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(54) **PROCESS FOR SELECTIVE SULFUR REMOVAL FROM FCC NAPHTHAS USING ZEOLITE CATALYSTS**

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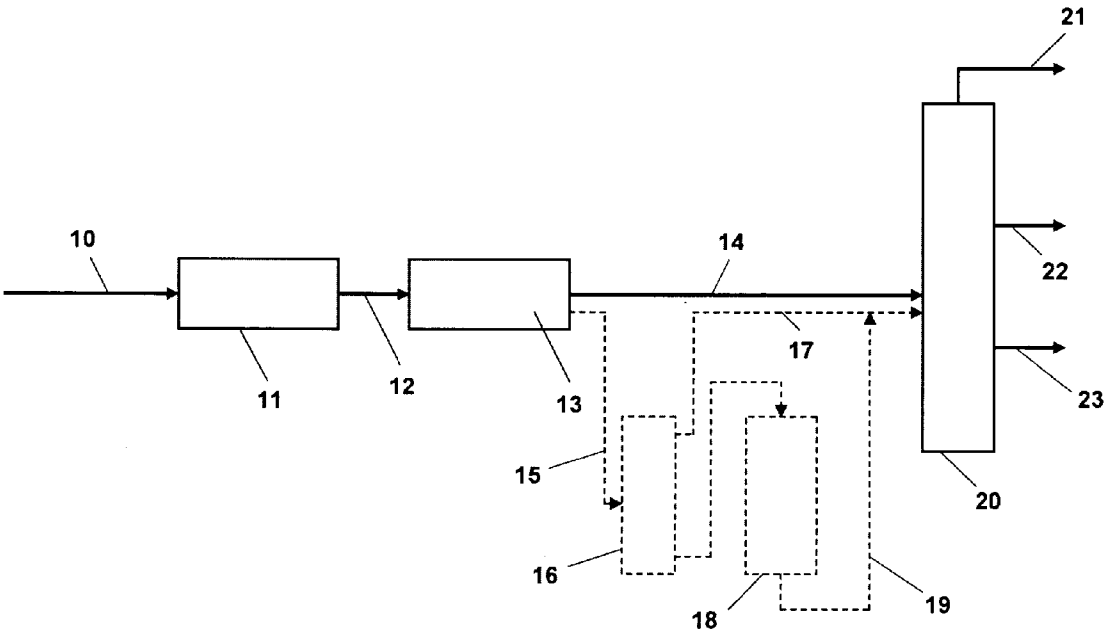
(57) **ABSTRACT**

A process for the removal of sulfur compounds from FCC catalytic naphtha which is simple to implement and is economical in operation operates by selectively hydrofining the cracked naphtha to remove sulfur without sacrificing octane (hydrodesulfurization typically around 85%) followed by a downstream alkylation which will remove residual sulfur from the gasoline boiling range. The alkylation is carried out using a solid, acidic molecular sieve catalyst under mild conditions to shift sulfur species from the lighter, olefin-rich portions of the naphtha to the heavy, olefin-poor gasoline. Separation of the heavy portion of the treated product followed by catalytic hydrodesulfurization or some other means (e.g. sorption) removes the sulfur from the heavy portion without losing significant octane value. Some of the heavy compounds formed in this process can drop out of the gasoline range, into the kero/light diesel range; this stream can be hydrotreated without penalty since octane is not a requirement for the middle distillate fuels.



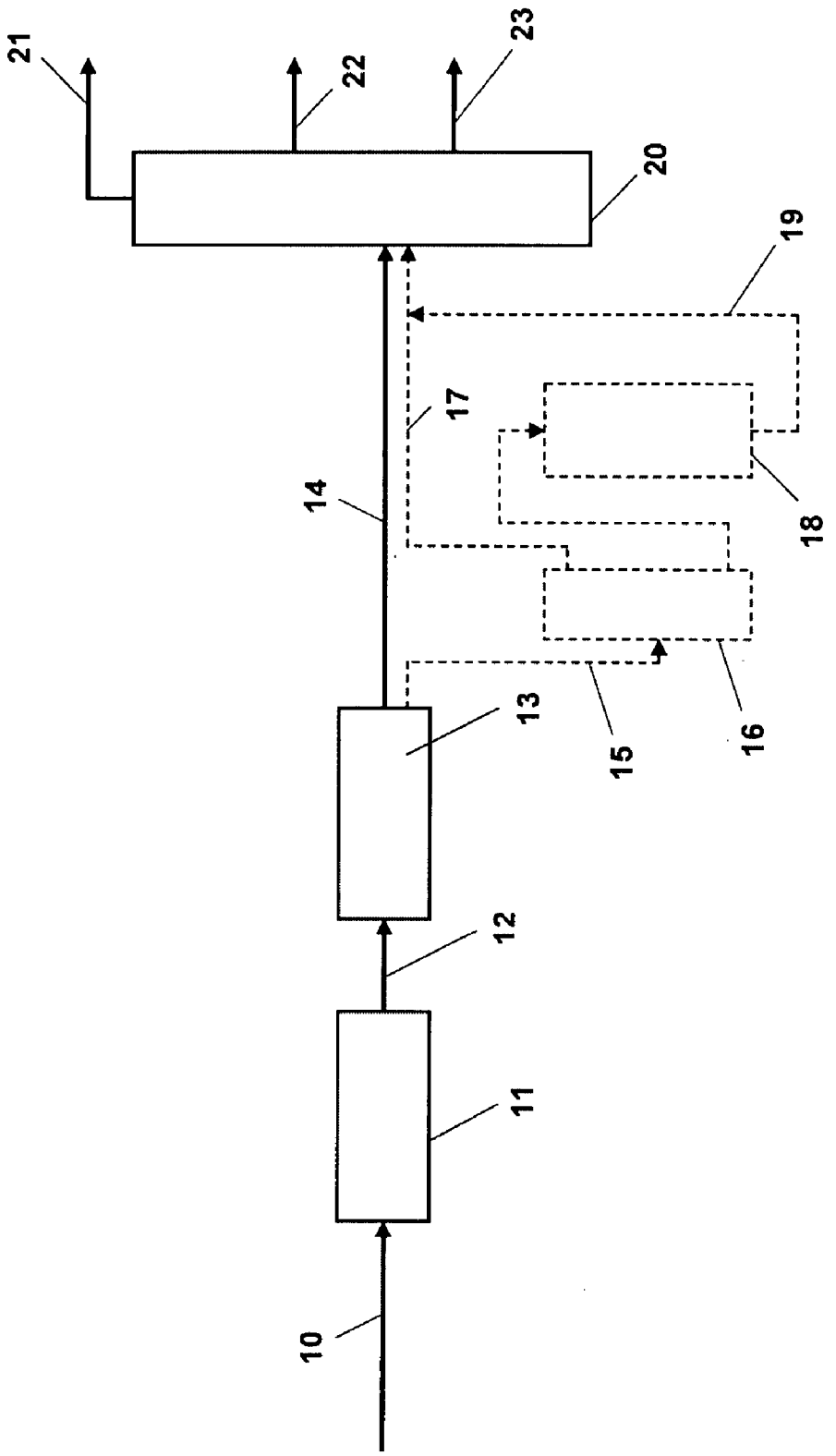


FIG. 1

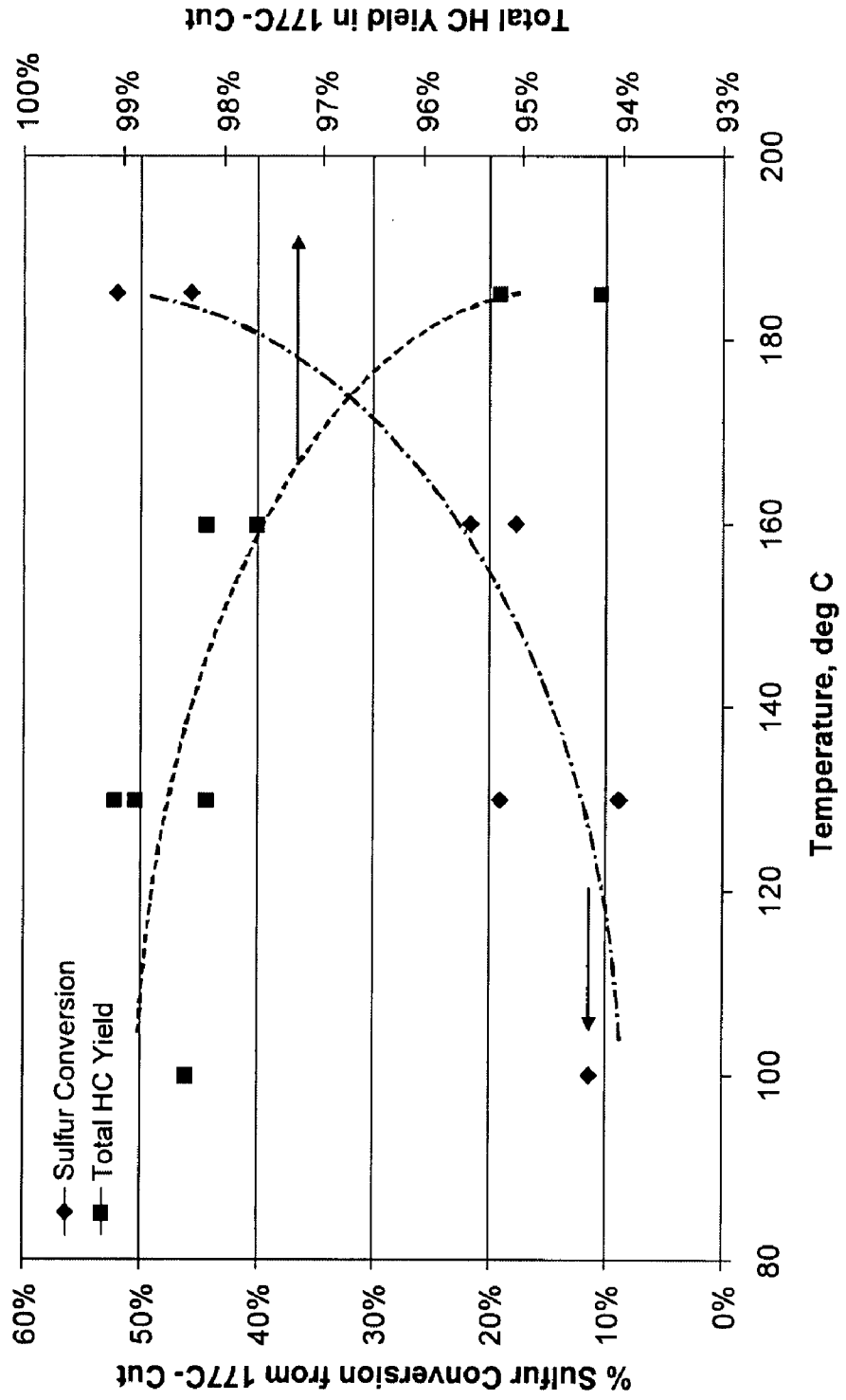

% Sulfur Conversion from 177C- Cut
Total HC Yield in 177C- Cut
Temperature, deg C
Sulfur Conversion
Total HC Yield
60%
50%
40%
30%
20%
10%
0%
100%
99%
98%
97%
96%
95%
94%
93%
80
100
120
140
160
180
200

FIG. 2

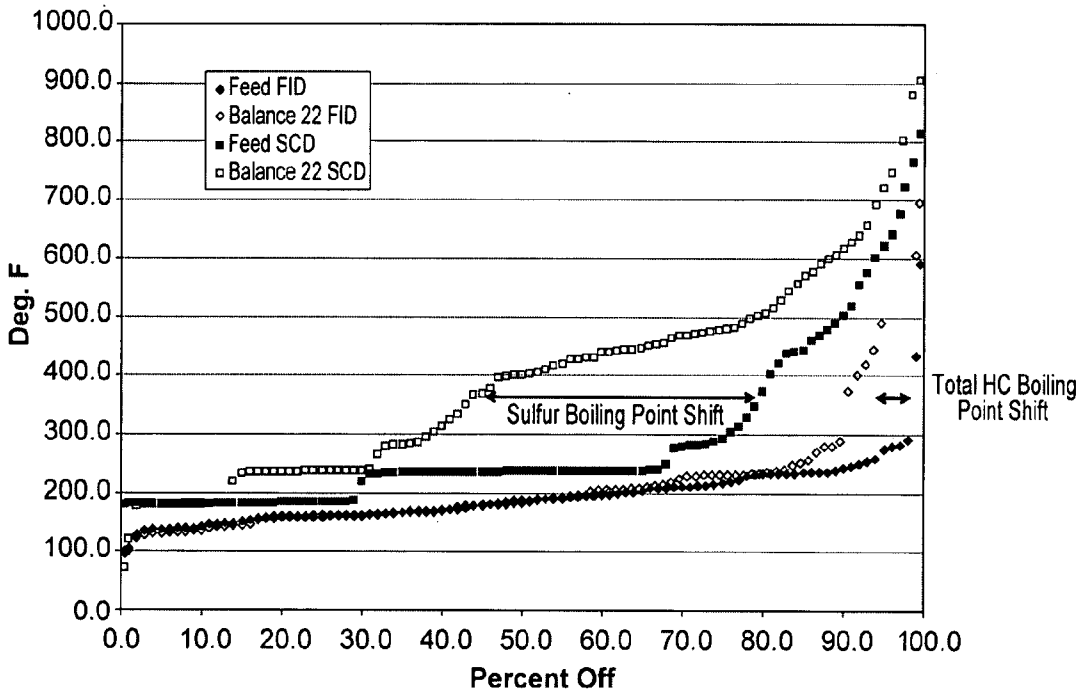

1000.0
900.0
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0.0
Deg. F
Feed FID
Balance 22 FID
Feed SCD
Balance 22 SCD
Sulfur Boiling Point Shift
Total HC Boiling Point Shift
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
Percent Off

FIG. 3

PROCESS FOR SELECTIVE SULFUR REMOVAL FROM FCC NAPHTHAS USING ZEOLITE CATALYSTS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the priority of U.S. Patent Application No. 60/852,404, filed 18 Oct. 2006.

FIELD OF THE INVENTION

[0002] 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 by reducing the sulfur content and also by removing benzene.

BACKGROUND OF THE INVENTION

[0003] 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, NOx and hydrocarbons.

[0004] 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, making it desirable to remove the sulfur while retaining the more desirable olefins. 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. 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.

[0005] A number of different techniques for reducing gasoline sulfur have been recognized as promising. Basically, these techniques have been categorized into four classes:

[0006] Hydrofining of FCC feed

[0007] Desulfurization of FCC gasoline

[0008] Use of catalysts and additives in the FCC process.

[0009] Sorption

[0010] All of these techniques have been applied with greater or lesser success depending upon product requirements, economics and the relative demand levels for gasoline and other fuel products. As a generalization, the hydrofining of the FCC feed is considered an expensive option in view of its hydrogen consumption even though yields benefits result for the LPG and gasoline fractions at the expense of cycle and slurry oils. Post-treatment of the FCC naphtha is regarded as a lower cost option and has been implemented in a number of competitive processes, each with their own distinguishing characteristics. One group, exemplified by the UOP ISAL Process and the Mobil OCTGAIN Process, suppress octane loss by isomerizing saturated hydrocarbons following the non-selective hydrodesulfurization. Selective hydrodesulfurization in processes such as ExxonMobil SCANfining, CDHydro, CDHDS, Axens Prime G+ and the BP-Axens OATS Process function by suppressing olefin saturation, mainly in the naphtha front end, by various techniques including catalytic selectivity as in the SCANfining Process or by distillative separation as in the other processes of this type. Sorption removal of sulfur is exemplified in the S Zorb Process (Phillips) and the IRVAD Process.

[0011] In the non-selective naphtha hydrodesulfurization processes, the FCC naphthas and other light fractions such as heavy cracked gasoline are hydrotreated by passing the feed over a hydrotreating catalyst at elevated temperature and somewhat elevated pressure in a hydrogen atmosphere. 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.

[0012] The sulfur impurities tend to concentrate in the heavy fraction of the gasoline, as noted in U.S. Pat. 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.

[0013] U.S. Pat. No. 4,049,542 (Gibson) discloses a process in which a copper catalyst is used to desulfurize an olefinic hydrocarbon feed such as catalytically cracked light naphtha. This catalyst is stated to promote desulfurization while retaining the olefins and their contribution to product octane.

[0014] Processes for improving the octane rating of catalytically cracked gasolines have been proposed. U.S. Pat. No. 3,759,821 (Brennan) discloses a process for upgrading catalytically cracked gasoline by fractionating it into a heavier and a lighter fraction and treating the heavier fraction over a ZSM-5 catalyst, after which the treated fraction is blended back into the lighter fraction. Another process in

which the cracked gasoline is fractionated prior to treatment is described in U.S. Pat. No. 4,062,762 (Howard) which discloses a process for desulfurizing naphtha by fractionating the naphtha into three fractions each of which is desulfurized by a different procedure, after which the fractions are recombined.

[0015] 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. Pat. No. 3,767,568 and U.S. Pat. No. 3,729,409 (Chen) in which the reformate octane is increased by treatment of the reformate with ZSM-5.

[0016] 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. Environmental regulations related to motor fuels have produced substantial changes in refinery operations. To comply with these regulations, some refineries have excluded the C6 compounds from the reformer feed to satisfy the low-level benzene requirement. A new refinery process able to alkylate benzene and sulfur compounds with the olefins contained in the same gasoline stream would be beneficial not only to meet benzene specification but also to comply with sulfur regulations.

[0017] A series of patents originating from Mobil Oil Corp. describe a process 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. The patents in this series are typified by the first, U.S. Pat. No. 5,346,609. Developments of the basic process with alternative methods of sulfur removal intended to further minimize octane loss are U.S. Pat. No. 5,318,690, in which the naphtha is split into two fractions with the light fraction subjected to an extractive sulfur removal operation which preserves olefin content the heavy fraction which contains relatively fewer of the desirable high-octane olefins is desulfurized by hydrodesulfurization and any resulting octane loss is restored by a selective cracking over a zeolite. A further development described in U.S. Pat. No. 5,360,532 uses a final extraction step to remove recombinant mercaptans.

[0018] When this process is applied to heavy catalytic naphtha (HCN), the yield loss can be between 6 to 15% while maintaining a similar octane value. The yield loss is highly dependent on octane-recovered value and the type of feed. Heavy catalytic naphtha is the ideal stream for this technology as higher losses are obtained with full range or intermediate catalytic naphthas.

[0019] A different approach was taken to sulfur removal by Exxon Research and Engineering Company in the selective naphtha hydrofining process described in various patents including: U.S. Pat. No. 5,985,136; U.S. Pat. No. 6,126,184; U.S. Pat. Nos. 6,231,753; 6,409,913; U.S. Pat. No. 6,231,754; US6013598; U.S. Pat. No. 6,387,249; U.S. Pat. No. 6,596,157. The ExxonMobil selective naphtha naptha hydrofining process, SCANfining™, which incorporates aspects of the processes described in these patents, which is commercially available under license from ExxonMobil Research and Engineering Company has demonstrated itself to be a very effective naphtha desulfurization process. This selective naphtha hydrofining process was developed for deep hydrodesulfurization with maximum preservation of the olefins (octane). The single stage version of the process can be used with a full range catalytic naphtha or with an intermediate catalytic naphtha (ICN), for example a nominal 65-175 C (150-350° F.) or a heavy catalytic naphtha (HCN), for example, a nominal 175 C+ (350° F.+) naphtha, or both. The two-stage version of the process, as described in U.S. Pat. No. 6,231,753, WO 03/048273 and WO 03/099963, adds a second reactor and inter-stage removal of H2S allowing very deep HDS with very good olefin retention. The operation of this process relies on a combination of a highly selective catalyst with process conditions designed to achieve hydrodesulfurization with minimum olefin saturation.

[0020] In cases where the sulfur content of the naphtha is modest and very deep HDS is not required, the SCANfining process can be an attractive option. If severe HDS conditions are needed, it is generally better to treat the LCN stream separately to preserve the maximum amount of olefins. Co-pending application USSN, claiming priority from U.S. Ser. No. 60/852,405, filed 18 Oct. 2006, entitled "Process for benzene reduction and sulfur removal from FCC naphthas", describes a process in which the cracked naphtha feed is split into a light fraction and a heavy fraction so as to permit optimized processing of each fraction for sulfur removal while retaining octane values.

SUMMARY OF THE INVENTION

[0021] We have now devised a process scheme to allow the removal of sulfur compounds and reduce benzene content of the FCC catalytic naphthas. This scheme is simple to implement and is economical in operation. According to the present process scheme, the selective naphtha hydrofining process is run to remove sulfur without sacrificing octane (hydrodesulfurization typically around 85%) followed by a downstream alkylation which will remove residual sulfur from the gasoline boiling range. In the alkylation step, the partly desulfurized naphtha is contacted with a solid, acidic molecular sieve alkylation catalyst under mild conditions to shift sulfur species from the lighter, olefin-rich portions of

the naphtha to the heavy, olefin-poor gasoline. Separation of the heavy portion of the treated product followed by catalytic hydrodesulfurization or some other means (e.g. sorption) removes the sulfur without losing significant octane value. Some of the heavy compounds formed in this process can drop out of the gasoline range, into the kero/light diesel range; this stream can be hydrotreated without penalty since octane is not a requirement for the middle distillate fuels. In addition, other reactions may occur in the presence of the catalyst to increase product octane, including isomerization of olefins to iso-olefins of higher octane and alkylation of aromatics to alkylaromatics, a reaction which is of particular utility in converting benzene in the naphtha to toluene and other alkylaromatics of reduced toxicity and higher octane. In this step of the process, it is also possible to add additional benzene from other refinery processes.

[0022] By carrying out an initial sulfur removal under conditions which do not result in excessive olefin saturation, the octane value of the olefins is preserved while, at the same time, enabling a substantial amount of the sulfur compounds to be removed from the cracked naphtha. The residual sulfur is then removed non-hydrogenatively by alkylation in a process step in which again, octane is largely retained. The alkylated sulfur compounds can then be removed from the gasoline boiling range fraction by fractionation, conveniently during product recovery. Thus, in this way, the objective of sulfur removal is satisfied by the balancing of conditions in the two selected process steps so that olefin octane is retained to the extent possible; very high levels of desulfurization can be achieved with little impact on gasoline yield and octane.

Typical reaction pathway for the alkylation step are:

[0023] Olefin+Sulfur compound→Alkylated Sulfur Compounds

[0024] Olefin ↔ Iso-olefins

[0025] Olefin+Aromatic→Alkylaromatic

[0026] The alkylation catalyst can be combined in one reactor with the selective hydrofining catalyst beds or can be loaded in a separate reactor.

[0027] The use of the solid molecular sieve alkylation catalyst is particularly favorable. Unlike catalysts such as solid phosphoric acid (sPA) catalyst, the molecular sieves are readily regenerable, either in situ or ex situ, and can be readily handled. They are also tolerant to the presence of water in the feed and do not tend to disintegrate or form lumps during operation. Suitable alkylation catalysts can be the intermediate pore size aluminosilicate zeolites such as ZSM-5, ZSM-11, ZSM-12 or members of the MWW family of zeolites such as MCM-22 and MCM-49. Large pore size zeolites such as zeolite Y (usually used as USY) or zeolite beta may also be utilized. Zeolite beta may be especially useful in view of its capability to isomerize paraffins in the presence of aromatics, thus, giving a further potential octane boost.

[0028] The front end of the cracked feed, which is relatively rich in olefins is spared the saturating effect of severe hydrodesulfurization but is nevertheless subjected to a controlled extent of desulfurization. The back end, by contrast, is relatively olefin-poor but high in sulfur compounds such as thiophenes and substituted thiophenes which are not amenable to extraction by conventional extractive processes. This higher-boiling, sulfur-rich fraction is effectively desulfurized by the alkylation followed by fractionation, optionally with the initial selective hydrofining step. The sulfur from thiophenes, substituted thiophenes and other higher boiling sulfur compounds initially present in the higher boiling fraction, if not removed by the initial hydrofining, are subjected to a similar type of alkylation usually in the presence of a zeolite catalyst to convert them into sulfur compounds boiling above the gasoline boiling range.

DRAWINGS

[0029] FIG. **1** of the drawings is a schematic of a process unit for carrying out the sulfur reduction process.

[0030] FIG. **2** is a graph showing the sulfur and conversion hydrocarbon yields from treatment of a naphtha with a zeolite catalyst as described in Example 8.

[0031] FIG. **3** is a graph showing the hydrocarbon and boiling point shifts resulting from the treatment described in Example 8.

DETAILED DESCRIPTION

[0032] Depending on the refinery operation, there are typically three components in the FCC naphtha: Light Cat Naphtha (LCN), Intermediate Cat Naphtha (ICN) and Heavy Cat Naphtha (HCN). The typical LCN (nominally C5-65° C., C5-150° F.) fraction contains mostly light (C1-C4) mercaptan sulfur species with lesser amounts of carbon disulfide, methylethylsulfide (MES), and dimethylsulfide (DMS). The LCN end point is generally set to ensure that only minimal amounts of thiophene (b.p. 84° C., 183° F.) enter the LCN stream. The typical ICN nominally in the boiling range of 65-175° C. (150-345° F.) contains most of the olefins of the FCC naphtha. Normal hydrotreating process of this stream will drastically affect its octane value. The typical HCN nominally boiling above 177° C. (350° F.) usually contains a higher concentration of sulfur and has the most difficult sulfur species to remove including benzothiophenes and substituted benzothiophenes. Thus, the problems in treating the FCC naphtha can be summarized according to the naphtha fraction: to remove mercaptans from the light naphtha while retaining olefins, to remove benzene, thiophene and other sulfur compounds from the intermediate naphtha again while retaining olefin content and with the heavy naphtha, to remove sulfur including the refractory substituted thiophenes.

[0033] According to the present invention, the sulfur in the cracked naphtha is effectively removed by the combination of the selective hydrofining (hydrodesulfurization) and the alkylation which uses the olefins contained in the naphtha (mainly in the front end) as the source of alkylating agent. Although this results in some olefin loss, the initial removal of sulfur in the selective hydrofining leaves only the residual sulfur to be removed and the olefin loss which takes place by using the olefins to alkylate the residual sulfur is less than the loss which would take place if the selective hydrofining were operated at the higher severity required to convert the sulfur compounds to inorganic form. In addition, if the alkylation conditions allow conversion of benzene (octane ~100) to alkylbenzenes such as toluene an octane boost may be achieved since the alkylaromatics are of higher blending octane (toluene octane=120), thereby compensating for the loss of olefins.

[0034] FIG. **1** shows an illustrative unit configuration for carrying out the present processing scheme. The FCC naphtha from the main column enters the unit by way of line **10**, coming into the selective hydrofining reactor **11** in which the sulfur compounds are removed by the selective hydrogenative process with its minimal tendency to saturate the olefins. The hydrofined effluent passes in line **12** to alkylation reactor **13** in which the sulfur compounds are converted to higher boiling alkyl analogs. The effluent from the alkylation reactor passes out through line **14** and the alkylated sulfur compounds which boil above the gasoline boiling range are separated from in fractionator **20** in the product recovery section. If the alkylation reactions result in alkylated sulfur products which remain in the back end (higher boiling portion) of the naphtha, the effluent from the alkylation reactor may be fractionated to remove the olefin-rich front end with the back end being passed to a hydrogenative sulfur removal step, e.g. hydrotreating, interposed between the alkylation reactor and the final product fractionator. In this case, the effluent from the alkylation reactor will pass through the portions of the unit indicated in feint, passing through line **15** to fractionator **16** which splits out the front end and sends it directly to the product recovery section through line **14**. The back end passes to hydrotreater **18** in which it is hydrotreated to convert the sulfur compounds to inorganic form. The hydrotreated naphtha passes to the product recovery section through line **19** and thence to fractionator **20**. The sulfur is recovered from the separator gases in the normal way (separators and scrubbers not shown). When the secondary hydrotreater is used, the alkylated effluent can be effectively hydrotreated to remove the sulfur since the olefin content of this fraction is relatively limited, so that the resulting octane loss is minimal. Light ends resulting from the processing leave fractionator **20** through line **21** and the desulfurized gasoline leaves through line **22**. Middle distillate either from the feed (if the gasoline cut point on fractionator **20** is lower than the feed cut point) or from the higher boiling materials produced from the alkylation is taken off the bottom of the fractionator through line **23**.

Selective Sulfur Removal

[0035] A desirable preliminary step is the removal of basic nitrogenous compounds from the naphtha since these may have an inhibiting effect on the acidic molecular sieve catalyst used in the subsequent alkylation step. An acidic wash treatment using dilute sulfuric acid or another acid is usually effective but a preferred treatment is with a heterogeneous acidic sorbent, preferably an acidic cation exchange resin such as the macroreticular cross-linked polymer sulfonate exchange resins sold under the Amberlyst™ trademark, such as Amberlyst™ 15. Resins of this type may be readily regenerated by acid treatment in the conventional manner.

[0036] The sulfur in the cracked naphtha is removed by a process which has minimal effect on the olefin content of the naphtha. To this end, a mercaptan extraction process such as the extractive Merox process may be used. The Merox sweetening type processes such as the Minalk process and the oxidative Merox process may also be used provided that the fractionation step which follows in the process sequence is effective to remove the disulfides and enable the gasoline fraction to meet applicable product sulfur specifications. The mercaptan extraction processes, however, are less effective with thiophene and other forms of sulfur and if a significant amount of non-mercaptan sulfur is present in the cracked naphtha, too much will be carried through to the alkylation step with the result that olefin consumption in this step will be increased. The selection of one of these sulfur removal processes is therefore dependent very much upon the sulfur species present in the feed.

[0037] A preferred sulfur removal technique which is effective against sulfur species present in naphtha streams together with other impurities is the selective hydrofining process referred to above which is capable of converting organic sulfur in the naphtha feed to inorganic form with a selective limited degree of hydrogenation of olefinic and aromatic compounds. As noted above, the selective naphtha hydrofining process is described in U.S. Pat. No. 5,985,136; U.S. Pat. Nos. 6,013,598; 6,126,184; U.S. Pat. No. 6,197,718; U.S. Pat. No. 6,231,753; U.S. Pat. No. 6,231,754; U.S. Pat. Nos. 6,387,249; 6,409,913; U.S. Pat. No. 6,596,157; U.S. Pat. No. 6,589,418; US 20030106839A1; US 20030127362A1; US 20030188992A1; US 20030220186A1; US20030217952A1; US20030183556A1; US 20040026298A1, US 20030221994A1; WO 2004/062796; WO 2005/037959, to which reference is made for a description and definition of the process and of variations in it. The ExxonMobil selective naphtha naptha hydrofining process, SCANfining™, which incorporates aspects of the processes described in these patents, is commercially available under license from ExxonMobil Research and Engineering Company and is highly suitable for this purpose.

[0038] The selective naphtha hydrofining process can be defined as one using a supported cobalt-molybdenum catalyst which is characterized by a combination of parameters including:

[0039] about 1 to 10 wt. % MoO_3; and

[0040] about 0.1 to 5 wt. % CoO; and

[0041] a Co/Mo atomic ratio of about 0.1 to 1.0, preferably 0.2 to 0.8 and most preferably from 0.25 to 0.72; and

[0042] a median pore diameter of about 60 to 200 Å, preferably 75 to 175 Å and most preferably 80 to 150 Å; and

[0043] a MoO_3 surface concentration of about 0.5×10^{-4} to 3×10^{-4} g/m^2 MoO_3, preferably 0.75×10^{-4} to 2.5×10^{-4} g/m^2 MoO_3 and most preferably from 1×10^{-4} to 2×10^{-4} g/m^2 MoO_3

[0044] an average particle size diameter of less than about 2.0 mm, preferably less than 1.6 mm and most preferably less than 1.4 mm.

Preferably, the catalyst has a metals sulfide edge plane area from about 7600 to 2800 μmol oxygen/g MoO3 as measured by oxygen chemisorption. It is also preferable for the MoO_3 surface concentration to be within the range of about 0.75×10^{-4} to about 2.5×10^{-4} g/m^2 MoO, with the Co/Mo atomic ratio from about 0.20 to 0.85.

[0045] In a preferred manner of operation, the process conditions of the hydrofining are such that the inlet temperature of the feedstock to the reaction unit is below the dew point of the feedstock and 100% of the feedstock

becomes vaporized in the catalyst bed. The process generally operates at a liquid hourly space velocity of from about 0.5 hr−1 to about 15 hr^{-1}, preferably from about 0.5 hr^{-1} to about 10 hr^{-1}, and most preferably from about 1 hr^{-1} to about 5 hr^{-1}.

[0046] The metal sulfide edge plane area as measured by the Oxygen Chemisorption Test is described in "Structure and Properties of Molybdenum Sulfide: Correlation of O_2 Chemisorption with Hydrodesulfurization Activity", S. J. Tauster et al., *Journal of Catalysis* 63, pp 515-519 (1980). The Oxygen Chemisorption Test involves edge-plane area measurements made wherein pulses of oxygen are added to a carrier gas stream and thus rapidly traverse the catalyst bed. For example, the oxygen chemisorption will be from about 800 to 2,800, preferably from about 1,000 to 2,200, and more preferably from about 1,200 to 2,000 μmol oxygen/gram MoO_3.

[0047] Further features of the preferred selective hydrodesulfurization process and the selective catalyst used in the process are found in the US patents referred to above in connection with the SCANfining™ process, to which reference is made for a description of them.

Alkylation-Process Parameters

[0048] Operation may take place under vapor phase, liquid phase or supercritical phase conditions (reactor inlet). Frequently, mixed phase conditions will prevail, depending on the feed composition and the conditions used. At the reactor outlet, liquid phase will prevail under normal conditions with the product including significant proportions of C_8, C_{10} and higher hydrocarbons. Pressure need not be above autogenous, sufficient to maintain the reactants in the liquid phase if liquid phase operation is desired. The pressure will therefore normally be dependent on unit constraints but usually will not exceed about 10,000 kPag (about 1450 psig) with low to moderate pressures, normally not above 7,000 kPag (about 1,000 psig) being favored from equipment and operating considerations although higher pressures are not excluded. In most cases, the pressure will be in the range of 1000 to 5500 kPag (about 145 to 800 psig) in order to make use of existing equipment. Space velocities can be quite high, giving good catalyst utilization. Space velocities are normally in the range of 0.5 to 5 hr^{-1} WHSV for the olefin feed, in most cases, 1 to 2 hr^{-1} WHSV. Optimum conditions may be determined empirically, depending on feed composition, catalyst aging and unit constraints.

[0049] Two factors affecting choice of temperature will be the feed composition and the level of sulfur and other impurities. The sulfur acts as a catalyst poison at relatively low reaction temperatures, typically about 120° C., but has relatively little effect at higher temperatures about 180° C. or higher, e.g. 200° C., 220° C., so that the preferred temperature regime is above about 150° C., with temperatures above 180° C. or higher being preferred, e.g. 200° or 220° C. or higher. In general terms, the temperature will be from about 120° to 350° C. (about 250 to 660° F.) and in most cases between 150° and 250° C. (about 300 to 480° F.).

[0050] If the naphtha fraction contains large proportions of benzene, it may be desirable to add olefins to the alkylation step from external sources in order to promote alkylation of the benzene to alkylaromatics. In such cases, lighter olefins may be used if available. FCC off-gas may be added with the advantage that the resulting alkylaromatic products have the lower carbon numbers characteristic of the preferred gasoline aromatics. The ratio between the total olefin and aromatic feed components is normally chosen to achieve the desired degree of benzene reduction consistent with the use of this process step to reduce sulfur. Optimal conditions may be determined empirically depending on feed composition, available feed rates, product objectives and unit type.

Alkylation Catalyst

[0051] The catalysts used in the alkylation contain a solid molecular sieve with acidic functionality as their essential catalytic component, preferably an intermediate or large pore size sieve. The intermediate pore size molecular sieves are a well established class and may comprise zeolites such as the aluminosilicate zeolites or other metallosilicate zeolites such as the aluminophosphosilicates and the aluminophosphates. The aluminosilicate zeolites are, however, preferred from the viewpoint of their catalytic activity and stability. Examples of intermediate pore size aluminosilicate zeolites which may be used are ZSM-5, ZSM-11 and ZSM-12. The more highly constrained intermediate pore size zeolites such as ZSM-22, ZSM-23 and ZSM-35 will not normally be preferred since their constrained pore structure does not allow the reactants and reaction products to access or to leave the internal pore structure of the zeolite. The large pore size zeolites such as zeolite Y (usually as USY), ZSM-4, ZSM-20 may also be used. Zeolite beta with its characteristic properties similar to both the large and intermediate pore size zeolites is also an appropriate selection.

[0052] A highly favored class of intermediate pore size zeolites are those of the MWW type. The MWW family of zeolite materials has achieved recognition as having a characteristic framework structure which presents unique and interesting catalytic properties. The MWW topology consists of two independent pore systems: a sinusoidal ten-member ring [10 MR] two dimensional channel separated from each other by a second, two dimensional pore system comprised of 12 MR super cages connected to each other through 10 MR windows. The crystal system of the MWW framework is hexagonal and the molecules diffuse along the [100] directions in the zeolite, i.e., there is no communication along the c direction between the pores. In the hexagonal plate-like crystals of the MWW type zeolites, the crystals are formed of relatively small number of units along the c direction as a result of which, much of the catalytic activity is due to active sites located on the external surface of the crystals in the form of the cup-shaped cavities. In the interior structure of certain members of the family such as MCM-22, the cup-shaped cavities combine together to form a supercage. The MCM-22 family of zeolites has attracted significant scientific attention since its initial announcement by Leonovicz et al. in Science 264, 1910-1913 [1994] and the later recognition that the family is currently known to include a number of zeolitic materials such as PSH 3, MCM-22, MCM 49, MCM 56, SSZ 25, ERB-1, ITQ-1, and others: Lobo et al. AIChE Annual Meeting 1999, Paper 292J.

[0053] The relationship between the various members of the MCM-22 family have been described in a number of publications. Three significant members of the family are MCM-22, MCM-36, MCM-49, and MCM-56. When initially synthesized from a mixture including sources of silica, alumina, sodium, and hexamethylene imine as an organic

template, the initial product will be MCM-22 precursor or MCM-56, depending upon the silica:alumina ratio of the initial synthesis mixture. At silica:alumina ratios greater than 20, MCM-22 precursor comprising H-bonded vertically aligned layers is produced whereas randomly oriented, non-bonded layers of MC-56 are produced at lower silica:alumina ratios. Both these materials may be converted to a swollen material by the use of a pillaring agent and on calcination, this leads to the laminar, pillared structure of MCM-36. The as-synthesized MCM-22 precursor can be converted directly by calcination to MCM-22 which is identical to calcined MCM-49, an intermediate product obtained by the crystallization of the randomly oriented, as-synthesized MCM-56. In MCM-49, the layers are covalently bonded with an interlaminar spacing slightly greater than that found in the calcined MCM-22/MCM 49 materials. The unsynthesized MCM-56 may be calcined itself to form calcined MCM 56 which is distinct from calcined MCM-22/MCM-49 in having a randomly oriented rather than a laminar structure. In the patent literature MCM-22 is described in U.S. Pat. No. 4,954,325 as well as in U.S. Pat. Nos. 5,250,777; 5,284,643 and 5,382,742. MCM-49 is described in U.S. Pat. No. 5,236,575; MCM-36 in U.S. Pat. No. 5,229,341 and MCM-56 in U.S. Pat. No. 5,362,697.

[0054] The preferred zeolitic material for use in the catalyst of the present process is MCM-22 although zeolite MCM-49 may be found to have certain advantages relative to MCM-22. It has been found that the MCM-22 may be either used fresh, that is, not having been previously used as a catalyst or alternatively, regenerated MCM-22 may be used. Regenerated MCM-22 may be used after it has been used in any of the catalytic processes for which it is suitable, including the present process in which the catalyst has shown itself remain active after even multiple regenerations. It may also be possible to use MWW catalysts which have previously been used in other commercial processes and for which they are no longer acceptable, for example, MCM-22 catalyst which has previously been used for the production of aromatics such as ethylbenzene or cumene, normally using reactions such as alkylation and transalkylation. The cumene production (alkylation) process is described in U.S. Pat. No. 4,992,606 (Kushnerick et al). Ethylbenzene production processes are described in U.S. Pat. No. 3,751,504 (Keown); U.S. Pat. No. 4,547,605 (Kresge); and U.S. Pat. No. 4,016,218 (Haag); U.S. Pat. Nos. 4,962,256; 4,992,606; 4,954,663; 5,001,295; and 5,043,501 describe alkylation of aromatic compounds with various alkylating agents over catalysts comprising MWW zeolites such as PSH-3 or MCM-22. U.S. Pat. No. 5,334,795 describes the liquid phase synthesis of ethylbenzene with MCM-22. As noted above, MCM-22 catalysts may be regenerated after catalytic use in these processes and other aromatics production processes by conventional air oxidation techniques similar to those used with other zeolite catalysts. Conventional air oxidation techniques are also suitable when regenerating the catalysts after use in the present process.

[0055] In addition to the MWW active component, the catalysts for use in the present process will often contain a matrix material or binder in order to give adequate strength to the catalyst as well as to provide the desired porosity characteristics in the catalyst. High activity catalysts may, however, be formulated in the binder-free form by the use of suitable extrusion techniques, for example, as described in U.S. Pat. No. 4,908,120. When used, matrix materials suitably include alumina, silica, silica alumina, titania, zirconia, and other inorganic oxide materials commonly used in the formulation of molecular sieve catalysts. For use in the present process, the level of MCM-22 in a finished matrixed catalyst will be typically from 20 to 70% by weight, and in most cases from 25 to 65% by weight. In manufacture of a matrixed catalyst, the active ingredient will typically be mulled with the matrix material using an aqueous suspension of the catalyst and matrix, after which the active component and the matrix are extruded into the desired shape, for example, cylinders, hollow cylinders, trilobe, quadlobe, etc. A binder material such as clay may be added during the mulling in order to facilitate extrusion, increase the strength of the final catalytic material and to confer other desirable solid state properties. The amount of clay will not normally exceed 10% by weight of the total finished catalyst. Self-bound catalysts (alternatively referred to as unbound or binder-free catalysts), that is, catalysts which do not contain a separately added matrix or binder material, are useful and may be produced by the extrusion method described in U.S. Pat. No. 4,582,815, to which reference is made for a description of the method and of the extruded products obtained by its use. The method described there enables extrudates having high constraining strength to be produced on conventional extrusion equipment and accordingly, the method is eminently suitable for producing the high activity self-bound catalysts. The catalysts are produced by mulling the zeolite, as described in U.S. Pat. No. 4,582,815, with water to a solids level of 25 to 75 wt % in the presence of 0.25 to 10 wt % of basic material such as sodium hydroxide. Further details are to be found in U.S. Pat. No. 4,582,815. Generally, the self-bound catalysts can be characterized as particulate catalysts in the form, for instance, of extrudates or pellets, containing at least 90 wt. pct., usually at least 95 wt. pct., of the active zeolite component with no separately added binder material e.g. alumina, silica-alumina, silica, titania, zirconia etc. Extrudates may be in the conventional shapes such as cylinders, hollow cylinders, trilobe, quadlobe, flat platelets etc.

[0056] As noted above, MCM-22 and other catalysts of this family may be regenerated after catalytic use for example, in the present process or in the cumene, ethylbenzene and other aromatics production processes, with the regeneration carried out by conventional air oxidation techniques similar to those used with other zeolite catalysts. Regeneration of the catalyst after use in the present process results in only a modest activity loss, with the catalyst maintaining more than 95% of fresh activity after the first regeneration. Even after multiple regenerations, a reasonable and acceptable level of activity is retained. The catalyst has been found to maintain more than 80% of fresh activity after 6 regenerations. Following the air oxidation, the catalyst may be reconditioned by aqueous reconditioning treatment using water or a mildly alkaline solution, for example, a dilute solution of ammonia or sodium carbonate. Treatment with water alone at ambient temperatures has been found to be effective: the air-regenerated catalyst is cooled and then immersed in a water bath after which it is dried and returned to service. The reconditioning treatment may be continued for the empirically determined time which results in an improvement in catalyst properties. It is theorized that the reconditioning treatment enables the silanol groups on the surface of the zeolite to be re-formed after the regen-

eration treatment with a consequent restoration of catalytic properties which, in favorable cases, may provide a catalyst almost comparable to a fresh catalyst.

[0057] A guard bed may be used ahead of the selective hydrofining reactor and, if used, may conveniently be the same catalyst used in the alkylation reactor as a matter of operating convenience but this is not required: if desired another catalyst or sorbent to remove contaminants from the feed may used, typically a cheaper guard bed sorbent, e.g. a used catalyst from another process or alumina. The objective of the guard bed is to remove the contaminants from the feed before the feed comes to the hydrofining catalyst and provided that this is achieved, there is wide variety of choice as to guard bed catalysts and conditions useful to this end. The volume of the guard bed will normally not exceed about 20% of the total catalyst bed volume of the unit.

Product Recovery and Treatment

[0058] After treatment in the alkylation step, the naphtha is treated for recovery of the product gasoline. Stabilization to remove light ends formed in the processing is typical as well as fractionation to separate the gasoline from heavier fractions formed in the alkylation step and any higher boiling sulfur compounds formed in the sweetening step (if used). At this time, the product specifications need to be observed in order to obtain proper flash point, boiling point and other specifications.

Experimental Work

[0059] Two types of FCC gasoline feeds were used in an investigation of the potential of zeolites for alkylating sulfur species, a C_5+ full range FCC gasoline and C_5 to 190° C. (375° F.) gasoline. Different samples of each type of gasoline feed were employed in the tests but differences between the samples for a given feed type were minimal and of no consequence. In general, 85 to 90 wt. % of the full range FCC gasoline boils below 190° C. (375° F.); the sulfur content was 2000 to 2500 ppm, 40-50% of which is in the 190° C.− (375° F.−) portion of the feed. For the C_5 to 190° C. (375° F.) FCC gasoline, more than 95 wt % boils below 190° C. (375° F.); these gasolines contained from 900-1300 ppm of sulfur, 85-95% of which is in the 190° C.− (375° F.−) portion of the feed.

[0060] The examples below illustrate the effectiveness of the catalytic treatments for shifting sulfur species from lighter, olefin-rich portions of the FCC gasoline to the heavy, olefin-lean gasoline or to the kero/light diesel range. Separation of the portion containing the sulfur compounds followed by catalytic hydrodesulfurization or some other means (e.g. sorption) can therefore remove the sulfur species without octane loss. Thus, very high levels of desulfurization can be achieved with little impact on overall gasoline yield and octane.

EXAMPLE 1

[0061] 1 part by weight of 100% H-MCM-22 (preparation below) was placed in a vial and contacted at room temperature with 3 parts by weight C_5+ full range gasoline. The contents of the vial were allowed to equilibrate over a 2-3 days, with periodic manual agitation. The supernatant liquid was then removed and subjected to GC analyses for boiling range distribution and sulfur content and distribution. Around 9% of the feed boiling below 190° C. (375° F.) was converted to the 190° C.+ (375° F.+) portion and 91% of the sulfur was removed from the 190° C.− (375° F.−) portion of the feed.

EXAMPLE 2

[0062] The same experiment as described in Example 1 was performed, except a C_5− 190° C. (C_5− 375° F.) FCC gasoline cut was employed. The 910 ppm S in this feed is very similar to the amount of 190° C.− (375° F.−) sulfur in the full range gasoline used in Example 1. Once again a high percentage of the light sulfur was shifted to heavy sulfur. Around 12% of the feed boiling below 190° C. (375° F.) was moved to the 190° C.+ (375° F.+) portion.

EXAMPLE 3

[0063] An H-MCM-22 powder (10 g) was placed in a 600 ml autoclave and dehydrated under a slow, continuous N_2 flow at 200° C. After 16 hours, the nitrogen flow was stopped, all inlets and outlets of the autoclave were closed, and the dried H-MCM-22 was cooled to 120° C. under the static N_2 atmosphere. At 120° C., a light (C_5− 190 C) FCC gasoline feed (100 g) was added via an ISCO™ pump to the autoclave over a 5 minute interval. After the gasoline addition, the autoclave's pressure was adjusted to 2070 kPag (300 psig) with N_2. The autoclave was then isolated from the gasoline source and held at 120° C. and 2070 kPag for 5 hr. Thereafter, the autoclave was cooled to ambient temperature and vented to ambient pressure slowly. A portion of the product was quickly sampled, passed through a syringe filter to remove catalyst particles, and subjected to sulfur and simulated distillation analysis. Boiling range conversion of 190° C.− (375° F.−) to the 190° C.+ (375° F.+) portion is less than 2% at 55-60% sulfur removal from the 190° C.− (375° F.−) portion of the feed.

[0064] The significant degree of sulfur removal from the 190° C.− (375° F.−) gasoline under markedly different conditions with respect to the above examples (lower catalyst to oil ratio, shorter contact time, higher temperature) illustrates the effectiveness of the MCM-22 catalyst for accomplishing this chemistry.

EXAMPLE 4

[0065] The same amount of the light FCC gasoline was treated with 10 g of USY zeolite (100% H-form, preparation below), using the procedure and conditions described in Example 3. Although the sulfur removal from the 190° C.− (375° F.−) portion of the feed is smaller with respect to the MCM-22 catalyst under the same conditions, the results showed that USY was nonetheless able to shift the sulfur out of the 190° C.− (375° F.)− gasoline. Boiling range conversion of 190° C.− (375° F.−) gasoline to 190° C.+ (375° F.+) gasoline is less than 1% with 20-25% of the sulfur removed from the 190° C.− (375° F.−) portion of the feed.

EXAMPLE 5

[0066] The same amount of the light FCC gasoline was treated with 10 g zeolite Beta (100% H-form, preparation below), using the procedure and conditions described in the Example 3. Sulfur removal from the 190° C.− (375° F.−) portion of the feed is roughly similar to that observed with MCM-22 under the same conditions. Boiling range conversion of 190° C.− (375° F.−) to 190° C.+ (375° F.+) portion

is around 5% at 50-55% sulfur removal from the 190° C.− (375° F.−) portion of the feed. In conjunction with the above examples, this example illustrates that a wide variety of aluminosilicate molecular sieves can be effective for shifting sulfur into heavier portions of the gasoline.

EXAMPLE 6

[0067] 1 part by weight of 100% USY (previously reduced with H_2) was contacted at room temperature with 3 parts by weight of the full range C_5+ gasoline. The contents of the vial were allowed to equilibrate over 16-24 hours, with periodic manual agitation. The supernatant liquid was then removed and subjected to GC analyses for boiling range distribution and sulfur content and distribution. Almost 80% of the sulfur was removed from the 190° C.− (375° F.−) portion of the feed. This example, together with example 4 above, illustrates that zeolite performance can be enhanced by modifying operating conditions.

EXAMPLE 7

[0068] The product from Example 1 was subjected to a compositional analysis by mass spectrometry and the results were used to calculate the octane properties of the treated gasoline. Compared to results for the feed based on the same type of analysis, the product road octane (i.e. (R+M)/2) showed only a modest change (86.0 for the treated gasoline vs. 87.4 for the feed). This example illustrates that high conversions of 190° C.− (375° F.−) sulfur to 190° C.+ (375° F.+) sulfur can be achieved without greatly affecting the gasoline octane quality.

EXAMPLE 8

[0069] The effectiveness of the alkylation step for removing sulfur from the gasoline fraction was demonstrated using a narrow cut intermediate (C_6-C_8) catalytic naphtha fraction containing 49% olefins, 12% aromatics, 360 wppm sulfur. The nitrogen content was reduced to about 1 wppm by treatment with an ion exchange resin (Amberlyst™) and alumina. This fraction was passed without treat gas over an MCM-49 catalyst diluted 4:1 with inerts, in an upflow reactor. The pressure (total system, gauge) was held at 6200 kPag (900 psig) and space velocity at 5 hr^{-1} v/v; the temperature was varied upwards during the course of the 11 day run during which 2 mass balances were taken each day. A 177° C.− (350° F.−) product fraction was taken and the sulfur conversion from this fraction determined. FIG. **2** shows that the sulfur conversion out of the product fraction increases with temperature and that the total hydrocarbon yield decreases. Similar results were obtained with a 204° C.− (400° F.−) fraction. FIG. **3** shows the hydrocarbon and boiling point shifts resulting from the treatment at a temperature of 185° C. (365° F.) attained at end-of-run when Mass Balance 22 was taken after 11 days of operation; it shows that while the shift in boiling point of the hydrocarbons is relatively limited (compare the boiling point shift between lines "Feed FID" and "Balance 22 FID"), a significantly greater shift in the boiling points of the sulfur species is obtained (compare the boiling point shift between lines "Feed SCD" and "Balance 22 SCD"), demonstrating that a subsequent fractionation will be readily capable of separating the alkylated sulfur compounds from the hydrocarbon components.

Preparation of H-MCM-22 Crystal Sample

[0070] A Na-form MCM-22 with a silica-to-alumina molar ratio of 24 was used for this catalyst preparation. The Na-form MCM-22 was calcined at 482° C. for 3 hours under N_2 atmosphere. Then the crystals were ammonium exchanged with 1 M ammonium nitrate solution (5 cc/g zeolite) two times at the natural pH and washed with deionized water. Then the wet MCM-22 zeolite was dried in an oven at 120° C. overnight. The material was air calcined (5 v/v/min) in a tray for 6 hours at 538° C.

Preparation of Beta Crystal Sample

[0071] A commercial Na-form Beta with a silica-to-alumina molar ratio of 35 was used for this catalyst preparation. The Na-form Beta was ammonium exchanged with 1 M ammonium nitrate solution two times at the natural pH and washed with deionized water. Then wet Beta zeolite was dried in an oven at 120° C. overnight. The material was calcined in a tray under N_2 at 482° C. for 3 hours, then under air (5 v/v/min) for 6 hours at 538° C.

Preparation of H USY Crystal Sample (Y-30681)

[0072] A commercial Na-form USY with a silica-to-alumina ratio of 5.5 and a unit cell size of 24.54 Å was used for this catalyst preparation. The Na-form USY was made a slurry with deionized water to target a 35 wt % solids level. A solution of 30 wt % ammonium sulfate was prepared, and then the pH was adjusted to 3.0 using 20 wt % H_2SO_4 solution. The pH 3.0 ammonium sulfate solution was added slowly to the USY slurry (1.3 g of 30% aluminum sulfate solution per 1 g zeolite) while the overall solution pH was adjusted to 3.0. The mixture slurry solution was stirred for ~30 minutes while the pH was adjusted to 3.0. The exchanged USY zeolite was filtered and washed with deionized water (10 cc/g zeolite). Then the USY zeolite was ammonium exchanged one more time by pouring pH 3.0 ammonium sulfate solution (1.3 g solution per 1 g USY) over the USY zeolite on the filter. The exchanged USY zeolite was washed with deionized water (10 cc/g zeolite) and then dried in an oven at 120° C. overnight. The material was air calcined (5 cc air/g zeolite/min) for 3 hours at 538° C.

1. A process for the removal of sulfur compounds from a catalytically cracked petroleum naphtha feed comprising organic sulfur compounds and olefins, which comprises:

Selectively hydrodesulfurising the cracked naphtha under conditions and with a catalyst which is effective to convert organic sulfur in the naphtha feed to inorganic form with a selective, limited degree of hydrogenation of olefinic compounds,

Subjecting the hydrodesulfurized naphtha to a fixed bed alkylation step in the presence of a solid molecular sieve alkylation catalyst to alkylate organic sulfur compounds in the hydrodesulfurized naphtha with the olefins contained in the naphtha;

Fractionating the hydrodesulfurized, alkylated naphtha to remove alkylated sulfur compounds which boil above the gasoline boiling range.

2. A process according to Paragraph **1** in which the hydrodesulfurized naphtha is subjected to alkylation over a zeolite alkylation catalyst comprising an intermediate pore size zeolite.

3. A process according to Paragraph **2** in which the hydrodesulfurized naphtha is subjected to alkylation over a zeolite alkylation catalyst comprising ZSM-5 or ZSM-12.

4. A process according to Paragraph **1** in which the hydrodesulfurized naphtha is subjected to alkylation over a zeolite alkylation catalyst comprising a zeolite of the MWW family.

5. A process according to Paragraph **4** in which the zeolite of the MWW family comprises MCM-22 or MCM-49.

6. A process according to Paragraph **1** in which additional benzene from outside sources is added to the alkylation step.

7. A process according to Paragraph **1** in which the hydrodesulfurized, alkylated naphtha is fractionated into a light fraction and a heavy fraction with the heavy fraction being subjected to a hydrodesulfurized step to remove sulfur compounds.

8. A process according to Paragraph **7** in which the heavy fraction, after being hydrodesulfurized to remove sulfur compounds, is recombined with the light fraction.

9. A process according to claim 1 in which the desulfurization during the selective hydrodesulfurization process is not greater than 90%.

10. A process according to claim 1 in which the desulfurization during the selective hydrodesulfurization process is not greater than 80%.

11. A process according to claim 1 in which the sulfur removal from the 190° C.− fraction of the hydrodesulfurized naphtha is at least 50%.

12. A process according to claim 1 in which the sulfur removal from the 190° C.− fraction of the hydrotreated naphtha is at least 75%.

13. A process according to claim 1 in which the sulfur removal from the 190° C.− fraction of the hydrodesulfurized naphtha is at least 85%.

14. A process according to claim 1 in which the boiling range conversion of the 190 C− (375 F−) portion of the hydrodesulfurized naphtha to the 190° C.+ (375° F.+) portion is less than 20%.

15. A process according to claim 1 in which the selective naphtha hydrodesulfurization process is carried out in the presence of a supported cobalt-molybdenum catalyst which comprises a porous inorganic refractory support, about 1 to 10 wt. % MoO_3 and about 0.1 to 5 wt. % CoO; and having

a Co/Mo atomic ratio of about 0.1 to 1.0; and

a median pore diameter of about 60 to 200 Å; and

a MoO3 surface concentration of about 0.5×10^{-4} to 3×10^{-4} $g\cdot m^{-2}$ MoO3; and

an average particle size diameter of less than about 2.0 mm.

16. A process according to claim 15 in which the hydrodesulfurization catalyst has a metals sulfide edge plane area from about 7600 to 2800 μmol oxygen/g MoO3 as measured by oxygen chemisorption.

17. A process according to claim 15 in which the hydrodesulfurization is such that the inlet temperature of the feedstock to the reaction unit is below the dew point of the feedstock and 100% of the feedstock becomes vaporized in the catalyst.

18. A process according to claim 15 in which the liquid hourly space velocity of the cracked naphtha over the hydrodesulfurization catalyst is from about 0.5 hr−1 to about 15 hr^{-1}.

19. A process according to claim 15 in which the hydrodesulfurization catalyst has a median pore diameter of from 80 to 150 Å.

20. A process according to claim 15 in which the hydrodesulfurization catalyst has a MoO_3 surface concentration of about 1×10^{-4} to 2×10^{-4} g/m^2 MoO_3.

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