

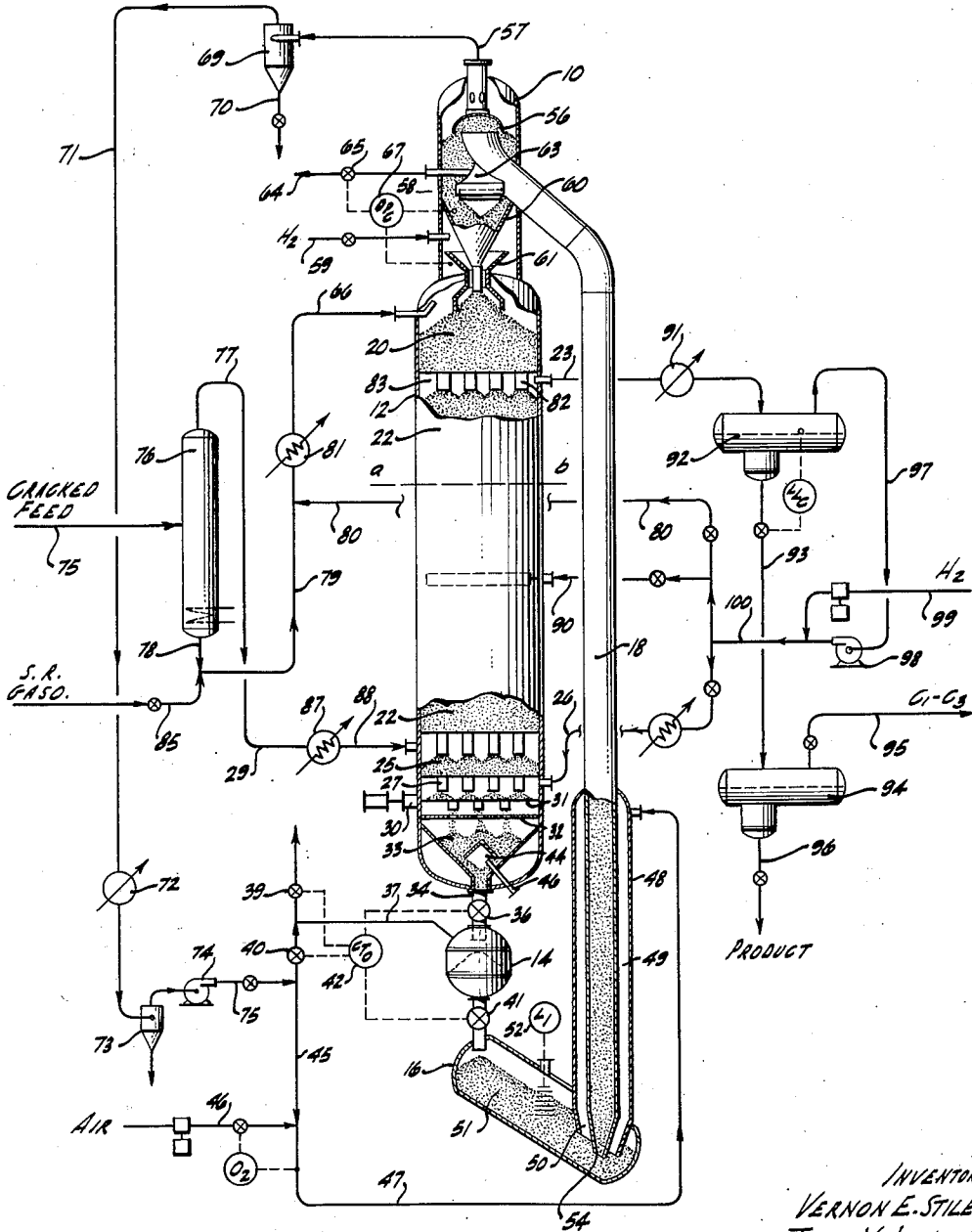
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DESULFURIZATION OF CRACKED GASOLINES

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1

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DESULFURIZATION OF CRACKED GASOLINES

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This invention relates to the hydrodesulfurization of cracked gasolines by selective hydrogenation in the presence of sulfide-forming catalysts. The process embraces broadly the treatment of cracked gasolines in the presence of hydrogen and a catalyst under such conditions that the organic sulfur components are selectively hydrocracked to produce hydrogen sulfide and hydrocarbon fragments, while the olefins remain relatively unaffected. The process conditions are adjusted in such manner as to minimize the hydrogenation of olefins, thereby producing a desulfurized product having an octane rating substantially equal or superior to the feed material. The process is distinguished from the type of conversion known as "reforming" or "hydroforming," wherein somewhat higher temperatures are employed in order to effect more fundamental changes in the structure of the hydrocarbons, as by cyclization, aromatization, isomerization and the like. The latter types of conversions are most advantageous when applied to straight run gasolines, which will produce upon reforming a high proportion of aromatic hydrocarbons. Cracked gasolines however are not benefited to the same extent as straight run gasolines by such reforming operations. Cracked gasolines, especially catalytically cracked gasolines, ordinarily have a sufficiently high knock rating, and the most important objectives in refining such cracked gasolines involve the removal of sulfur compounds, nitrogen compounds and other gum-forming materials.

The principal object of this invention is to provide methods whereby cracked gasolines may be effectively desulfurized without undergoing a loss in octane rating. A more specific object is to provide catalytic hydrodesulfurization treatments which will remove at least the most objectionable sulfur compounds, i. e. mercaptans and the like, while preserving the major part of the olefins. A further object is to provide reaction conditions and catalysts which inhibit the reaction of olefins with the hydrogen sulfide produced to form additional mercaptans. A still further object is to provide catalysts and reaction conditions which will compensate for any slight degree of olefin hydrogenation by simultaneously effecting other reactions such as isomerization, whereby the over-all knock rating may be actually improved. Other objects and advantages of the invention will be apparent to those skilled in the art from the description which follows.

In the hydrodesulfurization of cracked gasolines, one of the principal problems is concerned with finding reaction conditions which will effect a selective hydrogenation of sulfur and nitrogen compounds, and yet will leave most of the olefins in the product. A considerable amount of research in the past has been directed toward this problem with varying degrees of success. It is recognized that the sulfur compounds are slightly more easily hydrogenated than are the desirable mono-olefinic hydrocarbons. The mono-olefinic hydrocarbons, especially those wherein the double bond occurs toward the center of the molecule, are recognized as being valuable anti-

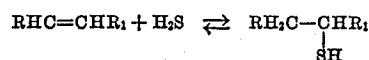
2

knock ingredients, and they do not contribute to gum formation to the extent that other olefins, e. g. diolefins, sometimes do. However, since as indicated the differences in reactivities are slight, all the known expedients which have been heretofore suggested are capable at best of improving the selectivity of hydrogenation to only a slight degree.

The present process provides an integrated set of reaction conditions, and a particular type of catalyst which is preconditioned in such manner as to provide maximum activity for desulfurization and a minimum activity for olefin hydrogenation. It has been found first that the difference in hydrogenation rates of olefins and sulfur compounds varies more with pressure than with the other process variables such as temperature, hydrogen concentration and the like. Increasing the pressure causes a greater increase in the olefin hydrogenation rate than the sulfur compound hydrogenation rate. Consequently, pressures below about 300 p. s. i. g. are employed, and preferably below about 200 p. s. i. g. Specifically, it has been found that at pressures between about atmospheric and 200 p. s. i. g., it is possible to hydrogenate from 60 to 90% of the sulfur compounds in the feed oil, while hydrogenating only about 10–30% of the olefins present. Moreover this effect is obtained over a considerable temperature range, from about 650° to 850° F., and at widely varying space velocities ranging between about 5 and 20. Under all these conditions, it is observed that the olefin hydrogenation rate is remarkably slow, so that the resulting product is found to exhibit an octane rating substantially equal to the feed material, and in some cases an improvement in octane rating is obtained. The hydrogen concentration of the reactant fluid likewise does not appear to be a critical variable at the low pressures employed. Hydrogen ratios between about 200 and 5000 s. c. f. per barrel may hence be employed.

The use of low pressures in the hydrogenation is found to result in a somewhat higher catalyst coking rate than is generally obtained at higher pressures. It is found however that this factor is fortuitously interrelated with the selective activity of the catalyst for the two types of reactions, olefin hydrogenation and sulfur compound hydrogenation. It is found that while coking of the catalyst reduces both its desulfurizing and its olefin hydrogenating activity, the olefin hydrogenating activity is reduced relatively more than the former. It is hence preferred to employ a catalyst which has been partially but not completely deactivated by coking, i. e., by deposition of coke on the active surface area of the catalyst during catalytic processing of hydrocarbon feedstocks. Under most coking conditions, the maximum coke level for obtaining a practical reaction rate is about 6% by weight of the catalyst, although higher proportions may be of some value, depending upon the manner in which the coke is deposited. As will be more particularly described hereinafter this type of catalyst is very advantageously obtained by employing a downwardly moving bed of catalyst with the principal feed stream flowing countercurrently to the lower section thereof, and with a minor feed stream flowing concurrently to an upper portion of the freshly regenerated catalyst in such manner as to provide an optimum pre-coking of catalyst for the subjacent desulfurization of the main feed stream.

In addition to the above factors, it has been found that under the process conditions described herein, which inherently involve the simultaneous presence of hydrogen sulfide and olefins, there is a tendency to synthesize an equilibrium proportion of mercaptans during or after the reaction according to the general equation:



Since mercaptans are most highly undesirable in the product, both because of their odor and their gum-forming tendencies, it is almost mandatory that the mercaptan content be reduced to near or below the doctor sweet level, which for most cracked gasolines is about 0.0004% by weight of mercaptan sulfur. It has now been found that this objective can be readily achieved herein by employing a circulating catalyst flowing countercurrently to the feed stream, and wherein the hydrogen sulfide formed during the reaction continuously combines with the catalyst to form metal sulfides. The catalyst circulation rate, the feed rate and/or the concentration of sulfidable metal oxides on the catalyst, is controlled so that in the upper portion of the downwardly moving catalyst bed a zone exists wherein the catalyst is incompletely sulfided under the desulfurization conditions prevailing. This provides that the top portion of the bed always displays some capacity for reacting with hydrogen sulfide, and also provides that the effluent product is both mercaptan-free and hydrogen sulfide-free. Hence, the term "incompletely sulfided," as used herein, means that the catalyst in the top portion of the bed (product effluent end of reactor) is not sulfided beyond the saturation level which would permit hydrogen sulfide to escape with the products. The sulfur which combines with the catalyst is removed from the bottom of the reactor with the spent catalyst, which is then oxidatively regenerated to burn off coke deposits and sulfur. The regenerated catalyst is then preferably reduced with hydrogen and passed again into the top of the conversion zone for the treatment of additional feed stock.

The catalysts employed herein may comprise any of the sulfidable, transitional metals, metal oxides, metal sulfides, or other metal salts which are known to catalyze hydrodesulfurization and are not poisoned by hydrogen sulfide or other sulfur compounds. The preferred catalysts comprise the oxides and/or sulfides of one or more metals selected from groups VIB and VIII of the periodic table, as for example the oxides or sulfides of molybdenum, tungsten, iron, cobalt, nickel, chromium and the like. Vanadium compounds may also be employed in some cases. A particularly active combination consists of a group VIB metal oxide or sulfide with a group VIII metal oxide or sulfide. For example compositions containing both molybdenum oxide and cobalt oxide, molybdenum oxide and nickel oxide, tungsten sulfide and nickel sulfide, and the like may be employed.

A particularly active catalyst consists of the composite known as cobalt molybdate, which actually may be a mixture of cobalt and molybdenum oxides wherein the molecular ratio of CoO to MoO₃ is between about 0.4 and 5.0. This catalyst, or any of the above catalysts may be employed in unsupported form, or alternatively it may be distended on a suitable adsorbent oxide carrier such as alumina, silica, zirconia, thoria, magnesia, titania, bauxite, acid activated clays, or any combination of such materials. Of the foregoing carriers, it has been found that the preferred material is alumina, and especially alumina containing about 3-20% by weight of silica. The presence of silica is highly desirable in that it promotes isomerization and other octane-improving reactions, which compensate for any slight degree of olefin hydrogenation. This result may be obtained also by incorporating other acidic components into the catalyst as e. g. hydrofluoric acid, hydrochloric acid, fluosilicic acid and the like. Such acid components may be added by impregnation from aqueous solutions, and the final catalyst may contain e. g. from about 0.1% to 8.0% by weight of F or Cl.

In the preparation of an unsupported cobalt molybdate catalyst the catalyst can be coprecipitated by mixing aqueous solutions of, for example, cobalt nitrate and ammonium molybdate, whereby a precipitate is formed. The precipitate is filtered, washed, dried and finally activated by heating to about 500° C. Alternatively, the cobalt

molybdate may be supported on alumina by coprecipitating a mixture of cobalt, aluminum and molybdenum oxides. A suitable hydrogel of the three components can be prepared by adding an ammoniacal ammonium molybdate solution to an aqueous solution of cobalt and aluminum nitrates. The precipitate which results is washed, dried and activated. In still another method a washed alumina hydrogel is suspended in an aqueous solution of cobalt nitrate and an ammoniacal solution of ammonium molybdate is added thereto. By this means a cobalt molybdate gel is precipitated on the alumina gel carrier. Catalyst preparations similar in nature to these and which can also be employed in this invention have been described in U. S. Patents 2,369,432 and 2,325,033.

Still other methods of catalyst preparation may be employed such as by impregnating dried carrier material, e. g. an alumina-silica gel, with an ammoniacal solution of cobalt nitrate and ammonium molybdate. Preparations of this type of cobalt molybdate catalyst are described in U. S. Patent 2,486,361. In yet another method for preparing impregnated molybdate catalyst the carrier material may be first impregnated with an aqueous solution of cobalt nitrate and thereafter impregnated with an ammoniacal molybdate. Alternatively, the carrier may be impregnated with both solutions in reverse order. Following the impregnation of the carrier by any of the foregoing methods the material is drained, dried and finally activated in substantially the same manner as is employed for the other catalysts. In the preparation of impregnated catalysts where separate solutions of cobalt and molybdenum are employed, it has been found that it is preferable to impregnate the carrier first with molybdenum, e. g., ammoniacal ammonium molybdate, and thereafter to impregnate with cobalt, e. g. aqueous cobalt nitrate, rather than in reverse order.

In yet another method for the preparation of suitable catalyst a gel of cobalt molybdate can be prepared as described hereinbefore for the unsupported catalyst, which gel after drying and grinding can be mixed with a ground alumina, alumina-silica or other suitable carrier together with a suitable pilling lubricant or binder which mixture can then be pilled or otherwise formed into pills or larger particles and activated.

In yet another modification finely divided or ground molybdenic oxide can be mixed with suitably ground carrier such as alumina, alumina-silica and the like in the presence of a suitable lubricant or binder and thereafter pilled or otherwise formed into larger agglomerated particles. These pills or particles are then subjected to a preliminary activation by heating to 600° C., for example, and are thereafter impregnated with an aqueous solution of cobalt nitrate to deposit the cobalt thereon. After draining and drying the particles are heated to about 600° C. to form the catalyst.

It is apparent from the foregoing description of the different types of cobalt molybdate catalyst that either an unsupported catalyst, in which case the active agents approximate 100% of the composition, or a supported catalyst wherein the active agents, e. g. cobalt and molybdenum oxides, comprise from about 7 to 22% by weight of the catalyst composition may be employed.

Regeneration of the catalyst is ordinarily accomplished by heating at about 750-1400° F. for a period of 0.5-12 hours in the presence of oxygen containing gases. The time of heating and/or the temperature, may be varied to accomplish either partial or complete removal of coke deposits, depending upon the desired activity level. The regeneration may be accomplished in a separate regeneration vessel, or the same may be accomplished in a gas lift line as will be more particularly described hereinafter.

The invention may be more readily understood by reference to the accompanying drawing which is a combination flow diagram of the process and a detailed drawing of an elevation view in partial cross section of the catalyst contacting and regeneration apparatus. The process il-

5

illustrated by the drawing represents one advantageous mode of carrying out the process, but the invention is not limited to the details described in the drawing.

Referring now more particularly to the drawing, the principal apparatus consists of an upper catalyst separator and pretreating chamber 10 into which the regenerated catalyst is discharged, a cylindrical naphtha treating column 12 through which the catalyst gravitates downwardly as a substantially compact bed, catalyst pressuring chamber 14 receiving spent catalyst from reaction chamber 12, induction chamber 16 into which the spent catalyst is discharged, and a lift line 18 through which the spent catalyst is conveyed and regenerated, and discharged for recirculation into upper separator chamber 10. The naphtha treating chamber 12 is divided horizontally into 2 sections. The top section comprises a fresh catalyst desulfurization zone 20, and the lower section comprises a partially deactivated catalyst desulfurization zone 22. In the modification illustrated a part of the feed stock contacts the catalyst in zone 20 concurrently therewith, and the major part of the feed stock contacts the catalyst in zone 22 countercurrently thereto. The combined products from zones 20 and 22 are withdrawn through line 23 and are treated as hereinafter described.

The lower, partially deactivated catalyst treating zone 22 is divided functionally into a lower portion located below a line indicated arbitrarily at $a-b$ in the drawing, said lower portion containing relatively completely sulfided catalyst, and an upper portion above line $a-b$ which contains incompletely sulfided catalyst, i. e. catalyst which still retains capacity for absorbing hydrogen sulfide. The catalyst in zone 20 also is incompletely sulfided. It will be apparent that the level of line $a-b$ will be determined by several interrelated variables. These variables include the liquid feed rate, the catalyst circulation rate, the percent of sulfur present in the feed stock, and the proportion of sulfidable ingredients on the catalyst.

After the catalyst has contacted the feed in treating zone 22, it flows downwardly into a stripping zone 25 wherein any remaining hydrocarbons are stripped therefrom by the countercurrent flow of recycle hydrogen gas admitted through line 26. The recycle hydrogen gas from line 26 flows upwardly through downcomers 27, thence through zone 25 to mingle with incoming feed stock entering through line 29. The stripped catalyst then flows downwardly at a rate regulated by solids feeder 30 which is provided with a reciprocating tray 31 and a lower stationary tray 32, so that upon reciprocation of tray 31 a substantially constant volumetric withdrawal of spent catalyst uniformly from the cross sectional area of column 12 is achieved. Spent catalyst from feeder 30 accumulates as a bed 33 which constitutes a surge volume, the level of which rises and falls as granular solids are withdrawn from the bottom of the column periodically through outlet 34, controlled by motor valve 36.

The spent, stripped solids are thus discharged into pressuring chamber 14. Pressuring chamber 14 is essentially a lock vessel which is provided in order to transfer solids from the low-pressure reaction vessel 12 to the high-pressure solids induction vessel 16. Pressuring chamber 14 is alternately pressured and depressured with flue gas admitted or withdrawn through manifold 37 in response to the opening or closing of motor valves 39 and 40. Solids are intermittently removed from pressuring chamber 14 by the opening of valve 41. Valves 36, 39, 40 and 41 are opened and closed in sequence by cycle timer operator 42 in such manner as to receive solids, pressure the chamber, discharge solids, and depressure chamber 14 at a rate sufficient to charge solids into induction chamber 16 at a rate equal to the solids circulation rate set by solids feeder 30.

In order to discharge solids from reaction vessel 12 into pressuring chamber 14, cycle timer operator 42 closes valve 41, opens valve 36, and closes valves 39 and

6

40. This causes catalyst to fall downwardly through conduit 34 and displaces flue gas upwardly into zone 33. The cycle timer then closes valve 36 and opens valve 40 whereupon pressuring vessel 14 is pressured via manifold 37 to the pressure prevailing in induction chamber 16. The cycle timer then opens valve 41 to drop solids into chamber 16. Valve 40 is then closed and valve 39 is opened in order to lower the pressure in chamber 14 to that prevailing in reaction vessel 12, at which point the initial solids inlet cycle into vessel 14 is again reached.

When valve 36 is open and solids are dropping into vessel 14 the upwardly displaced flue gas passes upwardly into gas disengaging zone 44 and is removed therefrom through line 46, together with a small proportion of the recycle gas admitted through line 26 which flows downwardly past feeder 30. This mixture may be utilized as fuel.

The spent catalyst in induction chamber 16 is simultaneously regenerated and lifted through the lift line 18. Lift line 18 is of the dense phase, or mass-flow type. The granular solids in this dense-packed form are caused to move by passing a concurrent flow of conveyance-regeneration fluid upwardly through the lift line at a rate sufficient to overcome the opposing forces of gravity acting on the solids and also to overcome opposing forces of friction of conveyance zone walls and the like which act against the solids when they are conveyed. This fluid flows through the serially connected interstices of the dense-packed mass of granular solids which presents a high resistance elongated path for the fluid flow. By maintaining a substantial pressure differential between the inlet and the outlet of the lift line, a sufficient quantity of fluid is forced to flow therethrough, generating a more or less constant pressure gradient at all points along its length so as to apply a conveyance force uniformly throughout the zone. The ratio of the resulting conveyance force tending to move the solids to the forces of gravity acting in the opposite direction has been termed the conveyance force ratio and is given by:

$$\frac{dp}{dl} \div \rho_s \cos \theta \quad (1)$$

wherein

$$\frac{dp}{dl}$$

is the pressure gradient in pounds per square foot per foot, ρ_s is the static bulk density of the granular solids being conveyed in pounds per cubic foot, and θ is the angular deviation of the direction of conveyance from an upward vertical reference axis. When the conveyance fluid flows at a rate sufficient to generate a pressure gradient which exceeds the forces of gravity expressed by the term $(\rho_s \cos \theta)$ in Equation 1, a slight additional flow of fluid is sufficient to exceed opposing forces of friction and permit the solids to move continuously in dense or compact form as an upwardly moving bed when a bed of solids is continuously supplied at the inlet, and dense granular solids are continuously withdrawn at a controlled rate from the discharged mass of solids at the outlet of the lift line.

Catalyst regeneration is accomplished in the above lift line by employing therein flue gases containing a small proportion, e. g. 0.1% to 10% by volume of oxygen and preheated to a temperature between about 550° and 900° F.

In the modification illustrated, recycle flue gas in line 45 is admixed with the desired proportion of air or other oxygen-containing gas admitted through line 46 and the mixture is then passed via line 47 into the top of a cylindrical jacket 48 surrounding the lower portion of lift line 18. The regeneration lift gas then flows downwardly through the annular space 49 and emerges from the opening 50 of jacket 48. The lower ends of jacket 48 and

lift line 18 are submerged in the compact bed of solids 51 in induction chamber 16. The proper catalyst level in chamber 16 is maintained by means of solids level indicator 52.

The regeneration-lift gas emerging from opening 50 then flows through opening 54 in the bottom of lift line 18 and effects simultaneous regeneration and transfer of solids as previously described. The outer jacket 48 aids in providing temperature control for the regeneration; the downflowing gases in space 49 being in countercurrent, indirect heat exchange relationship with the upflowing gases and solids in line 18, thereby controlling the exothermic temperature rise resulting from coke burn-off.

The regenerated catalyst emerges from the top of lift line 18 and is discharged against a baffle 56 which applies a force against the mass of catalyst issuing from lift line 18, and maintains the upwardly moving catalyst at a bulk density substantially equal to the static bulk density thereof.

The partially or completely regenerated catalyst gravitates downwardly from baffle 56, while the bulk of the lift gas moves upwardly and is withdrawn through line 57. The catalyst then gravitates downwardly into a reducing zone indicated generally at 58 wherein the higher oxides are reduced to lower oxides by means of hydrogen introduced through line 59. Hydrogen entering through line 59 flows downwardly past cone shaped baffle 60 and through the annular space enclosed within the lower periphery of baffle 61, and thence directly onto the top of the bed of regenerated catalyst in chamber 20. The main portion of this gas then passes upwardly on the inside of baffle 60 countercurrently to the regenerated catalyst in zone 58. This pretreating gas, along with a small amount of regeneration-lift gas coming down from the top of the lift line are removed from beneath baffle 63 through line 64 controlled by valve 65. The remaining portion of the hydrogen gas introduced through line 59 passes downwardly into the top of reaction zone 20 to mingle with feed stock introduced through line 66. This downflowing portion of hydrogen gas acts as a seal, preventing the upflow of feed stock into reducing zone 58. Differential pressure controller 67 actuates valve 65 in such a manner as to maintain a slightly lower pressure in zone 58 than prevails at the inlet of line 59, thereby insuring upward flow of the major portion of the reducing gas.

The lift gas in line 57 is passed into a cyclone separator 69 to separate catalyst fines which are removed through line 70. The elutriated lift gas emerges into line 71, and is cooled to the desired temperature for regeneration by means of cooler 72. The cooled lift gas is then passed through a separator 73 to remove any condensed hydrocarbons and is then returned to line 45 via compressor 74 and line 75.

The catalyst flow and regeneration having been described, the treatment and flow of feed stocks will now be described in connection therewith. The primary cracked gasoline feed is brought in through line 75 and passes into a distillation column 76. In column 76, the feed stock is split into a major portion going overhead through line 77, and a minor bottoms product comprising for example the highest boiling 10-30% of the feed stock is taken off through line 78. The overhead fraction in line 77 contains the major portion of the desirable olefins. The bottoms product in line 78 will contain a relatively lower proportion of olefins and a somewhat higher proportion of sulfur and nitrogen compounds than the overhead fraction. For example, in a cracked gasoline boiling between about 195° and 410° F., and containing initially 40 volume percent olefins, the highest boiling 20% thereof may contain only about 15-20% olefins. The present objective is to treat the high boiling portion exhaustively to substantially completely remove sulfur and nitrogen compounds. The olefins may be either completely or incompletely hydrogenated. This

treatment serves the additional purpose of partially coking the catalyst and conditioning it for the subsequent contacting with the low boiling fraction.

The high boiling fraction in line 78 is transferred via line 79, together with recycle hydrogen admitted through line 80, to heater 81, and thence through line 66 into the top of desulfurization zone 20 wherein the feed stock flows concurrently with the catalyst downwardly through downcomers 82 into product disengaging zone 83. The temperature in treating zone 20 may be maintained between about 700° and 950° F., the upper ranges, above about 850° F., being substantially in the dehydrogenating range.

In some cases it may be found desirable to admix with the high boiling cracked stock treated in zone 20, a proportion of straight-run gasoline which may be admitted via line 85. The total feed entering through line 66 may contain for example between about 10% and 60% by volume of straight-run gasoline. The high temperature treatment of such blends in zone 20 is substantially endothermic in character and effects a substantial reforming and hydrogen make, thereby lowering the temperature of the catalyst downwardly in the bed. By suitably adjusting the proportion of straight run gasoline, the temperature of the catalyst may be controlled so that when it enters zone 22 it will be at a desired lower temperature for the treatment of the low boiling fractions of cracked stock. The other reaction conditions in treating zone 20 may be substantially those known in the art as reforming conditions involving e. g. space velocities between about 2 and 10, hydrogen recycle rates between about 500 and 10,000 s. c. f. per barrel of feed, and pressures between about 100 and 1000 p. s. i. g. It is important to observe however that the catalyst/oil ratio in zone 20 should be adjusted so as to insure that the catalyst emerging from downcomers 82 is incompletely sulfided, i. e. still exhibits a substantial capacity for combining with hydrogen sulfide.

The overhead fraction from column 76 is passed via lines 77 and 23, heater 87 and line 83 into the bottom of treating zone 22 wherein the feed vapors, together with recycle hydrogen admitted through line 26, pass upwardly into product disengaging zone 83. The reaction ensuing in treating zone 22 is exothermic in nature, hydrogen being absorbed by the hydrocracking of sulfur and nitrogen compounds and the small degree of olefin hydrogenation. The temperature may be controlled therein by the use of various cooling devices illustrated herein by the injection of a cool auxiliary hydrogen stream through line 90.

In other modifications of the process, the full range cracked stock may be treated in zone 22 in which case column 76 is omitted. The stock treated in zone 20 may then comprise any other hydrocarbon fraction, such for example as 100% straight run gasoline for reforming, fuel oils, diesel oils or the like for desulfurization.

It is apparent that the countercurrent flow of feed stock upwardly in zone 22 will provide a concentration gradient of sulfide on the catalyst, provided the feed rates and catalyst circulation rates are so adjusted. It has been found for example that in a unit wherein 1100 barrels per day of feed stock containing 0.8% sulfur by weight are treated, and wherein a catalyst containing 8% by weight of MoO_3 and 3% by weight of CoO is employed, the catalyst circulation rate must be at least about 3000 pounds per hour in order to maintain the desired hydrogen sulfide absorbing capacity in the upper portion of zone 22. From these figures, the circulation rates may be readily calculated for other feed stocks, feed rates, and catalysts.

Due to the preconditioning of the catalyst in zone 20, the catalyst in zone 22 will contain catalytic coke in amounts ranging for example between about 0.2% to 2% at the top of zone 22, to perhaps 1-6% at the bottom of

zone 22. It is found that catalyst beds containing these general proportions and concentration gradients of coke and sulfur are optimum for the treatment of cracked stocks at low pressures in order to preserve the desirable olefin content, while at the same time avoiding the presence of mercaptans in the product.

The combined products from treating zones 20 and 22 are removed through line 23 and passed through a cooler-condenser 91 wherein the liquid feed material is condensed and cooled to for example about 50–200° F. The condensate is then passed into a high pressure separator 92. The liquid product is removed therefrom through line 93 and flashed into a low pressure separator 94, from which light gases and a small amount of hydrogen is removed through line 95 while the final product is taken off through line 96.

The gas phase from separator 92 comprises the hydrogen recycle stream, which is removed through line 97 and repressed to reactor pressure through compressor 98. The over-all conversion may either consume or make hydrogen, depending upon the proportion of straight run gasoline admitted through line 85. If hydrogen is consumed, make up hydrogen is admitted through line 99. The combined recycle stream is then passed via line 100 into lines 80, 90 and 26 as previously described.

In order to illustrate more particularly the critical process variables herein, the following examples are cited. These examples however are illustrative only and should not be construed as limiting in scope.

Example I

In order to define optimum conditions for desulfurizing cracked gasolines without also degrading the octane rating by olefin hydrogenation, a series of experiments was carried out on the hydrosulfurization of a full-range vis-breaker gasoline obtained by the thermal cracking of a viscous residual oil. This gasoline showed by inspection the following characteristics:

Boiling range	-----° F--	85–400
Gravity, API (60° F.)	-----	63.2
Olefins FIA, vol. percent	-----	52
Total S, wt. percent	-----	0.224
Mercaptan S, wt. percent	-----	0.076
Oct. No. F-1 Res.+3 ml. TEL	-----	82.0

in all runs, the hydrogen supply was 2000 s. c. f. per barrel of feed. The vaporized feed mixture plus hydrogen was preheated to the desired reaction temperature and passed downwardly through a 100 ml. (runs 1–6) or 50 ml. (runs 7–16) bed of cobalt molybdate catalyst in the form of 1/8 inch pellets of 94% alumina-6% silica base impregnated with 8.8 weight percent MoO₃ and 3.1% by weight of CoO. The catalyst was fresh and presulfided for run No. 1, and was used without regeneration for the succeeding runs. The results obtained were as follows:

TABLE 1

Run No.	Reaction conditions			Vol. percent olefins retained	Wt. percent mercaptan S removed	Wt. percent total S removed	Percent of original Oct. No.+3 ml. TEL
	LHSV	P.s.i.g.	Temp.,°F.				
1	3	500	550	11.5	98.7	91	88
2	3	500	575	11.5	95.4	96.4	88
3	3	500	600	5.7	98.5	98.6	87
4	3	500	626	2.0	99.8	98.6	86
5	6	500	627	7.7	98.5	98.6	89.5
6	6	500	650	5.7	99	98.6	89
7	12	500	625	33.5	91.4	85	96.4
8	12	100	625	81	97.2	64	103.5
9	12	100	649	79	97.8	64.8	103.5
10	12	500	625	48	95.7	77.2	97.5
11	12	300	624	66	95.2	73.2	101
12	12	300	675	48	98	84.5	98.5
13	10	200	675	56	97.8	83.2	100
14	10	200	700	54	98.4	85.5	99.7
15	12	300	700	46	97.2	84.5	99
16	12	500	675	61	92.5	78.6	99.7

The total barrels of feed per pound of catalyst for the above experiments was 5.18, and at the end of run 16 the catalyst was found to contain 5.11 weight percent of carbon. The above data shows in general that when employing completely sulfided catalysts it is not possible to obtain a doctor-sweet product, i. e. one wherein the mercaptan sulfur content is below about 0.0004% by weight, except in those cases wherein the olefins are substantially completely hydrogenated as in run No. 4. However, runs Nos. 13, 14 and 15 demonstrate that by operating at low pressures as herein claimed, it is possible to remove from 80–95% of the total sulfur while still retaining most of the olefins and suffering no loss in octane rating. This result is accomplished moreover at temperatures between 650° and 750° F. which are substantially below the reforming range. Low pressure runs 8 and 9, while improving the octane rating, and retaining a larger proportion of olefins, did not as effectively desulfurize the product. However, by employing temperatures between 700° and 780° F. under these conditions, the desulfurization may be increased substantially.

Example II

Run Nos. 13 and 14 as described in Example I, are repeated with the exception that the feed stock is first passed over 25 ml. of sulfided, partially coked catalyst and then over 25 ml. of partially coked but non-sulfided catalyst. The olefin content, octane number and total desulfurization obtained is substantially the same as reported for run Nos. 13 and 14. However, in these cases the product is observed to be doctor-sweet, substantially 100% of the mercaptan sulfur being removed. This example shows that the non-sulfided catalyst reacts with the hydrogen sulfide to drive the mercaptan decomposition reaction to completion.

Example III

This example demonstrates the selectivity of partially coked catalysts for promoting desulfurization as opposed to olefin hydrogenation, in comparison to a freshly regenerated catalyst. The feed stock employed was similar to that described in Example I, but was depentanized and had a boiling range of 170° to 406° F. and an API gravity of 56.1. This feed stock contained also 48 volume percent olefins, 0.214 weight percent sulfur, 0.0188 weight percent mercaptan sulfur, and had an original octane number (F-1 Research plus 3 ml. TEL) of 77.6. The same pelleted cobalt molybdate catalyst was employed and was freshly prepared and sulfided with H₂S. The hydrogen supply was 2000 s. c. f. per barrel of feed. Upon treating the feed stock with the fresh catalyst at space velocity 12, temperature 625° F. and at 500 p. s. i. g., 91.6% of the total sulfur was removed, but the octane rating dropped to 70.0, or 90.2% of the original octane number. The catalyst was then utilized in a series of desulfurization runs whereby about 6% by weight of coke was deposited thereon. The partially deactivated catalyst was then employed for desulfurization under conditions identical to the first run, and it was observed that 75.2% of the total sulfur was removed while the octane number of the product was 77.4, or 99.7% of the original.

In other runs conducted at lower pressures, e. g. 200–300 p. s. i. g., and at temperatures between about 700° and 780° F., it is found that an even more favorable selectivity is obtained. Under such conditions, employing partially coked catalysts, 90% or more of the sulfur may be removed while still retaining substantially the original octane rating, and if a partially non-sulfided catalyst is employed the product is free of mercaptans.

It will be apparent from the foregoing disclosure that optimum process conditions and catalysts are defined herein for the catalytic hydrosulfurization of cracked gasolines, while at the same time preserving the knock rating thereof. Substantially similar results to those shown in

the examples are obtained when other specific catalysts and feed stocks within the scope of the foregoing disclosure are employed. It will be apparent to those skilled in the art that many such variations may be employed without departing from the scope of the invention, and it is intended to include such variations within the scope of the following claims:

We claim:

1. A process for the catalytic hydrodesulfurization of a cracked gasoline without substantial hydrogenation of the olefins contained therein, which comprises contacting a stream of said gasoline with a hydrodesulfurization catalyst in the presence of hydrogen at a temperature between about 650° and 780° F., a liquid hourly space velocity between about 5 and 20, and a pressure between about 0 and 300 p. s. i. g., said catalyst consisting essentially of a minor proportion of the mixed oxides and sulfides of cobalt plus molybdenum supported on a major proportion of a predominantly alumina carrier, said catalyst throughout said contacting zone being maintained in a partially deactivated condition by the presence thereof of a small proportion, between about 0.2% and 6% by weight, of catalytic carbon intimately associated with the active surface area of said catalyst.

2. A process as defined in claim 1 wherein said carrier is activated alumina gel containing a minor proportion of coprecipitated silica gel.

3. A process for the catalytic hydrodesulfurization and sweetening of a cracked gasoline without substantial hydrogenation of the olefins contained therein, which comprises contacting a stream of said gasoline with a hydrodesulfurization catalyst in the presence of hydrogen at a temperature between about 650° and 780° F., a liquid hourly space velocity between about 5 and 20, and a pressure between about 0 and 300 p. s. i. g., said catalyst consisting essentially of a minor proportion of the mixed oxides and sulfides of cobalt plus molybdenum supported on a major proportion of an adsorbent oxide carrier, said catalyst throughout said contacting zone being maintained in a partially deactivated condition by the presence thereof of a small proportion, between about 0.2% and 6% by weight, of catalytic carbon intimately associated with the active surface area of said catalyst, the sulfide content of the portion of catalyst nearest the product effluent end of the contacting zone being (1) substantially less than the sulfide content of the catalyst nearer the feed influent end of said contacting zone, and (2) not above the level which would permit the escape of hydrogen sulfide in the product gases under the prevailing process conditions, whereby the products recovered from said contacting are substantially free from H₂S and mercaptans.

4. A process as defined in claim 3 wherein said carrier is activated alumina gel containing a minor proportion of coprecipitated silica gel.

5. A process for the catalytic hydrodesulfurization and sweetening of a cracked gasoline without substantial hydrogenation of the olefins contained therein, which comprises flowing a hydrodesulfurization catalyst serially through a conversion zone and a regeneration zone, flowing said cracked gasoline in admixture with hydrogen through said conversion zone countercurrently to said catalyst at a temperature between about 650° and 780° F., a liquid hourly space velocity between about 5 and 20, and at a pressure between about 0 and 300 p. s. i. g., said catalyst consisting essentially of a minor proportion of the mixed oxides and sulfides of cobalt plus molybdenum supported on a major proportion of a carrier which is predominantly activated alumina, adjusting the flow rate of said catalyst through said conversion zone so as to maintain the sulfide content of that portion of catalyst nearest the product effluent end of the contacting zone at a level which is (1) substantially less than the sulfide content of the catalyst nearer the feed influent

end of said contacting zone, and (2) not above the level which would permit the escape of hydrogen sulfide in the product gases under the prevailing process conditions, whereby the products recovered from said contacting are substantially free from H₂S and mercaptans said catalyst throughout said conversion zone being maintained in a partially deactivated condition by the presence thereof of a small proportion, between about 0.2% and 6% by weight, of catalytic carbon intimately associated with the active surface area of said catalyst.

6. A process as defined in claim 5 wherein said catalyst is passed through an intermediate preconditioning zone between said regeneration zone and said conversion zone, contacting said catalyst in said preconditioning zone with hydrogen and a hydrocarbon feed stock at a temperature between about 700° and 950° F. to effect conversion thereof and to deposit coke on said catalyst, and limiting the catalyst/oil ratio in said preconditioning zone so as to incompletely sulfide the catalyst therein.

7. A process as defined in claim 6 wherein said feed stock contacted in said preconditioning zone comprises a high boiling fraction separated from said cracked gasoline feed stock.

8. A process as defined in claim 6 wherein said feed stock contacted in said preconditioning zone comprises a straight run gasoline.

9. A process as defined in claim 6 wherein said feed stock contacted in said preconditioning zone is a blend of a straight run gasoline and a high boiling fraction separated from said cracked gasoline feed stock.

10. A process as defined in claim 6 wherein the conversion in said pretreating zone is conducted at a temperature between about 850° and 950° F., thereby effecting substantially complete desulfurization and denitrogenation, and the feedstock contacted therein is a high-boiling fraction of said cracked gasoline feedstock.

11. A process for the catalytic hydrodesulfurization and sweetening of a cracked gasoline without substantial hydrogenation of the olefins contained therein, which comprises flowing a hydrodesulfurization catalyst serially through a preconditioning-conversion zone, a desulfurization zone, an oxidative regeneration zone, a reducing zone, and back to said preconditioning-conversion zone, fractionating said cracked gasoline to obtain a major overhead fraction and a minor bottoms fraction, contacting said bottoms fraction plus hydrogen concurrently with said catalyst in said preconditioning-conversion zone to effect substantially complete desulfurization thereof and to deposit coke on said catalyst, contacting said overhead fraction plus hydrogen countercurrently with said catalyst in said desulfurization zone at a pressure between about 0 and 300 p. s. i. g., a liquid hourly space velocity between about 5 and 20, and a temperature between about 650° and 780° F., adjusting the flow rate of said catalyst so as to maintain the sulfide content of that portion of catalyst nearest the product effluent end of said desulfurization zone at a level which is (1) substantially less than the sulfide content of the catalyst nearer the feed influent end of said desulfurization zone, and (2) not above the level which would permit the escape of hydrogen sulfide in the product gases under the prevailing desulfurization conditions, whereby the products recovered from said desulfurization zone are substantially free from H₂S and mercaptans, said catalyst admitted to said reducing zone consisting essentially of a minor proportion of cobalt oxide plus molybdenum oxide supported on a major proportion of a predominantly alumina carrier.

12. A process as defined in claim 11 wherein a straight run gasoline is admixed with said bottoms fraction treated in said preconditioning conversion zone, and wherein endothermic, dehydrogenating conditions are maintained therein.

13. A process as defined in claim 11 wherein said oxidative regeneration zone is a gas lift line having a

2,793,170

13

compacted outlet whereby said catalyst is simultaneously regenerated and conveyed as a compact mass having a bulk density in said lift line substantially the same as its static bulk density, thereby minimizing attrition rates of said catalyst.

5

14

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