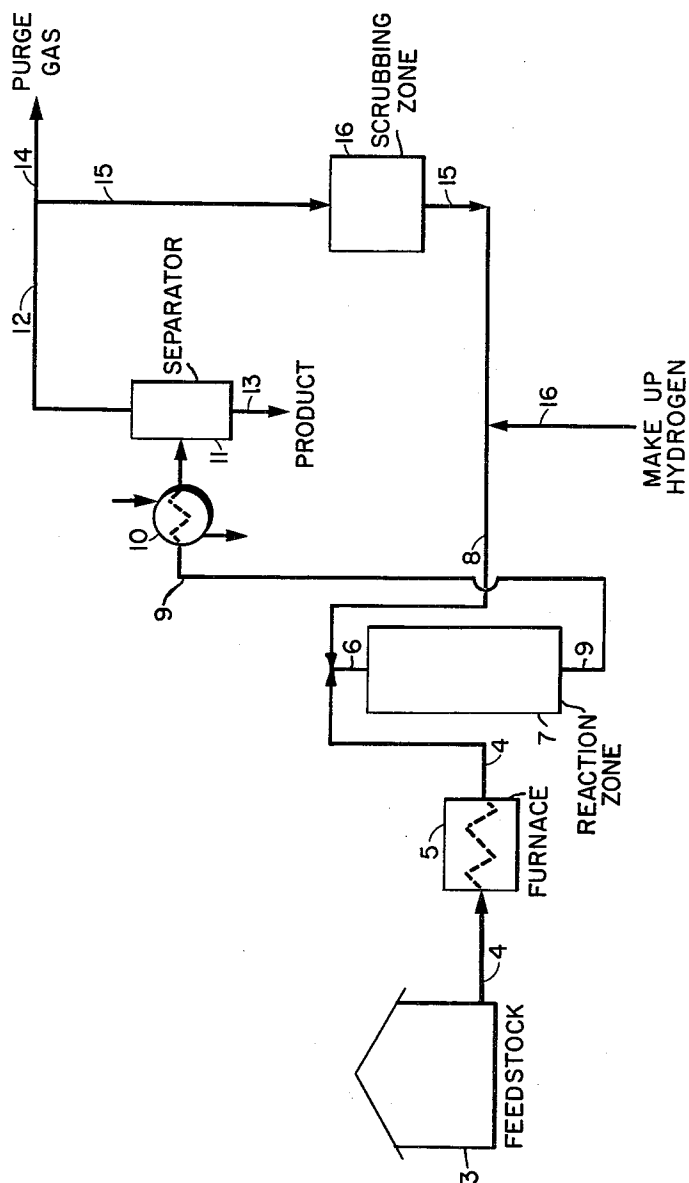


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FEED UNDER SPECIFIC CONDITIONS
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1

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HYDRODESULFURIZATION PROCESS USING A COBALT MOLYBDATE CATALYST PRESULFIDED WITH THE FEED UNDER SPECIFIC CONDITIONS

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The present invention concerns an improved process for the desulfurization of petroleum fractions that contain relatively large amounts of sulfur. It particularly relates to a desulfurization process in which a petroleum fraction containing in excess of about 1.5 weight per cent sulfur is hydrodesulfurized in the presence of a cobalt molybdate-type catalyst. It especially concerns a method of presulfiding the catalyst in situ before desulfurization step so that the catalyst is markedly more active in its desulfurizing ability and also in its effective life. The catalyst of particular interest to the present invention is cobalt molybdate impregnated on alumina.

It is well known in the petroleum industry to reduce the sulfur content of a petroleum fraction by subjecting the fraction to a hydrodesulfurization operation. In this process, a sulfur-containing petroleum fraction is contacted with a catalyst such as cobalt molybdate on alumina at a temperature of about 650°–800° F. and a pressure of about 100–1000 p. s. i. g. The petroleum fraction is fed to the hydrodesulfurization zone at a rate of about 0.25 to 5.0 volumes of liquid feed per hour per volume of catalyst. Hydrogen-containing gas is also passed through the zone at rates of between 500 and 5000 s. c. f./bbl. of feed. Under these conditions some hydrogen is generally consumed by the process. Hydrogen consumption rates are usually in a range of about 75–700 s. c. f./bbl. of feed and may be even as high as 1000 s. c. f./bbl. of feed. The hydrogen consumed in the process is considered to react with unsaturated compounds in the feed to form more saturated compounds and with sulfur compounds to form hydrogen sulfide. The molecules from which sulfur is released are in turn saturated.

The hydrodesulfurization process may be employed on petroleum fractions that exist within the desulfurization zone in the liquid and/or vapor phase. Thus, petroleum fractions including naphtha, fuel oil, kerosene, gas oil, diesel fuel, jet fuel, and the like, may be subjected to a hydrodesulfurization operation. Similarly, feed stocks derived from cracking operations may be employed as well as straight run fractions that are derived directly from a crude oil.

The hydrodesulfurization process causes sulfur compounds within a petroleum fraction to react with hydrogen to form hydrogen sulfide. The hydrogen sulfide and other gaseous components including hydrogen and light hydrocarbons are separated from the product stream and handled as desired. In many instances, the gaseous components are scrubbed with an ethanolamine solution which serves to remove any hydrogen sulfide therefrom.

As the hydrodesulfurization process proceeds, the catalyst may gradually deactivate, and in such cases it may be periodically regenerated by burning off the carbon which is deposited on the catalyst. This is conventionally done by passing an oxygen-containing gas through the catalyst at a temperature of between 800° F. to 1100° F. and a pressure of between 0–400 p. s. i. g. The regenerating gas may contain from about 1 to 21 volumes per

2

cent oxygen obtained from air, and is generally diluted with either recycled flue gas or steam. The main problem in such regeneration is the economic removal of the heat of burning. A longer interval between necessary regeneration permits a slower burning rate and consequently less expensive provisions for heat removal. It thus follows that any gain in catalyst initial activity which permits a longer operation between necessary regenerations will be particularly desirable.

Hydrodesulfurization in the presence of a cobalt molybdate-type catalyst has been successfully applied in the past to relatively low boiling hydrocarbon mixtures that contain comparatively small amounts of sulfur. Not only has it been possible to obtain products of low sulfur content; it has also been possible to maintain high activity for the catalyst over long periods of time. Hydrocarbon mixtures that have been especially susceptible to successful treatment in this respect have been low boiling petroleum fractions such as straight run naphthas, kerosenes, and other light fuels boiling below about 650° F.

While the use of the cobalt molybdate hydrodesulfurization process on the feed stocks just mentioned has been reasonably successful, this process has been less successfully applied to date to the desulfurization of high boiling hydrocarbon mixtures that contain relatively large amounts of sulfur. This condition has been particularly true for petroleum feed stocks and fractions that are derived, at least in part, from cracking operations.

In general, high boiling petroleum fractions from any given crude will contain much more sulfur than the lower boiling fractions. It is also well known that cracked fractions generally possess much more sulfur than do straight run or virgin materials from the same crude source. In general, it has been observed that the sulfur compounds in the high boiling stocks, and especially in the cracked stocks, are more refractory and difficult to remove than the sulfur compounds in straight run stocks. Hence, the processing of these stocks constitutes a very serious problem today to the petroleum refiner.

In attempting to hydrodesulfurize high boiling and high sulfur content hydrocarbon stocks, it has been a particularly difficult problem to realize satisfactory catalyst activity as well as satisfactory catalyst life. In the past, it has been the practice in the case of low boiling, straight run petroleum stocks to presulfide a cobalt molybdate catalyst before contacting it with such a feed stock in a hydrodesulfurization operation. This has generally been done by initially contacting the catalyst under conventional hydrodesulfurization conditions with a straight run petroleum fraction that contains a greater amount of sulfur than the feed stock itself. Thus, a catalyst which is to be employed in the catalytic hydrodesulfurization of a feed stock containing less than about 0.15 weight per cent sulfur has been conventionally presulfided by first contacting it with a straight run petroleum fraction (containing from about 0.25 to 0.50 weight per cent sulfur, and especially about 0.5 weight per cent) under the identical process conditions to be employed in the subsequent desulfurization step. The presulfiding step has generally been maintained for a period of about 12 to 48 hours, this being the period of time that experience has shown to provide a very active catalyst.

The accepted procedure to date in desulfurizing high boiling, high sulfur feed stocks has been to ignore any distinct presulfiding step. Rather, it has been the conventional practice to merely contact the catalyst directly with the feed stock itself under the same reaction conditions as are employed for the hydrodesulfurization itself. In other words, it has not heretofore been considered necessary to utilize conditions other than the hydrodesulfurization conditions themselves for preactivating the

catalyst in any way. The procedure that has been employed, however, has not constituted a practicable solution to the problem of handling these feed stocks. Specifically, this procedure has not made possible the realization of satisfactory catalyst activity, and it has not made possible the realization of economically attractive catalyst life.

Accordingly, it is an object of the present invention to provide a method for preactivating cobalt molybdate-type catalysts whereby the use of these catalysts for the hydrodesulfurization of high boiling and high sulfur content petroleum feed stocks is rendered both practicable and economical. More particularly, it is an object of the invention to provide a method of preactivating such catalysts in a manner such that the catalysts possess a high level of activity as well as a long period of active life.

The present invention achieves these objectives by presulfiding a cobalt molybdate-type catalyst in a manner designed to preactivate the catalyst and to render it more active and more stable in the hydrodesulfurization of high boiling and high sulfur content feed stocks. Briefly, a catalyst of the given type is contacted with the hydrodesulfurization feed stock itself under conditions that have been found to provide a very active and stable form of the catalyst. These conditions will be brought out in greater detail later in this description. At this point it may be stated that the catalyst is charged to the zone in which the desulfurization process is to occur, and it is there subjected to a two-step processing sequence. In the first step the catalyst is presulfided by contacting it with the petroleum feed stock and a hydrogen-containing gas under conditions of temperature, pressure, and feed rates that are adapted to presulfide and thereby preactivate the catalyst. In the second step the presulfided catalyst is then contacted with the feed stock and hydrogen-containing gas under conventional hydrodesulfurization conditions that are adapted to provide adequate desulfurization of the feed stock to the sulfur levels desired. The first step differs to a large degree from the second step in that the conditions employed in the first step are less severe than those required to effect the desired degree of desulfurization.

Before describing in detail the individual processing steps, it will be noted that the present invention is particularly concerned with the desulfurization of high-sulfur content petroleum fractions that contain in excess of about 1.5 weight per cent sulfur, and especially those fractions that contain from about 2 to 6 weight per cent sulfur. The hydrocarbons in the feed stocks may be straight run hydrocarbons, or they may be derived wholly or in part from petroleum refining operations such as thermal cracking, catalytic cracking, coking, deasphalting, etc. It is a characteristic of these various refining operations that they produce petroleum fractions that are characterized by high contents of refractory sulfur compounds. Consequently, such fractions require further refining before they can be marketed.

Insofar as the physical properties of the feed stocks are concerned, the present invention is particularly effective in the processing of high boiling petroleum fractions that may have initial boiling points as low as about 350° F. The fractions may be at least partially residual in character, but the invention is most effective in the processing of distillate fractions. It is preferred that the feed stocks have final boiling points that are not in excess of about 1050° F. It is an important feature of the invention that the feed stock to the desulfurization step of the process may be identical with the feed stock that is utilized for the presulfiding of the catalyst.

It will also be observed that the present invention is limited to the use of the so-called "cobalt molybdate-type" desulfurization catalysts. These catalysts are well known in the art and have been widely employed for the hydrodesulfurization of various petroleum fractions and

other hydrocarbon mixtures, as explained earlier in this description. They are conventionally prepared, for example, by impregnating a suitable carrier such as alumina, bauxite, silica gel, activated magnesia, or the like with an ammoniacal solution of cobalt and molybdenum salts. The catalyst preparation is then dried and decomposed to convert the cobalt and molybdenum salts to the oxides.

For the purposes of the present invention it is particularly desired to carry out the presulfiding step as well as the desulfurization step in a fixed bed type of reactor. Accordingly, the catalyst must be of a character to provide a bed which exhibits a satisfactory surface area, that is readily permeable to the flow of the liquid feed stock as well as vapors and gases, and that possesses sufficient strength to maintain a satisfactory bed structure. In this connection it has been found that the catalyst may have particle sizes extending within the range of about $\frac{1}{16}$ to $\frac{1}{2}$ inch, preferably about $\frac{3}{16}$ to $\frac{3}{8}$ inch. The particles may be formed by crushing, pilling, slugging, or any other conventional method for arriving at particles of this size.

The hydrogen-containing gas that is used in the present process consists partially of fresh gas that is added to the system and partially of recycle gas that is returned from the reactor exit to the reactor inlet. In flowing through the reaction zone a portion of the hydrogen reacts with sulfur-containing compounds in the hydrocarbon feed to form gaseous hydrogen sulfide. Another portion of the hydrogen reacts with unsaturated compounds and with the desulfurized compounds to form more saturated compounds. Thus, it is an essential feature of the process to always maintain an amount of hydrogen in the reaction zone that is over and above the amount which is consumed by the desulfurization and hydrogenation reactions.

It follows from the above description that the gas stream which is produced during the presulfiding and/or desulfurization reactions should be at least partially desulfurized before it is recycled to the reaction zone. This has been conventionally done by scrubbing the recycle stream with a material such as an aqueous alkali solution or an ethanolamine solution. These and other materials are particularly adapted to remove hydrogen sulfide and other sulfur compounds from a gas stream.

In addition to containing hydrogen sulfide, the gas stream from the presulfiding and/or desulfurization reactions may contain small amounts of low molecular weight hydrocarbon gases such as methane, ethane, and the like. These gases tend to dilute the recycle stream and thereby to reduce the concentration of hydrogen in this stream. Accordingly, it is now the practice to periodically or continuously remove at least a portion of the hydrogen-containing recycle stream from the reaction system and to replace it with an amount of a gas rich in hydrogen sufficient to maintain the desired amount of hydrogen in the recycle gas. The hydrogen which is added in this manner to the overall reaction system will hereinafter be referred to as "make-up" hydrogen.

In the process of the present invention, it is preferred that the recycle hydrogen stream contain at least 40 volume per cent hydrogen and preferably at least 75 volume per cent hydrogen. It is further desired that the recycle stream contain less than 5 volume per cent hydrogen sulfide, and generally less than 1 per cent. The make-up stream should contain at least 55 volume per cent hydrogen, and preferably at least 85 volume per cent hydrogen. The latter stream may be derived from any of the sources that are conventionally employed for manufacturing hydrogen. In petroleum refineries that possess hydroforming units, it may be convenient to utilize the excess hydrogen that is generally produced by such units. These gas streams, generally referred to as "hydroformer tail gas," usually contain at least 75% by volume of hydrogen and generally in excess of 85%.

A hydrogen gas suitable for the make-up hydrogen stream of the present process may also be produced by

5

contacting light hydrocarbon gases such as methane, ethane, propane and butane with a nickel-type reforming catalyst at a temperature of about 1300° to 1700° F. This process is well known and has already been employed for the generation of hydrogen.

Suitable hydrogen may also be derived as a by-product from the dehydrogenation of organic chemicals such as secondary butyl alcohol which is dehydrogenated commercially to form methyl ethyl ketone. In any event, the choice of a suitable source of make-up hydrogen will be governed by factors that are not critical in themselves to the success of the present process so long as the conditions noted earlier are observed.

The process of the present invention may be better understood by reference to the attached figure, which illustrates a storage tank 3, a heating zone 5, a reaction zone 7, a separator 11, and a scrubbing zone 16.

Referring to the figure, a high boiling, high sulfur content feed stock of the type described earlier in this description is withdrawn from the storage tank 3 and is passed by means of line 4 through heating zone 5. It is then passed, again by means of line 4, as well as line 6, into reaction zone 7.

Reaction zone 7 is provided with a fixed bed of a cobalt molybdate-type catalyst of the type referred to earlier. As charged to the reactor, it will be considered that the catalyst contains very little or no sulfur. Accordingly, the catalyst, in accordance with the present process, is first subjected to a preactivating or presulfiding step. In this initial phase of the process the catalyst is contacted with the feed stock at a temperature within the range of about 550°–650° F. and at a pressure of between 200 and 800 p. s. i. g., with a feed stock flow rate of about 0.5 to 2.0 volumes of liquid per hour per volume of catalyst. It is particularly preferred that a temperature of about 600° F., a pressure of about 400 p. s. i. g., and a feed stock flow rate of about 1 v./hr./v. be employed at this point. It is further important that the temperature within the reaction zone during the presulfiding step be maintained at least 50° F. below the temperature that is to be employed in the subsequent hydrodesulfurization step. It is preferred that the presulfiding temperature be maintained at least about 100° F. below the temperature of the desulfurization step; and it is essential that the temperature during the presulfiding procedure not exceed a value of about 650° F.

It will be appreciated that the use of a lower temperature in the presulfiding step than in the hydrodesulfurization step makes for much milder reaction conditions in the former step as compared with the latter step. It will also be appreciated that the reaction zone pressure and the hydrocarbon feed rate may be expected to exert an influence on the course of the presulfiding reaction. In this connection, the hydrogen pressure during the presulfiding step should be in the ranges stipulated earlier; but it should be no greater than the pressure that is to be employed subsequently in the desulfurization step. Insofar as the hydrocarbon feed rate is concerned, it is considered that variations in this factor should have no substantial effect on the course of the reaction so long as the feed rate employed falls within the range of feed rates prescribed hereinbefore.

During the presulfiding phase of the operation it is further necessary that a hydrogen-containing gas of a type described earlier be contacted with the catalyst simultaneously with the petroleum feed stock. The hydrogen rates should be maintained to provide between 500 and 3000 s. c. f. of hydrogen per barrel of liquid feed, and preferably between 1000 and 2000 s. c.f./barrel of feed. In the case of certain feed stocks such as petroleum fractions that contain substantial amounts of coker products, it may be necessary to employ hydrogen rates of as much as about 5000 s. c. f./barrel of feed. The amounts of hydrogen consumed during the presulfiding step are generally within the range of about 50 to 700 s. c. f. of hydrogen per barrel of feed.

6

The hydrogen gas which enters reaction zone 7 is derived, wholly or partially, from the recycle stream in line 15 and the make-up stream in line 16. In the figure, the hydrogen-containing stream is shown as entering a reactor 7 by merely passing through line 8 and line 6. It will be noted that it may be necessary to utilize a suitable heating zone in order to bring the temperature of this stream up to the level desired in zone 7. It may be feasible in some instances to introduce the hydrogen stream within the feed stream as the latter flows into heating zone 5. In this way the hydrogen and liquid feed would be simultaneously mixed and heated before entering zone 7.

The presulfiding phase of the process is generally conducted in mixed phase, the proportion of the phases depending upon the character of the feed stock itself. The reaction in zone 7 may be conducted employing an up-flow type of operation as well as a downflow type of operation. It is generally preferred that a downflow type of operation be used.

The presulfiding operation is carried out until the amount of sulfur contained in the liquid product from the zone contains an equilibrium amount of sulfur. It has been observed that the sulfur content of the liquid product at the very start of the presulfiding step will generally be very little less than the amount of sulfur in the liquid feed. Within a very short period of time, however, the sulfur content of the liquid product rapidly falls off. Within a period of about eight to thirty-six hours it has been further observed that the sulfur content of the liquid product reaches a substantially constant value. In other words, the degree of desulfurization of the presulfiding feed reaches an equilibrium value. At this point the catalyst is activated and generally contains about 15 to 65% of the sulfur that it would have acquired if all of the cobalt molybdate in the catalyst had been converted to cobalt thiomolybdate. It will be noted that a presulfiding time of about twenty-four hours will generally suffice for the activation of most cobalt molybdate catalysts and for most types of hydrocarbon stocks. It will further be noted that the sulfur content of the liquid product during this phase of the process may be accurately and closely followed by periodic convention chemical analyses performed on samples of the liquid product.

During the presulfiding step of the process the product stream that flows forth from reaction zone 7 passes through line 9, where it may be cooled by means of a suitable device such as the cooling coil 10. Having been cooled, the product stream then enters a separation zone 11, in which gaseous components, including hydrogen, light hydrocarbons and hydrogen sulfide are separated from the liquid product. The gases leave zone 11 through line 12. The liquid product, on the other hand, leaves zone 11 through line 13, whence it may be disposed of as desired.

The hydrogen-containing gas stream in line 12 is wholly or partially recycled by means of lines 15, 8, and 6 to the reaction zone 7. A portion of this gas stream may be withdrawn from the system through line 14 as desired. Similarly, additional hydrogen in the form of make-up hydrogen may be introduced within the system by means of line 16. The manner of withdrawing gas through line 14 and adding gas through line 16 has been considered at length earlier in this description.

The recycle gas stream in line 15 is preferably passed through a scrubbing zone 16, where it is contacted with a solid or liquid material which is adapted to remove sulfur-containing compounds principally hydrogen sulfide from the stream. Materials suitable for use in zone 16 include liquid contacting agents such as caustic soda, triethanolamine, diethanolamine, other alkali solutions, and solid adsorbents such as bauxite, silica gel, activated char, and the like. The manner of operating such a scrubbing zone is well known to persons skilled in the

art, and a detailed description of the operation of this zone is not considered to be critically necessary for a presentation of the present invention.

Once the catalyst within reaction zone 7 has become presulfided and preactivated to the desired degree, the conditions within this zone are changed to the conditions required and described earlier herein for hydrodesulfurization purposes. The temperature within zone 7 is increased by at least 50° F. and preferably 100° F. It is particularly desired that the operating temperature within zone 7 during the hydrodesulfurization step be maintained at a value within the range of 650°–800° F. and especially about 700°–750° F. The pressure within zone 7 should be maintained at a value within the range of between 150 and 1000 p. s. i. g., and the liquid feed rate is preferably maintained at a value within the range of about 0.5–3.0 v./hr./v. A hydrogen flow rate through zone 7 of between 1000 and 4000 s. c. f. per barrel of feed should be observed. A hydrogen consumption rate of the order of about 75 to 700 s. c. f. per barrel will generally prevail. These and other conditions to be observed within zone 7 have also been considered at length earlier in this description. It will be noted that the severity of the reaction within zone 7 increases with both increased temperature and pressure. Increased pressures avoid cracking and catalyst deactivation which may result from increased temperatures, but the latter method is much less costly. Accordingly, the choice of the precise temperature and pressure to be employed in any given case will depend upon the character of the feedstock, the equipment available, the degree of desulfurization desired, etc.

The product stream from zone 7, as in the presulfiding step, passes through line 9, cooler 10, separation zone 11 and scrubbing zone 16 in precisely the same manner as previously described in connection with the presulfiding procedure. In other words, the hydrogen-containing gas component of the product stream is separated from the liquid component, is scrubbed relatively free of sulfur compounds, and is recycled to the reaction zone. A portion of the recycle gas stream is removed from the system and make-up hydrogen is added to the system in order to maintain the critical concentration of hydrogen desired within the recycle stream.

The product stream from the desulfurization step is withdrawn through line 13 and is passed to any desired additional refining step, blending operation, storage tank, etc. It will be noted that the product in line 13 is particularly suited for use as a diesel fuel or as a feed stock to catalytic cracking operations.

Regeneration of the catalyst may be required periodically, depending largely upon the nature of the feed stock. Some feed stocks such as straight run distillate petroleum fractions cause very little or no degradation of the catalyst; the catalyst may be employed in such cases for months without regeneration. Frequently no regeneration is required. Feed stocks derived from cracking or coking operations, on the other hand, degrade a catalyst much more rapidly; and more frequent regenerations are therefore necessary. Even in these instances, however, the catalyst need almost never be regenerated more than once a week. But whenever a catalyst is regenerated, it is generally desirable to reactivate the catalyst by the present presulfiding procedure before it is returned to hydrodesulfurization service.

The present invention may be better understood by reference to the following examples, which serve to illustrate a specific example of the invention and the best mode contemplated of carrying out the same.

Example I

A conventional cobalt molybdate on alumina catalyst in the form of 5/14 mesh particles was charged to a suitable reaction zone. The catalyst was then contacted in a conventional manner with a West Texas heavy straight

run gas oil at 700° F., 400 p. s. i. g., 1 v./hr./v., and 1500 s. c. f./barrel hydrogen rate. The gas oil feed had a gravity of 24.4° API and possessed a boiling range of from about 390°–1050° F. The gas oil was further characterized by a sulfur content of about 2.1 weight per cent sulfur and a viscosity of about 42 SSU at 210° F.

Throughout the processing operation the degree of desulfurization of the feed stock was determined by means of chemical analyses which were performed on the liquid product which had been stripped with nitrogen for removal of dissolved hydrogen sulfide. During the first two days of operation the sulfur in the liquid product gradually decreased, probably because the catalyst was in the process of becoming sulfided. For the next eight days of operation the sulfur content of the product averaged about 0.155 weight per cent sulfur compared to the value of 2.1 weight per cent for the feed.

Example II

Another portion of the feed stock and another portion of the catalyst of Example I were then subjected to a processing sequence in accordance with the requirements of the present invention. In this sequence the fresh catalyst was charged to the reactor and was initially contacted with the gas oil for a period of 24 hours at a temperature of 600° F. At this point the product stream had a sulfur content of the order of about 1 wt. percent. All other operating conditions were maintained the same as were observed in Example I.

At the end of 24 hours the temperature of the reaction zone was increased to 700° F. Following a second 24-hour period, sulfur analyses for the next eight days indicated that the degree of sulfur in the liquid product now averaged only 0.130 weight per cent sulfur. In other words, the processing sequence which was followed in Example II was demonstrated to provide results that are markedly improved over the processing procedure which is presently conventional in the hydrodesulfurization art.

The foregoing examples are intended to illustrate a specific application of the present invention. It will be understood that the present invention is not to be limited, however, in its scope to these particular examples. Thus, it will be noted that the presulfiding and hydrodesulfurizing reactions of the present invention may be employed using fixed beds, moving beds, or fluidized beds of catalyst. Such modifications of the invention are considered to be well within the ability of persons skilled in the art to realize.

It will further be appreciated that the catalyst may be employed in structural forms other than the form presented in the examples. Furthermore, the catalyst may contain a small amount of silica to stabilize it in a manner known to those skilled in the art.

It will further be realized that the present invention may be used in combination with other petroleum refining processes such as catalytic processes including hydroforming, platforming, cracking and the like. It is particularly contemplated that gas oil fractions derived from the present desulfurization process be employed as feed stocks to catalytic cracking operations.

Piping, pumps, valves, instruments, heat exchangers, furnaces, and other equipment conventionally employed to operate hydrodesulfurization processes may be utilized without departing from the spirit or scope of the present invention. Similarly, the hydrogen utilized in the present process may be derived from any of the production sources that are contemplated for use in connection with hydrodesulfurization processes.

What is claimed is:

1. A method of hydrodesulfurizing a high boiling hydrocarbon mixture employing a cobalt molybdate-type catalyst wherein said mixture contains more than about 1.5 wt. per cent sulfur and boils in excess of about 350° F. which comprises precontacting the mixture with the catalyst for a period of from 8 to 48 hours at about 550°

to 650° F., 200 to 800 p. s. i. g. and about 0.5 to 2.0 v./hr./v. and with about 500 to 3000 s. c. f. of hydrogen per barrel of mixture, thereafter desulfurizing subsequent portions of said mixture with the precontacted catalyst at about 650° to 800° F., 100 to 1000 p. s. i. g. and about 0.25 to 5 volumes of liquid mixture per hour per volume of catalyst and with 500 to 5000 s. c. f. of hydrogen per barrel of mixture, the temperature of the precontacting step being maintained at least 50° F. below the temperature of the desulfurization step.

2. A method as defined in claim 1 in which the temperature of the precontacting step is at least 100° F. below the temperature of the desulfurization step.

3. A method as defined in claim 1 in which the temperature in the precontacting step is maintained at about 600° F.

4. A method employing a cobalt molybdate-type catalyst for hydrosulfurizing a petroleum fraction containing from 2 to 6 wt. per cent sulfur and boiling within the range from about 350° F. to 1050° F. which comprises presulfiding the catalyst by initially contacting it with 0.5 to 2.0 vols. of fraction per hour per volume of catalyst and with 500 to 3000 s. c. f. of hydrogen per barrel of fraction at 550° to 650° F. and 200 to 800 p. s. i. g. for 8 to 36 hours, thereafter desulfurizing subsequent portions of the fraction by contacting it with the presulfided catalyst and with 500 to 5000 s. c. f. of hydro-

gen per barrel of fraction at 650 to 800° F. and 100 to 1000 p. s. i. g., the liquid feed rate in the desulfurization step being from 0.25 to 5 volumes of fraction per hour per volume of catalyst, maintaining the temperature of the presulfiding step at least 50° F. below the temperature of the desulfurizing step.

5. A method as defined in claim 4 in which the temperature of the presulfiding step is maintained at least 100° F. below the temperature of the desulfurizing step.

6. A method as defined in claim 4 in which the presulfiding step is carried out at about 600° F., 400 p. s. i. g. and with a fraction feed rate of about 1 volume of liquid fraction per hour per volume of catalyst and a hydrogen rate between 500 and 3000 s. c. f. per barrel of fraction.

7. A method as defined in claim 6 in which the hydrogen rate is maintained between 1000 and 2000 s. c. f. per barrel of fraction.

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