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A. C. BYRNS

DESULFURIZATION AND REFORMING PROCESS

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Hydrogen

Feed

Desulfurization

H₂S Removal

Heating

Separation

Reforming

Liquid

Make Gas
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DESYLURIZATION AND REFORMING PROCESS

Alva C. Byrns, Oakland, Calif., assignor to Union Oil Company of California, Los Angeles, Calif., a corporation of California

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This application relates to the conversion of hydrocarbon mixtures containing sulfur compounds, and especially to the production of improved motor fuels by a process including both desulfurization and cracking or reforming in the presence of hydrogen and catalysts.

Certain processes are known which involve catalytic reforming in the presence of hydrogen. For example, in the conventional hydroforming process, a hydrocarbon feed stock boiling in the gasoline range may be vaporized and the vapors, mixed with hydrogen, may be passed under pressure at a relatively high temperature such as about 950° F. over a catalyst such as molybdenum oxide on an alumina carrier. Under these conditions the hydrocarbons are reformed to obtain substantial yields of aromatic type hydrocarbons. Limited amounts of sulfur compounds present in the feed stock may be destroyed concurrently, presumably with the formation of hydrogen sulfide which reacts with the molybdenum oxide in the catalyst, converting it at least partially to sulfides and liberating water vapor. This operation is continued until the catalyst has lost to a substantial degree either its desulfurizing activity or its reforming activity, due to conversion to sulfides and to deposition of coke or carbonaceous material on its surface. The operation in this catalyst bed is then suspended while the catalyst is regenerated by passing oxygen-containing gases over it to burn off the accumulated coke and convert the sulfides back to oxides.

There are many inherent disadvantages in the above conventional single-stage hydroforming process where high sulfur stocks, especially cracked stocks, are treated. For example, the conversion of the oxides to sulfides is a serious disadvantage, since the oxides are in general materially better catalysts than the sulfides, for improving the octane number of the stock. Furthermore, the maximum amount of hydrogen sulfide with which the usual hydroforming catalysts will react is rather limited, and this necessarily limits either the effective life of the catalyst or the sulfur content of the stocks which may be treated. Treatment of cracked stocks containing over about 2% sulfur is not economically feasible for these reasons. Even after relatively short periods of operation on high sulfur stocks (over about 0.5% sulfur), hydrogen sulfide may frequently be observed in the product. This is undesirable, since it necessitates purification not only of the gasoline product, but also of the large proportion of the reform product which is recycled. In the regeneration operation, which incidentally is not always completely effective in converting the sulfides back to oxides, a great deal of sulfur dioxide is formed, and this either causes serious corrosion of equipment as well as creation of nuisance if allowed to escape, or necessitates expensive recovery equipment. Elemental sulfur also is sometimes formed, presumably in the regeneration operation, and this results in the occasional production of corrosive gasolines. When cracked or olefin-containing stocks of high sulfur content are treated, moreover, there is excessively rapid and heavy deposition of coke on the catalyst, which shortens its active life between regenerations and complicates the problem of controlling the catalyst bed temperature during the regeneration. The yield of product of given octane number is also generally lower for treatment of cracked stocks and this product often responds poorly to the addition of anti-oxidants or of anti-detonants such as TEL. The hydrogen content of the recycled gas product is also very low, in the neighborhood of 20% to 30% in many instances, which further tends to shorten the catalyst life and impair its activity. By "catalyst life" is meant not only the cycle life, or life between regenerations, but also the total, effective life of the catalyst.

In the process of the present invention two reaction stages are employed, with different operating conditions and possibly different catalysts in the two stages. In the first stage the sulfur compounds present in the stock are substantially completely destroyed, with the formation of hydrogen sulfide, and a proportion of the unstable olefinic material present in the stock or formed in the desulfurization, is hydrogenated or converted to more stable hydrocarbons. In the second stage, the relatively sulfur-free hydrocarbon product from the first stage is catalytically cracked or reformed in the presence of hydrogen under optimum conditions to obtain a gasoline product which is not only of high octane number but is also highly susceptible to further
octane number improvement by the addition of knock inhibitors such as tetraethyl lead (TEL), i.e., in decreased sensitivity and also lists other desirable characteristics as shown below. The process is a considerable improvement over the conventional process of hydroforming of high sulfur stocks described above. Stocks of extremely high sulfur content, whether cracked or straight-run in character, may be handled equally well. The bulk of the sulfur compounds and the worst of the coke-forming olefins, etc. are eliminated in the desulfurization stage, so that the catalyst in the second stage is not subjected to severe conditions, nor is it subject to such rapid coke deposition. This materially lengthens the effective catalyst life and simplifies the temperature control in the regeneration. The corrosiveness and problems of disposal of the gases liberated in the regeneration are minimized or eliminated, and the requirements of expensive alloy steel are reduced. Products free from hydrogen sulfide or corrosive elemental sulfur are obtained; and the product yield and general efficiency of the process are greatly improved.

One method of carrying out the two-stage process of this invention is shown in the accompanying drawing, and may be described as follows:

A feed stock as described below, is introduced through line 1 and valve 2 vaporized in heater 3 and admixed with a hydrogen-containing gas which may be introduced through line 4 and valve 5 or lines 6 and valve 7, and the mixture is contacted with a desulfurization catalyst in the first stage 8. From the reaction product mixture withdrawn through line 9 and valve 10, cooled in cooler 11 and depressurized if desired, is separated in separator 12 into (1) a normally gaseous fraction containing hydrogen and hydrogen sulfide and (2) a normally liquid fraction of substantially reduced sulfur content. The gaseous fraction is withdrawn through line 13 and valve 14 into hydrogen sulfide remover 15 where it is treated to remove at least a portion of its hydrogen sulfide content which is withdrawn through line 16 and valve 17 and the treated gas is withdrawn through line 18, pump 19 and valve 20 preheated if desired, and recycled to the first stage through line 21. The liquid fraction from the separation stage is from separator 12 through line 22, pump 23 and valve 24, and vaporized, preheated and admixed in heating zone 25 with a hydrogen containing gas introduced through line 26 and valve 27, and the mixture is contacted with a refining catalyst in the second stage 28. From the reaction product withdrawn through line 29 is separated in separator 30 into (1) a normally gaseous hydrogen-containing fraction taken off through line 31, part of which may be withdrawn as make gas through line 32 and valve 33, while the remainder is recycled through line 34, pump 35 and valve 36 to the first stage through line 37 (part of it may also be recycled to the second stage through line 26 and valve 27 if desired), and (2) a normally liquid product containing hydrogenous compounds in the gaseous range which is withdrawn through lines 38 and valve 39. Other fractions, such as gaseous hydrocarbon fractions containing valuable butenes, propene, etc., and liquid fractions such as gas oil, etc., may also be segregated. Furthermore, it is the necessary or desirable to purify the hydrogen-containing gas of hydrocarbons or other impurities before recycling, or to discard make-up hydrogen.

The feed stock may be any hydrocarbon mixture containing organic sulfur compounds, providing it is sufficiently volatile to be vaporized under the reaction conditions. Petroleum fractions of the gasoline boiling range containing over about 0.5% sulfur in organic sulfur compounds (mercaptans, thioethers, thiophenes, thiophenols, etc.) are particularly suitable, whether cracked or straight-run in character. Stocks containing over 3% sulfur are especially suitable. Extract fractions from selective selective processes, coal tar distillates, and other stocks which contain large proportions of aromatic type hydrocarbons, especially those stocks containing over 0.5% sulfur as organic sulfur compounds, are especially benefited. Although fractions boiling in the gasoline boiling range, i.e., within the limits of about 100° F. to 425° F. are preferred, kerosenes, gas oils, etc., as well as the more liquefiable gases such as butanes, butenes, etc., may also be treated.

An important application of the process is in the production of pure aromatics such as toluene from petroleum fractions. This is now being carried out by hydroforming a low-sulfur, straight-run gasoline fraction, and azetroptically distilling a narrow boiling range cut from the product. Cracked gasoline fractions are also processed for this process in spite of their higher initial aromatic content, because of the low yields, short catalyst life, etc., as described above, and also because of greater difficulties in removing all traces of olefins and sulfur compounds from the product. Furthermore, there is evidence that aromatics are produced more readily from paraffinic or napthenic stocks than from olefinic stocks. By the process of this invention, however, cracked stocks, even those of high sulfur content, may be processed as readily and efficiently as the straight-run stocks now employed, and advantage may be taken of their higher initial aromatic content.

The catalysts used in the first (desulfurization) stage may be any of the efficient desulfurization catalysts, such as cobalt molybdate, chromium oxide, vanadium pentoxide, etc., which may be deposited on carriers such as alumina or various other oxides or gels. A particularly desirable catalyst consists of about 20% of cobalt molybdate precipitated on about 90% of undried alumina gel. This was prepared in one instance for example by dissolving 8 gram-mols of aluminum nitrate in 10 liters of hot water, and slowly stirring in 24 mols of ammonia in the form of concentrated ammonium hydroxide solution, to form a gelatinous alumina precipitate. After filtering and washing this precipitate to free it of dissolved salts, it was resuspended in 6 liters of hot water, and 2 liters of hot water containing 0.9 mol of dissolved cobalt nitrate was added thereto. Then a solution containing 0.35 mol of ammonium paramolybdate (NH₄)₂MoO₄·4H₂O, and 0.98 mol of ammonia, both dissolved in a total of 2 liters of hot water, was slowly stirred into the above cobalt nitrate solution containing the suspended alumina, precipitating cobalt molybdate on the alumina. The resulting solid product was filtered, washed twice and resuspended in 10 liters of hot water and filtering, dried for 48 hours at 200°F. to 400°F., and ground to 10 to 20 mesh slate blue granules.

The catalysts for the second (refining) stage may be of the reforming or hydroforming type, such as oxides of molybdenum, cobalt, nickel, manganese, zinc, chromium, vanadium, titanium,
As a specific example, a feed stock consisting of an approximately 200° F. to 400° F. boiling range fraction from pressure distillation derived from thermal cracking of a heavy naphthenic California crude oil and containing 0.63% sulfur in the form of organic sulfur compounds including mercaptans, as well as 20% of olefinic hydrocarbons, was pumped at a rate of 100 ml. (1.0 volume per hour of catalyst) per hour, in admixture with 80 liters (5000 cu. ft. per bbl. feed) per hour of hydrogen, to the lower end of a reaction tube, in which the feed was vaporized and mixed thoroughly with the hydrogen at a pressure of 250 lbs. gage and a temperature of about 400° F. to 500° F. The mixed gases were passed upward through a 100 ml. bed of catalyst, at the same pressure and at a temperature of 650° F. This catalyst consisted of about 20% of cobalt mixed on about 80% of undried alumina gel, and was prepared as described above. The gases emerging from the top of the reactor were cooled to room temperature under pressure, whereby the bulk of the liquid product was condensed and separated. The uncondensed vaporous mixture was depressurized to approximately atmospheric pressure and passed through a trap cooled by a bath of acetone maintained at approximately 90° F. by the addition of solid carbon dioxide, in order to condense the bulk of the residual hydrogen sulfide. The residual gas was largely hydrogen, and when freed of hydrogen sulfide to the desired degree, was suitable for recycling. No hydrogen sulfide appeared in the product during the initial five hours of operation, but some was always present in both the liquid and gaseous products thereafter. The operation was continued for 400 hours under these same conditions, and for over 850 hours under similar conditions without apparent loss of desulfurization activity of the catalyst.

The combined liquid trap condensate and pressure condensate was collected and measured every two hours. Its volume amounted to 95% to 99% of the volume of the feed introduced. Each of these two-hour cuts was freed of hydrogen sulfide by washing it with dilute caustic. The composite liquid product obtained by combining all of the cuts taken under the above operating conditions for the first 400 hours of operation had approximately the same boiling range as the feed stock, but contained only 0.016% sulfur in the form of organic sulfur compounds other than mercaptans, and only 10% of olefins. This product was used as feed stock for the second stage treatment which was carried out as follows:

In the second stage, the above liquid product was vaporized at a rate of 2.05 volumes per volume of catalyst per hour and the vapors, in admixture with about 2500 cubic feet per barrel of feed of a gas which was largely hydrogen, were passed at a pressure of 200 lbs. gage through a bed of 450 ml. of catalyst maintained at 1000° F. This catalyst consisted of chromic oxide deposited on alumina. The product gases were separated into a liquid and a gas fraction in a manner similar to that used in the first stage as described above. The gas fraction, amounting to 3250 cubic feet per barrel of feed, was largely hydrogen. The liquid fraction collected during five hours of operation amounted to about 83% of the feed volume, and had an octane number by the A. S. T. M. (C.F.R. motor) method, of 77.

By application of the process of the second stage alone (i.e. a conventional type hydroforming process) to a straight-run stock of similar boiling range and of very low olefin and sulfur content, a product having an octane number was obtained in a 78% yield. Since its volume of operation each increase of one octane number usually involves a decrease in yield of approximately one per cent, it is evident that about the same yield octane number relationship was obtained in the two-stage operation. The yield of the cracked stock as was obtained in the single-stage operation on low-sulfur straight-run stock. On the other hand, it has been shown clearly that in conventional single-stage hydroforming operations the yield obtainable for a product of a given octane number, such as about 80, is generally nearly 8% lower when a high sulfur cracked feed stock is employed than when a low sulfur straight-run feed stock is employed; or conversely, for a given yield, such as 80%, the octane number of a product from a high sulfur cracked stock is generally nearly 8 octane numbers lower than the product from similar operations on a low sulfur straight-run feed stock.

It is thus an object of this invention to provide a process for catalytic conversion, reforming, or hydroforming of hydrocarbon mixtures which contain relatively large amounts of organic sulfur compounds and which also may contain relatively large amounts of olefinic hydrocarbons (including cyclic or straight-chain alkenes, olefins, etc.), whereby such mixtures may be treated with approximately the same degree of efficiency as may hydrocarbon mixtures containing very low proportions of organic sulfur compounds, and olefins, or even with a greater degree of efficiency in many instances.

The long catalyst life obtained in the two-stage process of this invention is of great importance. For example, in the desulfurization stage, carried out under conditions similar to those of the above example, a cobalt-molybdenum catalyst has been employed to desulfurize over 1800 times its volume of a cracked gasoline fraction of the type of the above example, without apparent loss in activity, and without regeneration. These catalysts can also be repeatedly regenerated with only extremely slight loss in activity, by reforming or hydroforming catalysts employed in the second stage of the process of this invention, will not normally have as long life as that indicated above for the desulfurization catalysts. However, they will have exceptionally long life, both between regenerations, and total life, as compared with their lives when used in conventional single stage processes, especially where high-sulfur or cracked stocks are employed. This relatively slower rate of degradation in activity is presumably due to a
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A slower rate of deposition of carbonaceous material on the catalyst and less conversion of the catalyst from the oxide to the sulfide form. This is of importance not only because the catalysts will need regeneration or replacement less frequently when the two-stage process is employed, but also because the quality of the product produced over a given time period such as two hours, for example, will show less variation and control of all of the treating and recovery processes involved will be simplified.

A convenient method of carrying out the process of this invention which is also shown in the attached drawing involves closing valve 10 and passing the entire gaseous mixture from the first stage 8 without condensation, i.e., at a temperature above the dewpoint of the mixture, through line 40 and valve 41 into hydrogen sulfide removal zone 18 and through a bed of material such as iron oxide, etc., which will absorb the hydrogen sulfide from the gas, which may be then passed directly to the second stage heater 25 through line 43, pump 43 and valve 44. Several parallel beds of absorbent may be employed to provide for regeneration, as by air blowing, of some of the beds while others are in use.

In another mode of operation of this type, the gases from the first stage are cooled in line 40 and the mixture of resulting liquid and gas is passed through a liquid absorbent such as caustic soda, tripotassium phosphate, sodium phenolate, etc., in zone 18 for removing the hydrogen sulfide.

In a third preferred type of operation, the gases from the first stage are cooled and subjected to conventional gas separation, absorption, stripping and distillation processes, to obtain (1) a gas fraction rich in hydrogen at least part of which is subjected to treatment with iron oxide, tripotassium phosphate, etc., for removal of hydrogen sulfide, and recycled, i.e., re-introduced with fresh feed to the first stage; and (2) a liquid fraction substantially free from hydrogen sulfide, which is introduced to the second stage.

For best results, it is preferable that the feed stock and the hydrogen-containing gas charged to the second stage of the process be substantially free from hydrogen sulfide. This is not necessary for the desulfurization stage, however.

The presence of about 0.2% to 2% by volume, or even as much as 20% in some instances, of hydrogen sulfide in the mixture of hydrogen-containing gas and vaporized feed entering the desulfurization zone, may be tolerated. It may actually be desirable in many instances, since the presence of hydrogen sulfide appears to promote the hydrogenation of olefins, and this is normally a desirable effect in the two-stage process, as noted above.

In another modification of the process, a third stage is employed, into which the gaseous product from the second stage is passed without preliminary condensation, but with appropriate cooling and perhaps reduction in pressure. In this third stage the product is treated with a material such as clay, zinc chloride, etc., to improve its resistance to deterioration by oxidation, etc.

Modifications of the above invention which would occur to one skilled in the art and have not previously been disclosed are to be included in the scope of the following claims.

I claim:

1. A 2-stage process for treatment of a volatile hydrocarbon feed stock containing organic sulfur compounds as well as olefinic hydrocarbons which comprises subjecting said feed stock in the first stage to contact with between about 100 and 10,000 cu. ft. per barrel of hydrogen at a temperature between about 650° F. and 800° F. in the presence of a catalyst whereby said sulfur compounds are substantially converted with formation of hydrogen sulfide and said olefinic hydrocarbons are substantially hydrogenated, separating said hydrogen sulfide from the so treated hydrocarbons and from the hydrogen, mixing the separated hydrocarbons with added hydrogen which is substantially free from hydrogen sulfide, the amount of added hydrogen being between about 2000 and 8000 cu. ft. per barrel, and subjecting the resulting mixture in the second stage to contact with a catalyst at a temperature above about 900° F., whereby the octane number of said desulfurized hydrocarbons is substantially increased.

2. A 2-stage process for treatment of a cracked gasoline feed stock having a high content of organic sulfur compounds and olefinic hydrocarbons which comprises subjecting said feed stock in the first stage to contact with about 2000 cu. ft. of hydrogen per barrel of feed at a temperature between about 650° F. and 800° F. in the presence of a catalyst whereby said sulfur compounds are substantially converted with formation of hydrogen sulfide and acid olefinic hydrocarbons are substantially hydrogenated, and subjecting the so treated hydrocarbons in the second stage to contact with hydrogen which is substantially free of hydrogen sulfide in the proportion of at least about 2000 cu. ft. of hydrogen per barrel of feed at a temperature above about 900° F. in the presence of a catalyst, whereby the octane number of said desulfurized hydrocarbons is substantially increased.

3. A process according to claim 2 in which the pressure in the first stage is greater than about 100 pounds per sq. in. gage, and the pressure in the second stage is greater than about 50 pounds per sq. in. gage.

4. A 2-stage process for the treatment of a cracked gasoline of high sulfur content and high olefin content, which comprises subjecting said cracked gasoline in the first stage to vapor phase catalytic desulfurization at a temperature between about 650° F. and 800° F. in the presence of at least about 2000 cu. ft. of hydrogen per barrel of feed whereby the sulfur content of said cracked gasoline is substantially reduced with the production of hydrogen sulfide and said olefin content is also substantially reduced, and the resulting product mixture is substantially freed of hydrogen sulfide and without substantial removal of any other constituent is charged to the second stage wherein it is subjected to catalytic reforming in the presence of a catalyst at a temperature above about 900° F. whereby the desulfurized gasoline is substantially increased in octane number.

5. A 2-stage process for the conversion of a cracked gasoline containing substantial quantities of olefinic hydrocarbons and having a sulfur content greater than about 0.5% by weight which comprises contacting said cracked gasoline in the vapor phase with at least about 2000 cu. ft. of hydrogen at a temperature between about 650° F. and 800° F. in the presence of a desulfurization catalyst in the first stage, and thereby hydrogenating at least a portion of said olefins and reducing the sulfur content of said gasoline with the production of hydrogen sulfide; separating from the reaction product mixture (1) a gaseous fraction containing hydrogen sulfide and
a large proportion of hydrogen and (2) a liquid desulfurized hydrocarbon fraction substantially free from hydrogen sulfide; removing at least a portion of the hydrogen sulfide from said gaseous fraction and recycling the so treated gas to said first stage; vaporizing said liquid fraction and contacting the vapors admixed with at least about 2000 cu. ft. per barrel of hydrogen which is substantially free from hydrogen sulfide at a temperature above about 900° F. in the presence of a reforming catalyst in the second stage; and separating from the reaction product a gaseous hydrogen containing fraction, part of which is recycled to the first stage and part of which is recycled to the second stage, and a liquid fraction boiling in the gasoline range and having a substantially higher octane number than said desulfurized hydrocarbon fraction.

6. A process according to claim 1 in which the catalyst in the first stage comprises cobalt molybdate.

7. A process according to claim 1 in which the catalyst in the first stage comprises cobalt molybdate and the catalyst in the second stage comprises chromium oxide.

8. A process according to claim 1 in which the catalysts used in the two stages are different.

ALVA C. BYRNS.