

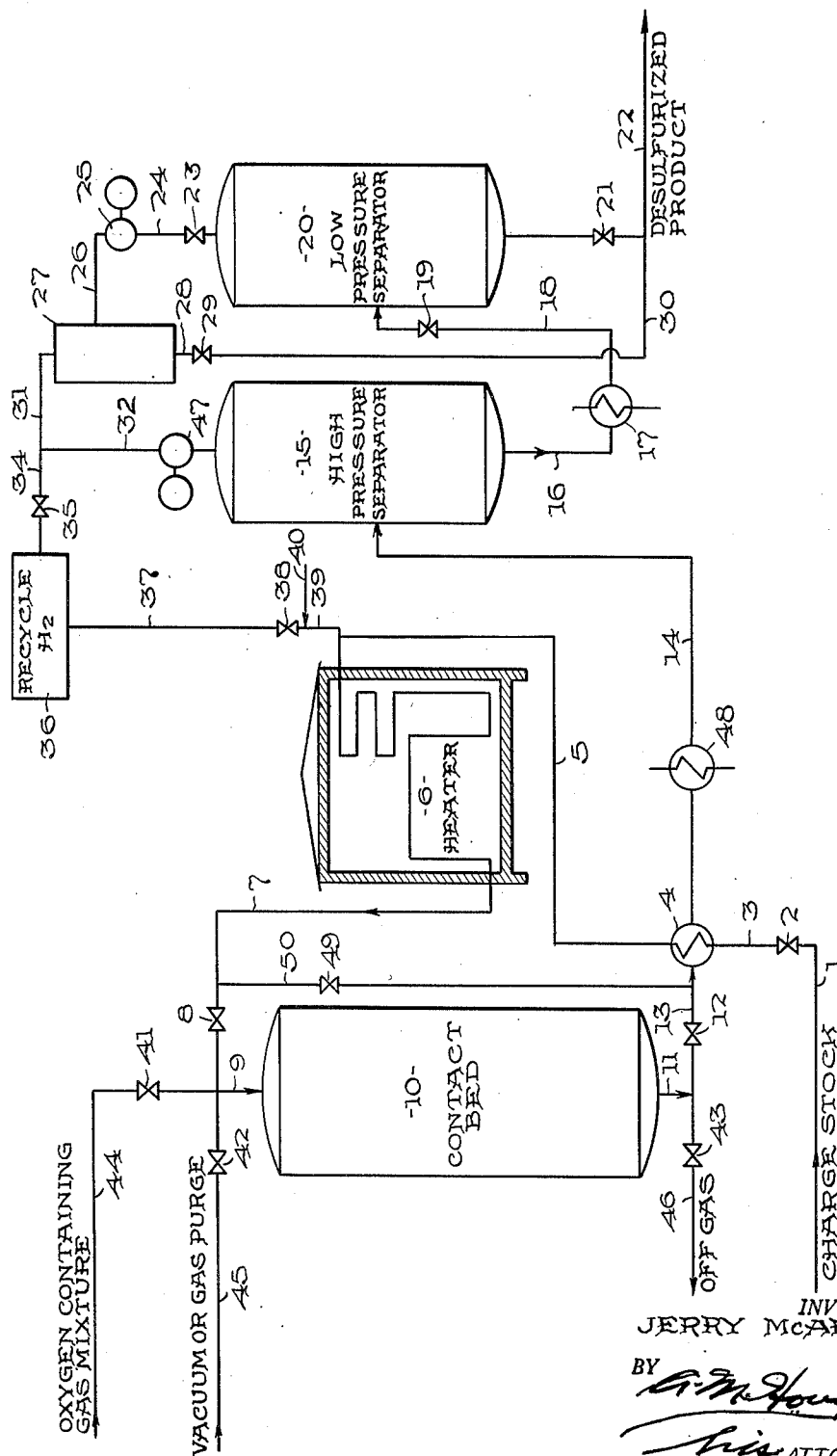
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DESULFURIZATION OF A HYDROCARBON OIL

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DESULFURIZATION OF A HYDROCARBON OIL

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This invention relates to an improved process for desulfurizing a hydrocarbon oil and in particular relates to improvements in hydrodesulfurization of a hydrocarbon oil by treating vapors thereof in the presence of a metal or metal oxide to form a sulfide followed by periodic regeneration of the metal or metal oxide.

It has been known previously that it is possible to remove sulfur compounds from a hydrocarbon oil by contacting vapors thereof with hydrogen and a contact having the sulfur-absorbing properties of metals of the iron group. The sulfur absorbing contact is converted into an iron group metal sulfide and carbonaceous material is simultaneously deposited thereon in relatively large amounts. The contact is periodically regenerated by burning off the carbonaceous material and converting the iron group metal sulfide into the iron group metal oxide by oxidation. In certain cases the metal oxide then is reduced but in any case the oxide or the reduced metal is again contacted with the sulfur-containing hydrocarbon vapors.

Considerable difficulty has been encountered during the regeneration of the desulfurization contact. The carbonaceous material is deposited on the contact in unusually large amounts and is of a tarry or asphaltic nature which tends to plug the catalyst bed. Under certain conditions, particularly with heavy stocks, this plugging is so serious that regeneration by combustion is precluded simply because the contact bed is plugged so badly that it is impossible to force sufficient regenerating medium through it. Furthermore, as indicated above, it is necessary not only to remove the carbonaceous material but also to convert the iron group metal sulfide back into the oxide. This requires additional amounts of regenerating medium and further complicates the problem. It has also been found that the hydrodesulfurization contacts tend to become agglomerated and it is believed that this agglomeration is associated with the formation of a low melting iron group metal sub-sulfide which tends to fuse and stick the catalyst pellets together. This regeneration, therefore, involves acute problems not encountered with the regeneration of conventional cracking and like contacts.

An object of my invention is to provide an improved hydrodesulfurization process in which the foregoing difficulties are reduced or eliminated. Another object is to provide a hydrodesulfurization process in which the regeneration of the contact is simplified. Another object is to

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provide an improved hydrodesulfurization process utilizing an iron group metal or metal oxide as the absorbent for the sulfur wherein the regeneration of the iron group metal can be accomplished in a relatively short period of time and with a smaller amount of regenerating medium. Another object is to reduce the amount of hydrocarbons lost during hydrodesulfurization. Other objects will appear hereinafter.

These and other objects are accomplished by my invention which includes terminating the hydrodesulfurization of the hydrocarbon when a substantial amount of carbonaceous material and sulfide has been formed on the sulfur-absorbing contact, treating this contact with hydrogen at an elevated temperature and pressure to convert a substantial amount of the carbonaceous material into hydrocarbon vapors, then subjecting the contact to a regeneration treatment to remove most of the remaining carbonaceous material and to reconvert the sulfur absorbing material into its original form and again treating vapors of the hydrocarbon oil with hydrogen in the presence of the regenerated contact.

In the following examples and description I have set forth several of the preferred embodiments of my invention but it is to be understood that these are given by way of illustration and not in limitation thereof.

In the accompanying drawing I have illustrated apparatus in which my improved process may be carried out. Referring to the drawing, hydrocarbon oil to be desulfurized flows through conduit 1, valve 2, line 3, heat exchanger 4, line 5 and heater 6, where it is heated to reaction temperature after mixing with hydrogen. This hydrogen is introduced into heater 6 through line 39 and is a mixture of recycle hydrogen flowing through valve 38 plus make-up hydrogen introduced through conduit 40. This mixture of hydrogen and hydrocarbon vapors flows through heater 6, line 7, valve 8, and conduit 9 into reactor 10, which contains a bed of sulfur-absorbing metal or metal oxide on a porous carrier. The mixture of the hydrogen and hydrocarbon vapor passes into intimate contact with the sulfur-absorbing material in reactor 10 and the sulfur contained in the hydrocarbon oil is removed by absorption to form iron group metal sulfide.

The effluent from reactor 10, i.e. the hydrogen and the desulfurized hydrocarbon vapors then pass through conduit 11, valve 12, conduit 13 and heat exchanger 4, which serves to preheat

the charge stock, and then through cooler 48, in which liquid hydrocarbons are condensed. The effluent then flows through line 14 into high pressure separator 15 where the liquid hydrocarbons are separated from the hydrogen gas. This liquid product passes through line 16, heat exchanger 17, line 18 and valve 19 into low pressure separator 20. The liquid desulfurized product from low pressure separator 20 is withdrawn through valve 21 and conduit 22. In low pressure separator 20 a small amount of hydrogen absorbed in the liquid product is evolved and is pumped by pump 25 through valve 23, lines 24 and 26, into separator 27. In separator 27 small amounts of entrained hydrocarbon liquids are separated and are withdrawn by way of line 28, valve 29, and line 30, which joins the desulfurized product line 22. The gases from separator 27 are withdrawn through line 31 and are combined with the high pressure hydrogen separated in high pressure separator 15, which hydrogen is withdrawn by way of line 32 and recycle hydrogen compressor 47. This combined hydrogen then flows through line 34 and valve 35 into recycle hydrogen reservoir 36. This recycle hydrogen is withdrawn as needed through line 37 and passes through valve 38 and line 39, into heater 6. Make-up hydrogen is added continuously or intermittently through line 40. Small amounts of recycle hydrogen are periodically bled from reservoir 36 to enable this addition of fresh or make-up hydrogen through line 40, thus maintaining the purity of the recycle hydrogen stream at any desired level.

After the hydrocarbon vapors and hydrogen have passed through the contact bed in reactor 10 for a sufficient period of time, the contact pellets will become coated with carbonaceous material and the iron group metal or metal oxide thereon will become converted to a substantial extent into the iron group metal sulfide. It is desirable to regenerate the contact when this deposit of carbonaceous material undesirably affects the passage of the reactants through the chamber or when sufficient iron group metal sulfide has been formed to reduce the sulfur-absorbing capacity of the contact. This reduction in sulfur-absorbing capacity usually takes place when about 30 to 60 per cent metal sulfide has been formed. It can be determined when substantial amounts of H_2S appear in the effluent. At this stage it is desirable to interrupt the process and to regenerate the contact in reactor 10.

During the on-stream period valves 41, 42 and 43 in lines 44, 45 and 46, respectively, remain closed. At the completion of the on-stream period valve 2 is closed and hydrogen is permitted to flow through furnace 6 and lines 7 and 9 into contact 10. This heated hydrogen tends to convert the carbonaceous deposit to a substantial extent into hydrocarbon vapors. These vapors pass with the unreacted hydrogen through conduit 11, valve 12, line 13, conduit 14, heat exchanger 4, and cooler 48, into the high pressure separator where the hydrogen is separated from the condensed hydrocarbons and is passed to recycle hydrogen reservoir 36. The liquid hydrocarbons are separated in separator 20 and are recovered as a useful product. The recycle hydrogen is thus used to remove a large part of the carbonaceous material from the contact, recovering it as useful hydrocarbon without any additional equipment.

After a substantial amount of carbonaceous material has been removed, the contact bed in

reactor 10 is subjected to a treatment which will reconvert the contact into substantially its original form. This is accomplished by first opening valve 49, which allows the hydrogen stream to by-pass the reactor through line 50, and then closing valves 8 and 12. The pressure in reactor 10 is released by opening valve 43 and purge gas such as steam is passed through the reactor by introduction through conduit 45 and valve 42 and removal through valve 43 and conduit 46. Alternatively a vacuum may be used instead of a purge gas to remove the residual hydrogen from the reactor.

Regeneration gas, such as a mixture of air or oxygen and steam, is then introduced into the reactor, after closing valve 42, through conduit 44 and valve 41. This oxygen containing mixture removes the carbonaceous material on the contact by combustion and the products of combustion pass out of the reactor by way of conduit 11, valve 43 and conduit 46. The oxygen also converts the iron group metal sulfide into iron group metal oxide with formation of sulfur dioxide. After removal of most of the remaining carbonaceous material has taken place and the iron group metal sulfide has been substantially reconverted into the oxide, the flow of oxygen containing gas mixture is terminated by closing valve 41. A purge gas such as steam is then introduced through conduit 45 by way of valve 42 in order to remove any remaining combustion gases, and valves 42 and 43 are then closed. In the event that a reduced metal contact is to be used valves 8 and 12 are opened and valve 49 is closed and recycle hydrogen gas is introduced into reactor 10 until most of the metal oxide has been converted into the metal by reduction. The on-stream reaction then is carried out as previously described by opening valve 2 and introducing the hydrocarbon charge. If a reduced contact is not to be used the hydrogen and hydrocarbon are both charged to the contact as initially described without the reduction to convert the oxide to the metal.

It will be obvious to one skilled in the petroleum art that many modifications can be made in the foregoing without departing from the spirit or scope of my invention. Thus it is usually desirable to have more than one reactor so that one contact mass may be on-stream while the contact mass in another reactor or reactors is undergoing treatment to remove carbonaceous material and/or to remove residual carbonaceous material and sulfides by combustion. The effluent from this second reactor then would be returned to the on-stream reactor as recycle hydrogen. While recycle hydrogen for the preliminary removal of the carbonaceous material is advantageous, hydrogen from any source, such as the fresh or make-up hydrogen, may be used. Also the recovery of the hydrocarbons formed during the destructive hydrogenation is advantageously carried out in the apparatus used to recover the desulfurized hydrocarbon during the on-stream reaction. However any other method of recovery may be used. My invention is applicable to desulfurization processes utilizing a fluidized fixed bed or a fluidized circulating contact as well as to a fixed bed contact as illustrated.

The contacts employed in my process may be any iron group metal or metal oxide (i.e. iron, cobalt or nickel) deposited on a porous carrier. Nickeliferous contacts are preferred and especially nickel oxide. Free metals of the iron group such as elemental nickel cause cracking of the

hydrocarbon to gas and excessive carbon formation. As disclosed in copending applications Serial Nos. 699,671 and 699,672, filed September 27, 1946, in the names of Horne and Junge, now U. S. Patents 2,516,876 and 2,516,877 respectively, superior results are obtained if the contact contains a substantial amount of the oxide of the metal. In its preferred form my invention involves the use of a contact containing a large amount of an iron group metal oxide, especially nickel oxide. However, the invention is equally applicable to the use of a contact containing the iron group metal entirely or substantially entirely in the metal form. While the less desirable properties of the metal contact are not overcome nevertheless my invention results in an improvement with both types of contacts. These contacts are made by impregnating the porous carrier with a solution of a soluble salt such as a nitrate of the metal followed by calcining (and reduction if a metal is to be used). A relatively large amount of the metal or metal oxide should be deposited on the porous carrier and preferably about 2 to 30 per cent. Examples of suitable porous carriers are silica gel, activated alumina, Magnesol, Porocel, Alfrax, kieselguhr and silica-alumina cracking catalysts of conventional types, prepared synthetically or by acid treatment of natural clays.

The temperature for the desulfurization treatment preferably should be between about 600° and 950° F. A temperature of 600° to about 800° F. is preferred for low boiling hydrocarbons such as gasoline and a temperature of about 750° to 950° is best for heavy hydrocarbons, such as reduced and topped crudes and crude petroleum. The invention is of particular value in connection with such heavy hydrocarbons since they tend to deposit abnormal amounts of tars and carbon during the desulfurization treatment. Hydrogen in amounts of at least 100 and preferably above 4000 cubic feet per barrel of oil should be used. Pressures between about 100 and 1000 p. s. i. g. are preferred. The space velocity preferably should vary from 0.2 to 6.0 volumes of liquid hydrocarbon per volume of catalyst.

The hydrogen treatment to remove the carbonaceous material should be carried out at a temperature and pressure sufficient to convert the carbonaceous material into hydrocarbon vapor. Thus conditions usually used for destructive hydrogenation are satisfactory. In general, the higher the temperature and pressure and the longer the time the greater will be the reduction of the carbonaceous deposit. The iron group metal, oxide and/or sulfide acts as a hydrogenation catalyst during this part of the process and assists in the destructive hydrogenation of the tar, asphalt, etc. into useful hydrocarbon vapors. The temperature is preferably at least as high as the temperature used during the desulfurization step. However any temperature between 600° and 1400° F. can be used. The temperature should not be high enough to cause sintering of the contact. A pressure of between about 100 and 2000 p. s. i. g. is desirable. The total amount of hydrogen varies from 5 to 5000 standard cubic feet per cubic feet of contact.

Example: Whole desalted West Texas crude having a gravity of 34.6° A. P. I. and a sulfur content of 1.51 per cent was vaporized and the vapors together with hydrogen were passed through a reactor filed with pellets of a contact containing 21.9 per cent nickel oxide deposited on a silica-alumina cracking catalyst (Harshaw

nickel-625). The operating conditions were as follows: reactor inlet temperature 841° F.; average reactor pressure 520 p. s. i. g.; liquid hourly space velocity 0.99 volume of oil per hour per volume of contact; total gas rate 5547 s. c. e./bbl. of charge; hydrogen gas purity 84.9 per cent H₂; process period length 4 hours. After each process period of 4 hours the oil flow was stopped and the hydrogen gas circulation continued for 30 minutes at the same rate, temperature, and pressure as during the processing period. The reactor was then depressured and purged with steam. The contact was then regenerated by passing steam through the reactor at a rate of 1088 pounds per hour preheated to a reactor inlet temperature of 850° F. Air was added to the steam at an average rate of 2773 s. c. f. h. so controlled that the maximum catalyst temperature approached but did not exceed approximately 1200° F. An average regeneration time of 3.33 hours was required to complete the regeneration during the 6 cycles comprising this test run. The hydrogen gas and oil vapors then were again passed through the reactor, thus starting another cycle. Six cycles were completed in this manner. The total liquid product obtained in the 6 cycles had a gravity of 39.8° A. P. I. and a sulfur content of 0.50 per cent. These inspections were in good agreement with those of previous test runs at the same conditions. To afford a basis of comparison, test runs were made under the same conditions except that the hydrogen treatment prior to regeneration was not used. It was found that the hydrogen treatment in accordance with the invention reduced the regeneration steam requirement 872 pounds per barrel charge to 459 pounds per barrel charge. The yield of liquid product (C₅ and heavier) was increased by the hydrogen treatment prior to regeneration from 90.2 weight per cent to 92.2 weight per cent while the production of purge oil (oil recovered from the reactor upon depressuring the reactor and steam purging) was decreased from 1.05 weight per cent to 0.04 per cent by weight.

An outstanding advantage of the invention is that it reduces the amount of carbonaceous material which must be removed during the regeneration by combustion. This reduces the regeneration requirements such as the time, reactants and size of equipment necessary for regeneration. In addition, relatively large amounts of useful hydrocarbons are recovered which would otherwise be lost. This is due not only to the conversion of the carbonaceous material but also to the recovery of the hydrocarbons deposited thereon which are normally at least partially lost in the purge gases.

I claim:

1. The process for removing sulfur compounds from a hydrocarbon oil which comprises treating a hydrocarbon oil which contains sulfur compounds while substantially in vapor form with hydrogen in the presence of a contact comprising a porous carrier on which is deposited a metalliferous material selected from the group consisting of iron group metals and their oxides at a temperature between about 600° and 950° F. and a pressure between about 100 and 1000 p. s. i. g. terminating said treatment when a substantial amount of carbonaceous material and sulfide has been formed on the contact, treating the contact with hydrogen at a pressure between about 100 and 2000 p. s. i. g., at a temperature between about 950° and 1400° F. whereby

a substantial amount of the carbonaceous material on the contact is converted into hydrocarbon vapors without substantial conversion of the sulfide material on the contact into hydrogen sulfide, subjecting the contact to a combustion regeneration treatment to remove most of the remaining carbonaceous material and to convert said metalliferous material into its original form and again treating a hydrocarbon oil which contains sulfur compounds while substantially in vapor phase with hydrogen in the presence of the regenerated contact under the conditions specified above.

2. The process for removing sulfur compounds from a hydrocarbon oil which comprises treating a hydrocarbon oil which contains sulfur compounds while substantially in vapor form with hydrogen in the presence of a contact comprising a porous carrier on which is deposited a metalliferous material selected from the group consisting of iron group metals and their oxides at a temperature between about 600° and 950° F. and a pressure between about 100 and 1000 p. s. i. g. terminating said treatment when a substantial amount of carbonaceous material and sulfide has been formed on the contact, treating the contact with hydrogen at a pressure between about 100 and 2000 p. s. i. g., at a temperature between about 950° and 1400° F. whereby a substantial amount of the carbonaceous material on the contact is converted into hydrocarbon vapors without substantial conversion of the sulfide material on the contact into hydrogen sulfide, adding these converted hydrocarbon vapors to the desulfurized hydrocarbon product, subjecting the contact to a combustion regeneration treatment to remove most of the remaining carbonaceous material and to convert said metalliferous material into its original form and again treating a hydrocarbon oil which contains sulfur compounds while substantially in vapor phase with hydrogen in the presence of the regenerated contact under the conditions specified above.

3. The process for removing sulfur compounds from a hydrocarbon oil which contains sulfur compounds and which is selected from the group consisting of crude, reduced crude and topped crude, which comprises treating said hydrocarbon oil substantially in vapor form with hydrogen in the presence of a contact comprising a porous carrier on which is deposited a metalliferous material selected from the group consisting of iron group metals and their oxides at a temperature between about 750° and 950° F. and a pressure between about 100 and 1000 p. s. i. g. terminating said treatment when a substantial amount of carbonaceous material and sulfide has been formed on the contact, treating the contact with hydrogen at a pressure between about 100 and 2000 p. s. i. g., at a temperature between about 950° and 1400° F. whereby a substantial amount

of the carbonaceous material on the contact is converted into hydrocarbon vapors without substantial conversion of the sulfide material on the contact into hydrogen sulfide, subjecting the contact to a combustion regeneration treatment to remove most of the remaining carbonaceous material and to convert said metalliferous material into its original form and again treating said hydrocarbon oil substantially in vapor phase with hydrogen in the presence of the regenerated contact under the conditions specified above.

4. The process for removing sulfur compounds from a hydrocarbon oil which contains sulfur compounds and which is selected from the group consisting of crude, reduced crude and topped crude, which comprises treating said hydrocarbon oil substantially in vapor form with hydrogen in the presence of a contact comprising a porous carrier on which is deposited a metalliferous material selected from the group consisting of iron group metals and their oxides at a temperature between about 750° and 950° F. and a pressure between about 100 and 1000 p. s. i. g. terminating said treatment when a substantial amount of carbonaceous material and sulfide has been formed on the contact, treating the contact with recycle hydrogen at a pressure between about 100 and 2000 p. s. i. g., at a temperature between about 950° and 1400° F., whereby a substantial amount of the carbonaceous material on the contact is converted into hydrocarbon vapors without substantial conversion of the sulfide material on the contact into hydrogen sulfide, adding these converted hydrocarbon vapors to the desulfurized hydrocarbon product, subjecting the contact to a combustion regeneration treatment to remove most of the remaining carbonaceous material and to convert said metalliferous material into its original form and again treating said hydrocarbon oil substantially in vapor phase with hydrogen in the presence of the regenerated contact under the conditions specified above.

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