

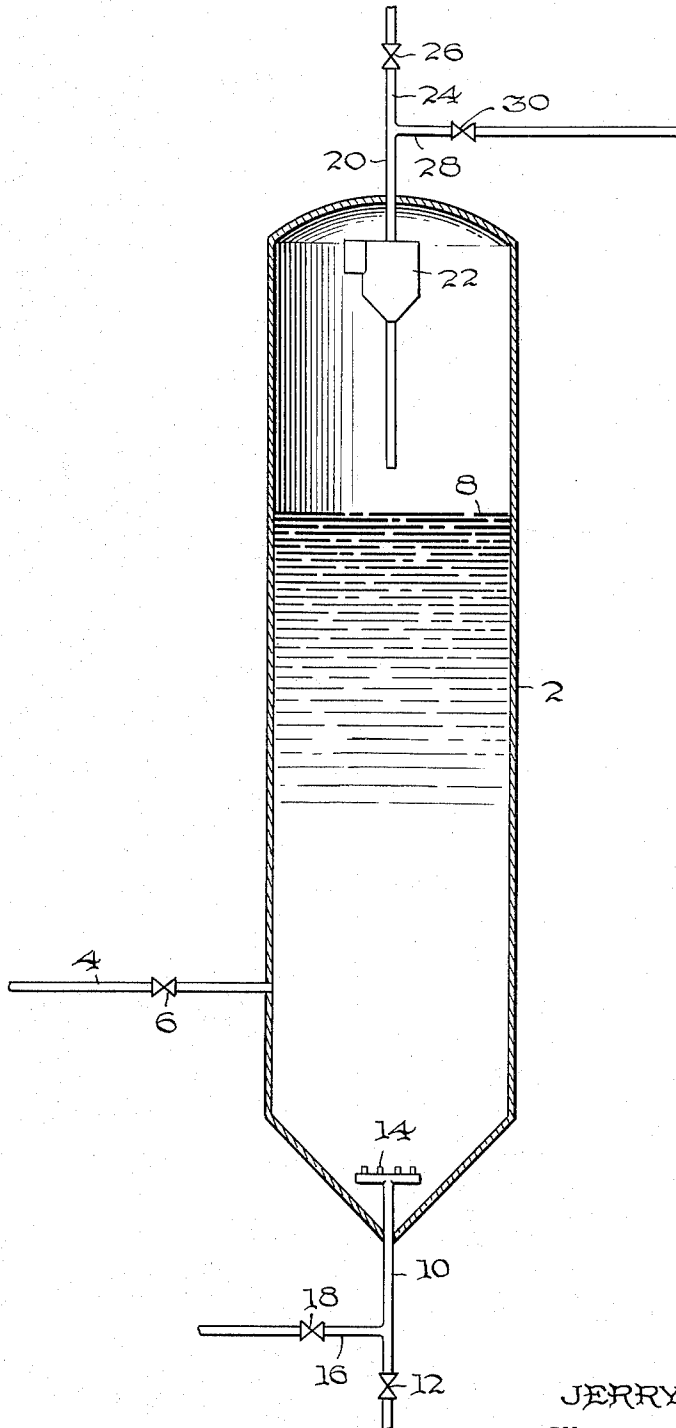
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HYDRODESULFURIZING HYDROCARBONS

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HYDRODESULFURIZING HYDROCARBONS

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This invention relates to improved procedure for hydrodesulfurizing high boiling hydrocarbons which contain asphaltic materials and for simultaneous conversion into lower boiling hydrocarbons.

It is known that heavy hydrocarbons containing asphaltic materials can be simultaneously desulfurized and converted into lighter hydrocarbons by treating them while in liquid phase with a hydrogenation catalyst and hydrogen at elevated temperature and at high pressures. The pressures employed have usually been above 3000 pounds and at such high pressures continuous conversion is accomplished with ease. However, the process is uneconomical because of high hydrogen consumption at these high pressures and because of high cost of equipment. The use of lower or moderate pressures such as about 250 to 2000 p. s. i. g. has been investigated in recent years but such lower pressures give rise to deposition of large amounts of carbon on the catalyst. Such practice results in lower yields and regeneration difficulties. This problem is especially acute in connection with the treatment of heavy hydrocarbons containing substantial amounts of asphaltic materials.

This invention has for its object to provide improved procedure for desulfurizing and converting heavy hydrocarbons which contain substantial amounts of asphaltic materials. Another object is to provide an improved procedure for converting heavy hydrocarbons containing substantial amounts of asphaltic materials at moderate pressures, i. e., 250 to 2000 p. s. i. g. in which procedure coke deposition is minimized. Another object is to provide moderate pressure hydrodesulfurization procedure for treatment of asphaltic heavy hydrocarbons in liquid phase in which regeneration of the catalyst is simplified. A still further object is to provide liquid phase hydrodesulfurization procedure giving improved yields when utilizing low grade charge stocks containing substantial amounts of asphaltic materials. Other objects will appear hereinafter.

These and other objects of my invention are accomplished by establishing a body of a heavy hydrocarbon liquid which contains a substantial amount of asphaltic material in which are suspended particles of hydrogenation catalyst, the amount of hydrogenation catalyst in the heavy hydrocarbon being at least 1.25 parts by weight of hydrogenation catalyst to one part by weight of asphaltic material. Hydrogen is passed through this body of heavy hydrocarbon liquid at a temperature between about 650° and 925° F. The hydrogen pressure is maintained between about 250 and 2000 p. s. i. g. during the treatment. The operation is continued until the body of heavy hydrocarbon oil has been substantially vaporized. These vapors are removed during the operation so that dry particles of catalyst are obtained in the final stage of the operation. The operation is then terminated and the dry catalyst particles are regenerated by suspending them in an oxygen containing gas to form a fluidized dense bed of catalyst. After the catalyst particles have been regenerated they are combined with an additional amount

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of liquid heavy hydrocarbon oil to form the liquid suspension specified above and the suspension is treated as described above.

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 they are given for the purpose of illustration and not in limitation thereof.

Referring to the drawing, which is a diagrammatic elevation, partly in section, of apparatus in which my invention can be carried out, numeral 2 designates a reactor which is designed to operate at a pressure of 250 to 2000 p. s. i. g. at a temperature between 650 and 925° F. Numeral 4 designates a conduit provided with valve 6 through which charge stock, comprising hydrogenation catalyst in solid particulate form suspended in an asphalt containing oil are introduced into reactor 2 to form a body of liquid, the upper surface of which is indicated by the numeral 8. Numeral 10 designates a conduit connected to the base of reactor 2 which conduit is provided with valve 12 and distributor head 14. Hydrogen under pressure is introduced into reactor 2 through valve 12, conduit 10 and distributor head 14. Numeral 16 designates a conduit which is connected to conduit 10 and is provided with valve 18. This conduit 16 is employed to introduce regeneration gas into reactor 2. Numeral 20 designates an effluent conduit at the top of the reactor 2 which is connected to the exhaust side of cyclone separator 22. Conduit 20 connects to conduit 24 provided with valve 26 and with conduit 28 provided with valve 30.

In operation a slurry of the heavy hydrocarbon oil and hydrogenation catalyst is introduced into reactor 2 through conduit 4. Valve 6 is then closed. This introduced charge can be preheated before introduction if desired but it preferably should be below cracking temperature, i. e., below about 650° F. Heated hydrogen is then introduced through conduit 10 and valve 12 so that a pressure in the desired range is established in reactor 2. During this operation valves 18 and 26 are closed and valve 30 is open.

This introduced hydrogen passes upwardly through the body of liquid 8 into cyclone separator 22 where solid particles of catalyst which may be entrained in the final stages of the operation are separated and returned to the reactor. The hydrogen and vapors of hydrocarbon then pass out through conduits 20 and 28 and valve 30 to a hydrocarbon and hydrogen separation system (not shown). The hydrogen which is separated is recycled through conduit 10. As the hydrogen passes up through the body of hydrocarbon liquid, desulfurization and hydrocracking or destructive hydrogenation takes place. The more volatile components pass out through conduit 20 as described.

The reaction is moderately exothermic. However heat must be supplied to initiate the reaction and to increase the temperature after the reaction has started. This additional heat preferably is supplied by hot hydrogen. It can also be supplied by reheating middle fractions of the product and returning them to the reactor. These fractions have very low asphalt content and recycling them would not upset the asphalt to catalyst ratio. The temperature during this operation is maintained between about 650° and 950° F. and preferably between about 700° and 850° F. It is preferable to gradually increase the temperature as explained below and this can be accomplished by gradually increasing the temperature of the hydrogen or hydrocarbon recycle.

This operation is continued until the hydrocarbon has been substantially entirely converted and removed overhead as vapors. In this manner all of the components are hydrocracked with minimum formation of carbonaceous material on the catalyst. As a result in the final

stage of the operation substantially all of the hydrocarbon is removed and there is a minimum amount of coke on the catalyst so that the catalyst is in a dry condition and can be readily fluidized. As a matter of fact, in the final stage of the operation the catalyst is fluidized, i. e., suspended in the hydrogen instead of in the liquid hydrocarbon and a considerable amount of the coke-like components deposited thereon are removed by the efficient contact with hydrogen while in this fluidized condition. This is an important advantage of my invention. The ratio of hydrogen to oil will vary from about 1000 to 50,000 cu. ft. per barrel of oil.

The catalyst is then regenerated. This is accomplished by closing valves 12 and 30 and opening valves 18 and 26. Steam is first introduced to flush the reactor and then a mixture of air and steam, or other oxidizing gaseous mixture, is introduced through conduit 16. The mixture of air and steam passes upwardly through the body of catalyst in reactor 2, causing it to become fluidized. The amount of steam and air introduced is such as to form a dense fluidized bed of catalyst therein as in conventional regeneration of fluidized catalysts. Combustion gases pass out through cyclone separator 22, conduit 20 and valve 26. Entrained catalyst is returned to the reactor by cyclone separator 22. When the carbonaceous deposit on the catalyst has been removed by combustion to the desired extent, the reactor is flushed with steam to remove combustion gases and to cool the catalyst to reaction temperature. Valves 18 and 26 are then closed and valve 6 is opened and a fresh charge of heavy hydrocarbon oil is introduced. Valve 6 is then closed and valves 12 and 30 opened and the mixture of hydrocarbon oil and regenerated catalyst in reactor 2 is then converted as previously described.

It will be apparent from the foregoing that a slurry of catalyst and hydrocarbon charge is introduced through conduit 4 only during the initial operation and that the operation from that point on requires only introduction of heavy hydrocarbon since the regenerated catalyst remains in the reactor. However, this mode of operation is not necessary and the catalyst can be removed and regenerated in an external regenerator and returned with the charge in slurry form or in any other manner. The removal of the catalyst in such an alternative procedure would be a simple operation since the catalyst is dry and flows in much the same manner as a fluid when it is suspended in a gas or vapor.

It is necessary to utilize at least 1.25 parts by weight of hydrogenation catalyst to one part of asphaltic material contained in the hydrocarbon. This is an important requirement since employment of charged hydrocarbon containing smaller amounts of catalyst per unit weight of asphalt will cause excessive coke deposit on the catalyst and this will prevent fluidization in the final stage of the process as well as during the subsequent regeneration.

It is advantageous, but not necessary, to gradually raise the temperature of the hydrocarbon during the process. This results in conversion of each component in the charge at the optimum conversion temperature for each component. If the temperature is increased rapidly it will be found that some of the components in the charge will give rise to increased amounts of coke before they are converted into volatile hydrocarbons. The temperature can be increased at a uniform rate or the temperature may be increased in stages. This gradual increase of temperature is not of importance until a cracking temperature range is reached. Reasonably high through-puts are to be desired and therefore the temperature should be raised as rapidly as possible without causing sufficient coking to prevent fluidization of the catalyst at the end of the operation. For practical reasons the temperature should be raised fast enough to complete the conversion in less than about 4 hours. It will be understood that this gradual increase in temperature constitutes a preferred embodiment of my invention and I contemplate utilizing a single

temperature or heating to a given temperature if this is desired. However, such expedients are less satisfactory and will give rise to greater coke deposition on the catalyst and in such event this will reduce the yields correspondingly.

Any heavy sulfur-containing hydrocarbon which contains a substantial amount of asphalt may be treated in accordance with my invention. Examples of such charge stocks are crudes, especially those low in gravity, topped crudes, reduced crudes and tars obtained from thermal cracking of heavy charge stocks, etc. Any hydrogenation catalyst may be employed. However, I prefer to utilize a sulfur resistant type of hydrogenation catalyst deposited upon a porous carrier. For instance molybdenum or tungsten oxides or sulfides may be used alone or combined with iron group metal oxides or sulfides such as those of nickel or cobalt. These catalysts are preferably deposited upon a porous carrier such as alumina, silica-alumina cracking catalyst, silica stabilized alumina, etc.

EXAMPLE

A reactor similar to that illustrated in the drawing was charged with 323 parts by weight of a hydrogenation catalyst in particle form and comprising 5 per cent nickel tungstate deposited on alumina. The catalyst had been previously regenerated and was still at an elevated temperature of approximately 150° F. Three hundred twenty-three parts by weight of a Baxterville crude, having the characteristics given in Table I, were then introduced into the reactor. The reactor was pressured with hydrogen to 900 p. s. i. g. The suspension in the reactor was then heated at a gradually increasing rate while passing hydrogen therethrough. After 1.33 hours the temperature was 400° F.; after 2.33 hours 661° F.; after 3.33 hours 861° F. and 889° F. after 4.33 hours. During this gradual heating a mixture of hydrogen and hydrocarbon vapors was removed as overhead product. The cycle was complete after 5.6 hours when the quantity of hydrocarbon vapor leaving the reactor was very small. The ratio of hydrogen to hydrocarbon was 31,000 cu. ft. per barrel of Baxterville crude. The inspection data on the product is given in Table II. The catalyst remaining in the reactor was approximately 300 pounds. It was withdrawn from the reactor and was found to be free of lumps, passed completely through 40 mesh and was in a dry and very good condition. Regeneration of this catalyst while in fluidized condition was readily accomplished.

Table I

INSPECTION DATA OF BAXTERVILLE CRUDE

Gravity, °API	15.8
Sp. Gr.	0.9609
Viscosity 100° F. centistokes	608
SUS.	2811
Color	Black (8¼ dilute)
Four point	Below 0° F.
Flash (P. M.) ° F.	120
Carbon residue percent on material above 590° F.	16.4
Sulfur percent (bomb)	2.64
Salt lbs./1000 bbl.	15
Distillation:	
Percent at 392° F.	2.0
Percent at 500° F.	8.0
Percent at 590° F.	18.0
Recovery percent	18.0
Residue percent	81.0
Loss percent	1.0
* Asphalt percent	36.8

* Determined by propane deasphalting at a pressure of 400 p. s. i. g.; a temperature of 150° F. and a propane to crude oil ratio of 4 to 1. Any method giving comparable results may be used.

Table II

Inspection data—total product:

Gravity, ° API	29.1
Sulfur (wt. percent)	.57
Distillation:	
Percent at 392° F.	11.00
Percent at 500° F.	29.00
Percent at 590° F.	49.00
Percent carbon residue on 590° bottoms	.67

What I claim is:

1. In a process for hydrodesulfurizing a heavy hydrocarbon which contains a substantial amount of asphaltic material which comprises establishing a liquid body of the heavy hydrocarbon in which are suspended particles of a hydrogenation catalyst, the amount of catalyst in the heavy hydrocarbon being at least 1.25 parts by weight of hydrogenation catalyst to one part by weight of asphaltic material, heating this body to a temperature between about 650° and 925° F. while under a pressure between about 250 and 2000 p. s. i. g. and while passing hydrogen through the liquid suspension, removing hydrocarbon vapors and hydrogen, continuing the process until dry discrete hydrogenation catalyst particles are obtained, terminating the treatment, regenerating the discrete catalyst particles by suspending them in an oxygen containing gas to form a fluidized dense phase of catalyst particles, combining the regenerated catalyst particles with an additional amount of heavy hydrocarbon which contains asphaltic material to form a suspension having the catalyst-asphalt content specified above and subjecting this suspension to the treatment with hydrogen as specified above.

2. In a process for hydrodesulfurizing a heavy hydrocarbon which contains a substantial amount of asphaltic material which comprises establishing a liquid body of the heavy hydrocarbon in which are suspended particles of a hydrogenation catalyst, the amount of catalyst in the heavy hydrocarbon being at least 1.25 parts by weight of hydrogenation catalyst to one part by weight of asphaltic material, heating this body to a temperature between about 650° and 925° F. while under a pressure between about 250 and 2000 p. s. i. g. and while passing hydrogen through the suspension, removing hydrocarbon vapors and hydrogen, continuing the process until dry discrete hydrogenation catalyst particles are obtained and a substantial amount of carbonaceous deposit on the catalyst has been removed by the hydrogen, terminating the treatment, regenerating the discrete catalyst particles by suspending them in an oxidizing gas comprising air to form a fluidized dense phase of catalyst particles, combining the regenerated catalyst particles with an additional amount of heavy hydrocarbon which contains asphaltic material to form a suspension having the catalyst-asphalt content specified above and subjecting this suspension to the treatment with hydrogen as specified above.

3. In a process for hydrodesulfurizing a crude petroleum which contains a substantial amount of asphaltic material which comprises establishing a liquid body of crude petroleum in which are suspended particles of a hydrogenation catalyst, the amount of catalyst in the crude petroleum being at least 1.25 parts by weight of hydrogenation catalyst to one part by weight of asphaltic material, heating this body to a temperature between about 700° and 850° F. while under a pressure between about 250 and 2000 p. s. i. g. and while passing hydrogen through the suspension, removing hydrocarbon vapors and hydrogen, continuing the process until dry discrete hydrogenation catalyst particles are obtained, terminating the treatment, regenerating the discrete catalyst particles by suspending them in an oxidizing gas comprising air to form a fluidized dense phase of catalyst particles, combining the regenerated catalyst particles with an additional amount of crude petroleum which contains asphaltic material to form a suspension having the catalyst-asphalt content specified above and subjecting this suspension to the treatment with hydrogen as specified above.

4. In a process for hydrodesulfurizing a crude petroleum which contains a substantial amount of asphaltic material which comprises establishing a liquid body of the crude petroleum in which are suspended particles of a hydrogenation catalyst, the amount of catalyst in the crude petroleum being at least 1.25 parts by weight of hydrogenation catalyst to one part by weight of asphaltic material, gradually heating this body from a temperature of about 650° to a temperature not in excess of about 925° F. while under a pressure between about 250 and 2000 p. s. i. g. and while passing hydrogen through the suspension, removing hydrocarbon vapors and hydrogen, continuing the process until dry discrete hydrogenation catalyst particles are obtained, terminating the treatment, regenerating the discrete catalyst particles by suspending them in a mixture of steam and air to form a fluidized dense phase of catalyst particles, combining the regenerated catalyst particles with an additional amount of crude petroleum which contains asphaltic material to form a suspension having the catalyst-asphalt content specified above and subjecting this suspension to the treatment with hydrogen as specified above.

5. In a process for hydrodesulfurizing a heavy hydrocarbon which contains a substantial amount of asphaltic material which comprises establishing a liquid body of heavy hydrocarbon which is preheated to a temperature below about 650° F. and in which are suspended particles of a hydrogenation catalyst, the amount of catalyst in the heavy hydrocarbon being at least 1.25 parts by weight of hydrogenation catalyst to one part by weight of asphaltic material, passing hydrogen through the suspension under a pressure of between about 250 and 2000 p. s. i. g., removing hydrocarbon vapors and hydrogen, gradually increasing the temperature within the range 650°–925° F. until dry discrete hydrogenation catalyst particles are obtained, terminating the treatment, regenerating the discrete catalyst particles by suspending them in an oxygen containing gas to form a fluidized dense phase of catalyst particles, combining the regenerated catalyst particles with an additional amount of heavy hydrocarbon which contains asphaltic material to form a suspension having the catalyst-asphalt content specified above and subjecting this suspension to the treatment with hydrogen as specified above.

6. In a process for hydrodesulfurizing a heavy hydrocarbon which contains a substantial amount of asphaltic material which comprises preheating the hydrocarbon to a temperature below about 650° F., suspending a hydrogenation catalyst in the preheated hydrocarbon to form a liquid body of hydrocarbon in which are suspended particles of a hydrogenation catalyst, the amount of catalyst in the heavy hydrocarbon being at least 1.25 parts by weight of hydrogenation catalyst to one part by weight of asphaltic material, passing hydrogen through the suspension under a pressure between about 250 and 2000 p. s. i. g., removing hydrocarbon vapors and hydrogen, gradually increasing the temperature within the range 700°–850° F., until dry discrete hydrogenation catalyst particles are obtained, terminating the treatment, regenerating the discrete catalyst particles by suspending them in an oxygen containing gas to form a fluidized dense phase of catalyst particles, combining the regenerated catalyst particles with an additional amount of heavy hydrocarbon which contains asphaltic material to form a suspension having the catalyst-asphalt content specified above and subjecting this suspension to the treatment with hydrogen as specified above.

7. In a process for hydrodesulfurizing a crude petroleum which contains a substantial amount of asphaltic material which comprises establishing a liquid body of the crude petroleum in which are suspended particles of a hydrogenation catalyst, the amount of catalyst in the crude petroleum being at least 1.25 parts by weight of hydrogenation catalyst to one part by weight of asphaltic material, heating this body to a temperature be-

tween about 700° and 850° F. while under a pressure between about 250 and 2000 p. s. i. g. by passing heated recycle hydrogen through the suspension, removing hydrocarbon vapors and hydrogen, continuing the process until dry discrete hydrogenation catalyst particles are obtained, terminating the treatment, regenerating the discrete catalyst particles by suspending them in a mixture of steam and air to form a fluidized dense phase of catalyst particles, combining the regenerated catalyst particles with an additional amount of crude petroleum which contains asphaltic material to form a suspension

having the catalyst-asphalt content specified above and subjecting this suspension to the treatment with hydrogen as specified above.

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