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HYDROCRACKING PROCESS FOR HIGH OCTANE PRODUCT

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ABSTRACT OF THE DISCLOSURE

The present disclosure relates to an improved hydrocracking process wherein a basic nitrogenous compound is continually present thereby inhibiting the cracking activity of the zeolite catalyst. Hydrocracking temperatures greater than commonly used are employed, e.g., in the range of 700° to 1,000° F., thereby producing a highly aromatic naphtha product of high octane number. In a preferred embodiment sulfur compounds are excluded from the reaction zone.

This invention relates to the catalytic hydrocracking of hydrocarbons. Particularly, it relates to an improved hydrocracking process capable of producing high octane gasoline product without the necessity for additional reforming capacity and utilizing a crystalline aluminosilicate zeolite hydrocracking catalyst in the presence of certain basic nitrogen compounds. More particularly, the invention is concerned with a two-stage hydrocracking process wherein the first stage is conducted at conventional hydrocracking conditions without introduction of said basic nitrogen compounds, and wherein the second stage is conducted in accordance with the aforesaid procedure.

Hydrocracking has now become widely accepted within the petroleum industry as a valuable alternative to conventional catalytic cracking processes, largely due to its ability to selectively convert heavy feeds to high quality naphtha or middle distillate with significantly less gas and coke yield, higher quality and yield of desired liquid product. A new breed of hydrocracking catalysts has recently appeared which comprises crystalline aluminosilicate zeolites commonly known as "molecular sieves" in combination with suitable hydrogenation components. Such catalysts have been shown to possess unusually high activity and activity maintenance, as compared to the conventional amorphous type catalysts previously utilized. For the production of hydrocracked naphthas which serve to meet gasoline demands, typical feedstocks would include virgin gas oils, coker gas oils, catalytic cycle oils, shale oils fractions, coal tar fractions, steam cracked tars, kerosene, etc. Conventional hydrocracking of these feedstocks, even with the aforementioned superior crystalline zeolite catalysts, is only capable of producing hydrocracked naphaha products having in the range of about 10 to 20% aromatic content with research octane numbers in the order of about 90 to 92 and motor octane numbers in the order of about 84 to 87. Ordinarily, these values are insufficient to meet the octane requirements of premium grade gasoline so that additional upgrading procedures are usually required, one of the most common being hydroforming. Thus, conventional processing schemes typically used in present-day refineries involve a cracking operation followed by reforming of the cracked products to increase octane number to the level of about 98 to 100 research octane units.

In accordance with the present invention, means have been discovered to produce high octane naphtha product capable of meeting the high octane requirements for premium grade fuels by means of a hydrocracking operation, without the necessity for additional reforming capacity. The hydrocracking process of the present invention utilizes a crystalline zeolite catalyst combined with a suitable metallic hydrogenation component and is conducted in the continual presence of a basic nitrogenous compound having the capability of inhibiting the unique cracking properties of the zeolite catalyst at the high hydrocracking temperature employed. This hydrocracking temperature is significantly higher than that customarily employed with either the conventional or the zeolite variety of hydrocracking catalysts. The temperature employed in the invention will generally be within the range of about 700 to about 1000° F., usually about 750 to about 950° F. It will be preferred to conduct the hydrocracking operation at a temperature above 800° F., e.g. above 800° F. to about 950° F., with the most preferred temperatures being in the range of about 825 to 925° F.

The cracking activity of the superior zeolitic hydrocracking catalysts is controlled in the present process both by the feed rates utilized and by the presence of the basic nitrogen inhibitor. The continual presence of this inhibitor in relatively undiminished quantities is required throughout the hydrocracking operation, since the requisite high temperatures needed for the production of aromatic naphthas meeting the octane requirements herein desired cannot be utilized in the absence of such inhibitor without the occurrence of excessive cracking to undesired products. As an additional preferred embodiment of the invention, the hydrocracking operation is conducted in the absence of a substantial amount of sulfur compounds in the feeds, again to avoid the occurrence of excessive cracking.

The present process may thus be briefly characterized by the following essential features: (1) the use of substantially higher temperatures than those employed in conventional hydrocracking operations, (2) the use of a crystalline zeolite-containing hydrocracking catalyst, and (3) the continual presence of a basic nitrogen compound inhibitor in relatively undiminished amount during the hydrocracking operation, said inhibitor being capable of controlling the activity and selectivty of the zeolitic catalyst so as to produce highly aromatic naphtha product of desired high octane number. In addition, a preferred fourth requirement is the substantial absence of sulfur during this high octane producing hydrocracking step.

The basic nitrogen inhibitor used in the present process may be any of the common nitrogenous base materials. Examples of such materials include ammonia; amines such as aryl amines, e.g., aniline; alkyl amines, e.g., methyl and propyl amines; alkyl aryl amines such as dimethyl aniline and diethyl naphthylamine; and the like. Various other nitrogenous compounds can also be used, including pyridine, piperidine, quinoline, pyrrolidine, pyrrol, nitrosobenzene, nitrobenzene, and the like. Additional compounds would include the oximes and nitriles, as well as azo-, diazo, and heterocyclic ring compounds with two or more nitrogen atoms per molecule. The latter encompasses the pyridiazines, pyrimidine, pyrazine, triazines, cinnoline, quinazoline, naphthylpyridine, purine, and the like. Such compounds possess the ability to alter the activity and selectivity of the particular zeolite hydrocracking utilized herein so as to inhibit its cracking activity to a minor extent, such that aromatics production is maximized at the high temperatures herein utilized.

The amount of nitrogenous base inhibitor employed in the hydrocracking operation for the production of high octane gasoline is maintained essentially constant throughout the process. This amount will generally be in the range of about 500 to 30,000 p.p.m., based on the weight of hydrocarbon feed to the hydrocracking zone, preferably about 1000 to 10,000 p.p.m., and most preferably about

1800 to 5000 p.p.m. A portion of the above-specified nitrogen content may be present in the feed supplied to the hydrocracking zone without separate addition of nitrogen compound. Normally, however, particularly with heavy high nitrogen feeds, the feed to the hydrocracking zone will have been treated at some time prior to the hydrocracking zone to substantially reduce the sulfur content to a low level, and partially remove nitrogen by conventional methods such as hydrofining. Where an initial pretreat is not necessary, typical feeds to the hydrocracking zone will normally possess nitrogen contents substantially lower than those specified above. The basic nitrogen compound can be incorporated into the feed to the hydrocracking zone, added separately to the hydrocracking zone, or added to the recycle hydrogen gas system, as by addition of ammonia to the hydrogen stream supplied in the hydrocracking zone. Impregnation of the nitrogen compound on the original fresh catalyst is also contemplated.

The hydrocracking operation of the present invention can be conducted with a fixed bed, moving bed, fluidized bed, etc. However, because of the substantially higher temperatures employed in the present process, as compared to conventional processing, it may be desirable to facilitate catalyst regeneration. The preferred systems would thus involve the moving bed or fluidized bed operation, whereby spent catalyst can be continuously withdrawn and regenerated. "Swing type" operations using fixed bed reactors are also contemplated.

The hydrocracking reaction is conducted in the present invention at a temperature of about 700 to about 1000° F., usually about 750 to about 950° F.; a pressure of about 200 to 3000 p.s.i.g., preferably about 400 to 2000 p.s.i.g., more preferably about 750 to 1500 p.s.i.g.; an exit hydrogen rate of about 1000 to 10,000, preferably about 2000 to 8000, more preferably about 2000 to 6000, s.c.f./bbl. feed; and at a feed rate of about 0.5 to 5.0, preferably about 0.5 to 3, more preferably 1 to 3, volumes of feed per volume of catalyst per hour. As previously mentioned, the feed rates used in the present invention are to be regarded as critical to the successful production of the desired highly aromatic product. The conversion level in the hydrocracking zone will generally be about 20 to about 20%, preferably about 40 to about 60%, to products boiling below about 430° F.

The feedstocks particularly adaptable for the use of the present process will be petroleum derived feeds, preferably boiling substantially in the range of about 400 to 1000° F. Such feeds would include virgin and coker gas oils, cycle oils, heating oils, shale oils, steam cracked tars, and the like. Most preferred feeds will consist of the 400 to 700° F. fractions from the above sources.

As has been noted previously, the process of the invention is preferably conducted in the substantial absence of sulfur and sulfur compounds. Usually the feed will have been pretreated at some point to remove sulfur, or an initially sulfur-free feed will be used. The preferred sulfur levels of the feed will be less than about 0.2 wt. percent, preferably less than 0.02 wt. percent. Where hydrogen sulfide is formed upon hydrotreating of the feed, it is separated from the hydrogen gas recycle system and removed to avoid reintroduction in the hydrocracking zone.

By the process of the invention, highly aromatic naphtha products are obtained having aromatic contents of about 40 to 60% and exhibiting research octane numbers (3 cc. TEL) as high as 98 to 100 units. Such result is attainable through the unique combination of process characteristics previously set forth.

The aforementioned crystalline aluminosilicate zeolite catalysts are now well known in the art and have been described extensively in the patent literature. They are characterized by highly ordered crystalline structure and uniformly dimensioned pores and have an aluminosilicate anionic cage structure wherein alumino and silica tetrahedra are intimately connected to one another so as to provide a large number of active sites, with the uniform pore openings allowing the entry of molecular structures having smaller cross-sectional diameters. For the purposes of the present invention, the crystalline aluminosilicate zeolites should have effective pore diameters of within the range of 6 to 15 Angstrom units, preferably 7 to 13 Angstrom units. Such "large pore" crystalline zeolites are exemplified by the naturally occurring minerals faujasite and mordenite. (Because of availability, only mordenite may be employed practically.) Synthetically produced aluminosilicate zeolites having large pore diameters are also available and will be preferred in the present invention. In general, all crystalline aluminosilicate zeolites, in natural or synthetic form, contain a substantial portion of an alkali metal oxide, normally sodium oxide.

More specifically, the cracking component of the catalyst used in the present invention is a crystalline aluminosilicate zeolite having an effective pore diameter of about 6 to about 15 Angstroms, wherein a substantial portion of the alkali metal, e.g., sodium, has been replaced with a cation (either a metal cation or a hydrogen-containing cation, e.g., NH_4^+) so as to reduce the alkali metal oxide, e.g., Na_2O, content to less than about 10 wt. percent, and preferably to about 1 to 5 wt. percent (based on zeolite). The anhydrous form of the base-exchanged crystalline aluminosilicate zeolite prior to compositing with platinum group metal may be generally expressed in terms of moles by the formula:

$$0.9\pm0.2Me_{2/n}O:Al_2O_3:xSiO_2$$

wherein Me is selected from the group consisting of hydrogen and metal cations (so that the Na_2O content is less than 10 wt. percent of the zeolite), n is its valence and x is a number from 2.5 to 14 or higher, preferably 3 to 10, and most preferably 4 to 6. Crystalline zeolites having these ratios have been found to be highly active, selective, and stable. However, zeolites having higher or lower silica-to-alumina ratios may also be employed advantageously.

The processes for synthetically producing crystalline aluminosilicate zeolites are well known in the art. They involve crystallization from reaction mixtures containing: Al_2O_3 as sodium aluminate, alumina sol, and the like; SiO_2 as sodium silicate and/or silica gel and/or silica sol; and Na_2O as sodium hydroxide. Careful control is kept over the soda (Na_2O) concentration of the mixture, as well as the proportions of silica to alumina and soda to silica, the crystallization period, etc., to obtain the desired product.

The most preferred crystalline zeolite to be used in the present invention will be a synthetic faujasite having a silica-to-alumina ratio of between about 4 and 6 and an X-ray diffraction pattern essentially similar to the naturally occurring mineral faujasite. Such material is known in the art as the so-called "type Y" molecular sieve.

For hydrocracking use the zeolite is preferably base exchanged with a hydrogen-containing and/or metal cation to reduce the soda content to below 10 wt. percent. Suitable metal cations include ions of metals in Groups I to VIII and rare earth metals, preferably metals in Groups II, III, IV, VI–B, VII–B, VIII and rare earth metals, most preferably Groups II and VIII. Mixtures of these various cations can be employed. Where a hydrogen-containing cation is used to replace the sodium, the "hydrogen" form of the zeolite is produced. A convenient method of preparing the "hydrogen" form is to subject the zeolite to base exchange with an ammonium cation solution followed by controlled heating at elevated temperature, e.g., 600 to 100° F., to drive off ammonia and water.

The base-exchanged crystalline zeolite is then composited with a suitable metallic hydrogen component, e.g., metals in Groups VI and VIII of the Periodic Table. Nonlimiting examples would include copper, nickel, cobalt, molybdenum, and, most preferably, the platinum group metals, such as platinum or palladium. Platinum group metals may be incorporated by treatment (e.g., wet impregnation or base exchange) with a platinum or palladium salt or ammonium complex, e.g., platinous ammonia chloride, palladious tetramine chloride, etc. The amount of catalytic metal in the finished catalyst is ordinarily between 0.01 and about 5.0 wt. percent, preferably 0.5 to 1.0 wt. percent (based on the zeolite). Normally the catalyst is subjected to a heat or hydrogen treatment at elevated temperatures, e.g., 500 to 1500° F., to reduce the platinum group metal, at least in part, to its elemental state. The preferred metal is palladium.

By the process described above, it is possible to convert a typical gas oil, cycle oil, etc. to a highly aromatic naphtha product having premium grade octane ratings in a single-stage procedure without the necessity for subsequent reforming. In a more specific embodiment of the invention, this procedure can be integrated into a two-stage hydrocracking process with or without pretreatment of the feed as by hydrofining. If hydrofining of the initial feedstock is desired or required, it is readily accomplished in conventional manner using typical hydrofining or hydrogenation catalysts, such as the oxides or sulfides of metals of Groups VI and VIII of the Periodic Table, either alone or in admixture with each other, composited with an inert metal oxide support such as silica, oxides of metals in Groups II–A, III–A and IV–B of the Periodic Table, and mixtures thereof. A particularly preferred catalyst, for example, would be nickel or cobalt molybdate and/or the corresponding tungstates on alumina. Conventional hydrofining conditions are used and the hydrofined effluent is introduced into the first-stage hydrocracker containing the same type zeolite hydrocracking catalyst hereinbefore described. The first-stage hydrocracking operating conditions include a temperature of about 550 to 750° preferably 600 to 725° F.; a pressure of about 400 to 3000 p.s.i.g., preferably 500 to 1500; a space velocity of 0.2 to 5 v./v./hour, preferably 0.5 to 2 v./v./hour; and a hydrogen rate of about 1000 to 15,000 s.c.f./bbl. of hydrofined feed, preferably 4000 to 6000. The first-stage hydrocracked effluent is treated to remove hydrogen sulfide formed in the previous steps either completely or to the extent required to achieve the desired sulfur content in the feed to the second-stage hydrochracker. The second-stage hydrocracking is conducted in accordance with the procedures hereinbefore set forth, that is, at the significantly higher temperatures previously set forth, and in the presence of the basic nitrogen compound which is continually introduced either into the second-stage feed or into the second-stage hydrocracking zone per se. This can be accomplished in various ways, as will be apparent to those skilled in the art. For example, a separated ammonia stream can be introduced with the feed to the second-stage hydrocracker. After suitable gas separation the effluent stream from the second-stage hydrocracking zone is fractionated, and a highly aromatic, high octane producing naphtha product is recovered. The fractionator bottoms, consisting mainly of material boiling above about 430° F., can be recycled either to the first-stage or second-stage hydrocracking zone.

The above embodiment is thus characterized by a two-stage hydrocracking procedure using the same general type of zeolitic catalyst in both stages, wherein the second stage is conducted in the continual presence of the basic nitrogen compound in the amounts hereinbefore set forth and at the more severe temperature conditions than the first stage in order to achieve the high octane benefits of the invention. Again, additional reforming capacity can thus be eliminated.

This improved octane performance is also obtained in the single-stage hydrocracking system. In this instance

the hydrofined liquid effluent, freed of most of the sulfur, is introduced to the single-stage, high temperature hydrocracking zone. The nitrogen content is adjusted by addition to either the treat gas or liquid feed, and the operation is conducted as outlined for the second stage as discussed above.

The invention will be further understood by reference to the following examples, which are not intended to be limiting.

EXAMPLE 1

The improved benefits of the hydrocracking process of the invention was demonstrated with a catalytic cycle oil having the following specifications:

Gravity, ° API	37.7
Nitrogen, p.p.m.	1
Sulfur, p.p.m.	31
Distillation, D–158:	
IBP	290
5	400
10	422
50	501
90	592
95	603
FBP	641

The feed was previously hydrofined with a cobalt molybdate-aluminum catalyst at conventional hydrofining conditions, and the above specifications refer to the hydrofined material. Two wt. percent aniline was added to the hydrofined cycle oil, and this feed was hydrocracked over a synthetic faujasite type hydrocracking catalyst. This catalyst consisted of a synthetic faujasite which was base exchanged with both hydrogen and magnesium cations and had the following approximate analysis:

	Weight percent
SiO_2	66.2
Al_2O_3	20.4
Na_2O	1.9
MgO	2.4

After the base exchange the catalyst was contacted with a solution containing the ammonium complex of palladious tetramine chloride to incorporate about 0.5 wt. percent palladium. The catalyst was finally dried and calcined at 1000° F. The final catalyst thus contained 0.5% palladium and had a Na_2O content of about 2.0 and a silica-to-alumina molar ratio of about 5.5.

The hydrocracking operation was conducted in a fixed bed unit utilizing a temperature of 900° F., a space velocity of 1 v./v./hour, a pressure of 800 p.s.i.g., at an exit hydrogen rate of 2000 s.c.f./bbl.

For purposes of comparison the same feed was treated over the same catalyst without the addition of aniline, and the results were compared. In the first case the aniline was continually added to the feed throughout the operation to maintain the 2% level. In both cases the operation was conducted single stage and in a once-through manner. The hydrocracking conditions employed in the second run (i.e., no aniline added) were conventional for the zeolite catalyst and included a temperature of 491° F., a pressure of 1500 p.s.i.g., a space velocity of 0.94 v./v./hour, and an exit hydrogen rate of 8500 s.c.f./bbl.

The results of these two operations are summarized in the following table.

HYDROCRACKING OF CATALYTIC CYCLE OIL

Aniline Added to Feed, wt. percent	2	0
Operating conditions:		
Temperature, ° F	900	491
Pressure, p.s.i.g	800	1,500
Space velocity, v./v./hour	1	0.94
Exit hydrogen rate, s.c.f./bbl	2,000	8,500
Product distribution:		
C_3 and lighter, wt. percent	20.8	0.7
i-C_4, vol. percent	15.0	11.5
n-C_4, vol. percent	9.8	
C_5–250° F., vol. percent	31.2	68.2
250-350° F., vol. percent	9.3	
350-430° V., vol. percent	4.3	
430° F.+, vol. percent	20.2	33.2
Product inspection of C_5–430° F. fraction:		
Gravity, ° API	51.8	54.3
Vol. percent aromatics	44	~13
Octane data:		
Research +3 cc. TEL	99.3	90.5
Motor +3 cc. TEL	88.3	87.1

As indicated above, use of the added basic nitrogen compound made higher hydrocracking temperatures feasible and increased catalyst selectivity to aromatics substantially, thus enabling production of 99+ research octane number C_5–430° F. naphtha product; such product can be used directly for premium fuel.

What is claimed is:

1. An improved hydrocracking process for the production of high octane naphtha product which comprises contacting a petroleum derived feedstock boiling substantially in the range of about 400 to 1000° F. with a catalyst comprising a crystalline aluminosilicate zeolite having uniform pore openings of about 6 to 15 Angstrom units combined with a metallic hydrogenation component, in the presence of a basic nitrogen compound in an amount capable of suppressing the cracking activity of said catalyst at the hydrocracking conditions utilized so as to avoid excessive cracking to low octane-producing product, said amount being maintained at a substantially constant level within the range of about 1800 to 5000 parts per million based on the weight of feed, wherein said hydrocracking conditions include a temperature of about 825 to about 925° F., a pressure of about 750 to 1500 p.s.i.g., a feed rate of about 1 to 3 volumes of feed per volume of catalyst per hour, and an exit hydrogen rate of about 1,000 to 10,000 standard cubic feet per barrel of feed and recovering an aromatic naphtha product.

2. An improved hydrocracking process for the production of high octane naphtha product which comprises hydrofining a petroleum derived feedstock, hydrocracking the hydrofined feedstock in a first hydrocracking zone containing a crystalline aluminosilicate zeolite combined with a metallic hydrogenation component at hydrocracking conditions including a temperature of about 550 to 750° F., and hydrocracking the effluent from said first hydrocracking zone in a second hydrocracking zone with a catalyst essentially similar to that used in said first zone at hydrocracking conditions including a substantially higher temperature in the range of 825–925° F., wherein the hydrocracking reaction in said second zone is conducted in the presence of a substantially constant quantity of a basic nitrogen compound in the range of about 1,000 to 10,000 p.p.m. based on the feed to suppress the cracking activity of the catalyst in said second zone at said substantially higher temperature so as to avoid excessive cracking to low octane-producing products, and recovering from the effluent of said second hydrocracking zone a naphtha product having a research octane number in excess of 98.

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