GASOLINE UPGRADING PROCESS

Field of the Invention

This invention relates to a process for the upgrading of hydrocarbon streams. It more particularly refers to a process for upgrading gasoline boiling range petroleum fractions containing substantial proportions of sulfur impurities. Another advantage of the present process is that it enables the end point of catalytically cracked gasolines to be maintained within the limits which are expected for Reformulated Gasoline (RFG) under the United States EPA Complex Model.

Background of the Invention

Catalytically cracked gasoline currently forms a major part of the gasoline product pool in the United States and it provides a large proportion of the sulfur in the gasoline. The sulfur impurities may require removal, usually by hydrotreating, in order to comply with product specifications or to ensure compliance with environmental regulations, both of which are expected to become more stringent in the future, possibly permitting no more than 300 ppmw sulfur in motor gasolines; low sulfur levels result in reduced emissions of CO, NO_x and hydrocarbons. In addition other environmental controls may be expected to impose increasingly stringent limits on gasoline composition. Currently, the requirements of the U.S. Clean Air Act and the physical and compositional limitations imposed by the Reformulated Gasoline (RFG) and EPA Complex Model regulations (U.S.) will result not only in a decrease in permissible sulfur levels but also in limitations on boiling range, typically measured by minimum Reid Vapor Presssure (RVP) and T_{90} specifications. Limitations on aromatic content may also arise from the Complex Model regulations.

Naphthas and other light fractions such as heavy cracked gasoline may be hydrotreated by passing the feed over a hydrotreating catalyst at elevated temperature and somewhat elevated pressure in a hydrogen atmosphere. One suitable family of catalysts which has been widely used for this service is a combination of a Group VIII and a Group VI element, such as cobalt and molybdenum, on a substrate such as alumina. After the hydrotreating operation is complete, the product may be fractionated, or simply flashed, to release the hydrogen sulfide and collect the now sweetened gasoline.

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. In some cases, this fraction may contribute as much as up to half the gasoline in the refinery pool, together with a significant contribution to product octane. Other unsaturated fractions boiling in the gasoline boiling range, which are produced in some refineries or petrochemical plants, include pyrolysis gasoline and coker naphtha. Pyrolysis gasoline is a fraction which is often produced as a by-product in the cracking of petroleum fractions to produce light unsaturates, such as 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. Coker naphtha is similar in containing significant amounts of sulfur and nitrogen as well as diolefins which make it unstable on storage.

Hydrotreating of any of the sulfur containing fractions which boil in the gasoline boiling range causes a reduction in the olefin content, and consequently a reduction in the octane number and as the degree of desulfurization

increases, the octane number of the normally liquid 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 more desirable olefins. The 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.-A 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. This catalyst is stated to promote desulfurization while retaining the olefins and their contribution to product octane.

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 - because of current ecological considerations - the need to produce burning, less polluting fuels, especially low sul. This inherent tension is yet more marked in the c supply situation for low sulfur, sweet crudes.

Processes for improving the octane rating of catalytically cracked gasolines have been proposed. U.S.-A 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. 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.

The octane rating of the gasoline pool may be increased by other methods, of which reforming is one of the most common. Light and full range naphthas can contribute substantial volume to the gasoline pool, but they do not generally contribute significantly to higher octane values without reforming. They may, however, be subjected to catalytically reforming so as to increase their octane numbers by converting at least a portion of the paraffins and cycloparaffins in them to aromatics. Fractions to be fed to catalytic reforming, for example, with a platinum type catalyst, need to be desulfurized before reforming because reforming catalysts are generally not sulfur tolerant; they are usually pretreated by hydrotreating to reduce their sulfur content before reforming. The octane rating of reformate may be increased further by processes such as those described in U.S.-A 3,767,568 and U.S.-A 3,729,409 (Chen) in which the reformate octane is increased by treatment of the reformate with ZSM-5.

Aromatics are generally the source of high octane number, particularly very high research octane numbers and are therefore desirable components of the gasoline pool. They have, however, been the subject of severe limitations as a gasoline component because of possible adverse effects on

the ecology, particularly with reference to benzene. It has therefore become desirable, as far as is feasible, to create a gasoline pool in which the higher octanes are contributed by the olefinic and branched chain paraffinic components, rather than the aromatic components.

In U.S.-A 5,409,596 and U.S.-A 5,346,609 and the counterpart EP 641 375, we have described a process for the upgrading of gasoline by sequential hydrotreating and selective cracking steps is described. In the first step of the process, the naphtha is desulfurized by hydrotreating and during this step some loss of octane results from the saturation of olefins. The octane loss is restored in the second step by a shape-selective cracking, preferably carried out in the presence of an intermediate pore size zeolite such as ZSM-5. The product is a low-sulfur gasoline of good octane rating.

Summary of the Invention

As shown in U.S.-A 5,409,956 and 5, 346,609, intermediate pore size zeolites such as ZSM-5 are effective for restoring the octane loss which takes place when the initial naphtha feed is hydrotreated. In the conventional manner, the catalysts comprise the zeolite component to provide the desired activity together with a binder or matrix material which is used to provide mechanical strength to the catalyst as well as enabling it to be formed into extrudates or other shaped forms which reduce the pressure drop in fixed bed reactors.

We have now found that it is desirable to use a catalyst which is free of the binder or matrix material in this process. Catalysts of this type have a higher activity than bound catalysts and permit lower temperatures to be used during the processing over the zeolitic catalyst for octane restoration.

According to the present invention, therefore, a process for catalytically desulfurizing cracked fractions in the gasoline boiling range to acceptable sulfur levels uses an initial hydrotreating step to desulfurize the feed with some reduction in octane number, after which the desulfurized material is treated with a self-bound or binder-free zeolite to restore lost octane.

The process may be utilized to desulfurize catalytically and thermally cracked naphthas such as FCC naphtha as well as pyrolysis gasoline and coker naphthas, including light as well as full range naphtha fractions, while maintaining octane so as to reduce the requirement for reformate and alkylate in the gasoline blend. The use of the self-bound catalyst offers processing advantages in terms of catalyst activity and permits lower processing temeperatures to be used at this stage of the process. The higher activity also permits higher space velocities to be used, based on the total catalyst weight.

Detailed Description

Feed

The feed to the process comprises, as described in U.S.-A 5,409,596 and U.S.-A 5,346,609 and the counterpart EP 641 375, a sulfur-containing petroleum fraction which boils in the gasoline boiling range, which can be regarded as extending from C_6 to 260°C (500°F) although lower end points below the 260°C (500°F) end point are more typical. Feeds of this type include light naphthas typically having a boiling range of C_6 to 165° (330 °F), full range naphthas typically having a boiling range of C_5 to 215°C (420 °F), heavier naphtha fractions boiling in the range of 127° to 210°C (260 °F to 412 °F), or heavy gasoline fractions boiling at, or at least within, the range of 165 to 260°C (330 to 500 °F), preferably 165 to 210°C (330 to 412 °F). While the most preferred feed appears at this

time to be a heavy gasoline produced by catalytic cracking; or a light or full range gasoline boiling range fraction, the best results are obtained when, as described below, the process is operated with a gasoline boiling range fraction which has a 95 percent point (determined according to ASTM D 86) of at least 163°C (325°F) and preferably at least 177°C (350°F), for example, 95 percent points (T_{95}) of at least 193°C (380°F) or at least 220°C (400°F). The process may be applied to thermally cracked naphthas such as pyrolysis gasoline, visbreaker naptha and coker naphtha as well as catalytically cracked naphthas such as FCC naphtha since both types are usually characterized by the presence of olefinic unsaturation and the presence of sulfur. From the point of view of volume, however, the main application of the process is likely to be with catalytically cracked naphthas, especially FCC naphthas and for this reason, the process will be described with particular reference to the use of catalytically cracked naphthas.

The process may be operated with the entire gasoline fraction obtained from the catalytic 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 38°C (100°F) to 150°C (300°F), more usually in the range of 93°C (200°F) to 150°C (300°F) 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 65°C (150°F) 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 82°C (180°F). 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. Such a variant of the process is described in U.S.-A 5,360,532 and U.S.-A 5,318,690. 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 these catalytically cracked fractions 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 193°C (380°F), the sulfur content may exceed 1,000 ppmw and may be as high as 4,000 or 5,000 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 193°C (380°F). 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 - 20, weight percent.

Process Configuration

The selected sulfur-containing, gasoline boiling range feed is treated in two steps by first hydrotreating the feed by effective contact of the feed with a hydrotreating catalyst, which is suitably a conventional hydrotreating catalyst, such as a combination of a Group VI and a Group VIII metal on a suitable refractory support such as alumina, under hydrotreating conditions. Under these conditions, at least some of the sulfur is separated from the feed molecules and converted to hydrogen sulfide, to produce a hydrotreated intermediate product comprising a normally liquid fraction boiling in substantially the same boiling range as the feed (gasoline boiling range), but which has a lower sulfur content and a lower octane number than the feed.

The hydrotreated intermediate product which also boils in the gasoline boiling range (and usually has a boiling range which is not substantially higher than the boiling range of the feed), is then treated by contact with the zeolite beta catalyst under conditions which produce a second product comprising a fraction which boils in the gasoline boiling range which has a higher octane number than the portion of the hydrotreated intermediate product fed to this second step. The product form this second step usually has a boiling range which is not substantially higher than the boiling range of the feed to the hydrotreater, but it is of lower sulfur content while having a comparable octane rating as the result of the second stage treatment.

Hydrotreating

The temperature of the hydrotreating step is suitably from 220°to 454°C (400° to 850°F), preferably (260 to 427°C)

(500° to 800 °F) with the exact selection dependent on the desulfurization desired for a given feed and catalyst. Because the hydrogenation reactions which take place in this stage are exothermic, a rise in temperature takes place along the reactor; this is actually favorable to the overall process when it is operated in the cascade mode because the second step is one which implicates cracking, an endothermic reaction. In this case, therefore, the conditions in the first step should be adjusted not only to obtain the desired degree of desulfurization but also to produce the required inlet temperature for the second step of the process so as to promote the desired shape-selective cracking reactions in this step. A temperature rise of 10° to 110°C (20° to 200°F) is typical under most hydrotreating conditions and with reactor inlet temperatures in the preferred 260° to 427°C (500° to 800°F) range, will normally provide a requisite initial temperature for cascading to the second step of the reaction. When operated in the two-stage configuration with interstage separation and heating, control of the first stage exotherm is obviously not as critical; two-stage operation may be preferred since it offers the capability of decoupling and optimizing the temperature requirements of the individual stages.

Since the feeds are readily desulfurized, low to moderate pressures may be used, typically from 445 to 10443 kPaa (50 to 1500 psig), preferably 2170 to 7,000 kPa (300 to 1000 psig). 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 90 to 900 $n.l.l^{-1}$. (500 to 5000 SCF/Bbl), usually 180 to 445 $n.l.l^{-1}$. (1000 to 2500 SCF/B). 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. 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; if it is necessary, however, to increase the denitrogenation in order to obtain a desired level of activity in the second step, the operating conditions in the first step may be adjusted accordingly.

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 hydrotreating catalyst will usually be determined by the type of hydrotreating process which is being carried out, although in most cases this will be as a down-flow, liquid phase, fixed bed process.

Octane Restoration - Second Step Processing

After the hydrotreating step, the hydrotreated intermediate product is passed to the second step of the process in which cracking takes place in the presence of the acidic catalyst comprising an intermediate pore size zeolite, preferably ZSM-5, although other zeolites of this type may

also be used, for example, ZSM-11, ZSM-22, ZSM-23, ZSM-35 or MCM-22. The effluent from the hydrotreating step may be subjected to an interstage separation in order to remove the inorganic sulfur and nitrogen as hydrogen sulfide and ammonia as well as light ends but this is not necessary and, in fact, it has been found that the first stage can be cascaded directly into the second stage. This can be done very conveniently in a down-flow, fixed-bed reactor by loading the hydrotreating catalyst directly on top of the second stage catalyst.

The conditions used in the second step of the process are selected to favor a number of reactions which restore the octane rating of the original, cracked feed at least to a partial degree. The reactions which take place during the second step which converts low octane paraffins to form higher octane products, both by the selective cracking of heavy paraffins to lighter paraffins and the cracking of low octane n-paraffins, in both cases with the generation of olefins. Ring-opening reactions may also take place, leading to the production of further quantities of high octane gasoline boiling range components. The catalyst may also function to improve product octane by dehydrocyclization/aromatization of paraffins to alkylbenzenes.

The conditions used in the second step are those which are appropriate to produce this controlled degree of cracking. Typically, the temperature of the second step will be 150 to 480°C (300° to 900 °F), preferably 177 to 400°C (350° to 750 °F) although the higher activity of the self-bound catalysts permits temperatures below 370°C (700°F) to be used with advantage. As mentioned above, however, a convenient mode of operation is to cascade the hydrotreated effluent into the second reaction zone and this will imply that the outlet temperature from the first step will set the initial temperature for the second zone. The feed characteristics and the inlet temperature of the

hydrotreating zone, coupled with the conditions used in the first stage will set the first stage exotherm and, therefore, the initial temperature of the second zone. Thus, the process can be operated in a completely integrated manner, as shown below.

The pressure in the second reaction zone is not critical since no hydrogenation is desired at this point in the sequence. The pressure will therefore depend mostly on operating convenience and will typically be comparable to that used in the first stage, particularly if cascade operation is used. Thus, the pressure will typically be 445 to 10445 kPa (50 to 1500 psig), 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}). The self-bound catalysts permit higher space velocities to be used relative to the bound catalysts because of their higher zeolite content. Hydrogen to hydrocarbon ratios typically of 0 to 890 $n.l.l^{-1}$. (0 to 5000 SCF/Bbl), preferably 18 to 445 $n.l.l^{-1}$. (100 to 2500 SCF/Bbl) will be selected to minimize catalyst aging.

The use of relatively lower hydrogen pressures thermodynamically favors the increase in volume which occurs in the second step and for this reason, overall lower pressures are preferred if this can be accommodated by the constraints on the aging of the two catalysts, esspecially that of the zeolite catalyst. In the cascade mode, the pressure in the second step may be constrained by the requirements of the first but in the two-stage mode the possibility of recompression permits the pressure requirements to be individually selected, affording the potential for optimizing conditions in each stage, although, as stated above, lower pressures are favored for the second stage.

Consistent with the objective of restoring lost octane while retaining overall product volume, the conversion to

products boiling below the gasoline boiling range (C_5-) during the second stage is held to a minimum. However, because the cracking of the heavier portions of the feed may lead to the production of products still within the gasoline range, no net conversion to C_5- products may take place and, in fact, a net increase in C_5+ material may occur during this stage of the process, particularly if the feed includes significant amount of the higher boiling fractions. It is for this reason that the use of the higher boiling naphthas is favored, especially the fractions with 95 percent points above 177°C (350°F) e.g. above 193°C (380°F) or higher, for instance, above 205°C (400°F). Normally, however, the 95 percent point (T_{95}) will not exceed 270°C (520°F) and usually will be not more than 260°C (500°F).

The catalyst used in the second step of the process possesses sufficient acidic functionality to bring the desired cracking reactions to restore the octane lost in the hydrotreating step. The preferred catalysts for this purpose are the intermediate pore size zeolitic behaving catalytic materials are exemplified by those 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 would have a Constraint Index between 2 and 12. U.S.-A 4,784,745 gives a definition of Constraint Index and a description of how this value is measured.

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. Zeolite MCM-22 is described in U.S.-A 4,954,325. 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 pore 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.

These materials are exemplary of the topology and pore structure of suitable acid-acting refractory solids; useful catalysts are not confined to the aluminosilicates and other refractory solid materials which have the desired acid activity, pore structure and topology may also be used. The zeolite designations referred to above, for example, define the topology only and do not restrict the compositions of the zeolitic-behaving catalytic components.

The preferred acidic component of the catalyst used in the second step is a zeolite such as ZSM-5. The aluminosilicate forms of this zeolite have been found to provide the requisite degree of acidic functionality and for this reason are the preferred forms of the zeolite. The aluminosilicate form of ZSM-5 is described in U.S.-A 3,702,886. Other isostructural forms of the zeolite containing other metals instead of aluminum such as gallium, boron or iron may also be used.

The acidic zeolite catalyst possesses sufficient acidic functionality to bring the desired reactions to restore the octane lost in the hydrotreating step. The catalyst should have sufficient acid activity to have cracking activity with respect to the second stage feed (the intermediate fraction), that is sufficient to convert the appropriate portion of this material as feed. suitably with an alpha value of at least 20, usually in the range of 20 to 800 and preferably at least 50 to 200 (values measured prior to addition of the metal component). The alpha value is one measure of the acid activity of a catalyst; it is a measure of the ability of the catalyst to crack normal hexane under prescribed conditions and is described in U.S. Patent-A 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 zeolite component of the catalyst is, according to the present invention, used without a binder or matrix material but, in order to minimize the pressure drop across the reactor, is formed into shaped particles such as extrudate or pellets, typically of at least 1.3mm (0.050 inch) in diameter, typically of 3mm (0.125 inch) diameter in the case of cylinders (with other shapes, the maximum cross-sectional distance). The catalyst can be said to be binder-free or self-bound since it is formed into the desired shapes without the aid of the normal binder. The catalysts will therefore consist essentially of the zeolite itself or, when a metal component is used, of the zeolite plus the metal component. In either case, no binder is present.

Methods for making catalyst particles consisting essentially of the crystalline zeolite are described in U.S.-A 4,582,815, to which reference is made for a description of the method. Briefly, the method described in that patent enables extrudates having high strength to be produced on conventional extrusion equipment by mulling the zeolite crystal with water to a soids level of 25 to 75 weight percent in the presence of 0.25 to 10 weight percent of a base such as sodium hydroxide (calculated as solid base, based on total solids content). The use of a metal component in addition to the acidic zeolite component may be desirable and any metal component may be added in the muller. A preferred metal component is molybdenum. Molybdenum is suitably used in an amount from 1 to 15 weight percent of the catalyst, more usually from 2 to 10 weight percent. The metal component has the capability of improving catalyst stability. When the metal can be

incorporated by ion-exchange of a metal cation onto the zeolite, aging is likely to be reduced by inhibiting the deposition of coke in the internal pore structure of the zeolite. Metals such as nickel and platinum which can be put into aqueous solutions of their cations such as nickel nitrate and platinum ammine complexes can be used in this way.

The catalysts are used in the form of solid, shaped particles which may be cylindrical or polygonal in cross-section, for example, triangular, square or hexagonal or, alternatively, may be of polylobal configuration, e.g. cloverleaf.

The particle size and shape of the zeolite catalyst will usually be determined by the type of conversion process which is being carried out with operation in a down-flow, mixed (vapor/liquid) phase, fixed bed process being typical and preferred.

The advantage of the self-bound catalysts relative to the bound catalysts is that stability is improved since there is no place for coke to be deposited, blocking access to the zeolite component of the catalyst. The self-bound catalysts is also more active and can be operated at lower temperatures where thermal and catalytic side reactions are less prevalent: dealkylation as well as the production of light gas by non-selective cracking are likely to be less favored at the lower operating temeperatures associated with the self-bound zeolite catalysts.

The conditions of operation and the catalysts can be selected, together with appropriate feed characteristics to result in a product slate in which the gasoline product octane is not substantially lower than the octane of the feed gasoline boiling range material; for example, not lower by more than 1 to 3 octane numbers, although slightly greater losses, typically 4 to 6 octane numbers,

may be optimal from the economic point of view with highly olefinic feeds. It is preferred also that the volume of the product should not be substantially less than that of the feed, for example, from 88 to 94 volume percent of the feed. In some cases, the volumetric yield and/or octane of the gasoline boiling range product may well be higher than those of the feed, as noted above and in favorable cases, the octane barrels (that is the octane number of the product times the volume of product) of the product will be higher than the octane barrels of the feed.

The operating conditions in the first and second steps may be the same or different but the exotherm from the hydrotreatment step will normally result in a higher initial temperature for the second step. Where there are distinct first and second conversion zones, whether in cascade operation or otherwise, it is often desirable to operate the two zones under different conditions. Thus the second zone may be operated at higher temperature and lower pressure than the first zone in order to maximize the octane increase obtained in this zone.

The second stage of the process should be operated under a combination of conditions such that at least half (1/2) of the octane lost in the first stage operation will be recovered, preferably such that all of the lost octane will be recovered. In favorable cases, the second stage can be operated so that there is a net gain of at least 1 % in octane over that of the feed, which is equivalent to a gain of at least 5 % based on the octane of the hydrotreated intermediate. The process should normally 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.

Examples

Example 1
Preparation of a Self-bound H-ZSM-5 Catalyst

An as-synthesized ZSM-5 was mulled to form a uniform material. A solution of NaOH containing 2 wt% NaOH was added and mulled. An additional amount of deionized water was added to form an extrudable paste. The mixture was auger extruded to 1.6mm (1/16 inch) cylindrical shape extrudates and dried at 127°C. The extrudates were then nitrogen calcined at 538°C for 3 hours and cooled. The calcined material was ammonium exchanged two times with 1M NH_4NO_3 solution (5 cc solution/ g catalyst) for 1 hr each. The exchanged catalyst was washed with deionized water and dried overnight at 127°C. The dried catalyst was calcined for 6 hours in air at 538°C. The catalyst was then steamed in 100% steam at 480°C for 5 hours. The properties of the final catalyst are listed in Table 1 below. The properties of hydrotreating catalysts are also reported in Table 1.

Example 2
Preparation of a Self-bound Mo/ZSM-5 Catalyst

An as-synthesized ZSM-5 was mulled to form a uniform material. A solution of NaOH containing 2 wt% NaOH was added and mulled. An additional amount of deionized water was added to form an extrudable paste. The mixture was auger extruded to 1.6mm (1/16inch) cylindrical shape extrudates and dried at 127°C. The extrudates were then nitrogen calcined at 538°C for 3 hours and cooled. The calcined material was ammonium exchanged two times with 1 M NH4NO3 solution (5 cc solution/ g catalyst) for 1 hr each. The exchanged catalyst was then washed with deionized water and dried overnight at 127°C. The dried catalyst was calcined for 6 hours in air at 538°C and was steamed in 100% steam at 480°C for 5 hours. The steamed extrudates were impregnated with 4 wt% Mo and 2 wt% P using an

incipient wetness method with a solution of ammonium heptamolybdate and phosphoric acid. The impregnated extrudates were then dried at 120°C overnight and calcined at 500°C for 3 hours. The properties of the final catalyst are listed in Table 1.

Example 3

Preparation of a Self-bound Mo/Beta Catalyst

An as-synthesized zeolite beta was mulled to form a uniform material. A solution of NaOH containing 6 wt% NaOH was added and mulled. An additional amount of deionized water was added to form an extrudable paste. The mixture was auger extruded to 1.6mm (1/16inch) cylindrical extrudates and dried in an oven overnight at 127°C. The dried material was ammonium exchanged two times with 1 M NH_4NO_3 solution (5 cc solution/ g catalyst) for 1 hr each. The extrudates were then nitrogen calcined at 482°C for 3 hours and air calcined for 6 hours at 538°C. The calcined extrudates were steamed in 100% steam at 480°C for 4 hours. The steamed extrudates were impregnated with 4 wt% Mo and 2 wt% P using an incipient wetness method with a solution of ammonium heptamolybdate and phosphoric acid. The impregnated extrudates were then dried at 120°C overnight and calcined at 500°C for 3 hours. The properties of the final catalyst are listed in Table 1.

Table 1
Physical Properties of Catalysts

	CoMo HDS	H-ZSM-5	Mo/ZSM-5	Mo/Beta
Zeolite	-	ZSM-5	ZSM-5	Beta
Zeolite, wt%	-	100	100	100
Alpha	-	100	100*	202*
Surface area, m2/g	260	356	317	445
n-Hexane sptn, wt%	-	12.0	10.8	-
cy-Hexane sptn, wt%	-	7.3	-	16.0
Co, wt%	3.4	-	-	-
Mo, wt%	10.2	-	3.95	3.7
P, wt%	-	-	1.9	1.9

* Before Mo impregnation.

These catalysts are intended to show good desulfurization and octane-uplift activities for various refinery streams, such as FCC naphtha, coker naphtha, and a LCO/FCC naphtha blend. Physical properties of the potential feeds are summarized in Tables 2 though 4 below.

Table 2
Properties of FCC Naphtha Feeds

General Properties	Full FCC Naphtha	Light FCC Naphtha	Heavy FCC Naphtha
Nom. Boiling Range,°C	40-200	75-200	175-255
SG, g/cc	0.7722	0.805	0.916
Total Sulfur, wt%	0.14	0.23	2.0
Nitrogen, ppm	76	86	180
Bromine Number	68	54.3	10.4
Research Octane	93.2	92.3	96.4
Motor Octane	81.0	80.3	84.0
Distillation,°C(D2887, wt%)			
IBP	13	575	110
5%	37	73	162
10%	52	88	182
30%	92	114	209
50%	127	142	228
70%	162	169	235
90%	203	207	255
95%	214	217	265
EP	231	245	280
Distillation,°C(D86, vol%)			
IBP	35	74	90
5%	57	102	194
10%	63	108	201
30%	86	123	215
50%	115	142	224
70%	149	167	233
90%	187	194	247
95%	198	203	253
EP	214	219	266

Notes:
1. The full FCC naphtha and the light FCC naphtha (75°C fraction) are from same FCC naphtha source.
2: A 182°C+ fraction of a different FCC naphtha.

Table 3
Properties of Coker Naphtha Feed

General Properties	Coker Naphtha I	Coker Naphtha II
Nom. Boiling Range, °C	170 - 330	180 - 400
SG, g/cc	0.742	0.772
Total Sulfur, wt%	0.7	0.6
Nitrogen, ppm	71	120
Bromine Number	72.0	61.9
Research Octane	68.0	60.0
Motor Octane	60.6	56.3
Distillation, °C (D2887)		
IBP	21	76
5%	37	95
10%	59	100
30%	96	129
50%	123	153
70%	147	173
90%	172	199
95%	177	204
EP	212	227

Table 4
Properties of Heavy FCC Naphtha, LCO, and 90/10 Blend

	Heavy FCC Naph	Full LCO	90/10 v/v Heavy naphtha/LCO
Nom. Boiling Range, °C	175-255	315-400	175-270
SG, g/cc	0.916	-	0.922
Total Sulfur, wt%	1.9	-	2.0
Nitrogen, ppm	180	400	230
Bromine Number	10.4	2.3	15.0
Research Octane	96.4	-	95.5
Motor Octane	84.0	-	83.7
Distillation, °C (D86)			
IBP	90	304	92
5%	194	331	192
10%	201	337	202
30%	215	353	217
50%	224	365	227
70%	233	377	238
90%	247	393	260
95%	253	398	279
EP	266	398	324

Claims:

1. A process of upgrading a cracked, olefinic sulfur-containing feed fraction boiling in the gasoline boiling range by hydrodesulfurizing the cracked, olefinic sulfur-containing feed fraction, to produce an intermediate product comprising a normally liquid fraction which has a reduced sulfur content and a reduced octane number as compared to the feed and then contacting the gasoline boiling range portion of the intermediate product with a second, acidic catalyst, to convert the gasoline boiling range portion of the intermediate product to a product comprising a fraction boiling in the gasoline boiling range having a higher octane number than the gasoline boiling range fraction of the intermediate product, characterized in that the second catalyst comprise shaped particles of a self-bound acidic zeolite.

2. The process as claimed in claim 1 in which the feed fraction comprises a catalytically cracked naphtha fraction having a boiling range within the range of C_5 to 215°C.

3. The process as claimed in claim 1 in which the feed fraction comprises a catalytically cracked naphtha fraction having a boiling range within the range of 165 to 260°C., preferably 165 to 215°C.

4. The process as claimed in any of claims 1 to 3 in which the feed fraction comprises a naphtha fraction having a 95 percent point of at least 193°C, preferably at least 205°C.

5. The process as claimed in any of claims 1 to 4 in which the feed fraction comprises a thermally cracked naphtha fraction such as a coker naphtha.

6. The process as claimed in nay of claims 1 to 5 in which the acidic zeolite is in the aluminosilicate form.

7. The process as claimed in any of claims 1 to 6 in which the acidic zeolite comprises ZSM-5.

8. The process as claimed in any of claims 1 to 7 in which the second stage is carried out at a temperature of 150 to 482°C, a pressure of 446 to 10,443 kPaa, a space velocity of 0.5 to 10 $hr.^{-1}$ LHSV, and a hydrogen to hydrocarbon ratio of 0 to 890 $n.l.l.^{-1}$. of hydrogen per barrel of feed, preferably at a temperature of 177 to 482°C, a pressure of 2170 to 7,000 kPaa, a space velocity of 1 to 6 $hr.^{-1}$ LHSV, and a hydrogen to hydrocarbon ratio of 17.8 to 445 n. l. $l.^{-1}$.

9. The process as claimed in any of claims 1 to 8 in which the shaped particles of the self-bound zeolite catalyst consist essentially of the acidic zeolite, optionally with a metal component, preferably molybdenum.

10. The process as claimed in any of claims 1 to 9 in which the particles of the self-bound zeolite catalyst are formed by the extrusion of a mixture of the zeolite with water in the presence of a basic material, preferably sodium hydroxide an amount from 0.25 to 10 weight percent based on the total solids.

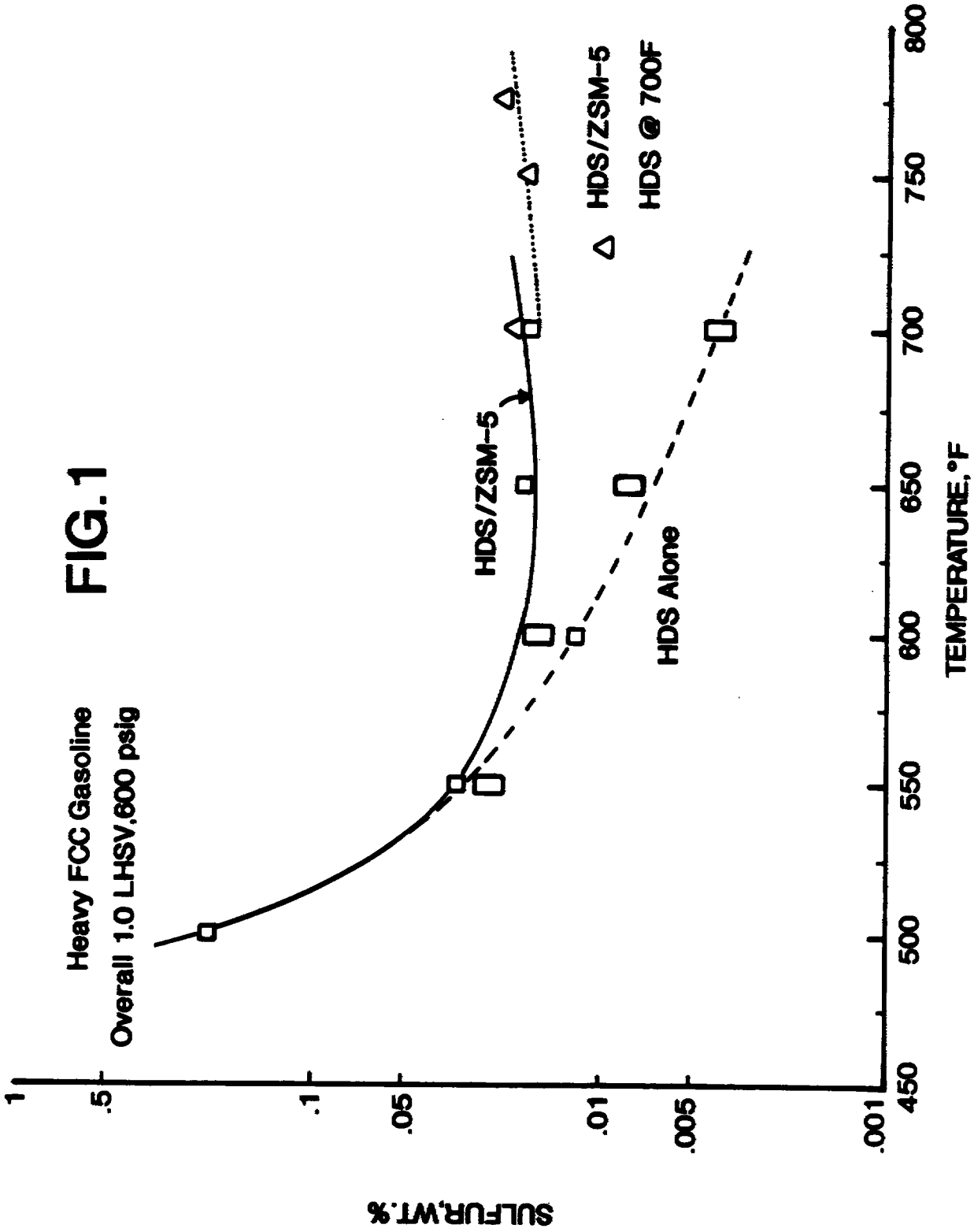
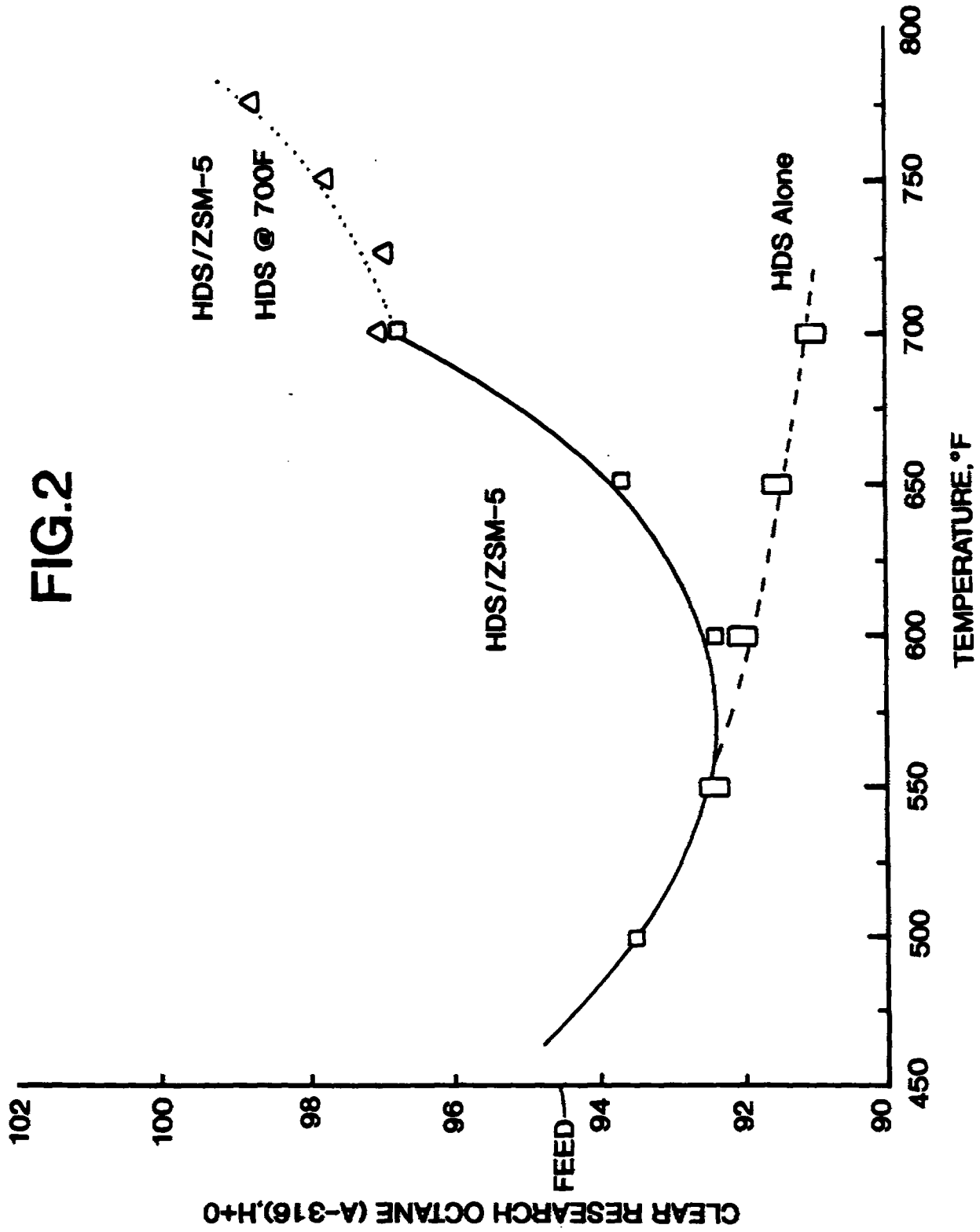

Heavy FCC Gasoline
Overall 1.0 LHSV,800 psig
HDS/ZSM-5
HDS Alone
HDS/ZSM-5
HDS @ 700F
SULFUR,WT.%
1
.5
.1
.05
.01
.005
.001
450
500
550
600
650
700
750
800
TEMPERATURE, °F

FIG. 1

FIG.2


CLEAR RESEARCH OCTANE (A-316),H+0
102
100
98
96
FEED
94
92
90
450
500
550
600
650
700
750
800
TEMPERATURE, °F
HDS/ZSM-5
HDS @ 700F
HDS/ZSM-5
HDS Alone

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International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C10G 67/00, 69/00

A1

(11) International Publication Number: WO 96/07713

(43) International Publication Date: 14 March 1996 (14.03.96)

(21) International Application Number: PCT/US95/09336

(22) International Filing Date: 25 July 1995 (25.07.95)

(30) Priority Data:
303,909 9 September 1994 (09.09.94) US

(81) Designated States: CA, FI, JP, KR, MX, NO, SG, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

96120 43-1

RTMPs copy

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(54) Title: GASOLINE UPGRADING PROCESS

(57) Abstract

A process for catalytically desulfurizing cracked fractions in the gasoline boiling range to acceptable sulfur levels uses an initial hydrotreating step to desulfurize the feed with some reduction in octane number, after which the desulfurized material is treated with a self-bound or binder-free zeolite to restore lost octane. The process may be utilized to desulfurize catalytically and thermally cracked naphthas such as FCC naphtha as well as pyrolysis gasoline and coker naphthas, while maintaining octane so as to reduce the requirement for reformate and alkylate in the gasoline blend. The self-bound catalyst offers advantages in activity and permits the process to be carried out at lower temperatures.

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