durch Entfernen von Verunreinigungen, die basischen Stickstoff enthalten, aus einem Naphtha, das durch ein katalytisches Crackverfahren hergestellt wird.

Revendications

1. Procédé de production d'un produit à teneur en soufre réduite à partir d'une charge d'alimentation, dans lequel ladite charge d'alimentation contient des impuretés organiques contenant du soufre et est composée d'un mélange normalement liquide d'hydrocarbures qui comprennent des oléfines, ledit procédé comprenant :

(a) la mise en contact de la charge d'alimentation avec un catalyseur de modification d'oléfines dans au moins une zone de réaction de modification d'oléfines dans des conditions qui sont efficaces pour produire un produit ayant un indice de brome qui est inférieur à celui de la charge d'alimentation et où le produit contient des composés réfractifs du soufre ;

(b) le fractionnement du produit provenant de ladite zone de réaction de modification d'oléfines pour produire :

(i) une première fraction qui comprend des impuretés organiques contenant du soufre et a un point final de distillation qui est inférieur à environ 140°C ;

(ii) une deuxième fraction qui a un point d'ébullition supérieur à celui de la première fraction qui comprend des impuretés organiques contenant du soufre et a un point final de distillation qui est inférieur à environ 240°C ; et

(iii) une troisième fraction qui a un point d'ébullition supérieur à celui de la deuxième fraction et comprend des impuretés organiques contenant du soufre et des composés réfractifs du soufre ;

(c) la mise en contact de ladite deuxième fraction avec un catalyseur d'hydrotraitement sélectif en présence d'hydrogène dans une zone de réaction d'hydrotraitement sélectif dans des conditions qui sont efficaces pour convertir au moins une partie des impuretés contenant du soufre dans la deuxième fraction en sulfure d'hydrogène ; et

(d) la mise en contact de ladite troisième fraction avec un catalyseur d'hydrodésulfuration en présence d'hydrogène dans une zone de réaction d'hydrodésulfuration dans des conditions qui sont efficaces pour convertir au moins une partie du soufre dans lesdites impuretés contenant du soufre de la troisième fraction en sulfure d'hydrogène.

2. Procédé selon la revendication 1, dans lequel la charge d'alimentation contient des paraffines et dans lequel les conditions dans ladite zone de réaction de modification d'oléfines sont efficaces pour produire un produit ayant un indice de brome qui est inférieur à celui de la charge d'alimentation, et moins de 10% des oléfines dans la charge d'alimentation sont craqués.

3. Procédé selon la revendication 1, qui comprend de plus l'élimination du sulfure d'hydrogène de l'effluent de ladite zone de réaction d'hydrotraitement sélectif pour fournir un produit désulfuré qui contient moins d'environ 50 parties par million en poids de soufre.

4. Procédé selon la revendication 3, dans lequel l'octane du produit désulfuré représente au moins 95% de celui de la charge d'alimentation dirigée vers la zone de réaction de modification d'oléfines.

5. Procédé selon la revendication 1, dans lequel la charge d'alimentation contient d'environ 0,05% en poids à environ 0,7% en poids de soufre sous la forme de composés organiques du soufre.

6. Procédé selon la revendication 1, qui comprend de plus l'élimination du sulfure d'hydrogène de l'effluent de ladite zone d'hydrodésulfuration pour fournir un produit désulfuré qui contient moins d'environ 50 parties par million en poids de soufre.

7. Procédé selon la revendication 6, dans lequel l'octane du produit désulfuré représente au moins 90% de celui de la charge d'alimentation dirigée vers la zone de réaction de modification d'oléfines.

8. Procédé selon la revendication 1, dans lequel ladite charge d'alimentation contient des impuretés basiques contenant de l'azote et ledit procédé comprend de plus l'élimination desdites impuretés basiques contenant de l'azote de la charge d'alimentation avant sa mise en contact avec le catalyseur de modification d'oléfines.

9. Procédé selon la revendication 8, dans lequel ladite charge d'alimentation est composée d'hydrocarbures provenant d'un traitement de craquage catalytique.

10. Procédé selon la revendication 1, dans lequel ladite charge d'alimentation est substantiellement dépourvue d'impuretés basiques contenant de l'azote.

11. Procédé selon la revendication 1, dans lequel ladite charge d'alimentation est composée d'un mélange d'hydrocarbures dont la gamme de points d'ébullition est celle de l'essence.

12. Procédé selon la revendication 1, dans lequel la charge d'alimentation est composée d'un naphta traité qui est préparé par élimination d'impuretés basiques contenant de l'azote provenant d'un naphta produit par un traitement de craquage catalytique.

13. Procédé selon la revendication 1, dans lequel la troisième fraction représente de 2 à 10% en volume du produit provenant de la zone de réaction de modification d'oléfines.

14. Procédé selon la revendication 1, dans lequel la charge d'alimentation a un point d'ébullition initial qui est inférieur à environ 79°C et un point de distillation final qui ne dépasse pas environ 345°C.

15. Procédé selon la revendication 1, dans lequel ledit catalyseur de modification d'oléfines est choisi dans le groupe

consistant en tous les catalyseurs acides solides ; et dans lequel :

(i) ladite première fraction qui comprend des impuretés organiques contenant du soufre, a un point de distillation final qui est inférieur à environ 120°C ;

(ii) ladite deuxième fraction qui a un point d'ébullition supérieur à celui de la première fraction qui comprend des impuretés organiques contenant du soufre, a un point de distillation final qui est inférieur à environ 200°C ; et

(iii) ladite troisième fraction qui a un point d'ébullition supérieur à celui de la deuxième fraction comprend des impuretés organiques contenant du soufre et des composés réfractifs du soufre.

16. Procédé selon la revendication 15, qui comprend de plus l'élimination de sulfure d'hydrogène de l'effluent de ladite zone d'hydrotraitement sélectif pour fournir un produit désulfuré ayant un octane qui représente au moins 98% de celui de la charge d'alimentation dirigée vers la zone de réaction de modification d'oléfines.

17. Procédé selon la revendication 15, qui comprend de plus l'élimination de sulfure d'hydrogène de l'effluent de ladite zone d'hydrodésulfuration pour fournir un produit désulfuré ayant un octane qui représente au moins 97% de celui de la charge d'alimentation dirigée vers la zone de réaction de modification d'oléfines.

18. Procédé selon la revendication 15, dans lequel ladite charge d'alimentation est composée d'hydrocarbures provenant d'un traitement de craquage catalytique.

19. Procédé selon la revendication 15, dans lequel la charge d'alimentation est composée d'un naphta traité qui est préparé par élimination d'impuretés basiques contenant de l'azote provenant d'un naphta produit par un traitement de craquage catalytique.

