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DESULFURIZATION OF OLEFINIC GASOLINE**WITH A DUAL FUNCTIONAL CATALYST AT LOW PRESSURE**

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This invention relates to a process for desulfurizing olefinic naphtha by olefin cracking
5 to produce a low sulfur, high octane product with improved gasoline yields. More specifically,
the invention relates to a low pressure process which advantageously relies on a dual
functional catalyst for hydrotreating and paraffin cracking in the same reactor volume. The
operating conditions of the process provide significant olefins cracking while minimizing olefin
saturation from the metals.

10 Catalytically cracked gasoline currently forms a major part of the gasoline product
pool in the United States and the cracking process contributes 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.
Low sulfur levels result in reduced emissions of CO, NO_x and hydrocarbons. In addition,
15 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 Pressure
20 (RVP) and T₉₀ specifications. Limitations on aromatic content may also arise from the
Complex Model regulations.

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
25 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
30 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.

35 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. 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.

5 Naphthas and other light fractions such as heavy cracked gasoline may be hydrotreated by passing the feed over a hydrotreating catalyst at an elevated temperature and a 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 element and a Group VI element, such as cobalt and molybdenum, on a substrate such as alumina. After the hydrotreating
10 operation is complete, the product may be fractionated, or simply flashed, to release the hydrogen sulfide and collect the now sweetened gasoline.

 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 and hydrodesulfurization processes have been employed that treat only the heavy
15 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 commercial operation, the selectivity for hydrodesulfurization relative to olefin saturation is shifted by suitable catalyst selection, for example, by the use of a magnesium oxide support instead of the more conventional alumina.

20 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 conflict 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 conflict is yet more marked in the current supply
25 situation for low sulfur, sweet crudes.

 Aromatics are generally the source of high octane number, particularly very high research octane numbers, and are, therefore, desirable components of the gasoline pool. However, they have been the subject of severe limitations as a gasoline component because of possible adverse effects on the ecology, particularly with reference to benzene. Thus, it has
30 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.

 It has now been discovered that the problems encountered in the prior art can be overcome by the present invention, which provides a process for desulfurizing olefinic naphtha
35 by olefin cracking at low pressure to produce a low sulfur, high octane product with improved gasoline yields. More specifically, the invention uses a dual functional catalyst for

hydrotreating and paraffin cracking in the same reactor volume at low pressures. Under these conditions, olefins cracking is favored over olefin saturation from the metals.

The present invention provides a process for reducing sulfur content of gasoline while substantially maintaining road octane number. The process includes contacting a catalytically cracked olefinic gasoline stream containing organic sulfur compounds and having an initial boiling point in the gasoline boiling range, an initial sulfur content, an initial bromine number and an initial road octane number with a dual functional catalyst. The catalyst is made up of an intermediate pore size zeolite having an alumina substrate and impregnated with at least one metal selected from the group consisting of Group VI metals of the Periodic Table and Group VIII metals of the Periodic Table. The gasoline stream contacts the catalyst under a combination of a pressure of from 100 to 600 psig (790.86 to 4238.35 kPaa), a space velocity of from 0.1 to 10 LHSV and an atmosphere comprising hydrogen to convert the sulfur compounds to hydrogen sulfide. The hydrogen sulfide can be removed from the gasoline stream to provide a product gasoline with a reduced sulfur content lower than the initial sulfur content. The product gasoline also has a less than 5% change in the road octane number.

The process of the present invention uses an intermediate pore size zeolite catalyst which can be selected from a group of several catalysts, including ZSM-5, ZSM-11, ZSM-22, ZSM-12, ZSM-23, ZSM-35, ZSM-48, ZSM-57, ZSM-58, MCM-22 and M-41S. In a preferred embodiment of the present invention, the intermediate pore size zeolite is impregnated with cobalt and molybdenum. The amounts of cobalt and molybdenum can vary according to several factors, such as, the composition of the feedstock, the process operating conditions and the desired characteristics of the product gasoline. The most preferred ranges, in terms of the total weight of the impregnated catalyst, are from 0.5% to 10% by weight cobalt and from 1% to 20% by weight molybdenum.

The present invention has the following process conditions: the space velocity is from 0.1 to 10 LHSV and preferably 0.5 to 5 LHSV; the ratio of hydrogen to hydrocarbon is 100 to 5,000 standard cubic feet of hydrogen per barrel of hydrocarbon (17.8 to 890 n.l.l.^{-1}) and preferably 500 to 2,500 standard cubic feet of hydrogen per barrel of hydrocarbon (89 to 445 n.l.l.^{-1}); the pressure range is from 100 to 600 psig (790.86 to 4238.35 kPaa) and preferably 100 to 400 psig (790.86 to 3163.44 kPaa); and the operating temperature is from 600° to 800°F (315.56° to 426.67°C), preferably operating temperature of from 700° to 750°F (371.11° to 398.89°C).

In a preferred embodiment, the reduced sulfur content of the recovered gasoline stream is from 5 to 10% of the initial sulfur content.

In another embodiment, the distillation of the olefinic gasoline stream is less than 50% and the olefin saturation of the product gasoline measured in terms of bromine number is less than 50% of the initial bromine number.

The present invention has several advantages over gasoline desulfurization processes known in the prior art, including high desulfurization with higher gasoline yields and reduced octane loss at almost any desulfurization level. The dual functional catalyst used in the present invention has the advantage of desulfurizing and cracking the feedstock in one vessel, in contrast to prior art processes that use separate vessels for desulfurizing and cracking. The lower operating pressure of the present invention also provides the advantage of increasing the stability of the dual functional catalyst. Additionally, the present invention provides the advantage of lower hydrogen consumption by cracking olefins directly before hydrogenation.

As new gasoline regulations permit lower amounts of sulfur, an increasing amount of cracked gasoline has to be hydrofinished. This typically results in a severe octane loss. The process of the present invention provides high desulfurization and high gasoline yields by using a dual functional catalyst that both desulfurizes and cracks the olefinic naphthas. In addition, by adjusting the process parameters, the amount of olefins in the product gasoline can be tailored to meet different target specifications.

The present invention maintains octane and desulfurizes olefinic naphtha by olefin cracking at low pressure using a dual functional catalyst that has a very strong desulfurization function as well as a selective cracking function. This produces a low sulfur, high octane product with greatly improved gasoline yields compared to other processes. The dual catalyst system performs separate desulfurization by Cobalt Molybdenum and paraffin cracking by zeolite. In a preferred embodiment, the process uses a CoMo/ZSM-5 catalyst. At higher pressures, this dual functional catalyst can be used for conventional hydrotreating of olefinic naphtha to paraffins and subsequent paraffin cracking to higher octanes. It has been discovered that at lower pressures, the dual functional catalyst has an unexpected different chemistry. At lower pressures, olefins are cracked directly to lighter material before the olefins are saturated over the metals. A significant advantage of the process of the present invention is that the desulfurization function has been added without sacrificing cracking activity. This results in minimal octane losses at almost any desulfurization level. Another advantage of the dual functional catalyst is that both hydrotreating and paraffin cracking can be done in the same reactor vessel. In addition, the lower operating pressure increases the stability of the dual functional catalyst.

The dual function catalyst of the present invention employs metals to remove heteroatoms, such as sulfur and nitrogen, while saturating the olefins. Once saturated, the zeolite portion of the catalyst selectively cracks the low octane paraffins raising the octane at the expense of gasoline yields loss.

The chemistry of the catalytic reaction changes at lower pressure favoring olefin cracking instead of olefin saturation from the metals. This has a very positive impact on product yields and properties. The most important result is that significant octane loss from

saturation does not occur and, therefore, the operating temperature can be adjusted to achieve high or mid level desulfurization without significant octane loss. At the lower operating pressure, hydrogen consumption is significantly less and the tolerance to nitrogen poisons has been found to be greater. In addition, the light gases in the gasoline product become more olefinic.

The present invention can operate at surprisingly low temperatures (400° to 750°F versus 675° to 800°F) (204.44° to 398.89°C versus 357.22° to 426.67°C) for the typical catalytic hydrodesulfurization process) and provides higher gasoline yields than conventional hydrodesulfurization processes, especially at less than 95% desulfurization. However, the preferred operating temperature is typically below 700°F (371.11°C). The octane enhancement chemistry of the present invention is dominated by olefin cracking, in contrast to a conventional process, in which paraffin cracking is responsible for the octane enhancement. Under the low-pressure operating conditions of the present invention, the catalyst has been found to be more nitrogen tolerant and can be operated at higher liquid hourly space velocities (LHSV). This results in the production of more gasoline. In addition, the dual functional catalysts of the present invention, such as a CoMo promoted ZSM-5 catalyst, operated at low pressure do not require a high degree of denitrogenation for octane enhancement.

FEEDSTOCK

The feed to the process comprises a sulfur-containing petroleum fraction that boils in the gasoline boiling range, which can be regarded as extending from C₆ to 500°F (260°C) although lower end points below the 500°F (260°) end point are more typical. Feeds of this type include light naphthas typically having a boiling range of C₄ to 330°F (166°C), full range naphthas typically having a boiling range of C₅ to 420°F (215.56°C), heavier naphtha fractions boiling in the range of 260° to 420°F (126.67° to 215.56°C), or heavy gasoline fractions boiling at, or at least within, the range of 330° to 500°F (165.56° to 260°C), preferably from 330° to 420°F (166° to 215.56°C). 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 325°F (162.78°C) and preferably at least 350°F (176.67°C), for example, 95 percent points (T₉₅) of at least 380°F (193.33°C) or at least 400°F (204.44°C). The process can be applied to thermally cracked naphthas such as pyrolysis gasoline, coker naphtha and visbreaker naphtha as well as catalytically cracked naphthas such as thermoform catalytic cracking (TCC) or fluid catalytic cracking (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 can 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 or a high degree of sulfur removal is required, 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 can vary according to the sulfur compounds present. A cut point in the range of from 100° to 300°F (37.78° to 148.89°C) is preferred, and a cut point in the range of 200° to 300°F (93.33° to 148.89°C) is the most preferred. 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 180°F (82.22°C) is mostly in the form of mercaptans, which can be removed by extractive type processes. However, hydrotreating is appropriate for the removal of thiophene and other cyclic sulfur compounds present in higher boiling components, that is, component fractions boiling above 180°F (82.22°C). Treatment of the lower boiling fraction in an extractive type process coupled with hydrotreating of the higher boiling component can represent a preferred economic process option. Such a variant of the process is described in U.S. Serial No. 08/042,189 filed 30 March 1993 now U.S. Patent No. 5,360,532 and U.S. Serial No. 07/001,681 filed 7 January 1993 now U.S. Patent No. 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, in most cases, the sulfur content will be in excess of 500 ppmw. For the fractions which have 95 percent points over 380°F (193.33°C), the sulfur content can exceed 1,000 ppmw and can be as high as 4,000 to 5,000 ppmw, or higher. 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 70 ppmw can be found in certain higher boiling feeds with 95 percent points in excess of 380°F (193.33°C). The nitrogen level will, however, usually not be greater than 250 or 300 ppmw. As a result of the cracking which precedes the steps of the present process, the feed to the hydrodesulfurization step will be

olefinic, with an olefin content of at least 5% by weight and more typically in the range of 15 to 20 weight percent (wt.%), although higher olefin levels, for example 40 wt.%, or even higher, can be encountered in specific charge stocks, such as gasoline obtained from resid catalytic cracking (RCC) processes.

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PROCESS CONFIGURATION

The present invention includes the use of a dual functional catalyst that has a very strong desulfurization function as well as a selective cracking function to treat the sulfur-containing, gasoline boiling range feed. The dual catalyst functions as a conventional hydrotreating catalyst to separate sulfur from the feed molecules and convert it to hydrogen sulfide. The dual catalyst also contains an intermediate pore size zeolite that promotes catalytic cracking.

The catalyst used in the hydrosulfurization 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 preferably molybdenum or tungsten and the Group VIII metal preferably nickel or cobalt. Combinations, such as NiMo, CoMo and NiCoMo, are typical with CoMo used in preferred embodiments. 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 can 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, a down-flow, fixed bed process is preferred.

The hydrogenation reaction and the cracking reaction performed by the dual functional catalyst are complimentary because the hydrogenation reactions are exothermic, and result in a rise in temperature, while the cracking reaction is an endothermic reaction. Therefore, the hydrotreating conditions are adjusted not only to obtain the desired degree of desulfurization but also to produce the optimum temperature for promotion of the desired shape-selective cracking reactions.

The preferred catalysts for this invention contain zeolite-type crystals and, most preferably, intermediate pore size zeolites. For purposes of this invention, the term "zeolite" is meant to represent the class of porotectosilicates, i.e., porous crystalline silicates, that contain silicon and oxygen atoms as the major components. Other components can be present in minor amounts, usually less than 14 mole.%, and preferably less than 4 mole.%. These components include alumina, gallium, iron, boron and the like, with aluminum being preferred, and used herein for illustrative purposes. The minor components can be present separately or

in mixtures in the catalyst. They can also be present intrinsically in the structure of the catalyst.

The dual functional catalyst promotes cracking reactions that convert low octane paraffins into higher octane products, both by the selective cracking of heavy paraffins to lighter paraffins and by cracking low octane n-paraffins, in both cases with the generation of olefins. Ring-opening reactions can also take place, leading to the production of further quantities of high octane gasoline boiling range components. The dual functional catalyst also improves product octane by dehydrocyclization/aromatization of paraffins to alkylbenzenes.

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 can improve the activity of the cracking catalyst. Normally, the denitrogenation which accompanies the desulfurization will result in an acceptable organic nitrogen content. However, if it is necessary to increase the denitrogenation in order to obtain a desired level of activity in the cracking step, the operating conditions for the hydrogenation reaction can be adjusted accordingly.

The operating conditions are selected to produce a controlled degree of cracking. Typically, the temperature of the reactor will be 300° to 800°F (148.89° to 426.67°C), preferably 400° to 750°F (204.44° to 398.89°C). The reactor pressure will typically operate at from 100 to 600 psig (790.86 to 4238.35 kPaa), preferably 200 to 400 psig (1581.71 to 3163.44 kPaa) with comparable space velocities, typically from 0.1 to 10 LHSV (hr⁻¹), and preferably from 0.5 to 5 LHSV (hr⁻¹). The present catalyst combination of molybdenum on ZSM-5 has been found to be effective at low pressures below 200 psig (1480.36 kPaa) and even below 150 psig (1034.25 kPaa). Hydrogen to hydrocarbon ratios typically of 100 to 5,000 scf/bbl (17.8 to 890 n.l.l.⁻¹), preferably 500 to 2,500 scf/bbl (89 to 445 n.l.l.⁻¹) are selected to minimize catalyst aging.

Consistent with the objective of restoring lost octane while retaining overall product volume, the conversion to products boiling below the gasoline boiling range (C₅-) during the cracking is held to a minimum and distillation of the gasoline feed stream is maintained below 50%. However, because the cracking of the heavier portions of the feed can lead to the production of products still within the gasoline range, the conversion to C₅- products is at a low level, in fact, a net increase in the volume of C₅+ material can occur during this stage of the process.

The acidic component of the dual functional catalyst is an intermediate pore size zeolite. Zeolites of this type are characterized by a crystalline structure having rings of ten-membered rings of oxygen atoms through which molecules obtain access to the intracrystalline pore volume. These zeolites have a Constraint Index from 2 to 12, as defined in U.S. Patent No. 4,016,218, to which reference is made for a description of the method of

determining Constraint Index and examples of the Constraint Indices for a number of zeolites. Zeolites of this class are well-known intermediate pore size aluminosilicate zeolites; typical members of this class are the zeolites having the structures of ZSM-5 (U.S. Patent Nos. 3,702,886 and Re 29,948); ZSM-11 (U.S. Patent No. 3,709,979); ZSM-12 (U.S. Patent No. 3,832,449); ZSM-22 (U.S. Patent No. 4,556,477); ZSM-23 (U.S. Patent No. 4,076,842); ZSM-35 (U.S. Patent No. 4,016,245); ZSM-48 (U.S. Patent No. 4,397,827); ZSM-57 (U.S. Patent No. 4,046,685); ZSM-58 (U.S. Patent No. 4,417,780); M-41S (U.S. Patent No. 5,098,684) and MCM-22 (U.S. Patent Nos. 4,954,325 and 4,962,256). ZSM-5 is the preferred zeolite for use in the present process. The aluminosilicate forms of these zeolites provide the requisite degree of acidic functionality and for this reason are the preferred compositional forms of the zeolites. Other isostructural forms of the intermediate pore size zeolites containing other metals instead of aluminum such as gallium, boron or iron can also be used.

The zeolite catalyst possesses sufficient acidic functionality to bring about the desired reactions to restore the octane lost in the hydrotreating reaction. The catalyst should have sufficient acid activity to have cracking activity that is sufficient to convert the appropriate portion of the feed, suitably with an alpha value of at least 10, 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. 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 No. 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 component of the dual functional 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 dual functional catalyst also contains Group VIB and Group VII metals, such as cobalt and molybdenum, components which improve catalyst desulfurization activity, stability as well as for improving product quality as described above. Typically, the cobalt and molybdenum will be in the oxide or the sulfide form; it can readily be converted from the oxide
5 form to the sulfide by conventional pre-sulfiding techniques. A molybdenum content of 1 to 10 wt.%, conventionally 5 to 10 wt.%, (as metal) is suitable although higher metal loadings typically up to 15 wt.% can be used. A cobalt content of 0.5 to 5 wt.% (as metal), conventionally 3 to 4 wt.%, is suitable.

The molybdenum component can be incorporated into the dual functional catalyst by
10 conventional procedures such as impregnation into an extrudate or by mulling with the zeolite and the binder. When the molybdenum is added in the form of an anionic complex such as molybdate, impregnation or addition to the muller will be appropriate methods.

The particle size and the nature of the catalyst will usually be determined by the type of
15 conversion process which is being carried out with operation in a down-flow, fixed bed process being typical and preferred.

The conditions of operation and the catalysts should be selected based on the characteristics of the feed so that 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 1 to 10 octane numbers and usually, not more than 1 to 3 octane numbers, depending on the nature of
20 the feed. It is preferred also that the volume of the product should not be substantially less than that of the feed although yields as low as 80% can be achieved with certain feeds under particular conditions. In some cases, the volumetric yield and/or octane of the gasoline boiling range product can 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
25 product will be higher than the octane barrels of the feed.

EXAMPLES

A full range feedstock was processed using the dual function catalyst system of the present invention at two different pressures (550 and 350 psig) (3893.6 kPaa to 2514.60 kPaa). The feedstock properties are as follows:

TABLE 1**PROPERTIES OF FEEDSTOCK**

API Gravity	48.0
Motor Octane (M+O)	78.8
Research Octane (R+O)	90.0
Road Octane	84.4
Bromine Number	40.61
Sulfur, ppm	2802
Nitrogen, ppm	62

Distillation (D86), °C

IBP	54
50	140
EP	220

EXAMPLE 1

In this example, the full range feedstock shown in Table 1 was desulfurized under high pressure conditions. Initially, the feedstock was contacted with a commercial cobalt molybdenum catalyst to saturate diolefin at a low temperature. The diolefin-removed feedstock was desulfurized at a space velocity of 2.0 LHSV (liquid hourly space velocity); with 2,500 scf/bbl (445 n.l.l.⁻¹) hydrogen circulation and 550 psig (3893.6 kPaa) total pressure over a CoMo ZSM-5 at various temperatures. The results are summarized in Table 2.

TABLE 2
HIGH PRESSURE BASE CASE

ZSM-5 temperature	500°F (260°C)	600°F (316°C)	650°F (343°C)	700°F (371°C)	725°F (385°C)	750°F (410°C)
Octanes R+O	76.8	75.8	76	85	87.8	90.7
M+O	71.1	71.8	72	79.3	80.6	81.9
API	50.5	56.3	55.7	55.3	55.1	53.1
Sulfur, ppm	49	250	101	123	52	154
Nitrogen, ppm	8	15	<5	<5	<5	<5
C₁+C₂	Nil	0.01	0.04	0.29	0.63	1.48
C₃	0.02	0.04	0.36	4.61	5.51	10.59
C₃⁼	Nil	Nil	0.01	0.02	0.02	0.06
IC₄	0.02	0.25	0.32	3.47	3.66	6.16
NC₄	0.11	1.24	1.02	2.84	3.22	5.37
C₄⁼	Nil	Nil	Nil	0.01	0.01	0.08
C₅⁺	100.01	99.57	99.36	89.67	87.86	77.67
H₂ consumption, Scf/bbl	407 (72.45 n.l.l. ⁻¹)	719 (127.98 n.l.l. ⁻¹)	713 (126.91 n.l.l. ⁻¹)	625 (111.25 n.l.l. ⁻¹)	634 (112.85 n.l.l. ⁻¹)	869 (154.68 n.l.l. ⁻¹)

5 **EXAMPLE 2**

In this example, the full range feedstock shown in Table 1 was desulfurized at low pressure conditions using the present invention. The diolefin-removed feedstock was desulfurized at 3.0 LHSV, 2,500 scf/bbl (445 n.l.l.⁻¹) hydrogen circulation, 300 psig (2169.85 kPaa) and cascaded over CoMo ZSM-5 at 3.0 LHSV at various temperatures. The results are summarized in Table 3.

TABLE 3**LOW PRESSURE DIOLEFIN SATURATION**

ZSM-5 temperature	550°F (288°C)	600°F (316°C)	650°F (343°C)	700°F (371°C)	725°F (385°C)	750°F (410°C)
Octanes R+O	89.6	86.8	86	87.8	87.5	88
M+O	79	78	77.5	80	79.4	79.6
API	50.5	49.9	48.1	47.1	48.6	49.1
Sulfur, ppm	593	192	169	99	131	101
Nitrogen, ppm	44	42	38	30	14	10
C₁+C₂	0.01	0.02	0.05	0.06	0.15	0.23
C₃	0.14	0.17	0.73	2.01	3.0	3.8
C₃⁼	0.03	0.11	0.38	0.3	0.26	0.24
IC₄	0.13	0.08	0.60	1.71	2.31	2.71
nC₄	0.20	0.13	0.48	1.23	1.84	2.29
C₄⁼	0.23	0.40	1.05	0.79	0.56	0.52
C₅⁺	99.45	99.30	96.79	93.82	92.02	90.24
H₂ consumption, scf/bbl	201 (36.78 n.l.l. ⁻¹)	222 (39.51 n.l.l. ⁻¹)	165 (29.37 n.l.l. ⁻¹)	125 (22.25 n.l.l. ⁻¹)	199 (35.42 n.l.l. ⁻¹)	145 (25.81 n.l.l. ⁻¹)

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The low-pressure data shows that motor octane (M+O) did not drop off with higher temperature, while research octane (R+O) dropped only mildly compared to the high-pressure data. The synergism between the metals and the ZSM-5 allowed this to work. The advantage is higher gasoline yields and lower hydrogen consumption at equivalent desulfurization. The low pressure operation can tolerate a higher residual nitrogen content to enhance product octane. In comparison, the octane enhancement for the high pressure operation is accompanied by a very high degree of denitrogenation. This is because the ZSM-5 is preferentially cracking olefins prior to saturation. A better illustration is shown below in Example 3 for a lighter feed.

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EXAMPLE 3

In this example, the FCC gasoline feedstock shown in Table 4 was desulfurized using the low pressure process of the present invention. Initially, the feedstock was contacted with a commercial cobalt molybdenum catalyst for diolefin saturation at low temperature. The diolefin-removed feedstock was desulfurized at 3.0 LHSV, and 2,500 scf/bbl (445 n.l.l.⁻¹) hydrogen circulation; with 300 psig (2372.58 kPaa) total pressure over CoMo ZSM-5 at various temperatures. The catalyst used was a standard hydrogen ZSM-5, commonly used for catalytic dewaxing or cracking, impregnated with 3.0 wt.% cobalt and 8.8 wt.% molybdenum. The results of the test are shown below in Table 5.

The bromine numbers of the desulfurized gasoline products were measured to determine the change in composition. The bromine number is a method of calculating the contents of an olefin. The number of grams of bromine absorbed by 100 grams of gasoline indicates the percentage of double bonds present. Thus, when the type and molecular weight is known, the contents of the olefin can be calculated.

TABLE 4**C5/C6 FCC Gasoline**

API Gravity	74.5
Motor Octane	79.8
Research Octane	94.7
Road Octane	87.3
Bromine Number	81.4
Sulfur, ppm	487
Nitrogen, ppm	15

Distillation (D86), °C

IBP	29
50	57
EP	101

TABLE 5**LOW PRESSURE SATURATION WITH A LIGHT FEEDSTOCK**

ZSM-5 temperature	400°F (204°)	500°F (260°C)	600°F (316°C)	700°F (371°C)	725°F (385°C)	770°F (410°C)
Octanes R+O	93.5	93.4	89.2	83.2	86.2	88.8
M+O	79.1	79.4	78.8	78.3	80.8	81.8
API	73.8	73.4	73.7	71.1	68.8	65.8
Sulfur, ppm	360	239	62	34	36	25
Nitrogen, ppm	9	<5	<5	<5	<5	<5
C ₁ +C ₂	0.00	0.00	0.01	1.16	2.47	3.32
C ₃	0.00	0.02	0.14	5.79	9.87	12.40
C ₃ ⁼	0.00	0.00	0.09	0.66	0.60	0.54
IC ₄	0.19	0.13	0.26	6.80	7.36	8.35
nC ₄	0.32	0.25	0.78	6.22	5.85	6.91
C ₄ ⁼	1.61	1.19	1.27	1.92	0.9	0.77
C ₅ ⁺	97.84	98.35	97.68	77.68	73.71	68.45
H ₂ consumption, scf/bbl	-20 (-3.56 n.l.l. ⁻¹)	-28 (-4.984 n.l.l. ⁻¹)	116 (20.65 n.l.l. ⁻¹)	416 (74.05 n.l.l. ⁻¹)	354 (63.01 n.l.l. ⁻¹)	344 (61.23 n.l.l. ⁻¹)
Bromine number	80.7	92.7	72.7	19.4	9.3	6.0

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At less than 700°F (371°C), the bromine numbers indicate that considerable olefins have not been saturated while the olefins in the light gases indicate olefins have been cracked from heavier olefins.

CLAIMS

1. A process for reducing sulfur content of gasoline while substantially maintaining road octane number, comprising:

contacting a catalytically cracked olefinic gasoline stream comprising organic sulfur compounds and having an initial boiling point in the gasoline boiling range, an initial sulfur content, a bromine number and an initial road octane number with a dual functional catalyst comprising ZSM-5 having an alumina substrate and impregnated with at least one metal selected from the group consisting of Group VI metals of the Periodic Table and Group VIII metals of the Periodic Table, under a combination of a pressure of from 100 to 600 psig (790.86 to 4238.35 kPaa), a space velocity of from 0.1 to 10 LHSV, a temperature of from about 400°F to about 750°F, and an atmosphere comprising hydrogen to convert the sulfur compounds to hydrogen sulfide;

wherein hydrogen sulfide is removed from the gasoline stream to provide a product gasoline having reduced sulfur content lower than the initial sulfur content and a less than 5% change in the road octane number.

2. A process according to Claim 1 wherein ZSM-5 is an intermediate pore size zeolite.

3. A process according to Claim 1, wherein the ZSM-5 is impregnated with cobalt and molybdenum.

4. A process according to Claim 3, wherein the impregnated catalyst comprises from 0.5 to 10% by weight cobalt and from 1 to 20% by weight molybdenum.

5. A process according to Claim 3, wherein the space velocity is from 0.5 to 5 LHSV.

6. A process according to Claim 3, further comprising a hydrogen to hydrocarbon ratio of 100 to 5,000 standard cubic feet of hydrogen per barrel (17.8 to 890 n.l.l.⁻¹) of hydrocarbon.

7. A process according to Claim 5, further comprising a hydrogen to hydrocarbon ratio of 500 to 2,500 standard cubic feet of hydrogen per barrel (89 to 445 n.l.l.⁻¹) of hydrocarbon.

8. A process according to Claim 3, wherein the process is carried out within a pressure range of from 100 to 400 psig (790.86 to 3163.44 kPaa).
9. A process according to Claim 3, wherein the reduced sulfur content of product
5 gasoline is from 1% to 20% of the initial sulfur content.
10. A process according to Claim 1, wherein the distillation of the olefinic gasoline stream is less than 50% and the olefin saturation of the product gasoline measured in terms of bromine number is less than 50% of the initial bromine number.