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HYDRODESULFURIZATION PROCESS

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This invention relates to improvements in the desulfurization of hydrocarbons utilizing a nickel-containing desulfurization contact or catalytic agent.

Contact and catalytic agents containing free or reduced nickel may be used for desulfurizing petroleum oil either by absorbing sulfur from the oil through the formation of sulfur compounds of nickel, or by catalyzing the conversion of the sulfur in the oil into hydrogen sulfide which is washed from the product. See for instance Cornell application Serial No. 92,436, filed May 10, 1949, now U. S. Patent 2,614,066, McAfee application Serial No. 63,157, filed December 2, 1948, now abandoned, and U. S. Patents 2,070,295, 2,298,347, and 2,406,200 which refer to the employment of metallic nickel as a desulfurization contact or catalyst. In such usage the nickel progressively loses desulfurizing activity because of contamination by sulfur and/or carbonaceous materials. It is therefore necessary periodically to regenerate and reactivate the nickeliferous agent by oxidizing to remove sulfur and carbonaceous contaminants and by then reducing with hydrogen gas to reconvert a substantial portion of the nickel therein to the free metallic state. This reduction is an exothermic reaction and when uncontrolled may cause such excessive temperature rise as to damage or destroy the catalytic or contact agent through sintering of the nickel or disintegration and/or deactivation of the porous carrier on which the nickel commonly is supported. A further problem is that after completion of the uncontrolled reduction the contact is not at the proper temperature for the on-stream phase of the desulfurization process and must be either heated or cooled with resulting expense and time loss to attain the required temperature for continuation of the desulfurization process.

This invention has for an object to provide a method for desulfurizing hydrocarbons wherein the temperature is controlled during the reactivation of an oxidized nickeliferous contact or catalyst.

A further object is to provide a method for desulfurizing hydrocarbons in which the nickeliferous contact or catalytic agent used in the process is reactivated by a controlled reduction whereby damage to the agent due to excessive temperature during reduction is avoided.

A still further object is to provide a process for desulfurizing hydrocarbons in which the nickeliferous contact or catalytic agent used in the process is reactivated by a controlled reduction, whereby the pressure of the system and the temperature of the agent at the end of the reduction are substantially equal to the pressure and temperature required for the on-stream phase of the desulfurization process employing the reduced contact or catalytic agent.

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These and other objects are accomplished by the following invention in which a sulfur containing hydrocarbon in vapor phase is desulfurized by contacting it at elevated pressure and at a temperature between about 820 and 875° F. with hydrogen and a nickeliferous agent comprising between about 15 and 25 per cent nickel calculated as oxide deposited on a porous support, a substantial portion of said nickel being in the metallic form, terminating the contact of vapor, hydrogen, and nickeliferous agent when regeneration is required, depressuring, regenerating the nickeliferous agent by combustion, at least partially reducing the regenerated nickeliferous agent by treating said agent at an initial reduction temperature between about 750 and 800° F. and at a pressure approximately equal to the reaction pressure with a mixture of steam and reducing gas, the mol ratio of steam to reducing gas being between about 4.5:1 and 28:1 and being such as to give said agent a final temperature after reduction at least about 40° F. higher than the initial reduction temperature but between about 820 and 875° F., terminating the flow of steam and immediately contacting vapors of the sulfur containing hydrocarbon with hydrogen and the regenerated and at least partially reduced nickeliferous agent while still at approximately said final temperature and reaction pressure.

The nickeliferous agent herein referred to includes the sulfur absorbent contact type which desulfurizes by combining with sulfur in the oil; the catalytic type which catalyzes conversion of sulfur in the oil into hydrogen sulfide which may be washed from the product; and the type which initially in the process is sulfur absorbent but becomes catalytic after being sulfurized in the course of the desulfurization process. These nickeliferous agents may be prepared by impregnating a porous support material with a solution of a nickel salt such as nickel nitrate, drying and calcining to form nickel oxide on the support, and at least partially reducing the oxidized mass by treatment with a reducing gas at elevated temperature. The agents suitable for use in my process contain between about 15 and 25 per cent by weight nickel calculated as oxide based on the total weight of the support and agent. The agents may contain nickel in the form of free metallic nickel, nickel oxide, nickel sulfate, or nickel sulfide but will contain at least a substantial amount of free nickel at the beginning of the desulfurization process. Among the suitable porous support materials are, alumina, kieselguhr, silica gel, aluminum silicates, bauxite, Alfrax, Magnesol, Porocel, or silica-alumina carriers, especially of the cracking catalyst type whether active or inactive for cracking.

My process may be employed to desulfurize

various sulfur-containing hydrocarbons such as gasoline, naphtha, gas oil etc. but is particularly adapted for desulfurizing sulfur-containing heavy petroleum oils such as total crude, reduced crude, and topped crude. To desulfurize an oil of this type by my process, the sulfur bearing oil in the vapor phase (which term includes conditions in which a small amount of unvaporized material may be present as a mist or in partially condensed form) and in admixture with hydrogen is contacted with a nickeliferous agent of the type above described, comprising between about 15 and 25 per cent by weight of nickel calculated as oxide deposited on a porous support under the following preferred conditions: temperature between about 820° and 875° F., pressure between about 300 and 1000 p. s. i.; liquid hourly space velocity of the oil, between about 0.2 and 6.0 volumes of oil per volume of nickeliferous agent; hydrogen concentration between about 1000 and 10,000 or more cubic feet per barrel of oil. During this process sulfur is removed from the oil either by combining with the nickel in the agent or by forming hydrogen sulfide which is removed from the product by caustic washing or other suitable method. In either case, the nickeliferous agent progressively loses its desulfurizing activity during the process because of the formation of sulfur and/or carbonaceous contaminants on the agent.

When the deposition of the contaminants has seriously lowered the desulfurizing activity of the nickeliferous agent, the contacting with oil vapors is terminated, the system is depressured and the agent is regenerated by contacting with an oxygen-containing regeneration gas at an elevated temperature to burn off carbonaceous deposits and at least partially remove sulfur combined with nickel thus forming nickel oxide. Following the regeneration the agent is reactivated by treatment with a reducing gas at approximately the pressure desired in the reaction phase or on-stream phase to reconvert a substantial portion of the nickel to the metallic state. This reduction reactivation must be initiated at a temperature between 750° and 800° F. If an initial temperature below about 750° F. is used the reduction does not proceed satisfactorily and if a temperature above about 800° F. is used initially it is very difficult and uneconomical to restrict the final temperature to the desired on-stream temperature. I therefore control the temperature of the preceding oxidation treatment so that the nickeliferous agent at the end of the oxidation treatment will be at the proper temperature for initiating the reduction reactivation. Such control of the regeneration temperature may be accomplished by regulating the amount of oxygen in the regeneration gas and/or the temperature of the diluent gas which is usually steam.

During regeneration by oxidation of a body of catalytic or contact material of the type employed in my process, a burning zone progresses through the body of material from one end to the other. Unless steps are taken to avoid it, in the final stages of the regeneration the first oxidized portion of the material will have cooled and will be at a lower temperature than the subsequently oxidized portions. This may be avoided and a uniform temperature throughout the catalytic or contact material may be obtained by preheating the regeneration gas to a suitable temperature (e. g. between about 750° and 800° F.) to give the desired initial temperature for reduction throughout the body of regenerated material.

Immediately prior to the reduction phase of my

process the nickeliferous agent is in the oxidized state, at a temperature between about 750° and 800° F., and comprises a complex mixture of nickel oxide and a porous support material plus nickel sulfate, small amounts of nickel sulfide and carbonaceous materials, and perhaps other impurities. It should be emphasized the invention is unique to nickeliferous contact agents of the type described which are employed in a desulfurization process and further, to such contacts which are regenerated by combustion. This is because the unusual nature of the contact causes it to behave in a unique manner as compared with normally analogous metallic oxides.

The reduction reaction of this complex mixture with hydrogen or other reducing gases is highly exothermic. Therefore, if the reduction is effected with no temperature control, an excessive temperature rise will occur in the agent which will cause sintering of the nickel or disintegration of the porous support, or both, and at the end of the reduction treatment the temperature will be so high as to require cooling of the agent before introducing sulfur-containing oil for the ensuing desulfurization cycle.

To allow the final temperature of the bed to exceed the maximum allowable limit of about 875° F. is disadvantageous not only because of the danger of damaging the nickeliferous agent and/or the support but because of the high coke and gas production and rapid deactivation of the contact agent at temperatures exceeding this limit during the subsequent processing period or on-stream phase. To attempt to avoid the latter difficulty by cooling the reduced nickel agent after the maximum temperature has been exceeded is entirely unsatisfactory, since this involves depressuring, flushing with, for example, steam and repressuring with hydrogen. Under this procedure the length of the off-stream period (non-productive time) is increased substantially, substantial quantities of hydrogen are wasted, a more complex control is necessary, and the risk of deactivating the agent and/or support with the cooling gas is created.

In view of the facts discussed above, it will be obvious that an essential feature of my invention is the control of the initial temperature at which the reduction is started and control of the temperature during reduction utilizing certain amounts of steam mixed with hydrogen to produce a reduction final temperature of the nickeliferous agent between about 820° and 875° F. This temperature range is suitable for the desulfurization phase of the process, and thus the contacting of the sulfur-containing hydrocarbon vapors with the regenerated and reactivated nickeliferous agent may be resumed while the agent is still at approximately its final reduction temperature.

As an illustration of my invention, the following example shows a typical operating cycle with conditions for the on-stream period, the regeneration period and the reduction period.

EXAMPLE

The catalyst used was prepared by impregnation of dried 6-10 mesh silica gel with an aqueous nickel nitrate solution followed by drying at 260° F. and subsequent calcining at 800° F. to convert the nickel nitrate to nickel oxide.

This sequence of impregnation, drying and calcining was repeated twice, so that the final catalyst contained 18 per cent nickel oxide and 82 per cent silica gel. The catalyst was then partially reduced by treating at 800° F. with hydro-

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gen and steam. The catalyst was then ready for the reaction period. After a reaction period the reactor was depressured, and the catalyst was regenerated by combustion. At the end of the regeneration period, in which the final temperature was suitably regulated, reduction of the catalyst was carried out with a mixture of steam and hydrogen of desired mol ratio at elevated pressure. At the end of this step, steam flow was terminated and oil cut into the reactor for a processing period. The conditions for the regeneration, reduction, and processing periods are given in the table below.

Table 1

Regeneration step:

Pressure, p. s. i. g.	100
Reactor Temperature, °F.—	
Inlet	750
Outlet	1150
Steam rate, lbs./lb. oxidized catalyst....	13
Air rate, SCF/lb. oxidized catalyst.....	29
Time, min.	120

Reduction step:

Pressure, p. s. i. g.	500
Reactor temperature, °F.—	
Average	825
Maximum	850
Steam rate, lbs./lb. oxidized catalyst....	1.50
H ₂ rate, SCF/lb. oxidized catalyst.....	1.20
Steam-hydrogen mol ratio.....	26.4:1
Reduction time, min.	15

Operating step:

Temperature, °F.	850
Pressure, p. s. i. g.	500
Space velocity, vol./vol.	1
Throughout, vol./vol. Cat.	4
H ₂ circulation, CF/bbl.	2000

Product data are shown in Table 2 immediately below:

Table 2

Charge and Production Inspection:

	Charge (Kuwait Crude)	Product
Gravity, °API.....	31.5	41.4
Gravity Increase (Prod.-Chg.).....		9.9
Sulfur, Wt. Percent B. S.	2.40	0.76
Desulfurization, Percent.....		68
Distillation, Percent at:		
392° F.	25	37
500° F.	36	57
590° F.	45	73
Carbon Residue, 590° F., Bottoms.....	7.98	0.47
Liquid Recovery, Vol. Percent.....		95.6
Dry Gas, cu. ft./B.		149
Carbon, Wt. Percent of Charge.....		3.3

The data presented in Table 1 illustrate an operative example of the desulfurization process utilizing the feature of controlled reduction of a supported nickeliferous agent containing 15–25 per cent nickel calculated as oxide. The data of Table 2 illustrate the benefits obtained by this process, i. e., high degree of upgrading, high degree of desulfurization on low gas and carbon production.

The optimum temperature range for the desulfurization phase of the process as disclosed above is from about 820° F. to 875° F. Below the minimum of about 820° F. the rate of desulfurization is low and sufficient hydrogenation of the oil does not occur, while above the maximum of about 875° F. the rate of desulfurization does not materially improve and a larger, more rapid decom-

position of the oil to carbon and gas is encountered. Thus in reducing the nickeliferous agent by my process I raise the temperature of the agent from its initial temperature of between about 750 and 800° F. to at least about 820° F. and I avoid a final reduction temperature of the agent higher than about 875° F. by diluting the reducing gas with steam.

The amount of steam required varies with the temperature rise to be obtained and the initial temperature, a relatively large amount of steam being required to limit the temperature rise to a small value and a relatively smaller amount of steam being required for a greater rise in temperature. The largest possible temperature rise that would be permitted in my process is from 750° F. to 875° F. or a rise of 125° F. I have discovered that this particular temperature rise of 125° F. can be obtained by employing in the reduction a steam-hydrogen ratio of 4.5 mols of steam per mol of hydrogen. To limit the temperature rise to less than 125° F. a larger amount of steam in the steam-hydrogen mixture is required. For example, I have found that a ratio of 28 mols of steam per mol of hydrogen is required to limit the temperature to a 40° F. rise. To limit the temperature rise to any smaller value than 40° F. requires much larger and uneconomical amounts of steam. For example 166 mols of steam per mol of hydrogen is required to limit the temperature rise to 20° F.

Since such large amounts of steam are required to limit the temperature rise to less than 40° F., it is undesirable to operate at a temperature differential of less than 40° F. both from the standpoint of steam economy and the possibility of poor hydrogen efficiency if the reduction gas is too dilute. Thus, my invention involves the use of a steam-hydrogen ratio which will produce a final temperature after reduction at least about 40° F. higher than the initial reduction temperature but between about 820° F. and 875° F. If a temperature rise intermediate between 40 and 125° F. is required, a steam-hydrogen mol ratio proportionately intermediate between 28:1 and 4.5:1 is employed.

Since it is desirable to maintain a uniform catalyst bed temperature during the reduction step, the reduction gases may be preheated so that the inlet temperature of these gases approaches the desired initial temperature for the reaction step.

Thus, after regenerating the nickeliferous agent by oxidation under conditions which give a temperature of 750 to 800° F. for the oxidized agent, I select the proper steam-hydrogen ratio which will raise the agent temperature during reduction at least 40° F. from a point between about 750° and 800° F. to a desired point between about 820° and 875° F. The agent is then contacted with steam and hydrogen in the selected ratio at approximately reaction pressure for a period sufficient to reduce a major portion of the nickeliferous agent and to raise the temperature of the bed to the desired degree, after which I terminate the flow of steam and immediately resume contacting of hydrocarbon vapors with regenerated and reactivated nickeliferous agent without the necessity of first heating or cooling the agent, or repressuring the reactor.

The reducing gas employed in the controlled reduction of my invention may be obtained from different sources. Pure hydrogen from a hydrogen producing plant may be employed but lower purity hydrogen-containing gases such as recycle

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hydrogen from the desulfurization process gases absorbed in the desulfurized product and removed therefrom during subsequent fractionation may be used. Also low molecular weight hydrocarbons such as methane and ethane alone or in admixture with other hydrocarbons or hydrogen may be employed.

What I claim is:

1. The process for sulfurizing a hydrocarbon which comprises contacting vapors of a sulfur-containing hydrocarbon at elevated pressure and at a temperature between about 820° and 875° F. with hydrogen and a nickeliferous agent comprising between about 15 and 25 per cent nickel calculated as oxide deposited upon a porous support, a substantial portion of said nickel being in the metallic form, terminating contact between the vapors, hydrogen, and nickeliferous agent when regeneration is required, depressurizing, regenerating the nickeliferous agent by combustion, at least partially reducing the regenerated nickeliferous agent by treating said agent at an initial reduction temperature between about 750° and 800° F. and at a pressure approximately equal to the reaction pressure with steam and simultaneously treating said agent with a reducing gas, the mol ratio of steam to reducing gas being between about 4.5:1 and 28:1 and being such as to give said agent a final temperature after reduction at least about 40° F. higher than the initial reduction temperature but between about 820° and 875° F., terminating the flow of steam and immediately contacting vapors of the sulfur-containing hydrocarbon with hydrogen and the regenerated and at least partially reduced nickeliferous agent while still at approximately said final temperature and reaction pressure.

2. The process for desulfurizing a hydrocarbon which comprises contacting vapors of a sulfur-containing hydrocarbon at elevated pressure and at a temperature between about 820° and 875° F. with hydrogen and a nickeliferous contact agent comprising between about 15 and 25 per cent nickel calculated as oxide deposited upon a porous support, a substantial portion of said nickel being in the metallic form, terminating contact between the vapors, hydrogen, and nickeliferous contact agent when regeneration is required, depressurizing, regenerating the nickeliferous contact agent by combustion in the presence of an oxygen-containing gas, controlling the regeneration to give said agent a temperature after regeneration of between about 750° and 800° F., at least partially reducing the regenerated nickeliferous contact agent by treating said agent at approximately reaction pressure and while at about this temperature with steam and simultaneously treating said agent with hydrogen, the mol ratio of steam to hydrogen being between about 4.5:1 and 28:1 and being such as to give said agent a final temperature after reduction at least about 40° F. higher than the temperature at the beginning of the reduction treatment but between about 820° and 875° F., terminating the flow of steam and immediately contacting vapors of the sulfur-containing hydrocarbon with hydrogen and the regenerated and at least partially reduced nickeliferous contact agent while still at approximately said final temperature and reaction pressure.

3. The process for desulfurizing heavy hydrocarbons which comprises contacting vapors of a sulfur-containing heavy petroleum oil at elevated

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pressure and at a temperature between about 820° and 875° F. with hydrogen and a nickeliferous contact agent comprising between about 15 and 25 per cent nickel calculated as oxide deposited upon a porous support, a substantial portion of said nickel being in the metallic form, terminating contact between the vapors, hydrogen, and nickeliferous contact agent when regeneration is required, depressurizing, regenerating the nickeliferous contact agent by combustion in the presence of an oxygen-containing gas, controlling the regeneration to give said agent a temperature after regeneration of between about 750° and 800° F., at least partially reducing the regenerated nickeliferous contact agent by treating said agent at approximately reaction pressure and while at about this temperature with steam and simultaneously treating said agent with hydrogen, the mol ratio of steam to hydrogen being between about 4.5:1 and 28:1 and being such as to give said agent a final temperature after reduction at least about 40° F. higher than the temperature at the beginning of the reduction treatment but between about 820° and 875° F., terminating the flow of steam and immediately contacting vapors of the sulfur-containing heavy petroleum oil with hydrogen and the regenerated and at least partially reduced nickeliferous contact agent while still at approximately said final temperature and reaction pressure.

4. The process for desulfurizing a hydrocarbon oil which comprises contacting vapors of a sulfur-containing hydrocarbon oil from the group consisting of total crude, topped crude, and reduced crude at elevated pressure and at a temperature between about 820° and 875° F. with hydrogen and a nickeliferous contact agent comprising between about 15 and 25 per cent nickel calculated as oxide deposited upon a porous support, a substantial portion of said nickel being in the metallic form, terminating contact between the vapors, hydrogen, and nickeliferous contact agent when regeneration is required, depressurizing, regenerating the nickeliferous contact agent by combustion in the presence of an oxygen-containing gas, controlling the regeneration to give said agent a temperature after regeneration of between about 750° and 800° F., at least partially reducing the regenerated nickeliferous contact agent by treating said agent at approximately reaction pressure and while at about this temperature with steam and simultaneously treating said agent with hydrocarbon, the mol ratio of steam to hydrogen being between about 4.5:1 and 28:1 and being such as to give said agent a final temperature after reduction at least about 40° F. higher than the temperature at the beginning of the reduction treatment but between about 820° and 875° F., terminating the flow of steam and immediately contacting vapors of the sulfur-containing hydrocarbon oil with hydrogen and the regenerated and at least partially reduced nickeliferous contact agent while still at approximately said final temperature and reaction pressure.

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