BENZENE CONVERSION IN AN IMPROVED GASOLINE UPGRADING PROCESS

This invention relates to a process for the upgrading of hydrocarbon streams. It more particularly relates to a process for upgrading gasoline boiling range petroleum fractions containing substantial proportions of benzene and sulfur impurities while minimizing the octane loss which occurs upon hydrogenative removal of the sulfur.

Catalytically cracked gasoline forms a major part of the gasoline product pool in the United States. When the cracking feed contains sulfur, the products of the cracking process usually contain sulfur impurities which normally require removal, usually by hydrotreating, in order to comply with the relevant product specifications. These specifications are expected to become more stringent in the future, possibly permitting no more than 300 ppmw sulfur (or even less) in motor gasolines and other fuels. Although product sulfur can be reduced by hydrodesulfurization of cracking feeds, this is expensive both in terms of capital construction and in operating costs since large amounts of hydrogen are consumed.

As an alternative to desulfurization of the cracking feed, the products which are required to meet low sulfur specifications can be hydrotreated, usually using a catalyst comprising a Group VIII or a Group VI element, such as cobalt or molybdenum, either on their own or in combination with one another, on a suitable substrate, such as alumina. In the hydrotreating process, the molecules containing the sulfur atoms are mildly hydrocracked to convert the sulfur to inorganic form, hydrogen sulfide, which can be removed from the liquid hydrocarbon product in a separator. Although this is an effective process that has been practiced on gasolines and heavier petroleum fractions for many years to produce satisfactory products, it does have disadvantages.

Cracked naphtha, as it comes from the catalytic cracker and without any further treatments, such as purifying operations, has a relatively high octane number as a result of

the presence of olefinic components and as such, cracked gasoline is an excellent contributor to the gasoline octane pool. It contributes a large quantity of product at a high blending octane number. In some cases, this fraction may contribute as much as up to half the gasoline in the refinery pool.

Other highly unsaturated fractions boiling in the gasoline boiling range, which are produced in some refineries or petrochemical plants, include pyrolysis gasoline produced as a by-product in the cracking of petroleum fractions to produce light olefins, mainly ethylene and propylene. Pyrolysis gasoline has a very high octane number but is quite unstable in the absence of hydrotreating because, in addition to the desirable olefins boiling in the gasoline boiling range, it also contains a substantial proportion of diolefins, which tend to form gums after storage or standing.

Hydrotreating these sulfur-containing cracked naphtha fractions normally causes a reduction in the olefin content, and consequently a reduction in the octane number; as the degree of desulfurization increases, the octane number of the gasoline boiling range product decreases. Some of the hydrogen may also cause some hydrocracking as well as olefin saturation, depending on the conditions of the hydrotreating operation.

Various proposals have been made for removing sulfur while retaining the olefins which make a positive contribution to octane. Sulfur impurities tend to concentrate in the heavy fraction of the gasoline, as noted in U.S. Patent No. 3,957,625 (Orkin) which proposes a method of removing the sulfur by hydrodesulfurization of the heavy fraction of the catalytically cracked gasoline so as to retain the octane contribution from the olefins which are found mainly in the lighter fraction. In one type of conventional, commercial operation, the heavy gasoline fraction is treated in this way. As an alternative, the selectivity for hydrodesulfurization relative to olefin saturation may be shifted by suitable catalyst selection, for example, by the use of a magnesium

oxide support instead of the more conventional alumina. U.S. Patent No. 4,049,542 (Gibson) discloses a process in which a copper catalyst is used to desulfurize an olefinic hydrocarbon feed such as catalytically cracked light naphtha.

In any case, regardless of the mechanism by which it happens, the decrease in octane which takes place as a consequence of sulfur removal by hydrotreating creates a tension between the growing need to produce gasoline fuels with higher octane number and the need to produce cleaner burning, less polluting, low sulfur fuels. This inherent tension is yet more marked in the current supply situation for low sulfur, sweet crudes.

Other processes for treating catalytically cracked gasolines have also been proposed in the past. For example, U.S. Patent No. 3,759,821 (Brennan) discloses a process for upgrading catalytically cracked gasoline by fractionating it into a heavier and a lighter fraction and treating the heavier fraction over a ZSM-5 catalyst, after which the treated fraction is blended back into the lighter fraction. Another process in which the cracked gasoline is fractionated prior to treatment is described in U.S. Patent No. 4,062,762 (Howard) which discloses a process for desulfurizing naphtha by fractionating the naphtha into three fractions each of which is desulfurized by a different procedure, after which the fractions are recombined.

U.S. Patent No. 5,143, 596 (Maxwell) and EP 420 326 B1 describe processes for upgrading sulfur-containing feedstocks in the gasoline range by reforming with a sulfur-tolerant catalyst which is selective towards aromatization. Catalysts of this kind include metal-containing crystalline silicates including zeolites such as gallium-containing ZSM-5. The process described in U.S. Patent No. 5,143,596 hydrotreats the aromatic effluent from the reforming step. Conversion of naphthenes and olefins to aromatics is at least 50% under the severe conditions used, typically temperatures of at least 400°C (750°F) and usually higher, e.g. 500°C (930°F). Under similar conditions, conventional reforming is typically

accompanied by significant and undesirable yield losses, typically as great as 25% and the same is true of the processes described in these publications: C_5+ yields in the range of 50 to 85% are reported in EP 420 326. This process therefore suffers the traditional drawback of reforming so that the problem of devising a process which is capable of reducing the sulfur level of cracked naphthas while minimizing yield losses as well as reducing hydrogen consumption has remained.

U.S. Patent No. 5,346,609 describes a process for reducing the sulfur of cracked naphthas by first hydrotreating the naphtha to convert sulfur to inorganic form followed by treatment over a catalyst such as ZSM-5 to restore the octane lost during the hydrotreating step, mainly by shape-selective cracking of low octane paraffins. This process, which has been successfully operated commercially, produces a low-sulfur naphtha product in good yield which can be directly incorporated into the gasoline pool.

Another aspect of recent regulation is the need to reduce the levels of benzene, a suspected carcinogen, in motor gasolines. Benzene is found in many light refinery steams which are blended into the refinery gasoline pool, especially reformate which is desirable as a component of the gasoline pool because of its high octane number and low sulfur content. Its relatively high benzene content requires, however, that further treatment be carried out in order to comply with forthcoming regulations. Various processes for reducing the benzene content of refinery streams have been proposed, for example, the fluid bed processes described in U.S. Patent Nos. 4,827,069; 4,950,387 and 4,992,607 convert benzene to alkylaromatics by alkylation with light olefins. The benzene may be derived from cracked naphthas or benzene-rich streams such as reformates. Similar processes in which the removal of benzene is accompanied by reductions in sulfur are described in U.S. Applications Serial Nos. 08/286,894 (Mobil Case 6994FC) and 08/322,466 (Mobil Case No. 6951FC) and U.S. Patent No. 5,391,288. A process for reducing the benzene content of

light refinery streams such as reformate and light FCC gasoline by alkylation and transalkylation with heavy alkylaromatics is described in U.S. Patent No. 5,347,061.

We have now devised a process for catalytically desulfurizing cracked fractions in the gasoline boiling range which enables the sulfur to be reduced to acceptable levels without substantially reducing the octane number. At the same time, the present process permits the benzene levels in light refinery streams such as reformate to be reduced. The benefits of the present process include reduced hydrogen consumption and reduced mercaptan formation, in comparison with the process described in U.S. Patent No. 5,346,609, as well as the concomitant capability to reduce benzene levels in other streams.

According to the present invention, the process for upgrading cracked naphthas comprises a first catalytic processing step in which the cracked naphtha feed is co-processed with a light, benzene-containing hydrocarbon stream to convert the benzene, the olefins and some paraffins in the combined feed over a zeolite or other acidic catalyst. The reactions which take place are mainly shape-selective cracking of low octane paraffins and olefins and alkylation reactions which convert the benzene to alkylaromatics. Many of these increase the octane of the cracked naphtha and greatly reduce its olefin content which, in turn, reduces hydrogen consumption and octane loss during the subsequent hydrodesulfurization step. The extent of aromatization of olefins and naphthenes is limited as a result of the mild conditions employed during the treatment over the acidic catalyst; the aromatic content of the final, hydrotreated product may in certain cases be lower than that of the combined feeds.

In its normal practical form, the process will comprise contacting the feed (sulfur-containing cracked naphtha fraction and a benzene-rich reformate co-feed) in a first step with a solid acidic intermediate pore size zeolite catalyst at a temperature of 350° to 800°F (177° to 427°C), a pressure of

300 to 1000 psig (2172 to 6998 kPa), a space velocity of 1 to 6 LHSV, and a hydrogen to hydrocarbon ratio of 1000 to 2500 standard cubic feet of hydrogen per barrel of feed (180 to 445 $n.l.l.^{-1}$), to alkylate the benzene in the combined feed with olefins to form alkylaromatics and to crack olefins and low octane paraffins in the feed, with conversion of olefins and naphthenes to aromatics being held to levels less than 25 wt.% and benzene conversion (to alkylaromatics) from 10 to 60%. The intermediate product is then hydrodesulfurized in the presence of a hydrodesulfurization catalyst at a temperature of 500° to 800°F (260° to 427°C), a pressure of 300 to 1000 psig (2172 to 6998 kPa), a space velocity of 1 to 6 LHSV, and a hydrogen to hydrocarbon ratio of 1000 to 2500 standard cubic feet of hydrogen per barrel of feed, to convert sulfur-containing compounds in the intermediate product to inorganic sulfur and produce a desulfurized product with a total liquid yield of at least 90 vol.%.

In comparison to the treatment sequence described in U.S. Patent No. 5,346,069, where the cracked naphtha is first subjected to hydrodesulfurization followed by treatment over an acidic catalyst such as ZSM-5, the present process operates with reduced hydrogen consumption as a result of the early removal of olefins. Also, by placing the hydrodesulfurization after the initial treatment, mercaptan formation by H_2S-olefin combination over the zeolite catalyst is eliminated, potentially leading to higher desulfurization or mitigating the need to treat the product further, for example, as described in U.S. Application Serial No. 08/001,681.

The process may be utilized to desulfurize light and full range naphtha fractions while maintaining octane so as to obviate the need for reforming such fractions, or at least, without the necessity of reforming such fractions to the degree previously considered necessary.

In practice it may be desirable to hydrotreat the cracked naphtha before contacting it with the catalyst in the first aromatization/cracking step in order to reduce the diene content of the naphtha and so extend the cycle length of the

catalyst. Only a very limited degree of olefin saturation occurs in the pretreater and only a minor amount of desulfurization takes place at this time.

Detailed Description

Feed

One of the feeds to the process comprises a sulfur-containing petroleum fraction which boils in the gasoline boiling range. Feeds of this type typically include light naphthas typically having a boiling range of C_6 to 330°F (166°C), full range naphthas typically having a boiling range of C_5 to 420°F (216°C), heavier naphtha fractions boiling in the range of 260° to 412°F (127° to 211°C), or heavy gasoline fractions boiling at, or at least within, the range of 330° to 500°F (166° to 211°C), preferably 330° to 412°F (166° to 260°C). In many cases, the feed will have a 95 percent point (determined according to ASTM D 86) of at least 325°F(163°C) and preferably at least 350°F(177°C), for example, 95 percent points of at least 380°F (193°C) or at least 400°F (220°C).

Catalytic cracking is a suitable source of cracked naphthas, usually fluid catalytic cracking (FCC) but thermal cracking processes such as coking may also be used to produce usable feeds such as coker naphtha, pyrolysis gasoline and other thermally cracked naphthas.

The process may be operated with the entire gasoline fraction obtained from a catalytic or thermal cracking step or, alternatively, with part of it. Because the sulfur tends to be concentrated in the higher boiling fractions, it is preferable, particularly when unit capacity is limited, to separate the higher boiling fractions and process them through the steps of the present process without processing the lower boiling cut. The cut point between the treated and untreated fractions may vary according to the sulfur compounds present but usually, a cut point in the range of from 100°F (38°C) to 300°F (150°C), more usually in the range of 200°F (93°C) to 300°F (150°C) will be suitable. The exact cut point selected will depend on the sulfur specification for the gasoline product as well as on the type of sulfur compounds present:

lower cut points will typically be necessary for lower product sulfur specifications. Sulfur which is present in components boiling below 150°F (65°C) is mostly in the form of mercaptans which may be removed by extractive type processes such as Merox, but hydrotreating is appropriate for the removal of thiophene and other cyclic sulfur compounds present in higher boiling components, e.g., component fractions boiling above 180°F (82°C). Treatment of the lower boiling fraction in an extractive type process coupled with hydrotreating of the higher boiling component may therefore represent a preferred economic process option. Higher cut points will be preferred in order to minimize the amount of feed which is passed to the hydrotreater and the final selection of cut point together with other process options such as the extractive type desulfurization will therefore be made in accordance with the product specifications, feed constraints and other factors.

The sulfur content of the cracked fraction will depend on the sulfur content of the feed to the cracker as well as on the boiling range of the selected fraction used as the feed in the process. Lighter fractions, for example, will tend to have lower sulfur contents than the higher boiling fractions. As a practical matter, the sulfur content will exceed 50 ppmw and usually will be in excess of 100 ppmw and in most cases in excess of 500 ppmw. For the fractions which have 95 percent points over 380°F (193°C), the sulfur content may exceed 1000 ppmw and may be as high as 4000 or 5000 ppmw or even higher, as shown below. The nitrogen content is not as characteristic of the feed as the sulfur content and is preferably not greater than 20 ppmw although higher nitrogen levels typically up to 50 ppmw may be found in certain higher boiling feeds with 95 percent points in excess of 380°F (193°C). The nitrogen level will, however, usually not be greater than 250 or 300 ppmw. As a result of the cracking which has preceded the steps of the present process, the feed to the hydrodesulfurization step will be olefinic, with an olefin content of at least 5 and more typically in the range of 10 to 20, e.g. 15 to 20 wt.%; preferably, the feed has an olefin

content of 10 to 20 wt.%, a sulfur content from 100 to 5000 ppmw, a nitrogen content of 5 to 250 ppmw and a benzene content of at least 5 vol.%. Dienes are frequently present in thermally cracked naphthas but, as described below, these are preferably removed hydrogenatively as a pretreatment step.

The co-feed to the process comprises a light, fraction boiling within the gasoline boiling range which is relatively high in aromatics, especially benzene. This benzene-rich feed will typically contain at least 5 vol.% benzene, more specifically 20 vol.% to 60 vol.% benzene. A specific refinery source for the fraction is a reformate fraction. The fraction contains smaller amounts of lighter hydrocarbons, typically less than 10% C_5 and lower hydrocarbons and small amounts of heavier hydrocarbons, typically less than 15% C_7+ hydrocarbons. These reformate co-feeds usually contain very low amounts of sulfur as they have usually been subjected to desulfurization prior to reforming.

Examples include a reformate from a fixed bed, swing bed or moving bed reformer. The most useful reformate fraction is a heart-cut reformate, i.e. a reformate with the lightest and heaviest portions removed by distillation. This is preferably reformate having a narrow boiling range, i.e., a C_6 or C_6/C_7 fraction. This fraction can be obtained as a complex mixture of hydrocarbons recovered as the overhead of a dehexanizer column downstream from a depentanizer column. The composition will vary over a wide range, depending upon a number of factors including the severity of operation in the reformer and reformer feed. These streams will usually have the C_5's, C_4's and lower hydrocarbons removed in the depentanizer and debutanizer. Therefore, usually, the heart-cut reformate will contain at least 70 wt.% C_6 hydrocarbons, and preferably at least 90 wt.% C_6 hydrocarbons. Other sources of a benzene-rich feed include a light naphtha, coker naphtha or pyrolysis gasoline.

By boiling range, these benzene-rich fractions can be defined by an end boiling point of 250°F (121°C), and preferably no higher than 230°F (110°C). Preferably, the

boiling range falls between 100°F (38°C) and 212°F (180°C), and more preferably between the range of 150°F (66°C) to 200°F (93°C) and even more preferably within the range of 160°F to 200°F (71° to 93°C).

The following Table 1 sets forth the properties of a useful 250°F- (121°C) C_6-C_7 heart-cut reformate.

Table 1

C_6-C_7 Heart-Cut Reformate

RON	82.6
MON	77.3
Composition, wt.%	
I-C_5	0.9
n-C_5	1.3
C_5 Naph	1.5
I-C_6	22.6
n-C_6	11.2
C_6 Naph	1.1
Benzene	32.0
I-C_7	8.4
n-C_7	2.1
C_7 Naph	0.4
Toluene	17.7
I-C_8	0.4
n-C_8	0.0
C_8 Arom.	0.4

Table 2 sets out the properties of a more preferred benzene-rich heart-cut fraction which is more paraffinic.

Table 2

Benzene-Rich Heart-Cut Reformate

RON	78.5
MON	74.0
Composition, wt.%	
I-C_5	1.0
n-C_5	1.6
C_5 Naph	1.8
I-C_6	28.6
n-C_6	14.4
C_6 Naph	1.4
Benzene	39.3
I-C_7	8.5
n-C_7	0.9
C_7 Naph	0.3
Toluene	2.3

Process Configuration

The selected sulfur-containing, gasoline boiling range feed together with the benzene-rich co-feed is treated in two steps by first passing the naphtha plus co-feed over a shape selective, acidic catalyst. In this step, the olefins in the cracked naphtha alkylate the benzene and other aromatics to form alkylaromatics while, at the same time, incremental olefins are produced by shape-selective cracking of low octane paraffins and olefins from one or both feed components. Olefins and naphthenes may undergo conversion to aromatics but the extent of aromatization is limited as a result of the relatively mild conditions, especially of temperature, used in this step of the process. The effluent from this step is then passed to a hydrotreating step in which the sulfur compounds present in the naphtha feed, which are mostly unconverted in the first step, are converted to inorganic form (H_2S), permitting removal in a separator following the hydrodesulfurization. Because the first treatment step over the acidic catalyst does not produce any products which interfere with

the operation of the second step, the first stage effluent may be cascaded directly into the second stage without the need for interstage separation.

The particle size and the nature of the catalysts used in both stages will usually be determined by the type of process used, such as: a down-flow, liquid phase, fixed bed process; an up-flow, fixed bed, trickle phase process; an ebulating, fluidized bed process; or a transport, fluidized bed process. All of these different process schemes, which are well known, although the down-flow fixed bed arrangement is preferred for simplicity of operation.

First Stage Processing

The combined feeds are first treated by contact with an acidic catalyst under conditions which result in alkylation of benzene by olefins to form alkylaromatics. The bulk of the benzene comes from the co-feed, e.g. reformate although some aromatization of the olefins which are present in the naphtha feed may take place to form additional benzene. The mild conditions, especially of temperature, used in this step usually preclude a very large degree of aromatization of olefins and naphthenes. Normally, the conversion of olefins and naphthenes to new aromatics is no more than 25 wt.% and is usually lower, typically no more than 20 wt.%. Under the mildest conditions in the first stage, the overall aromatic content of the final hydrotreated product may actually be lower than that of the combined feeds as a result of some aromatic hydrogenation taking place during the second stage of the reaction.

Shape-selective cracking of low octane paraffins, mainly n-paraffins, and olefins takes place to increase product octane with incremental olefin production which may also result in the alkylation of aromatics, especially of benzene. These reactions take place under relatively mild conditions and yield losses are held at a low level. Over both steps of the process, total liquid yields are typically at least 90% volume and may be higher, e.g., 95% volume. In some cases, the liquid yield may be over 100% volume as a result of volume

expansion from the reactions taking place.

Compositionally, the first stage of the processing is marked by a shape-selective cracking of low octane components in the feed coupled with alkylation of alkylation of aromatics. The olefins are derived from the feed as well as an incremental quantity from the cracking of combined feed paraffins and olefins. Some isomerization of n-paraffins to branched-chain paraffins of higher octane may take place, making a further contribution to the octane of the final product. Benzene levels are reduced as the degree of alkylation increases at higher first stage temperatures, with benzene conversion typically in the range of 10 to 60%, more usually from 20 to 50%.

The conditions used in this step of the process are those favorable to these reactions. Typically, the temperature of the first step will be from 300° to 850°F (150° to 455°C), preferably 350° to 800°F (177° to 425°C). The pressure in this reaction zone is not critical since hydrogenation is not taking place although a lower pressure in this stage will tend to favor olefin production by cracking of the low octane components of the feedstream. The pressure, which will therefore depend mostly on operating convenience, will typically be 50 to 1500 psig (445 to 10445 kPa), preferably 300 to 1000 psig (2170 to 7000 kPa) with space velocities typically from 0.5 to 10 LHSV (hr^{-1}), normally 1 to 6 LHSV (hr^{-1}). Hydrogen to hydrocarbon ratios typically of 0 to 5000 SCF/Bbl (0 to 890 n.l.l.$^{-1}$), preferably 100 to 2500 SCF/Bbl (18 to 445 n.l.l.$^{-1}$) will be selected to minimize catalyst aging.

A change in the volume of gasoline boiling range material typically takes place in the first step. Some decrease in product liquid volume occurs as the result of the conversion to lower boiling products (C_5-) but the conversion to C_5- products is typically not more than 10 vol. percent and usually below 5 vol. percent. A further decrease in volume normally takes place as a consequence of the conversion of olefins to the aromatic compounds or their incorporation into

aromatics but with limited aromatization, this is normally not significant. If the feed includes significant amounts of higher boiling components, the amount of C_5- products may be relatively lower and for this reason, the use of the higher boiling naphthas is favored, especially the fractions with 95 percent points above 350°F (177°C) and even more preferably above 380°F (193°C) or higher, for instance, above 400°F (205°C). Normally, however, the 95 percent point will not exceed 520°F (270°C), and usually will be not more than 500°F (260°C).

The catalyst used in the first step of the process possesses sufficient acidic functionality to bring the desired cracking, aromatization and alkylation reactions. For this purpose, it will have a significant degree of acid activity, and for this purpose the most preferred materials are the solid, crystalline molecular sieve catalytic materials solids having an intermediate pore size and the topology of a zeolitic behaving material, which, in the aluminosilicate form, has a constraint index of 2 to 12. The preferred catalysts for this purpose are the intermediate pore size zeolitic behaving catalytic materials, exemplified by the acid acting materials having the topology of intermediate pore size aluminosilicate zeolites. These zeolitic catalytic materials are exemplified by those which, in their aluminosilicate form have a Constraint Index between 2 and 12. Reference is made to U.S. Patent No. 4,784,745 for a definition of Constraint Index and a description of how this value is measured as well as details of a number of catalytic materials having the appropriate topology and the pore system structure to be useful in this service.

The preferred intermediate pore size aluminosilicate zeolites are those having the topology of ZSM-5, ZSM-11, ZSM-12, ZSM-21, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50 or MCM-22, MCM-36, MCM-49 and MCM-56, preferably in the aluminosilicate form. (The newer catalytic materials identified by the MCM numbers are disclosed in the following patents: Zeolite MCM-22 is described in U.S. Patent No. 4,954,325; MCM-36 in U.S.

Patent Nos. 5,250,277 and 5,292,698; MCM-49 in U.S. Patent No. 5,236,575; and MCM-56 in U.S. Patent No. 5,362,697). Other catalytic materials having the appropriate acidic functionality may, however, be employed. A particular class of catalytic materials which may be used are, for example, the large pores size zeolite materials which have a Constraint Index of up to 2 (in the aluminosilicate form). Zeolites of this type include mordenite, zeolite beta, faujasites such as zeolite Y and ZSM-4. Other refractory solid materials which have the desired acid activity, pore structure and topology may also be used.

The catalyst should have sufficient acid activity to convert the appropriate components of the feed naphtha as described above. One measure of the acid activity of a catalyst is its alpha number. The alpha test is described in U.S. Patent No. 3,354,078 and in J. Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980). The experimental conditions of the test used to determine the alpha values referred to in this specification include a constant temperature of 538°C and a variable flow rate as described in detail in J. Catalysis, 61, 395 (1980). The catalyst used in this step of the process suitably has an alpha activity of at least 20, usually in the range of 20 to 800 and preferably at least 50 to 200. It is inappropriate for this catalyst to have too high an acid activity because it is desirable to only crack and rearrange so much of the feed naphtha as is necessary to maintain octane without severely reducing the volume of the gasoline boiling range product.

The active component of the catalyst, e.g. the zeolite, will usually be used in combination with a binder or substrate because the particle sizes of the pure zeolitic behaving materials are too small and lead to an excessive pressure drop in a catalyst bed. This binder or substrate, which is preferably used in this service, is suitably any refractory binder material. Examples of these materials are well known and typically include silica, silica-alumina, silica-zirconia, silica-titania, alumina.

The catalyst used in this step of the process may be free of any metal hydrogenation component or it may contain a metal hydrogenation function. If found to be desirable under the actual conditions used with particular feeds, metals such as the Group VIII base metals, especially molybdenum, or combinations will normally be found suitable. Noble metals such as platinum or palladium will normally offer no advantage over nickel or other base metals.

Second Step Hydrotreating

The hydrotreating of the first stage effluent may be effected by contact of the feed with a hydrotreating catalyst. Under hydrotreating conditions, at least some of the sulfur present in the naphtha which passes unchanged thorough the cracking/aromatization step is converted to hydrogen sulfide which is removed when the hydrode-sulfurized effluent is passed to the separator following the hydrotreater. The hydrodesulfurized product boils in substantially the same boiling range as the feed (gasoline boiling range), but which has a lower sulfur content than the feed. Product sulfur levels are typically below 300 ppmw and in most cases below 50 ppmw. Nitrogen is also reduced to levels typically below 50 ppmw, usually below 10 ppmw, by conversion to ammonia which is also removed in the separation step.

If a pretreatment step is used before the first stage catalytic processing, the same type of hydrotreating catalyst may be used as in the second step of the process but conditions may be milder so as to minimize olefin saturation and hydrogen consumption. Since saturation of the first double bond of dienes is kinetically/thermodynamically favored over saturation of the second double bond, this objective is capable of achievement by suitable choice of conditions. Suitable combinations of processing parameters such as temperature, hydrogen pressure and especially space velocity, may be found by empirical means. The pretreater effluent may be cascaded directly to the first processing stage, with any slight exotherm resulting form the hydrogenation reactions providing a useful temperature boost for initiating the mainly

endothermic reactions of the first stage processing.

Consistent with the objective of maintaining product octane and volume, the conversion to products boiling below the gasoline boiling range (C_5-) during the second, hydrodesulfurization step is held to a minimum. The temperature of this step is suitably from 400° to 850°F (220° to 454°C), preferably 500° to 750°F (260° to 400°C) with the exact selection dependent on the desulfurization required for a given feed with the chosen catalyst. A temperature rise occurs under the exothermic reaction conditions, with values of 20° to 100°F (11° to 55°C) being typical under most conditions and with reactor inlet temperatures in the preferred 500° to 750°F (260° to 400°C) range.

Since the desulfurization of the cracked naphthas normally takes place readily, low to moderate pressures may be used, typically from 50 to 1500 psig (445 to 10443 kPa), preferably 300 to 1000 psig (2170 to 7,000 kPa). Pressures are total system pressure, reactor inlet. Pressure will normally be chosen to maintain the desired aging rate for the catalyst in use. The space velocity (hydrodesulfurization step) is typically 0.5 to 10 LHSV (hr^{-1}), preferably 1 to 6 LHSV (hr^{-1}). The hydrogen to hydrocarbon ratio in the feed is typically 500 to 5000 SCF/Bbl (90 to 900 n.l.l.$^{-1}$), usually 1000 to 2500 SCF/B (180 to 445 n.l.l.$^{-1}$). The extent of the desulfurization will depend on the feed sulfur content and, of course, on the product sulfur specification with the reaction parameters selected accordingly. Normally the process will be operated under a combination of conditions such that the desulfurization should be at least 50%, preferably at least 75%, as compared to the sulfur content of the feed. It is not necessary to go to very low nitrogen levels but low nitrogen levels may improve the activity of the catalyst in the second step of the process. Normally, the denitrogenation which accompanies the desulfurization will result in an acceptable organic nitrogen content in the feed to the second step of the process.

The catalyst used in the hydrodesulfurization step is suitably a conventional desulfurization catalyst made up of a Group VI and/or a Group VIII metal on a suitable substrate. The Group VI metal is usually molybdenum or tungsten and the Group VIII metal usually nickel or cobalt. Combinations such as Ni-Mo or Co-Mo are typical. Other metals which possess hydrogenation functionality are also useful in this service. The support for the catalyst is conventionally a porous solid, usually alumina, or silica-alumina but other porous solids such as magnesia, titania or silica, either alone or mixed with alumina or silica-alumina may also be used, as convenient.

The particle size and the nature of the catalyst will usually be determined by the type of conversion process which is being carried out, such as: a down-flow, liquid phase, fixed bed process; an up-flow, fixed bed, liquid phase process; an ebulating, fixed fluidized bed liquid or gas phase process; or a liquid or gas phase, transport, fluidized bed process, as noted above, with the down-flow, fixed-bed type of operation preferred.

Examples

Three parts by volume of a 210°F+ (99°C+) fraction of an FCC naphtha was combined with one part of a heart-cut reformate to produce a combined feed with the composition and properties given in Table 3. The combined feed was co-fed with co-fed with hydrogen to a fixed-bed reactor containng a ZSM-5 catalyst having the properties set out in Table 4.

Table 3
FCC Naphtha/Reformate Properties

Composition, wt%	
N-pentane	0.4
Iso-pentane	0.3
Cyclopentane	0.5
C_6-C_{10} n-Paraffins	5.0
C_6-C_{10} Iso-paraffins	16.3
C_6-C_{10} Olefins and cycloolefins	11.4
C_6-C_{10} Naphthenes	5.8
Benzene	9.2
C_7-C_{10} Aromatics	34.2
C_{11}+	17.0
Total Sulfur, wt%	0.14
Nitrogen, ppmw	71
Properties	
Clear Research Octane	90.9
Motor octane	80.6
Bromine number	36.3
Density, 60°C, $g.cc^{-1}$	0.7977

Table 4
ZSM-5 Catalyst Properties

Zeolite	ZSM-5
Binder	Alumina
Zeolite loading, wt. pct.	65
Binder, wt. pct.	35
Catalyst alpha	110
Surface area, m^2g^{-1}	315
Pore vol., $cc.g^{-1}$	0.65
Density, real, $g.cc.^{-1}$	2.51
Density, particle, $g.cc.^{-1}$	0.954

The total effluent from the first reactor was cascaded to a second fixed bed reactor containing a commercial $CoMo/Al_2O_3$ catalyst (Akzo K742-3Q). The feed rate was constant such that the liquid hourly space velocity over the ZSM-5 catalyst was 1.0 $hr.^{-1}$ and 2.0 $hr.^{-1}$ over the hydrotreating catalyst. Total reactor pressure was maintained at 590 psig (4171 kPa) and hydrogen co-feed was constant at 2000 SCF/Bbl (356 $n.l.l.^{-1}$) of naphtha feed. The temperature of the ZSM-5 reactor was varied from 400° to 800°F (205° to 427°C) while the HDT reactor temperature was 500° to 700°F (260° to 370°C). The results are shown in Table 5.

Table 5

Combined Naphtha/Reformate Upgrading Results

ZSM-5 Temp. °F/°C	400/204	750/388	800/427	800/427
HDT Temp.,°F/°C	700/371	700/371	700/371	500/260
Benzene conversion, percent	13	39	41	38
H_2 Consumption, scfb	360	250	260	30
C_5+ Yield, vol% of feed	101.7	95.6	92.1	90.8
Aromatization of C_6-C_{10} olefins/naphthenes	(22)	(2)	5	20
Yield, wt% of HC feed				
C_1-C_2	0.1	0.3	0.6	0.5
Propane	0.0	1.3	2.7	2.5
N-Butane	0.0	1.5	2.3	2.3
Isobutane	0.0	1.6	2.2	2.1
N-Pentane	0.5	1.2	1.4	1.4
Isopentane	0.2	2.5	2.3	2.1
Pentenes	0.0	0.0	0.0	0.2
Total C_6+	99.7	91.8	88.7	88.8
C_6-C_{10} N-Paraffins	8.0	4.7	3.8	3.8
C_6-C_{10} Isoparaffins	23.2	17.0	15.6	15.3
C_6-C_{10} Olefins	0.0	0.0	0.0	0.6
Benzene	7.9	5.6	5.4	5.6
C_6-C_{10} Naphthenes	13.6	12.3	11.1	7.8
C_7-C_{10} Aromatics	31.7	37.5	38.9	41.2
C_{11}+	15.2	15.4	14.2	14.0
Total Sulfur, ppmw	75	32	20	31
Nitrogen, ppmw	2	3	3	56
C_5+ Research Octane	77.4	88.2	89.5	91.8
C_5+ Motor Octane	72.9	81.2	81.9	83.3

Note: Values shown () represent negative values (decreases) and reflect less aromatics in the product than in the feed.

As shown in Table 5, increasing the temperature of the ZSM-5 at constant HDT severity leads to increasing octanes and reduced C_5+ yields. Significant benzene conversions around 40% were also observed at 750° to 800°F (399° to 427°C) ZSM-5 temperatures compared to 13% due to saturation over the HDT

catalyst. Desulfurization levels above 94% may also be achieved. Hydrogen consumption decreases with increasing ZSM-5 temperature due to the increased conversion of the cracked naphtha olefins over the acidic catalyst rather than from hydrogen consuming reactions over the HDT catalyst; hydrogen consumption may be reduced further by reducing HDT temperature to 500°F (260°C) with little effect on hydrodesulfurization. This lower HDT temperature also leads to increased product octane as aromatic saturation is reduced. Aromatization of feed olefins and naphthenes is held at a low level and over both process steps, the level of aromatics may even be decreased relative to the feed. Liquid yields are high in all cases, with the highest yields being obtained at low first step temperatures when increases in product volume may be achieved.

CLAIMS:

1. A process of hydrosuslfurizing a combined hydrocarbon feed comprising fractions containing sulfur, olefins and benzene and reducing the benzene content of the feed, said process comprising:

(a) contacting a combined feed comprising

(i) a sulfur-containing cracked naphtha feed fraction boiling in the gasoline boiling range which includes paraffins including low octane n-paraffins, olefins and aromatics, and

(ii) a fraction boiling in the gasoline boiling range containing benzene,

in a first step under mild cracking conditions compriisng temperature between 204° to 427°C with a solid acidic catalyst consisting essentially of intermediate pore size ZSM-5 zeolite havaing an acid activity comprising an alpha value between 20 and 200 to alkylate benzene with olefins to form alkylaromatics and to crack paraffins and olefins in the feed and form an intermediate product of reduced benzene content relative to the combined feeds, and

(b) in a second step contacting the intermediate product with a hydrodesulfurization catalyst under a combination of elevated temperature, elevated pressure and an atmosphere comprising hydrogen, to convert sulfur-containing compounds in the intermediate product to inorganic sulfur and produce a desulfurized product comprising a normally liquid fraction in the gasoline boiling range.

2. The process as claimed in claim 1 in which said cracked naphtha feed fraction comprises a light naphtha fraction having a boiling range within the range of C_6 to 166°C.

3. The process as claimed in claim 1 in which said cracked naphtha feed fraction comprises a full range naphtha fraction having a boiling range within the range of C_5 to 216°C.

4. The process as claimed in claim 1 in which said cracked naphtha feed fraction comprises a heavy naphtha fraction having a boiling range within the range of 166° to 260°C.

5. The process as claimed in claim 1 in which said cracked naphtha feed is a catalytically cracked olefinic naphtha fraction.

6. The process as claimed in claim 1 in which the benzene-containing fraction is a reformate fraction.

7. The process as claimed in claim 1 in which the hydrosulfurization catalyst comprises a Group VIII and a Group VI metal.

8. The process as claimed in claim 1 in which the first stage is carried out at a pressure of 379 to 10446 kPa, a space velocity of 0.5 to 10 LHSV, and a hydrogen to hydrocarbon ratio of 0 to 890 $n.l.l.^{-1}$ of hydrogen per barrel of feed.

9. The process as claimed in claim 1 in which the hydrodesulfurization is carried out at a temperature of 204° to 427°C, a pressure of 379 to 10446 kPa, a space velocity of 0.5 to 10 LHSV, and a hydrogen to hydrocarbon ratio of 89 to 890 $n.l.l.^{-1}$ of hydrogen per barrel of feed.

10. A process of upgrading a sulfur-containing feed fraction boiling in the gasoline boiling range which contains mononuclear aromatics including benzene, olefins and paraffins and of reducing the benzene content of the fraction, which process comprises:

contacting a feed fraction boiling in the gasoline boiling range containing mononuclear aromatics including benzene, olefins and low octane paraffins, and comprising a sulfur-containing cracked naptha fraction and a benzene-rich reformate co-feed, in a first step under mide cracking conditions comprising temperature between 204° and 427°C with a solid acidic intermediate pore size catalyst consisting essentially of ZSM-5 zeolite having an acid activity comprising an alpha value between 20 and 200 at a pressure of 2172 to 6998 kPa, a space velocity of 1 to 6 LHSV, and a hydrogen to hydrocarbon ratio of 17.8 to 445 n.l.l.$^{-1}$ of hydrogen per barrel of feed, to alkylate benzene with olefins to form alkylaromatics and to crack olefins and low octane paraffins in the feed, conversion of olefins and naphthenes to aromatics being less than 25 wt.%, with benzene conversion from 10 to 60%, to form an intermediate product of reduced benzene content relative to the feed, hydrodesulfurizing the intermediate product in the presence of a hydrodesulfurization catalyst at a temperature of 260° to 427°C, a pressure of 2172 to 6998 kPa, a space velocity of 1 to 6 LHSV, and a hydrogen to hydrocarbon ratio of 178 to 445 n.l.l.$^{-1}$ of hydrogen per barrel of feed, to convert sulfur-containing compounds in the intermediate product to inorganic sulfur and produce a desulfurized product with a total liquid yield of at least 90 vol.%; and naphthenes to aromatics being less than 25 wt.%, with benzene conversion from 10 to 60%, to form an intermediate product of reduced benzene content relative to the feed, hydrodesulfurizing the intermediate product in the presence of a hydrodesulfurization catalyst at a temperature of 260° to 427°C, a pressure of 2172 to 6998 kPa, a space velocity of 1 to 6 LHSV, and a hydrogen to hydrocarbon ratio of 178 to 445 n.l.l.$^{-1}$ of hydrogen per barrel of fee, to convert sulfur-containing compounds in the intermediate product to inorganic sulfur compounds and produce a desulfurized product with a total liquid yield of at least 90 vol.%.