United States Patent Office 2,913,405
Patented Nov. 17, 1959

2,913,405

DESULFURIZATION OF OLEFINIC GASOLINE

Harold Shalit, Drexel Hill, Pa., assignor to Houdry Process Corporation, Wilmington, Del., a corporation of Delaware

No Drawing. Application August 27, 1957
Serial No. 680,630

9 Claims. (Cl. 208—213)

The present invention relates to the selective hydrodesulfurization of cracked gasoline containing olefins and is particularly concerned with effecting sulfur removal from such gasoline while reducing to a practical minimum the extent of simultaneous hydrogenation of the olefins contained therein.

Among the objects of the invention are the provision of a hydrodesulfurization process obtaining a desulfurized gasoline product of sufficiently low sulfur content for use as motor fuel or in a motor fuel blend, and wherein the obtained product has improved lead susceptibility and an octane rating equal to or better than that of the charge so treated.

The removal of sulfur as well as nitrogen by hydrodesulfurization has been practiced in the treatment of gasoline and naphtha fractions of comparatively low octane rating in connection with the pretreatment of such fractions to be employed as feed to catalytic reforming operations. In these operations the possible hydrogenation of any olefins present or the extent of such hydrogenation is not material since the refined naphtha is subsequently to be subjected to hydrogenative reforming. On the other hand, cracked gasolines ordinarily have a sufficiently high octane rating so that they can be and are employed in modern motor fuels without further conversion by reforming or otherwise, and any required desulfurization of such gasoline should desirably be accomplished without accompanying loss in anti-knock value, wherefore the hydrogenation of olefins must be avoided or minimized.

In accordance with the present invention the desired removal of sulfur compounds from olefin-containing gasoline or gasoline fractions is obtained by catalytic hydrodesulfurization in the presence of controlled quantities of an organic nitrogen base. Under these conditions it has been found that the sulfur compounds can be effectively and selectively removed without the corresponding expected extent of hydrogenation of the olefins obtained in the absence of such nitrogen compounds.

The process can be carried out with any of the organic nitrogen bases boiling below the end point of the gasoline. Typical nitrogen bases useful in the process include alkylamines, such as n-butylamine; arylamines, such as aniline; heterocyclic nitrogen bases, such as pyridine. To obtain significant effect, there must be present in the desulfurization reactor a minimum concentration of nitrogen compounds supplying at least 100 parts N by weight per million parts of hydrocarbons being treated, preferably between about 140 to about 550 p.p.m. nitrogen should be employed for best overall results on most gasolines to be treated by the described process. As the content of nitrogen compounds in the reaction zone is increased, there is evidenced beside the reduction in extent of olefin hydrogenation also in many instances some lowering of desulfurization activity of the catalyst, so that in general the limitation

on the quantity of nitrogen compound to be added will be governed by the loss in extent of desulfurization that can be tolerated in any instance to obtain a desulfurized gasoline of such residual sulfur content that the blend therefrom will meet prevailing market standards and specifications. Based on these considerations as applied to the more typical situations encountered in the required desulfurization of a cracked gasoline of at least 80 F_1 octane clear rating and having up to about 0.7% S, the nitrogen content of the reaction mix should not exceed about 2500 p.p.m. As a rough measure the quantity of nitrogen compounds to be added should be such as to bring the nitrogen content of the feed to a value providing at least 1 atom of nitrogen for every 25 atoms of sulfur and not more than about 1 atom of nitrogen for each 2 atoms of sulfur.

It has been observed that the sulfur content of cracked gasoline increases sharply near the 400° F. boiling point cut and above. In the case of such gasolines of over-all high sulfur content, as above about 0.4% in the gasoline cut, it may be found desirable to apply the desulfurization treatment according to the invention (i.e., in the presence of added organic nitrogen compounds) to a selected portion of the gasoline such as the cut boiling up to about 360° or 380° F. The remainder of the gasoline boiling above the 360–380° F. cut point and up to say about 410° F. could then be subjected to more severe desulfurization in the absence of added nitrogen compounds. Since this higher boiling cut ordinarily constitutes only a relatively minor part of the whole gasoline fraction (at 380° F. less than about 8 to 10% of the whole gasoline fraction), the loss in olefins encountered as a result of saturation would be relatively small. Furthermore, if such higher boiling gasoline cut contains sufficient nitrogen compounds to inhibit desulfurization to any great extent, an alternative procedure can be employed in which this higher boiling fraction is subjected to acid extraction to remove the nitrogen compounds prior to hydrodesulfurization thereof. The extract will contain the basic nitrogen compounds in the form of addition salts which can be easily treated to reconstitute the free N-bases. The thus treated extract or a recovered concentrate of these reconstituted bases can be utilized as the nitrogen compounds to be added in the hydrodesulfurization of the remainder of the gasoline fraction boiling below the 360–380° F. cut point.

The process of the invention, although not so limited, finds its principal application in the desulfurization of a catalytically cracked gasoline or naphtha, or selected portion thereof. Such gasoline or naphtha fraction will have an octane rating usually in excess of 80 F_1 clear and will have a fair content of olefins which sometimes may run as high as 65% or more by weight, while the sulfur content even in those catalytically cracked gasolines derived from a high sulfur crude ordinarily does not exceed about 0.5%; the nitrogen content of the gasoline obtained by commercial catalytic cracking operations, employing acidic siliceous catalysts, in most instances is relatively low. The process of the invention is also applied with advantage in the treatment of certain thermally cracked gasolines and naphthas having sufficiently high octane rating as those of above about 80 F_1 clear. If an occasional gasoline fraction should happen to contain an adequate nitrogen content to inhibit to desired extent the saturation of olefins accompanying hydrodesulfurization, further addition of nitrogen compounds for this purpose may then be unnecessary. In the treatment of residual oils of comparatively high sulfur content by catalytic cracking methods such as the recent "Houdresid" process, olefinic gasolines of undesirably high sulfur content are produced (in

the order of up to 1.0% S); such gasolines are advantageously desulfurized by the method of the present invention.

The operating conditions employed for the treatment of the olefinic gasoline may be those ordinarily employed in hydrodesulfurization generally; using the typical hydrodesulfurization catalysts at a temperature in the range of 650–850° F., pressures in the range of 5 to 25 atmospheres, and hydrogen to oil molar ratios in excess of 1:1 and up to about 5:1. The operation is preferably carried out at high space rates in excess of about 6 volumes of oil (as liquid) per hour per volume of catalyst and going up to as high as 25 v./hr./v. Among the preferred catalysts are the oxides and sulfides of cobalt and/or molybdenum and nickel catalysts, suitably supported on alumina or other known type of carriers.

EXAMPLE 1

A synthetic feed stock was prepared from 80% by weight normal heptane and 20% mixed isoheptenes, to which feed various amounts of sulfur were added in the form of thiophene. This stock was treated in one series of runs over sulfided nickel-on-alumina catalyst (10.7 wt. percent Ni) and in another series of runs over sulfided cobalt-molybdena-alumina catalyst (1.86 wt. percent CoO–7.71 wt. percent MoO_3). All of the runs were carried out at a pressure of 300 p.s.i.g. and at a liquid hourly space velocity of 12. Over each of the catalysts, runs were made at 700° F. and at 800° F. and in certain of the runs the hydrogen addition was reduced from 3:1 H_2/oil molar ratio to 1.5:1.

For comparison with the above-described runs there was added to the described heptane-isoheptene charge approximately 0.19% N in the form of pyridine and certain of these runs repeated at the same operating conditions. It was found in the case of the cobalt-moly catalyst that the addition of the nitrogen compound in the charge resulted in one instance (at 800° F.) in decreasing by about 20% the extent of olefin hydrogenation with only a comparatively slight loss in extent of desulfurization of the charge (7.5%), while at the lower temperature of operation the extent of olefin hydrogenation was decreased about 39% by the addition of the nitrogen compound but with a corresponding loss of about 25% in the extent of desulfurization. In both cases the desulfurization selectivity was improved by the presence of the nitrogen compound. Selectivity can be numerically represented as:

$$\text{Selectivity} = 100 - \frac{\text{percent olefin hydrogenation}}{\text{percent desulfurization}} \times 100$$

The runs made with the nickel catalyst showed considerably higher selectivity but at comparatively lower desulfurization activity. Moreover, in these runs using the nickel catalyst the presence of the nitrogen compound not only improved selectivity but unexpectedly raised the extent of total desulfurization.

Another series of runs was carried out over the nickel catalyst on the same heptane-isoheptene charge, to which butyl mercaptan was added as the sulfur compound and the pyridine was added in an amount furnishing 0.182 weight percent N. The same trends were noted as in the previously described runs over this catalyst.

The results of several of the runs are tabulated below for comparison.

Table 1

[Charge (80% heptane–20% isoheptenes).]

	Cobalt-Molybdena Cat.				Nickel Catalyst (700° F.)			
	(700° F.)		(800° F.)					
Sulfur, weight percent:								
Butyl mercaptan					0.486	0.464		
Thiophenes	0.414	0.386	0.414	0.386			0.901	0.901
Nitrogen, weight percent	0.000	0.189	0.000	0.189	0.000	0.182	0.000	0.191
Br_2 number	36.0	31.9	36.0	31.9	21.5	36.5	36.2	36.2
Liquid product:								
Sulfur, weight percent	0.088	0.157	0.084	0.102	0.014	0.008	0.721	0.524
Br_2 number	5.5	15.3	4.7	9.7	15.7	31.8	33.4	34.1
Desulfurization, percent	78.8	59.4	79.8	73.8	71.2	98.2	20.0	41.8
Olefin hydrogenation, percent	84.7	52.0	86.9	69.6	27.0	12.8	7.8	5.8

The nickel catalyst employed in the above runs was prepared by soaking porous alumina pellets of about 4 mm. size for one hour in the liquid obtained by melting nickel nitrate hexahydrate, using a volume of liquid melt in slight excess of that required to cover the pellets. After draining the unsorbed liquid, the pellets were dried at 280–290° F. and calcined in air at 950° F. for two hours. The calcined pellets contained about 15.65% NiO. The pellets were then sulfided at 800° F. for 4 hours in a mixture of 25% H_2S–75% N_2 (mol) and cooled in nitrogen. Gain in weight by sulfidation was about 10% (S content about 8.5%).

The cobalt-molybdena catalyst was prepared by soaking porous alumina pellets for one hour in a solution prepared by mixing: 137.4 parts aqueous ammonia (33.4% NH_3), 126 parts aqueous ethylene diamine solution (93% EDA), approximately 194 parts of molybdenum oxide (MoO_3) and 266.5 parts of an aqueous solution of cobalt nitrate hexahydrate

[71% $Co(NO_3)_2 \cdot 6H_2O$]

with about 350 parts water, employing sufficient solution to keep the alumina pellets covered throughout the soaking period. The pellets were then drained, dried in air at 200–300° F. and heat treated by being passed first through a steaming zone during approximately 2 hours at a maximum bed temperature of 550° F., then during approximately 6 hours through an air heating zone having a maximum bed temperature of 950° F., thus effecting conversion of the salts to the oxides of molybdenum and cobalt, respectively. The treated pellets contained approximately 1.75% CoO and 7.75% MoO_3. These pellets were then treated at 800° F. for 3 hours in a mixture of 25% H_2S–75% N_2 (mol) and purged and cooled in nitrogen to a sulfur content of 4.46%.

EXAMPLE II

The gasoline fraction employed was obtained by catalytic cracking of a Kuwait crude fraction; the gasoline had an API gravity of 52.8 and distilled over the range of 121 to 400° F. (ASTM). One portion of the gasoline was treated to remove nitrogen compounds by washing with 10% HCl and drying over solid caustic. The treated and untreated portions of the gasoline were then each separately subjected to hydrodesulfurization over the heretofore described cobalt-molybdena catalyst supported on alumina, at 700° F., 100 p.s.i.g. and at 3/1 hydrogen to oil mol ratio at several different space rates. It was found that the original nitrogen content present in the gasoline (170 p.p.m.) was sufficient to

retard olefin hydrogenation and preserve the octane number when the gasoline was subjected to hydrodesulfurization, and that by removal of the nitrogen content the gasoline lost 2 to 2.5 octane numbers more by hydrodesulfurization than the gasoline which had not been acid-washed; at the lower nitrogen level the extent of olefin hydrogenation was almost doubled. The results obtained are compared in Table 2 below.

Table 2

	Untreated	Treated	Untreated	Treated
Feed stock:				
Sulfur, weight percent	0.619	0.610	0.619	0.610
Nitrogen, p.p.m.	170	14	170	14
F_1 clear octane number	87.6	87.3	87.6	87.3
Br_2 number	91.9		91.9	
Liquid product:	At 18 LHSV		At 12 LHSV	
Sulfur, weight percent	0.452	0.407	0.430	0.380
F_1 clear octane number	85.7	83.1	87.1	85.0
Br_2 number	82.8	78.9	85.6	78.7
Olefin hydrog., percent	9.9	14.2	6.9	14.3
Desulfurization, percent	26.9	33.2	30.5	37.7

To determine the approximate level at which the basic nitrogen compound becomes effective, another series of runs was made over the heptane-isoheptene blend. It was found that with a nitrogen content below 1 p.p.m. the feed stock was 65% desulfurized and 41% of its olefins was hydrogenated. Increasing the nitrogen level to 77 p.p.m. produced no noticeable change within the limits of measurement. By raising the nitrogen level to about 140 p.p.m., the extent of olefin hydrogenation was reduced from 41% to 31% while desulfurization was lowered from 65 to 55%. Further increase in nitrogen content produced further reduction in extent of olefin hydrogenation with a corresponding or lower loss in desulfurization level.

EXAMPLE III

A commercial catalytically cracked gasoline from an Arabian crude was separated into heavy and light fractions having the characteristics shown below.

Table 3

	Whole Gasoline	Initial to 360° F.	360° F. to Bottoms
Gasoline fraction:			
Vol. percent	100	62.9	37.1
Sulfur, weight percent	0.312	0.08	0.741
Br number	46.7		20.6
F_1 clear	89.7	91.0	88

The 360° F.-bottoms cut is extracted with several volumes of dilute aqueous hydrochloric acid (15% HCl) and the extract is "sprung" by neutralization with aqueous caustic solution. The recovered nitrogenous extract is then water washed to remove NaOH and added to the lower boiling gasoline cut.

Each of the fractions is separately hydrodesulfurized over the cobalt-molybdena-on-alumina catalyst described in the previous example, operating at 700° F., 300 p.s.i.g. and a space rate of 3 (vol./hr./vol.).

Each of the fractions is desulfurized to a content of less than 0.03% S and the combined fractions have a sulfur content of less than 0.03% and an octane number of about 90.5 (F_1 clear). This low sulfur content of the finished gasoline meets with the most rigid present-day sulfur tolerances in 100 octane leaded fuels, and the blend has the desired high lead susceptibility which renders its further upgrading to desired octane level by tetraethyl lead addition highly economical.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be made as are indicated in the appended claims.

What is claimed is:

1. The method of desulfurizing an olefin-containing cracked gasoline fraction having a low content of organic nitrogen bases corresponding to less than 140 parts N per million parts of hydrocarbons by weight, which comprises subjecting such a fraction as charge to catalytic hydrodesulfurization while adding to such charge an organic nitrogen base to increase the nitrogen content of the charge to at least 100 parts per million but not in excess of 2500 parts per million, the quantity of nitrogen compound thus added being correlated with the sulfur content of the charge so as to provide a total of at least 1 atom of nitrogen for every 25 atoms of sulfur in the charge and not in excess of 1 atom of nitrogen for each 2 atoms of sulfur.

2. The method according to claim 1 wherein said cracked gasoline fraction is one having an octane rating of at least 80 F_1 clear.

3. The method according to claim 1 wherein said fraction comprises catalytically cracked gasoline.

4. The method according to claim 1 wherein said organic nitrogen base is added in an amount sufficient to adjust the nitrogen content of the feed to 140–550 parts per million.

5. The method of desulfurizing an olefinic gasoline having a sulfur content above 0.4%, which comprises fractionating the gasoline cut to provide a lower boiling fraction having an end point up to 360–380° F. and a higher boiling fraction constituting the portion boiling above said end point, subjecting the lower boiling fraction to catalytic hydrodesulfurization in the presence of added organic nitrogen bases present in an amount providing at least 100 parts N per million parts hydrocarbon, subjecting at least a portion of the higher boiling fraction to hydrodesulfurization in the absence of added nitrogen compounds, and blending products of the recited several hydrodesulfurization treatments.

6. The method according to claim 5 wherein said higher boiling fraction is subjected to acid extraction for removal of nitrogen compounds therefrom prior to hydrodesulfurization.

7. The method according to claim 6 wherein the extract obtained by said acid extraction is treated to release free nitrogen bases and said released bases are employed as at least part of the nitrogen bases added in the hydrodesulfurization of said lower boiling fraction.

8. The method according to claim 7 wherein said higher boiling fraction and said lower boiling fraction are each desulfurized by the recited respective hydrodesulfurization treatments to a sulfur content of less than 0.03% S and the blended product contains less than 0.03% S.

9. The method of desulfurizing a catalytically cracked gasoline fraction of high olefin content but low in content of basic nitrogen compounds, which method comprises subjecting such fraction as charge to catalytic hydrodesulfurization over supported sulfided metal-oxide hydrodesulfurization catalyst at a temperature in the range of 650–850° F., at a pressure ranging from 5 to 25 atmospheres and at a molar hydrogen to oil ratio in excess of one, while adding to such fraction organic nitrogen base in an amount at least sufficient to bring the nitrogen content of the charge to 100 parts N per million parts hydrocarbon by weight, and providing in said charge at least 1 atom of nitrogen for every 25 atoms of sulfur therein.

References Cited in the file of this patent

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