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GASOLINE UPGRADING PROCESS

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(71) Applicant(s)
MOBIL OIL CORPORATION

(72) Inventor(s)
BIRBAL CHAWLA; DOMINICK NICHOLAS MAZZONE; MICHAEL SEBASTIAN SARLI; STUART SHAN-SAN SHIH; HYE KYUNG C TIMKEN

(74) Attorney or Agent
PHILLIPS ORMONDE & FITZPATRICK , 367 Collins Street, MELBOURNE VIC 3000

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(57) Claim

1. A process of upgrading a cracked, olefinic sulfur-containing feed fraction boiling in the gasoline boiling range and having a 95 percent point of at least 325°F which comprises:

contacting the cracked, olefinic sulfur-containing feed fraction with a hydrodesulfurization catalyst in a first reaction zone, operating under a combination of elevated temperature, elevated pressure and an atmosphere comprising hydrogen, 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;

contacting at least the gasoline boiling range portion of the intermediate product in a second reaction zone with an acidic catalyst comprising zeolite beta in combination with a molybdenum hydrogenation component, 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.

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(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).

(72) Inventors: CHAWLA, Birbal; 116 Apley Drive, Cherry Hill, NJ 08034 (US). MAZZONE, Dominick, Nicholas; 10 North Monroe Avenue, Wenonah, NJ 08090 (US). SARLI, Michael, Sebastian; 307 Mt. Vernon Avenue, Haddonfield, NJ 08033 (US). SHIH, Stuart, Shan-San; 7 Abinger Lane, Cherry Hill, NJ 08003 (US). TIMKEN, Hye, Kyung, C.; 44 N. Girard Street, Woodbury, NJ 08096 (US).

(74) Agents: SINNOTT, Jessica, M. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).

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(54) Title: GASOLINE UPGRADING PROCESS

(57) Abstract

Low sulfur gasoline of relatively high octane number is produced from a cracked, sulfur-containing olefinic naphthas by hydrodesulfurization followed by treatment over an acidic catalyst comprising zeolite beta with a metal hydrogenation component, preferably a mild hydrogenation component such as molybdenum. The treatment over the acidic catalyst in the second step restores the octane loss which takes place as a result of the hydrogenative treatment and results in a low sulfur gasoline product with an octane number comparable to that of the feed naphtha. In favorable cases, using feeds of extended end point such as heavy naphthas with 95 percent points above about 380 °F (about 193 °C), improvements in both product octane and yield relative to the feed may be obtained.

GASOLINE UPGRADING PROCESS

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 EPA Complex Model.

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 about 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 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.

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. 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 cleaner burning, less polluting fuels, especially low sulfur fuels. This inherent tension is yet more marked in the current supply situation for low sulfur, sweet crudes.

Processes for improving the octane rating of catalytically cracked gasolines have been proposed. U.S. 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. 3,767,568 and U.S. 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 International Application Published on 3 March 1993, WO 93/04146, we have described processes for the upgrading of gasoline by sequential hydrotreating and selective cracking steps. 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.

As shown in these prior applications, zeolite ZSM-5 is effective for restoring the octane loss which takes place when the initial naphtha feed is hydrotreated. When the hydrotreated naphtha is passed over the catalyst in the second step of the process, some components of the gasoline are cracked into lower boiling range materials, if these boil below the gasoline boiling range, there

will be a loss in the yield of the gasoline product. If, however, the cracking products are within the gasoline range, a net volumetric yield increase occurs. To achieve this, it is helpful to increase the end point of the naphtha feed to the extent that this will not result in the gasoline product end point or similar restrictions (e.g. T_{90}, T_{95}) being exceeded. While the intermediate pore size zeolites such as ZSM-5 will convert the higher boiling components of the feed, a preferred mode of operation would be to increase conversion of the higher boiling components to products which will remain in the gasoline boiling range.

We have now found that zeolite beta is relatively more effective than ZSM-5 for the conversion of the higher boiling components of the naphtha, it converts more of the heavier, back-end fraction to lighter gasoline components. The improved back-end cracking selectivity of zeolite beta has potential benefit in situations where reduced gasoline end-point is required. The presence of a hydrogenation component on the zeolite beta catalyst, preferably a mild hydrogenation component such as molybdenum, has also been found to be effective for optimizing gasoline octane and yield and for catalyst activity, stability and selectivity.

According to the present invention, therefore, a process for catalytically desulfurizing cracked fractions in the gasoline boiling range to acceptable 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 zeolite beta catalyst to restore lost octane. In favorable cases, the volumetric yield of gasoline boiling range product is not substantially reduced and may even be increased so that the number of octane barrels of product produced is at least equivalent to the number of octane barrels of feed introduced into the operation.

The process may be utilized to desulfurize catalytically and thermally cracked naphthas including

light as well as 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. Since reforming generally implies a significant yield loss, this constitutes a marked advantage of the present process.

The single figure of the accompanying drawings is a plot of the road octane number of the treated product as a function of the operating temperature of hydrotreating and second stage conversion with different catalysts, obtained in comparison tests described in Example 6.

Feed

The feed to the process comprises a sulfur-containing petroleum fraction which boils in the gasoline boiling range. Feeds of this type include light naphthas typically having a boiling range of about C_6 to 330 °F, full range naphthas typically having a boiling range of about C_5 to 420 °F, heavier naphtha fractions boiling in the range of about 260 °F to 412 °F, or heavy gasoline fractions boiling at, or at least within, the range of about 330 to 500 °F, preferably about 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 about 325°F(163°C) and preferably at least about 350°F(177°C), for example, 95 percent points (T_{95}) of at least 380°F (about 193°C) or at least about 400°F (about 220°C). The process may be applied to thermally cracked and catalytically cracked naphthas since both 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 about 100°F (38°C) to about 300°F (150°C), more usually in the range of about 200°F(93°C) to about 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 about 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 about 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 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 about 500 ppmw. For the fractions which have 95 percent points over about 380°F(193°C), the sulfur content may exceed about 1,000 ppmw and may be as high as 4,000 or 5,000 ppmw or even higher, as shown below. The nitrogen content is not as characteristic of the feed as the sulfur content and is preferably not greater than about 20 ppmw although higher nitrogen levels typically up to about 50 ppmw may be found in certain higher boiling feeds with 95 percent points in excess of about 380°F(193°C). The nitrogen level will, however, usually not be greater than 250 or 300 ppmw. 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 about 400° to 850°F (about 220°to 454°C), preferably about 500° to 800 °F (about 260 to 427°C) 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 about 20° to 200°F (about 11° to 111°C) is typical under most hydrotreating conditions and with reactor inlet temperatures in the preferred 500° to 800°F (260° to 427°C) 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 about 50 to 1500 psig (about 445 to 10443 kPa), preferably about 300 to 1000 psig (about 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 about 0.5 to 10 LHSV (hr^{-1}), preferably about 1 to 6 LHSV (hr^{-1}). The hydrogen to hydrocarbon ratio in the feed is typically about 500 to 5000 SCF/Bbl (about 90 to 900 $n.l.l^{-1}$.), usually about 1000 to 2500 SCF/B (about 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. 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, 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 are generally well known in the petroleum arts, and the choice of the particular mode of operation is a matter left to the discretion of the operator, although the fixed bed arrangements are preferred for simplicity of operation.

A change in the volume of gasoline boiling range material typically takes place in the first step. Although some decrease in volume occurs as the result of the conversion to lower boiling products (C_5-), the conversion to C_5- products is typically not more than 5 vol percent and usually below 3 vol percent and is normally compensated for by the increase which takes place as a result of aromatics saturation. An increase in volume is typical for the second step of the process where, as the result of cracking the back end of the hydrotreated feed, cracking products within the gasoline boiling range are produced. An overall increase in volume of the gasoline boiling range (C_5+) materials may occur.

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 containing zeolite beta. 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 separation of the light ends at this point may be desirable if the added complication is acceptable since the saturated C_4-C_6 fraction from the hydrotreater is a highly suitable feed to be sent to the isomerizer for conversion to iso-paraffinic materials of high octane rating; this will avoid the conversion of this fraction to non-gasoline (C_5-) products in the second stage of the process. Another process configuration with potential advantages is to take a heart cut, for example, a 195°-302°F. (90°-150°C) fraction, from the first stage product and send it to the reformer where the low octane naphthenes which make up a significant portion of this fraction are converted to high octane aromatics. The heavy portion of the first stage effluent is, however, sent to the second step for restoration of lost octane by treatment with the acid catalyst. The hydrotreatment in the first stage is effective to desulfurize and denitrogenate the catalytically cracked naphtha which permits the heart cut to be processed in the reformer. Thus, the preferred configuration in this alternative is for the second stage to process the C_8+ portion of the first stage effluent and with feeds which contain significant amounts of heavy components up to about C_{13} e.g. with C_9 -C_{13} fractions going to the second stage, improvements in both octane and yield can be expected.

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; zeolite beta is particularly effective for the production of branched-chain C_4 and C_5 materials, possibly by the ring-opening reactions. 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. In favorable cases, the original octane rating of the feed may be completely restored or perhaps even exceeded. Since the volume of the second stage product will typically be comparable to that of the original feed or even exceed it, the number of octane barrels (octane rating x volume) of the final, desulfurized product may exceed the octane barrels of the feed.

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 about 300° to 900 °F (about 150 to 480°C), preferably about 350° to 800 °F (about 177°C). 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 although a lower pressure in this stage will tend to favor olefin production with a consequent

favorable effect on product octane. 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 about 50 to 1500 psig (about 445 to 10445 kPa), preferably about 300 to 1000 psig (about 2170 to 7000 kPa) with comparable space velocities, typically from about 0.5 to 10 LHSV (hr^{-1}), normally about 1 to 6 LHSV (hr^{-1}). Hydrogen to hydrocarbon ratios typically of about 0 to 5000 SCF/Bbl (0 to 890 $n.l.l^{-1}$.), preferably about 100 to 2500 SCF/Bbl (about 18 to 445 $n.l.l^{-1}$.) 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. 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.

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 about 350°F (about 177°C) and even more preferably above

about 380°F (about 193°C) or higher, for instance, above about 400°F (about 205°C). Normally, however, the 95 percent point (T_{95}) will not exceed about 520°F (about 270°C) and usually will be not more than about 500°F (about 260°C).

The active component of the catalyst used in the second step is zeolite beta. 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 zeolite beta is described in U.S. Patent No. 3,308,069 (Wadlinger). Other isostructural forms of the zeolite containing other metals instead of aluminum such as gallium, boron or iron may also be used.

The zeolite beta catalyst possesses sufficient acidic functionality to bring about 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. One measure of the acid activity of a catalyst is its alpha number. This is a measure of the ability of the catalyst to crack normal hexane under prescribed conditions. This test has been widely published and is conventionally used in the petroleum cracking art, and compares the cracking activity of a catalyst under study with the cracking activity, under the same operating and feed conditions, of an amorphous silica-alumina catalyst, which has been arbitrarily designated to have an alpha activity of 1. The alpha value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst. The alpha test gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time) of the test catalyst relative to the standard catalyst which is taken as an alpha of 1 (Rate Constant = 0.016 sec $^{-1}$). The alpha test is described in U.S. Patent 3,354,078 and

in J. Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980), to which reference is made for a description of the test. 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 beta catalyst suitably has an alpha activity of at least about 20, usually in the range of 20 to 800 and preferably at least about 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 intermediate product as is necessary to restore lost octane without severely reducing the volume of the gasoline boiling range product.

The zeolite component of the catalyst will usually be composited with a binder or substrate because the particle sizes of the pure zeolite 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 zeolite beta catalyst contains a metal hydrogenation function for improving catalyst activity and selectivity. In addition, the metal hydrogenation components may also favorably affect the operation of the process, especially with respect to catalyst activity, selectivity and stability. The aging characteristics of the zeolite beta catalysts are, in particular, favorably affected by the inclusion of the mild hydrogenation component. Suitable hydrogenation components on the catalyst are metals having hydrogenation-dehydrogenation activity, including metals such as the Group VI and VIII base metals or noble metals or combinations of such metals. Noble metals which may be used include platinum

and palladium but these may offer no significant advantage over base metals such as nickel, cobalt, molybdenum or chromium and will normally not be preferred, particularly when, as with platinum, sensitivity to sulfur poisoing may arise with the hydrotreated sulfur-containing feeds. Combinations of metals may also be used, for example, a combination of a Group VI metal such as chromium, molybdenum or tungsten with a Group VIII metal such as cobalt or nickel. It has been found that the mild hydrogenation activity provided by base metals such as the Group VI metals, molybdenum and tungsten, either alone or in appropriately low concentrations with Group VIII base metals such as nickel or cobalt, e.g. CoMo, NiMo, provide good results. Molybdenum has been found to give good results, particularly when catalyst stability is concerned since molybdenum is resistant to sulfur poisoning. More active hydrogenation components such as nickel in appropriate concentrations may, however, also be used. If a base metal hydrogenation component is used, a metal content of about 0.5 to about 5 weight percent is suitable although higher metal loadings typically up to about 10 weight percent may be used. If a more active noble metal such as platinum is used, a metal content of about 0.1 to about 2 weight percent would be typical and appropriate. Even though the effluent from the hydrotreater contains inorganic sulfur and nitrogen, the use of the more active zeolite catalyst in the second step permits noble metals to be present on the catalyst.

The metal component may be incorporated into the catalyst by conventional procedures such as cation exchange, impregnation into an extrudate or by mulling with the zeolite and the binder. When the metal is added in the form of an anionic complex such as molybdate or vanadate, impregnation or addition to the muller will be appropriate methods.

The particle size and the nature of the zeolite beta 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 fixed-bed type of operation preferred.

The conditions of operation and the catalysts should 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; that is, not lower by more than about 1 to 3 octane numbers. It is preferred also that the volume of the product should not be substantially less than that 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.

In one example of the operation of this process, it is reasonable to expect that, with a heavy cracked naphtha feed, the first stage hydrodesulfurization will reduce the octane number by at least 1.5 %, more normally at least about 3 %. With a full range naphtha feed, it is reasonable to expect that the hydrodesulfurization operation will reduce the octane number of the gasoline boiling range fraction of the first intermediate product

by at least about 5 %, and, if the sulfur content is high in the feed, that this octane reduction could go as high as about 15 %.

The second stage of the process should be operated under a combination of conditions such that at least about 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, most preferably that the second stage will be operated such that there is a net gain of at least about 1 % in octane over that of the feed, which is about equivalent to a gain of about at least about 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 about 50 %, preferably at least about 75 %, as compared to the sulfur content of the feed.

Conversion of the higher boiling coponents of the naphtha is enhanced by the use of the zeolite beta catalyst in the second step of the process. Compared to a ZSM-5 based catalyst, the conversion of all fractions boiling above 300°F (about 150°C) is significantly greater. Zeolite beta offers other additional advantages compared to ZSM-5: the final gasoline product may be brought to a lower total sulfur level, compared either to a process using a ZSM-5 catalyst or even to a simple hydrodesulfurization with no octane restoration. The zeolite beta catalysts are also very effective in reducing mercaptan sulfur as well as the heavier sulfur components: the use of the zeolite beta octane restoration step is effective to reduce total sulfur and mercaptan sulfur below the levels of the intermediate product from the hydrodesulfurization step.

Examples 1 - 2

Examples showing the use of ZSM-5 are given in WO 93/04146, to which reference is made for the details of these examples.

Examples 1 - 3 below illustrate the preparation of

various metal-containing zeolite beta catalysts for use in the present process. Performance comparisons of these catalysts are given in subsequent Examples, using two ZSM-5 catalysts (Examples 4, 5) for comparison. In these examples, parts and percentages are by weight unless they are expressly stated to be on some other basis. Temperatures are in °F and pressures in psig, unless expressly stated to be on some other basis.

Example 1

Preparation of a Mo/zeolite beta catalyst

A physical mixture of 65 parts zeolite beta and 35 parts pseudoboehmite alumina powder (LaRoche Versal™ alumina) as mulled to form a uniform mixture and formed into 1/16 inch (1.5 mm) cylindrical shape extrudates using a standard augur extruder. All components were blended based on parts by weight on a 100% solids basis. The extrudates were dried on a belt drier at 127°C, and were then nitrogen calcined at 480°C for 3 hours followed by a 6 hour air calcination at 538°C. Then the catalyst was steamed at 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 ammonium heptamolybdate and phosphoric acid solution. 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 below which also gives the properties of the HDS catalyst used in the performance comparisons.

Example 2

Peparation of a Pt/zeolite Beta Catalyst

The procedure used in Example 1 was followed except that after the air calcination the calcined extrudates were Pt exchanged using $Pt(NH_3)_4Cl_2$ dissolved in 0.5M NH_4NO_3 solution (5cc/g catalyst). The exchanged extrudates were dried at 120°C overnight and calcined at 350°C for 3 hours. The properties of the final catalyst are given in Table 1 below.

Example 3

Preparation of Steamed Pt/zeolite Beta Catalyst

The procedure of Example 2 was repateated except that after the air calcination the catalyst was steamed with 100% steam at 538°C for 10 hours. The steamed extrudates were then Pt exchanged using $Pt(NH_3)_4Cl_2$ dissolved in deionized water (5cc/g catalyst). The exchanged extrudates were dried at 120°C overnight and calcined at 350°C for 3 hours. The properties of the final catalyst are given in Table 1 below.

Example 4

Preparation of a ZSM-5/Al_2O_3 Catalyst

A physical mixture of 65 parts ZSM-5 and 35 parts pseudoboehmite alumina powder (LaRoche Versal™ alumina) was mulled to form a uniform mixture. All components were blended based on parts by weight on a 100% solids basis. Sufficient amount of deionized water was added to form an extrudable paste. The mixture was auger extruded to 1/16 inch (1.5 mm) cylindrical shape extrudates and dried on a belt drier at 127°C. The extrudates were then nitrogen calcined at 480°C for 3 hours followed by a 6 hour air calcination at 538°C. Then the catalyst was steamed at 100% steam at 480°C for approximately 4 hours. The properties of the final catalyst are listed in Table 1 below.

Example 5

Preparation of a ZSM-5/SiO_2 Catalyst

A physical mixture of 65 parts ZSM-5 and 17.5 parts precipitated siica (Nasilco Ultrasil VN3) and 17.5 parts cooloidal silica (duPont Ludox HS-40) was mulled to form a uniform mixture. An additional 6 parts NaOH solution (50 percent by weight) was added to improve extrudability. All components were blended based on parts by weight on a 100% solids basis. Sufficient amount of deionized water was added to form an extrudable paste. The mixture was auger extruded to 1/16 inch (1.5 mm) cylindrical shape extrudates and dried overnight at 120°C. The dried extrudates were then twice ammonium exchanged at room temperature (one hour each) using 1M

NH_4NO_3 solution (5ml/g catalyst). The extrudates were then blown down with air to dry and further dried at 120°C overnight. The dried extrudates were nitrogen calcined at 460°C for 3 hours, followed by a six hour air calcination at 538°C. The catalyst was then steamed at 480°C for 5 hours. The properties of the final catalyst are listed in Table 1 below.

TABLE 1
Physical Properties of Catalysts

	HDS Cat	Stmd Al_2O_3/ ZSM-5	Stmd SiO_2/ ZSM-5	Stmd Mo/ Beta	Unstmd Pt/ Beta	Stmd Pt/ Beta
Zeolite		ZSM-5	ZSM-5	Beta	Beta	Beta
Zeolite, wt%	-	65	65	65	65	65
Alpha	-	101	108	141*	350*	40*
Surface area, m^2/g	260	337	274	415	483	-
n-Hexane sorption, cc/g	-	10.4	5.2	-	-	12.3
cy-Hexane sorption, cc/g	-	9.3	9.0	14.9	17.7	5.3
Co, wt%	3.4	NA	NA	NA	NA	NA
Mo, wt%	10.2	NA	NA	3.8	NA	NA
P, wt%	NA	NA	NA	1.7	NA	NA
Pt, wt%	NA	NA	NA	NA	0.47	0.6

* : Before the metal loading.
NA: Not applicable.

Example 6

Performance Comparison - Heavy FCC Naphtha

The performances of the zeolite beta catalysts of Examples 1-3 were compared with that of the ZSM-5/Al_2O_3 catalyst of Example 4 using a heavy cracked naphtha feed. The properies of the cracked naphtha feed are given in Table 2 below together with the properties of a light cracked naphtha feed and a coker naphtha feed used in

following performance comparisons.

TABLE 2
Properties of Naphtha Feeds

General Properties	Heavy Naphtha	Light Naphtha	Coker Naphtha
Nominal Boiling Range, °F	350-490	180-400	200-400
Specific Gravity, g/cc	0.916	0.805	0.772
Total Sulfur, wt%	2.0	0.23	0.48
Nitrogen, ppm	180	86	120
Bromine Number	10.4	54.3	61.9
Research Octane	94.4	92.3	NA
Motor Octane	84.0	80.3	54.5
Distillation, °F (D2887)			
IBP	136	135	168
5%	323	163	203
10%	360	191	212
30%	408	237	264
50%	442	287	307
70%	456	336	344
90%	491	404	390
95%	510	422	399
EP	565	474	441

The experiments were carried out in a fixed-bed pilot unit employing a commercial CoMo/Al203 hydrodesulfurization (HDS) catalyst in an upper reaction zone and the zeolite catalyst in a lower zone. Typically 30-60 cc of each catalyst was sized to 14/28 mesh and loaded in a reactor. The pilot unit was operated in a cascade mode where desulfurized effluent from the hydrotreating stage cascaded directly to the zeolite-containing catalyst to restore octane without removal of ammonia, hydrogen sulfide, and light hydrocarbon gases at

the interstage. The HDS/zeolite catalyst system was presulfided with a 2%H_2S/98%H_2 gas mixture prior to the evaluations. The conditions employed for the experiments included temperatures from 500-775°F (260°-413°C), 1.0 LHSV (based on fresh feed relative to total catalysts), 3000 scf/bbl (534 n.l.l^{-1}) of once-through hydrogen circulation, and hydrogen inlet pressure of 600 psia (4140 kPaa). The ratio of HDT to the cracking catalyst was typically 1/1, vol/vol.

The results of the comparison are given below in Table 3. The results are also shown graphically in the figure.

TABLE 3
Process Performance Comparison (Heavy FCC Naphtha)

	Feed	Steamed H/ZSM-5	Steamed Mo/Beta	Unsteamed Pt/Beta	Steamed Pt/Beta
Stage 1 Temp., °F	-	704	700	704	700
Stage 2 Temp., °F	-	700	701	698	701
Product Analyses					
Sulfur, wt%	2.0	0.01	0.003	0.005	<0.002
Nitrogen, ppmw	180	1	1	4	3
Research Octane	96.4	97.1	98.9	98.5	94.0
Motor Octane	84.0	84.7	86.4	85.1	85.3
C_5+ Gasoline Yields					
vol%	100	99.6	100.3	101.6	101.2
wt%	100	96.0	95.1	95.2	95.3
Process Yields, wt%					
C_1 + C_2	-	0.1	0.1	0.2	0.1
C_3	-	1.1	0.8	1.0	1.2
C_4	-	2.1	3.3	2.8	3.0
C_5-300°F	3.8	13.5	22.1	29.6	18.2

	Feed	Steamed H/ZSM-5	Steamed Mo/Beta	Unsteamed Pt/Beta	Steamed Pt/Beta
Stage 1 Temp., °F	-	704	700	704	700
Stage 2 Temp., °F	-	700	701	698	701
Product Analyses					
Sulfur, wt%	2.0	0.01	0.003	0.005	<0.002
300-390°F	13.9	20.9	22.9	24.2	23.4
390-420°F	21.1	20.1	17.0	14.9	18.6
420°F+	61.2	41.2	33.1	26.5	35.2
Conversion, %					
300°F+	-	14	24	38	24
390°F+	-	25	39	48	35
420°F+	-	32	46	55	42
Hydrogen Consumption (scf/bbl)	-	840	860	810	1041

Conditions: 600 psig, 1.0 Overall LHSV.

These results show that all forms of the zeolite beta catalyst are more active for 420°F+ (215°C+) conversion than ZSM-5. Desulfurization is better with the zeolite beta catalysts, especially the Pt/beta although this is rather less effective in restoring octane.

The data contained in Table 3 and graphically in the figure demonstrate the improvement in catalyst activity and selectivity shown by the catalyst of the present invention. The HDS and Mo/zeolite beta combination clearly exhibits superior activity in recovering the feed octane. For example, at 700°F the Mo/zeolite beta catalyst produced gasoline with 98-99 research octane while the ZSM-5 catalyst produces 97 research octane. The Mo/zeolite beta catalyst exhibits approximately 50°F higher activity compared to fresh H-ZSM-5 in recovering the feed octane. The zeolite beta catalysts also exhibit

a better yield-octane relationship, with a 1 vol% greater yield than ZSM-5. The large-pore zeolite beta catalysts achieve greater back-end conversion than H-ZSM-5 (46-55% vs. 32%, Table 3). The Mo/zeolite beta catalyst exhibits comparable H2 consumption to the H-ZSM-5 catalyst (810-860 scf/bbl vs. 840 scf/bbl, Table 3)(144-153 vs. 149 n. l. $l.^{-1}$), although the steamed Pt/beta catalyst is rather higher.

Example 7

Performance Comparison - Light FCC Naphtha

The catalysts of Example 1, 2 and 4 were tested in the same way as described in Example 6 above but using the light FCC naphtha (Table 2) as the feed. The conditions and results are shown in Table 4 below.

TABLE 4
Process Performance Comparison (Light FCC Naphtha)

	Feed	Stmd. H/ZSM-5	Stmd. Mo/Beta	Unstmd. Pt/Beta
Stage 1 Temp., °F	-	699	700	649
Stage 2 Temp., °F	-	749	749	732
Product Analyses				
Sulfur, ppmw	2300	220	84	NA
Nitrogen, ppmw	86	<1	<1	NA
Research Octane	92.3	88.8	93.2	95.4
Motor Octane	80.3	80.3	83.7	83.1
C_5+ Gasoline Yields				
vol%	100	92.6	87.7	76.5
wt%	100	92.4	87.3	72.0
Process Yields, wt%				
$C_1 + C_2$	-	0.3	0.3	0.7
C_3	-	2.6	2.5	6.8
C_4	-	4.7	10.0	20.5
C_5-300°F	56	54.7	60.7	55.7

	Feed	Stmd. H/ZSM-5	Stmd. Mo/Beta	Unstmd. Pt/Beta
Stage 1 Temp., °F	-	699	700	649
Stage 2 Temp., °F	-	749	749	732
Product Analyses				
Sulfur, ppmw	2300	220	84	NA
300°F$^+$	44	37.7	26.6	16.3
Conversion, %				
300°F$^+$	-	37	39	62
330°F$^+$	-	13	43	62
Hydrogen Consumption (scf/bbl)	-	320	410	1105

NA: not analyzed.
Conditions: 600 psig, 1.0 Overall LHSV.

The data contained in Table 4 demonstrate the improvement in activity of Mo/beta and Pt/beta catalysts over ZSM-5. Even at 750°F, the H-ZSM-5 catalyst cannot recover the feed octane. The Mo/beta catalyst exceeds the feed octane at 750°F and the Pt/beta catalyst at 725°F. The Mo/beta catalysts achieves much greater 330°F$^+$ back-end conversion than H-ZSM-5 with a slight increase in H_2 consumption.

Example 8

Performance Comparison - Coker Naphtha

This example illustrates that Pt/zeolite beta catalyst (Example 2) can be used to upgrade a coker naphtha feed (Table 2) to produce a gasoline-range boiling product with a low sulfur level. The comparison was carried out in the same way as described above in Examples 6 and 7. The conditions and results are given in Table 5 below.

TABLE 5
Process Performance (Coker Naphtha)

	Feed	Unsteamed Pt/Beta
Stage 1 Temp., °F	-	600
Stage 2 Temp., °F	-	702
Product Analyses		
Sulfur, wt%	0.48	0.003
Nitrogen, ppmw	120	1
Research Octane	NA	60.0
Motor Octane	54.5	63.2
C_5+ Gasoline Yields		
vol%	100	87.9
wt%	100	85.3
Process Yields, wt%		
$C_1 + C_2$	-	0.1
C_3	-	3.2
C_4	-	11.9
C_5-300°F	46.8	62.9
300°F+	53.2	22.4
Conversion, %		
300°F+	-	58
Hydrogen Consumption (scf/bbl)	-	553

Conditions: 600 psig, 1.0 Overall LHSV.
NA: Not analyzed

The data in Table 5 demonstrate the activity of Pt/zeolite beta. For example, at 700°F, the Pt/zeolite beta catalyst improves the motor octane of the coker naphtha from 54.5 to 63.2. The Pt/zeolite beta catalyst is active in converting 300°F+ fraction (58% conversion at 700°F, Table 5). The overall volume of C_5-300°F fraction can be increased significantly with this process.

Example 9

Performance Comparison - Mercaptan Reduction

A further comparison between the ZSM-5/Al_2O_3 catalyst of Example 4 and the Mo/Beta catalyst of Example 1. The feed used was the light FCC naphtha of Table 2. The comparison was made in the same way as described above

under the conditions shown in Table 6 below, which also gives the results of the comparison.

A sulfur GC method was used to speciate and quantify the sulfur compounds present in the gasolines using a Hewlett-Packard gas chromatograph, Model HP-5890 Series II equipped with universal sulfur-selective chemiluminescnce detector (USCD) (Model 350, Sievers Research Inc., Boulder, CO). The accurate quantifications of sulfur species were made by analyzing a gasoline sample with a known amount of an internal standard, 2-bromothiophene. The sulfur chromatograms were processed on a consistent basis with appropriate integration parameters. Peaks were identified based upon GC retention times. The sulfur detection system was published by B. Chawla and F. P. DiSanzo in J. Chrom. 1992, **589**, 271-279.

Table 6
Sulfur Reduction with Mo/Beta

	HDS Only	ZSM-5/Al_2O_3	Stmd.	Mo/Beta
ABT Rx1, °F	700	697	700	701
ABT Rx2, °F	-	700	699	777
Octane (Res)	77.3	81.3	83.7	89.7
Octane (Mot)	71.5	74.7	77.3	80.4
Mercaptan, ppm	0	24	3	4
Heavy S, ppm	172	194	44	17
Total S, ppm	172	218	47	21

The results in Table 6 above demonstrate the improvement in desulfurization and octane recovery activities with the Mo/zeolite beta catalyst with the light naphtha feed. For example, at 700°F, the Mo/zeolite beta catalyst produces gasoline with 48 ppm total sulfur while HDT alone produces 172 ppm total sulfur and ZSM-5 produces a product with 218 ppm sulfur. In addition, the mercaptan level is much lower than that

of ZSM-5 (24 vs. 3 ppm).

Example 10

Performance Comparison - Mercaptan Reduction

A comparison was made between the ZSM-5/SiO2 catalyst of Example 5 and the Mo/Beta catalyst of Example 1. The feed used was the heavy FCC naphtha of Table 2. The comparison was made in the same way as described in Example 9 under the conditions shown in Table 7 below, which also gives the results of the comparison.

Table 7
Sulfur Reduction with Mo/Beta

	HDS Only	ZSM-5/SiO_2	Stmd. Mo/Beta	
ABT Rx1, 'F	700	700	703	701
ABT Rx2, 'F	-	700	701	751
Octane (Res)	91.3	96.8	95.2	99.1
Octane (Mot)	79.4	83.7	82,9	87.3
Mercaptan, ppm	0	252	39	51
Heavy S, ppm	174	155	22	0
Unknown S, ppm	2	12	8	7
Total S, ppm	176	419	69	58

The results in Table 7 above demonstrate the improvement in desulfurization and octane recovery activities with the Mo/zeolite beta catalyst with the heavy naphtha feed. For example, at 700'F, the Mo/zeolite beta catalyst produces gasoline with 69 ppm total sulfur while HDT alone produces 176 ppm total sulfur and ZSM-5 produces a product with 419 ppm sulfur. In addition, the mercaptan level is much lower than that of ZSM-5 (252 vs. 39 ppm).

Throughout the description and claims of this specification, the word "comprise" and variations of the word, such as "comprising" and "comprises", is not intended to exclude other additives, integers or process steps.

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"The Claims defining the invention are as follows"

1. A process of upgrading a cracked, olefinic sulfur-containing feed fraction boiling in the gasoline boiling range and having a 95 percent point of at least 325°F which comprises:

contacting the cracked, olefinic sulfur-containing feed fraction with a hydrodesulfurization catalyst in a first reaction zone, operating under a combination of elevated temperature, elevated pressure and an atmosphere comprising hydrogen, 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;

contacting at least the gasoline boiling range portion of the intermediate product in a second reaction zone with an acidic catalyst comprising zeolite beta in combination with a molybdenum hydrogenation component, 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.

2. The process as claimed in claim 1 in which the feed fraction comprises a full range catalytically cracked naphtha fraction having a boiling range within the range of C_5 to 420 °F.

3. The process as claimed in claim 1 in which the feed fraction comprises a heavy catalytically cracked naphtha fraction having a boiling range within the range of 330 to 500 °F.

4. The process as claimed in claim 1 in which the feed fraction comprises a heavy catalytically cracked naphtha fraction having a boiling range within the range of 330 to 412°F.

5. The process as claimed in claim 1 in which the feed fraction comprises a naphtha fraction having a 95 percent point of at least about 380°F.

6. The process as claimed in claim 5 in which the

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feed fraction comprises a naphtha fraction having a 95 percent point of at least about 400°F.

7. The process as claimed in ~~claim 1~~ any one of claims 1-6 in which the zeolite beta is in the aluminosilicate form.

8. The process as claimed in ~~claim 1~~ any one of claims 1-7 in which the molybdenum is present in an amount from about 2 to 5 weight percent of the catalyst.

9. The process as claimed in ~~claim 1~~ any one of claims 1-8 in which the zeolite beta catalyst includes a base metal of Group VIII of the Periodic Table.

10. The process as claimed in ~~claim 1~~ any one of claims 1-9 in which the hydrodesulfurization is carried out at a temperature of about 400 to 800 °F, a pressure of about 50 to 1500 psig, a space velocity of about 0.5 to 10 LHSV, and a hydrogen to hydrocarbon ratio of about 500 to 5000 standard cubic feet of hydrogen per barrel of feed.

11. The process as claimed in ~~claim 1~~ any one of claims 1-10 in which the second stage upgrading is carried out at a temperature of about 300 to 900 °F, a pressure of about 50 to 1500 psig, a space velocity of about 0.5 to 10 LHSV, and a hydrogen to hydrocarbon ratio of about 0 to 5000 standard cubic feet of hydrogen per barrel of feed.

12. The process as claimed in claim 11 in which the second stage upgrading is carried out at a temperature of about 350 to 900 °F, a pressure of about 300 to 1000 psig, a space velocity of about 1 to 6 LHSV, and a hydrogen to hydrocarbon ratio of about 100 to 2500 standard cubic feet of hydrogen per barrel of feed.

13. The process as claimed in ~~claim 1~~ any one of claims 1-12 which is carried out in two stages with an interstage separation of light ends and heavy ends with the heavy ends fed to the second reaction zone.

14. The process as claimed in ~~claim 1~~ any one of claims 1-13 in which the product fraction boiling in the gasoline boiling range has a higher octane number and a lower total sulfur content than that of the gasoline boiling range fraction of the intermediate product.

15. The process as claimed in ~~claim 1~~ any one of claims 1-14 in which the

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total sulfur content of the product fraction boiling in the gasoline boiling range is not more than 100 ppmw.

16. The process as claimed in claim 15 in which the total sulfur content of the product fraction boiling in the gasoline boiling range is not more than 50 ppmw.

17. The process as claimed in ~~claim 1~~ any one of claims 1-16 in which the product gasoline fraction has an octane number (research) of at least 93.

18. The process as claimed in ~~claim 1~~ any one of claims 1-17 in which the feed fraction comprises a coker naphtha.

19. A process of upgrading a catalytically cracked, olefinic sulfur-containing feed fraction boiling in the gasoline boiling range which comprises:

hydrodesulfurizing a cracked, olefinic, sulfur-containing gasoline feed having a sulfur content of at least 50 ppmw, an olefin content of at least 5 percent and a 95 percent point of at least 325°F with a hydrodesulfurization catalyst in a hydrodesulfurization zone, operating under a combination of elevated temperature, elevated pressure and an atmosphere comprising hydrogen, 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;

contacting the gasoline boiling range portion of the intermediate product in a second reaction zone with a bifunctional catalyst having acidic and hydrogenation functionality, comprising zeolite beta and a molybdenum hydrogenation component, to convert 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.

20. The process as claimed in claim 19 in which the feed fraction has a 95 percent point of at least 350°F, an olefin content of 10 to 20 weight percent, a sulfur content from 100 to 5,000 ppmw and a nitrogen content of 5 to 250 ppmw.

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21. The process as claimed in claims 19 or 20 in which the feed fraction comprises a naphtha fraction having a 95 percent point of at least about 380°F.

22. The process as claimed in any one of claims 19-21 in which the hydrodesulfurisation is carried out at a temperature of about 500 to 800°F, a pressure of about 300 to 1000 psig, a space velocity of about 1 to 6 LHSV, and a hydrogen to hydrocarbon ratio of about 1000 to 2500 standard cubic feet of hydrogen per barrel of feed.

23. The process as claimed in any one of claims 19-22 in which the second stage upgrading is carried out at a temperature of about 350 to 900°F, a pressure of about 300 to 1000 psig, a space velocity of about 1 to 6 LHSV, and a hydrogen to hydrocarbon ratio of about 100 to 2500 standard cubic feet of hydrogen per barrel of feed.

24. The process as claimed in any one of claims 19-23 in which the molybdenum is present in the catalyst in an amount of from 2 to 10 weight percent of the catalyst.

25. The process as claimed in any one of claims 19-24 in which the bifunctional catalyst has an alpha value of 100 to 400.

26. The process as claimed in any one of claims 19-25 in which the product fraction boiling in the gasoline boiling range has a higher octane number and a lower total sulfur content than that of the gasoline boiling range fraction of the intermediate product.

27. A process according to claim 1 substantially as hereinbefore described with reference to any one of the examples.

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PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
MOBIL OIL CORPORATION

AUSTRALIA PATENT OFFICE

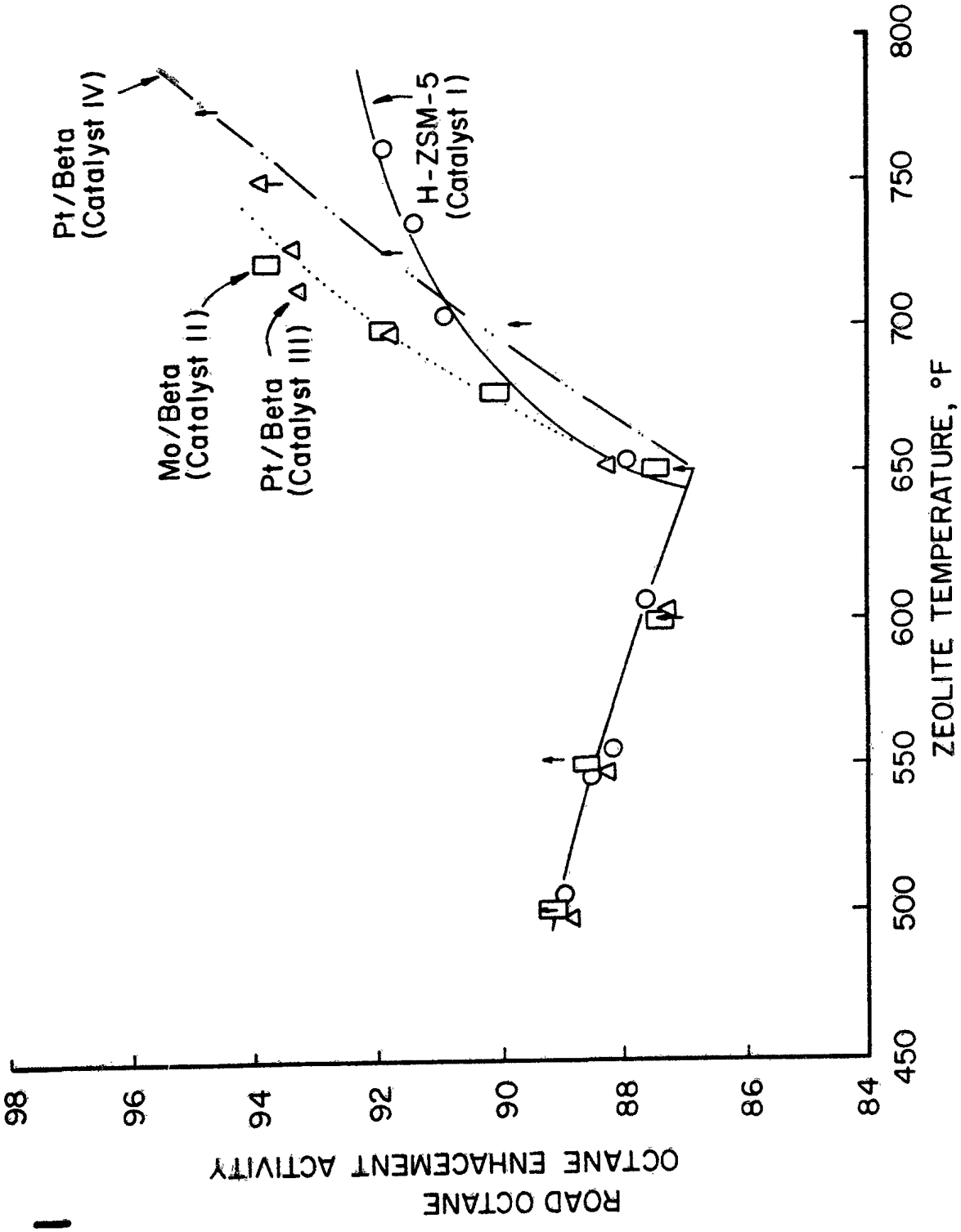

Pt/Beta
(Catalyst IV)
Mo/Beta
(Catalyst II)
Pt/Beta
(Catalyst III)
H-ZSM-5
(Catalyst I)
ROAD OCTANE
OCTANE ENHACEMENT ACTIVITY
98
96
94
92
90
88
86
84
450
500
550
600
650
700
750
800
ZEOLITE TEMPERATURE, °F

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/10548

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10G 69/02, 69/08
US CL :208/89, 58, 60, 134, 136, 213
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/89, 58, 60, 134, 136, 213

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

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

STN - search terms: zeolite beta, molybdenum, catalyst, catalytic reforming, hydrodesulfurization

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,957,625 (ORKIN) 18 MAY 1976.	1-26
A	US, A, 4,419,220 (LAPIERRE ET AL) 06 DECEMBER 1983.	1-26
A	US, A, 4,827,076 (KOKAYEFF ET AL) 02 MAY 1989.	1-26
A	US, A, 4,911,823 (CHEN ET AL) 27 MARCH 1990.	1-26

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
12 DECEMBER 1994	06 JAN 1995
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer WALTER GRIFFIN Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*