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OCTANE IMPROVEMENT PROCESS FOR MOTOR FUELS

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This invention relates to a process for increasing the octane number of an olefin containing hydrocarbon stream. Specifically, the invention relates to an improved process and catalyst for increasing the octane number, especially the motor octane number, of an olefinic hydrocarbon fraction, by passage over said catalyst comprising sulfided nickel deposited on a solid acidic support.

The catalyst is similar to the one described in the recently announced Isocracking process, which converts heavy hydrocarbon streams into materials boiling in the gasoline range by hydrocracking. In the Isocracking process, the heavy hydrocarbon streams boiling above about 250° F. are passed over a catalyst consisting of nickel deposited on a silica-alumina cracking catalyst base. At the sufficiently high temperatures used in the process, fragmentation of the large molecules result and material of high octane number boiling in the gasoline range is produced. The process of this invention differs from the Isocracking process in that the feed material is a light olefinic naphtha and the main reactions occurring are isomerization, saturation and polymerization, rather than cracking.

In present refinery operations, certain streams boiling from 30–350° F. and containing an appreciable concentration of olefins containing from 4 to 8 carbon atoms are obtained from catalytic cracking and thermal cracking operations. A common characteristic of these olefinic streams is that they have a fairly high research octane number, but the motor octane number is lower than that desirable in modern combustion engines. The research and motor octane numbers as used in this specification are determined by ASTM method D1656–59T (Research) and D357–59 (Motor). This difference between the research and motor octane number of a gasoline, commonly called the sensitivity, is becoming the limiting factor in refinery gasoline blending operations. Thus, any process for improving the motor octane of these olefinic naphthas and lowering the sensitivity will be economically advantageous and useful.

An object of this invention is the preparation of a catalyst suitable for the isomerization and saturation of olefins to isoparaffins. A specific object of this invention is a process wherein light olefinic naphthas are converted to saturated hydrocarbons having much higher motor octane numbers and, in some cases, higher research octane numbers by passage over the catalyst described herein. Another specific object of this invention is to decrease the sensitivity of the gasoline and to increase the octane index. Thus, by this process, the sensitivity of the gasoline is decreased and the octane

index is increased. By octane index is meant the weighted average of research and motor octane number and is a technique used by refiners to rate the road performance of a motor fuel. A still further specific object of this invention is the optimization of either the gasoline or middle distillate fraction depending upon operating conditions. Further objects will be apparent from a description of this invention hereinbelow.

It has been discovered that by using a solid dual function catalyst, that is, one containing an acidic component as well as a hydrogenating component, said catalyst comprising sulfided nickel on a hydrocarbon cracking catalyst base, one can obtain the very desirable reactions of olefin isomerization to isoolefins with the subsequent saturation of these isoolefins to isoparaffins. The following table shows the research and motor octane numbers of some typical normal and isoolefins in the 30° to 200° F. range, both before and after hydrogenation.

	Research O.N.	Motor O.N.
(1) 1-pentene	98.6 $\xrightarrow{H_2}$ 88.7	82.9 $\xrightarrow{H_2}$ 83.6
(2) 1-hexene	91.7 $\xrightarrow{H_2}$ 65.3	76 3 $\xrightarrow{H_2}$ 86.3
(3) 2-heptene (trans.)	89.5 $\xrightarrow{H_2}$ 43.5	78.9 $\xrightarrow{H_2}$ 46.9
(4) 2-methyl-1-butene	103.4 $\xrightarrow{H_2}$ 108.7	84.2 $\xrightarrow{H_2}$ 104.6
(5) 3-methyl-1-pentene	103.0 $\xrightarrow{H_2}$ 93.4	82.2 $\xrightarrow{H_2}$ 91.3
(6) 2,3-dimethyl-1-pentene.	102.1 $\xrightarrow{H_2}$ 103.4	86.4 $\xrightarrow{H_2}$ 103.5

It is apparent from the above data that hydrogenation of the normal olefins to paraffins lowers the research octane number, but has a variable effect on the motor octane number (reactions 1, 2 and 3). Processes have been proposed involving straight hydrogenation of catalytic and thermal naphthas to decrease the gasoline sensitivity. This, however, leads in many cases to a loss in octane number.

The above data shows that saturation of isoolefins to isoparaffins (reactions 4, 5 and 6) will increase the motor octane number markedly. The latter series of reactions is involved in the upgrading of olefinic naphthas over the dual function catalyst of the present invention. That is, isoolefins, either from isomerization by the acidic support or present in the feed, are saturated by hydrogen exchange or hydrogenation. By analyses of the products from this reaction, it is inferred that other reactions beside isomerization and hydrogen

exchange (or hydrogenation) take place. Polymerization, cracking of polymer, alklation and aromatization are all believed to participate to some extent in the overall reaction scheme.

According to the process of this invention, a light naptha boiling substantially in the range of 30° to 350° F. is passed over a reaction zone containing a sulfided nickel catalyst deposited on silica-alumina. Typical feeds which can be used in this process are ones which contain any significant amount of olefins. However, maximum improvement in octane number is obtained with streams containing a high proportion of olefins. Examples of such feeds are light catalytic naphtha, thermal naphtha (obtained from thermal cracking or visbreaking of heavy materials), fluid coker naphtha or, in general, any material containing at least 10% by volume of olefinic hydrocarbons, but preferably above 20%. The preferred feed for this process is an olefin containing stream boiling in the 30° to 200° F. range wherein the olefin content is from 50 to 90% by volume.

Conditions under which the process of this invention can be carried out vary widely, that is, feed rates of 0.1 to 10 volumes of hydrocarbon per volume of catalyst per hour (v./v./hr.), pressures of 0 to 2000 p.s.i.g. hydrogen pressure, temperatures in the range of 250° to 1200° F., and from 100 to 5000 standard cubic feet of hydrogen per barrel of feed naphtha (s.c.f./b.). The preferred conditions in this process are 0.2 to 2 v./v./hr. naphtha feed rate, temperature of 400° to 900° F., 500 to 1000 p.s.i.g. hydrogen pressure, and about 2000 to 4500 standard cubic feet of hydrogen per barrel of naphtha feed. At temperatures of 350° to 500° F. optimization of middle distillates is the result, whereas at temperatures of 500° to 800° F. optimum yields of materials boiling in the gasoline range are obtained.

Catalysts which are suitable for use in this process are those containing acidic sites plus a mild hydrogenating component. One example of such a catalyst as herein set forth before is a nickel salt which has been deposited on silica alumina cracking catalyst (88% silica, 12% alumina), hydrogenated, and sulfided by passing an H_2S containing gas over the catalyst under pressure and temperature conditions set forth hereafter.

The catalyst employed in this invention is prepared by depositing from .5 to 20% nickel by weight on a solid acidic support, reducing to nickel metal, and treating with a sulfur containing material to substantially convert all of the nickel to a sulfide form. The solid acidic support is impregnated with a soluble nickel salt. Suitable bases for impregnation of the nickel and subsequent reduction and sulfiding are all of the well known catalytic cracking catalysts such as 88% silica-12% alumina, 75% silica-25% alumina, silica-magnesia, silica-alumina-thoria catalysts, acidic clay and all other solid acidic catalysts known in the art. The nickel salt may be either soluble in water or an organic solvent. A particularly suitable salt, which is soluble in water, is a nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$. The salt is dissolved in enough water to make a thick slurry when the acidic silica-alumina support is added to the mixture. The slurry is well mixed, dried in an oven slightly above the boiling point of water, that is, at about 250° F. and pilled. The catalyst pills are then calcined for 1 to 20 hours at 500° to 1500° F. The nickel on the catalyst, presumably now in the form of nickel oxide, is reduced to metallic nickel by treatment with hydrogen. The treatment with hydrogen in one aspect involves a two step procedure, one step being carried out at low pressure and the other at relatively high pressures. The preferred conditions for the low temperature treatment with hydrogen are 15 minutes to 2 hours at temperatures of 300° to 800° F. and a hydrogen feed rate of about 0.1 to 6 cubic feet per hour per hundred cc. of catalyst. In the second stage, or high temperature treatment with hydrogen, the preferred conditions are 500 to 1000 p.s.i.g. hydrogen pressure, same temperature range and 0.1 to 3 cubic feet of hydrogen per hour per hundred cc. of catalyst. During this hydrogen treatment, there is a net uptake of hydrogen by the catalyst. Other techniques known in the art for a reduction of nickel salt can be employed, however.

The final step in the preparation of the catalyst, namely treatment with sulfur, can be carried out either by in situ treatment with the naturally occurring sulfur which is found in sour petroleum fractions or alternately, the catalyst can be treated with a sulfur containing gas such as H_2S. Preferred ranges of conditions for sulfiding the catalyst are one to ten hours treatment at temperatures in the range of 300° to 700° F. and pressures of 400 to 1000 p.s.i.g. The sulfiding gas should be a mixture of from 1 to 40% H_2S in hydrogen. The sulfiding gas is passed over the catalyst at a rate of from 0.1 to 5 cubic feet per hour per hundred cc. of catalyst at times of from 1 to 10 hours.

The hydrocarbon product obtained according to this process is substantially a saturated one, most of the olefins (that is, butenes to octenes) being converted to isoparaffins. Other chemical processes which take place in this system are polymerization, alkylation, aromatization and cracking. These reactions are well known to occur over acidic type catalysts. These polymerization and alkylation processes lead to materials boiling outside of the gasoline range. Since gasoline is one of the most profitable products in the refinery, it is advantageous except in special situations to obtain as high a yield of gasoline as is possible. This can be accomplished in this invention by operating at the upper temperature limits of the process and the yield of material boiling in the gasoline range (15°–430° F.) is proportional to the temperature used in the process. However, it may be desirable in some areas, such as Europe, to limit the production of gasoline fractions and optimize or maximize the yield of middle distillates (hydrocarbons boiling in the range 300° to 600° F.). This is accomplished by operating in the lower temperature limits of the process. The quality of the middle distillates thus produced is good, the product having a high cetane number and low pour point indicating applications either as home heating oil or diesel fuel.

The following examples will illustrate, but not limit the invention:

Example 1.—64.3 grams of $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in 400 cc. of distilled water. This solution was then added to 360 grams of Davidson 88% silica, 12% alumina cracking catalyst. This mixture was then heated to 150° F. with stirring, dried at 250° F., pilled and calcined for 10 hours at 1000° F. 185 cc. of this catalyst was then transferred to a high pressure flow reactor and treated with H_2 at a rate of 6 cubic ft./hr. for 65 minutes at a temperature of 580° F. The reactor pressure was then set at 850 p.s.i.g. and the catalyst was treated with H_2 at a rate of 0.492 cubic ft./hr. for three hours at the same temperature. About 0.3 cubic ft. of hydrogen was taken up by the catalyst during this period. The catalyst was then treated with a 90% H_2–10% H_2S mixture at a rate of 1.3 cubic ft./hr. for 5¼ hours at a temperature of 580° F. and a pressure of 700 p.s.i.g. This catalyst was employed in runs 2 and 3 shown in Example 2.

Example 2.—The catalyst prepared in Example 1 was placed in a flow reactor and a 40° to 200° F. light catalytic naphtha was passed over the catalyst at 0.4 v./v./hr. under the conditions given below. A run (1) using 88% silica, 12% alumina alone is included to show the superiority of the products obtained with the sulfided nickel catalyst. Also, typical results which one would obtain by nonselective hydrogenation of the naphtha are included to show (4) the superiority of the process of this invention, which gives both sensitivity and octane level improvement. It should be noted that data are given to illustrate the fact that when using nickel (S) on silica-alumina as the catalyst, it is possible to control the ratio of gasoline to middle distillate by variation of the process conditions.

Run Number		1	2	3	4
Catalyst		88% Silica 12% Alumina	Ni(S)-on 88% Silica 12% Alumina		Pd on Charcoal
Operating Cond.:					
Temperature, ° F.		400	400	700	100
Pressure, p.s.i.g.		500	500	850	500
H_2 Rate, s.c.f./b.		3,200	4,200	2,900	Batch
	Feed				
Yield, Percent of Feed:					
B.P. 40–200° F.	100	52.7	52.8	[1] 74	102
B.P. 200° F.+		32.0	44.9	15	0
C_4 and lower		15.3	2.3	11	0
Inspections, 40–200° F. Product—FIA, vol. Percent (Fluorescent Indicator Analyses):					
Aromatics	4.1	3.1	2.6	1.7	3.6
Olefins	64.2	32.9	3.1	0	12.6
Saturates	32.2	64.0	94.3	98.8	83.8
Blending Octane No. (25 vol. Percent in a Synthetic Pool): [2]					
Research +3 cc. of tetraethyl lead)	94.0	97.4	94.2	96.4	93.4
Motor +3 cc. (of tetraethyl lead)	80	87.2	93.6	94.4	88.2
Δ Octane Index		6.0	6.2	8.9	3.6
Sensitivity	14	10.2	0.6	2.0	5.2

[1] Both gas and 200° F.+ fractions contained material mostly boiling in the gasoline range. It is estimated that the fraction boiling from 40°–430° F. could comprise about 85–90% of the total product obtained. The remainder would consist of isobutane and a slight amount (1–3%) of 430° F.+ polymer.

[2] Synthetic Pool: Consists of a blend of catalytic pentenes, alkylate gasoline and catalytic reformate and having a research octane number substantially above 103 and a motor octane number substantially above 93.

It is evident from the examples set forth that this process will convert light olefinic naphthas into materials having much higher motor octane numbers than the feed, and in some cases, higher research octane numbers. Gasoline yield can be controlled by severity of operating conditions or alternately middle distillate yield can be maximized, if desired, depending upon refinery situations. In the above table, data are included using silica-alumina alone which is the acidic component of the catalyst or palladium on charcoal which would be an example of hydrogenation without isomerization. The process of this invention increases both research and motor octane number whereas the acidic silica-alumina catalyst does not lower the sensitivity appreciably. Palladium on charcoal, which is strictly a hydrogenation catalyst lowers the sensitivity somewhat, but there is very little increase in octane index.

It is further evident that the operation can be carried out in two temperature stages, that is, one stage operating at a low temperature to promote the isomerization and hydrogenation reactions and a high temperature stage to crack the polymer formed in the first stage to isoparaffinic material boiling in the gasoline range.

Specifically, it should be noted that the motor blending octane number of the light catalytic naphtha was increased from 80 to 94.4 and the research blending octane number was increased several units also. The net result was an increase in octane index of 8.9 and a decrease in the sensitivity from 14 units to 2 units.

It is a further advantage of this particular invention that it can be practiced in units already existing for the Isocracking process which uses a similar catalyst. The process, according to this invention, can be practiced simply by altering the reactor conditions slightly and feeding a light olefinic naphtha rather than a heavy 250+° F. material.

It is possible to prepare the catalyst in powder form, that is, omit the pilling operation. This powdered catalyst when suitably reduced and sulfided as described herein, can be used in a fluidized operation to upgrade light olefinic naphthas. A catalyst of this type would be particularly suitable for use in an existing fluid hydroforming unit.

Modifications falling within the scope of this invention can be made without departing from the coverage of the appended claim.

What is claimed is:

In a method for treating a light naphtha feed boiling at a temperature of from 30° to 350° F. containing at least 20 percent by volume of olefinic hydrocarbons with a catalyst prepared by sulfiding a nickel oxide distended on a silica-alumina cracking catalyst base, the improved method for treating said light naphtha which comprises optimizing process conditions to produce as a principal product a middle distillate fraction having a high cetane number and low pour point and boiling in the range of 300° to 600° F. by passing said naphtha over a silica-alumina cracking catalyst base containing from 0.5 to 20 percent by weight of nickel deposited thereon, said nickel having been prepared by reducing with hydrogen a nickel salt deposited on said base to nickel metal and treating with a sulfur-containing material selected from the group consisting of a gas containing hydrogen sulfide and a light naphtha feed boiling in the temperature range of from 30° to 350° F. containing naturally occurring sulfur therein, to substantially convert all of the nickel to the nickel sulfide form, the feed rate of said naphtha being from 0.1 to 10 v./v./hr. at a hydrogen pressure of from 500 to 2,000 p.s.i.g. and a temperature of 350° to 500° F., said treatment being conducted in the presence of from 2,000 to 5,000 standard cubic feet of hydrogen per barrel of said naphtha.

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