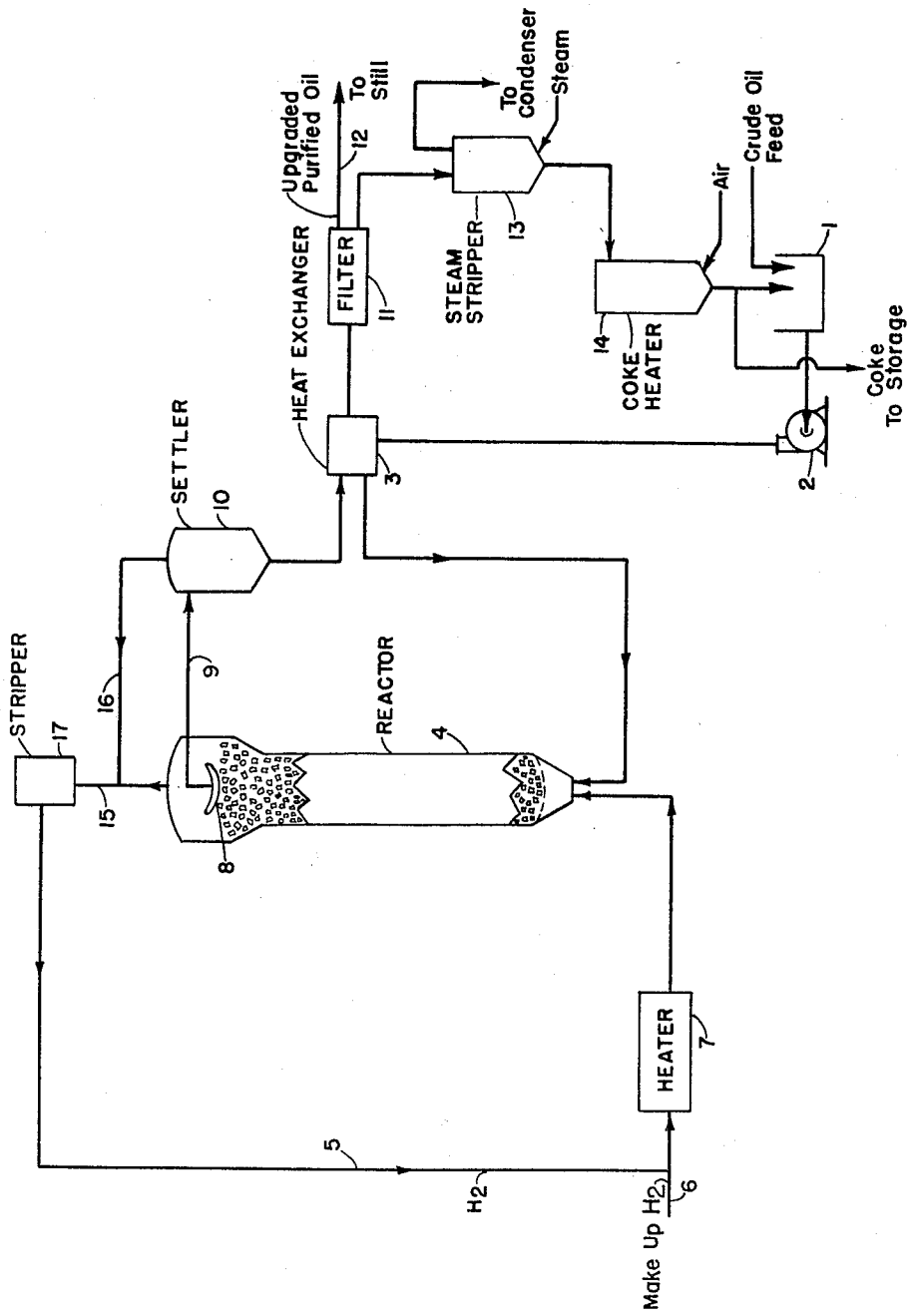
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PROCESS FOR HYDRODESULFURIZING CRUDE OIL IN THE PRESENCE OF COKE

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PROCESS FOR HYDRODESULFURIZING CRUDE OIL IN THE PRESENCE OF COKE

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1 Claim. (Cl. 208—213)

This invention relates to an improved process for effecting the hydrodesulfurization of petroleum fractions. More particularly, it relates to the hydrodesulfurization of topped crude petroleum oil having a boiling point above about 400° F. Still more particularly, the invention concerns itself with the hydrodesulfurization of a topped crude petroleum oil in the presence of added coke.

At present, hydrodesulfurization of petroleum fractions as a hydrorefining technique is rapidly gaining in prominence in the petroleum industry. In general, the treatment involves a procedure whereby a petroleum fraction is selectively hydrogenated in the presence of a sulfur-resistant catalyst so as to both saturate the unsaturates present therein and to convert any sulfur to hydrogen sulfide which is readily removable as a gas.

The advantages of hydrodesulfurization are widely known. However, as practiced, the process exhibits several serious shortcomings. For example, it is not customary to hydrorefine a topped crude oil because of possible tar formation due to use of elevated refining temperatures. Accordingly, the topped crude oil is first distilled fractionally to recover several fractions, which fractions are individually hydrorefined subsequently. The high boiling fractions in the range of about 900° F. can only be hydrorefined successfully under special stringent conditions. As for example, the hydrodesulfurization catalyst is usually specially conditioned prior to use as a hydrogenation catalyst. Alternatively, for economical treatment, the heavy boiling point fraction is pre-treated to remove ash-forming constituents and tar prior to hydrodesulfurization. These techniques are expensive and time consuming, all which seriously limit the wider acceptance of the hydrodesulfurization practice. A method for the direct hydrorefining treatment of a whole topped crude oil which would overcome the shortcomings of the prior practice would be highly desirable, if one such process could be developed.

It has been presently found that the disadvantages of hydrodesulfurization as practiced can be overcome in a simple, straight-forward manner. Unexpectedly, the use of coke as an adjuvant during hydrodesulfurization makes possible for the first time the economical treatment of a whole topped crude petroleum oil fraction of initial boiling point of about 400° F. Under the conditions of normal operation, it has been observed that the catalyst for effecting hydrodesulfurization remains uncontaminated and effective for weeks rather than hours or days under the conditions of normal operation. In addition, the total overall yield of refined oil is substantially higher with respect to recoverable subsequently distilled fractions.

According to the process of the invention, a topped crude petroleum oil fraction having an initial boiling point of about 400° F. is hydrodesulfurized in the presence of coke. It has been found that coke may be generally introduced into the bottom portion of a catalyst-charged reactor along with the topped crude in the form of coke slurried oil containing of from about 0.1% to about 10% solids content by weight. Hydrogen gas is

added concomitantly. The reactor is maintained under elevated temperatures and pressures sufficient to effect hydrodesulfurization. Advantageously, any tar that forms in the reactor is preferentially absorbed on the coke. The desulfurized petroleum fraction which contains suspended coke is tapped as an overflow and fed to a settling zone maintained at a pressure substantially lower than the reactor, whereby gaseous products are eliminated. The residual fraction is then treated to remove coke and to recover an upgraded and readily-distillable petroleum oil of low sulfur content. Resultant coke can then be added to treat incoming topped crude.

It is an advantage and feature of the present invention that less total hydrogen need be used to effect desulfurization. Smaller quantities of hydrogen than commonly consumed can be employed due to the hydrodesulfurization of a whole crude topped petroleum fraction rather than the treatment of individual fractions prepared by initially fractionally distilling crude petroleum oil. As little as 1500 to about 2000 cubic feet per barrel of crude may be used with some 400 to about 1000 cubic feet of fresh feed.

The invention will be further described with reference to the accompanying drawing, the single figure of which is a flow sheet wherein a hydrorefining plant embodying the principal features of the invention is diagrammatically illustrated.

Referring to the drawing, crude oil is fed to a slurry tank **1** to which is added coke to form an oil slurry. The latter is then pumped at **2** to a heat exchanger **3** from which it is introduced into the bottom of the reactor **4**. Hydrogen from two streams **5** and **6** is next heated at **7** and is simultaneously fed to the reaction chamber **4** containing a hydrodesulfurization catalyst. The slurried oil is next tapped from a pan **8** that rests on the catalyst in the upper portion of the reactor and is withdrawn through line **9** to a settler or storage chamber **10** from which such gaseous products as H_2 and H_2S are vented and subsequently treated to recover and reuse hydrogen. The slurried oil is next fed to filter **11** which separates coke from the refined oil. Settler **10** is generally maintained at pressures sufficiently low to permit the flashing of low boiling constituents including hydrogen and hydrocarbons of from 1 to 4 carbon atoms.

As shown in the drawing, it is advantageous to provide a heat exchanger **3** on the line between the settler **10** and the filter **11**. The oil from the storage chamber **10** passes through the heat exchanger **3**. This lowers the temperature of the refined oil because of heat interchange with cooler incoming coke-slurried oil so that it can be filtered on a conventional filter. Otherwise, special heat resistant filters would be necessary. At the same time, the hot petroleum oil serves to supply most of the necessary heat to the incoming slurried crude oil prior to hydrodesulfurization. The refined oil issuing at **12** may be then distilled in a still (not shown).

Solids in the form of coke are withdrawn from the filter and transferred to a steam stripper **13** to both revivify the coke and to recover adhering oil. Superheated steam is introduced into the bottom of the stripper. The superheated steam conditions the coke so that it leaves the coke in a free flowing semi-porous condition. The latter may be discharged to a coke heater **14** maintained at 1050° F.–1100° F. to burn off any adsorbed hydrogen on the coke in the presence of air and to render the coke finely porous. In the latter condition, the porous coke is capable of adsorbing tarry as well as metallic materials present in the oil. A portion of the coke is sent to storage whereas the other portion is slurried with incoming crude feed to form a slurried crude oil feed.

The gaseous products issuing from the reactor **4** and

storage chamber 10 are eliminated through lines 15 and 16, respectively to a stripper 17. The purpose of the stripping operation is to recover hydrogen primarily for purposes of adding the latter through line 5 to the reactor to effect hydrodesulfurization.

While the drawing illustrates the use of a single reactor, it would be apparent to one skilled in the art that two or more hydrorefining reactors in parallel can also be used with advantage.

For a fuller understanding of the nature of the invention, the following specific example is given to illustrate one embodiment which is not intended to be construed as limitative but is to be taken merely as illustrative of the process described above.

Example

In a refinery equipped to process at least 15,000 barrels per day of crude oil, 15,000 barrels per day of West Texas crude oil are initially fractioned to top a fraction boiling below 410° F. It is found that this fraction accounts for about 4500 barrels per day. The remaining 10,500 barrels per day of topped crude are next hydrorefined according to the process of the invention.

The topped crude oil is fed at the rate of 439 bbls./hour to a mixing tank to which is added a porous coke at the rate of from 1000–2000 pounds/hour. Resultant oil slurry is then pumped to and through heat exchangers where it is heated to from about 740° F. to about 800° F. The heated crude is next fed to the bottom portion of a reactor capable of holding 500–800 cubic feet of catalyst at a space velocity of 2.0–2.1 volumes of oil per hour per volume of catalyst. The catalyst employed consists of 3% cobalt oxide and 15% molybdenum oxide on alumina in the form of 3/16 inch x 3/16 inch pellets. The average temperature of the reactor is 800° F. and the average pressure is 600 p.s.i. Hydrogen is also fed at the rate of 1500–2000 cubic feet per hour to a preheater maintained at 1000–1300° F. and then enters the bottom portion of the reactor. The temperature of the hydrogen and the slurried crude oil is controlled so as to maintain the temperature in the reactor at from about 720° F. to 920° F.

The refined oil is then tapped off the upper portion of the reactor, more particularly from a pan so shaped that as the oil leaves the catalyst its velocity will be maintained to prevent settling of the coke onto the catalyst.

The so-treated oil withdrawn from the reactor is next fed to a storage tank maintained at an average pressure of 100 p.s.i. to remove gaseous products which are stripped to recover hydrogen. Residual oil is then filtered to recover about 423 gallons per hour of a refined oil. The latter is then fractionally distilled. A fraction which distills below 410° F. contains about 0.04% S and is recovered to yields of about 1950 bbls./day. Above 410° F. but below 670° F., the fraction yields 5400 bbls./day but this fraction contains a higher sulfur value, namely, 0.09% S. In the fraction distilling within the range of 670° F.–950° F., a yield of 2100 bbls./day having a 0.31% S content is obtained, whereas some 750 bbls./day having 0.51% S is recovered at a boiling point of 950° F. and heavier. The coke recovered is about 900 pounds per hour. However, coke from the filter is usually transferred to a steam stripper to remove adhering oil. The latter treatment leaves the coke in a free flowing semi-porous form. Porous coke is found to be a suitable adsorbent for the tarry matter formed during refining in the reactor. It also is capable of adsorbing heavy metals so as to yield a gas oil that is a better stock for catalyst cracking.

In the event that the topped crude oil is not hydrodesulfurized by the process described supra, there is recovered several fractions with attendant high sulfur values. In distilling the crude topped before treatment, it is found that there is but a small amount of a fraction boiling below 410° F., but at boiling points between 410° F. and 670° F., 4200 barrels showing a 0.91% S analysis are recovered at a boiling point of 670° F. to 950° F., 2500 barrels of 1.20% S are recovered; and above 950° F., 3600 barrels containing suspended coke and showing 1.68% S are obtained.

It is a feature and advantage of the present invention that any commercially-available sulfactive or hydrodesulfurization catalyst may be used to remove sulfur from the crude topped oil. It has been found that hydrogenation catalysts, for example cobalt molybdenum, nickel sulfide, molybdenum sulfide, tungsten sulfide and the like are not inactivated rapidly by sulfur, the sulfur being removed as hydrogen sulfide. Among the commercial catalysts, a preferred catalyst is cobalt molybdenum on alumina composed of from 2–5% cobalt oxide by weight and 10–20% molybdenum oxide by weight on alumina.

It is a further advantage of the invention that the activity of the catalysts persisted for at least about 13 days without regeneration or revivifying the same. Where the invention is not practiced as set forth, the catalysts are inactivated in seventy (70) hours or less.

The temperature and pressure reactor conditions may be varied over a wide range. For most crude oils, the temperature within the reactor is initially maintained at about 750° F. but is gradually increased to 840° F. as the activity of the catalyst lessens. The reactor, however, can be operated as high as about 900° F. but at temperatures substantially above 840° F., the rate of coke formation becomes too excessive for convenient and practical operation. At the temperatures indicated, the pressure can be varied from about 200 to about 900 p.s.i. At pressures below about 450 p.s.i., large amounts of coke are formed. In general, a good practice is to operate the reactor at a pressure range of from about 550 to about 850 p.s.i. for best hydrorefining results.

Although the process of the invention has been described with reference to a particular petroleum fraction known as topped crude oil of initial boiling point of about 410° F., it is nonetheless within the purview and contemplation of this invention that the described process is equally applicable to any petroleum fraction. However, it is preferred to treat a whole topped crude oil of initial boiling point of about 400° F. since such treatment leads to desirable economical refining procedure.

I claim:

In the hydrorefining of a whole topped crude petroleum oil fraction of initial boiling point of about 400° F. the improvement which comprises slurrying said oil with from about 0.1% to about 10% by weight of finely divided porous coke, passing the resulting slurry at elevated pressure and in admixture with hydrogen over a fixed bed of a sulfactive catalyst on a support consisting of alumina maintained at from 700° F. to 900° F. and thereby hydrofining said oil while adsorbing tar on said coke, withdrawing the resultant slurry of tar-containing coke in oil from contact with the catalyst and separating the coke from the oil.

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