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HYDROCRACKING EFFLUENT COOLING PRIOR TO HYDRODESULFURIZATION

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No Drawing. Continuation of application Ser. No. 102,251, Dec. 28, 1970, now Patent No. 3,716,476. This application Sept. 7, 1972, Ser. No. 287,135
The portion of the term of the patent subsequent to Feb. 13, 1990, has been disclaimed
Int. Cl. C10g 37/00
U.S. Cl. 208—97 9 Claims

ABSTRACT OF THE DISCLOSURE

A residue-containing petroleum fraction, 50 percent boiling above 1,000° F., is hydrocracked and then hydrodesulfurized. During the onstream period, the conversion level of material boiling above 1,000° F. is maintained substantially constant while the sulfur content of the hydrocracked effluent increases. The sulfur content of a product fraction is maintained substantially constant by gradually increasing the hydrodesulfurization temperature. The effluent from the hydrocracking reaction is cooled by adding an aromatic-rich fraction and the cooled mixture is passed to the desulfurization reaction.

This application is a continuation of Ser. No. 102,251 filed Dec. 28, 1970, now U.S. Pat. 3,716,476.

This invention relates to the treatment of hydrocarbons. More particularly, it is concerned with the catalytic hydrodesulfurization of hydrocarbons, especially heavy hydrocarbon oils of the crude and residual types.

The hydrodesulfurization of hydrocarbon liquids is well known and has been practiced for several years in the refining of petroleum. The catalytic hydrodesulfurization processes of the prior art comprise contacting the sulfur-containing charge stock with a catalyst in the presence of hydrogen at elevated temperatures and pressures to convert the sulfur present in the charge stock to hydrogen sulfide. Ordinarily the hydrogen-rich effluent gas is subjected to a hydrogen sulfide removal treatment and recycled to the reaction zone. Typical catalysts comprise cobalt and molybdenum or nickel and molybdenum or nickel and tungsten on a support such as alumina.

Generally, sulfur is present in petroleum fractions in the form of mercaptants, sulfides, disulfides and in complex ring compounds containing ring structures such as thiophenes. In catalytic hydrodesulfurization of lighter fractions such as gasoline, naphtha and kerosine, the sulfur is present to a large extent in the form of easily-removable mercaptans which require less severe reaction conditions and thus long catalyst life is obtained. However even in residual fractions not only is the sulfur present in more difficulty removable form, but the fraction contains materials such as tar and metals which severely affect the activity of conventional catalysts.

The catalytic desulfurization of heavy hydrocarbon oil such as crudes and residuals has presented a particular problem to the petroleum refining industry in that to date commercial desulfurization of heavy hydrocarbon oils by known processes has not been practical. When heavy hydrocarbon oils, for example, oils containing at least 1% by weight Conradson Carbon Residue, are contacted in a known manner, the catalysts become contaminated by deposited coke, metals and possibly "gum" (polymers) and require higher temperatures to effect satisfactory desulfurization. However, these higher temperatures lead to additional contaminant deposition which results in a rapid deactivation of the catalyst. This deactivation becomes progressively worse and to obtain satisfactory conversion

it is necessary to increase the catalyst temperature still higher resulting in more coke and metal deposition thereby deactivating the catalyst to such an extent that commercial operation is no longer feasible within a relatively short time.

Conventionally in commercial desulfurization processes, after startup of the desulfurization unit, reaction conditions are selected to yield a product having the desired sulfur content as for example 0.3 wt. percent sulfur or 1.0 wt. percent sulfur as the case may be. However, as the onstream period progresses, the desulfurization activity of the catalyst declines so that in order to obtain a product meeting the desired specifications it becomes necessary to increase the temperature of the reaction zone or catalyst bed. The rate of temperature increase necessary to maintain the desired sulfur content of the product is termed "deactivation rate" and is expressed in terms of ° F. per unit of time. Attempts to desulfurize heavy oils such as vacuum residuum have been successful in that they have succeeded in reducing the sulfur content of the oil but have not been successful from a commercial standpoint in that they have resulted in deactivation rates of as much as 2° F. per day which means that the unit must be shut down frequently either for regeneration or replacement of the catalyst.

It is, therefore, an objection of this invention to provide a process for reducing the sulfur content of heavy petroleum hydrocarbon oils. Another object is to provide a desulfurization process in which the catalyst does not require frequent regeneration or replacement. Still another object is to provide a process in which the catalyst deactivation rate is low. These and other objects will be obvious to those skilled in the art from the following disclosure.

According to our invention, there is provided a process for the production of petroleum hydrocarbon fractions of reduced sulfur content which comprises contacting a residue-containing petroleum fraction in the presence of hydrogen with a supported catalyst comprising a member selected from the group consisting of Group VI metals, Group VIII metals, their compounds and mixtures thereof under hydrocracking conditions comprising a temperature between about 750 and 950° F., a pressure between about 500 and 5000 p.s.i.g., a space velocity of 0.1–10 and a hydrogen rate between about 1000 and 30,000 s.c.f.b., cooling the effluent and passing same into contact with a supported catalyst comprising a member selected from the group consisting of Group VI metals, Group VIII metals, their compounds, and mixtures thereof under desulfurization conditions comprising a temperature between about 600 and 850° F., a pressure between about 500 and 5000 p.s.i.g., a space velocity of between about 0.1 and 10 and a hydrogen rate between about 1000 and 30,000 s.c.f.b. and recovering from the effluent a fraction of reduced sulfur content.

The charges used as feed to the process are those heavy petroleum fractions containing asphalt and residue which are traditionally extremely difficult to desulfurize. Such materials include whole crudes such as San Ardo crude, shale oil, tar sand oil, vacuum residua and mixtures thereof. Typically they contain at least 1% Conradson carbon residue and generally at least about 50% of the charge boils above 1000° F.

The charge is introduced with hydrogen into the first or hydrocracking zone. The hydrogen used in the process of this invention need not be pure, hydrogen having a purity of at least 50% and preferably about 70–90 vol. percent being satisfactory. The hydrogen may be obtained from any suitable source hydrogen such as that obtained by partial oxidation of petroleum hydrocarbons followed by shift conversion and carbon dioxide removal, elec-

trolytic hydrogen or catalytic reforming by-product hydrogen, are satisfactory.

The charge in admixture with hydrogen is introduced into contact with a hydrocracking catalyst. The catalyst preferably is in particulate form and may be used as a fixed bed, a moving bed or a fluidized bed. The reactant flow may be either upward or downward or the hydrogen flow may be countercurrent to the downward flow of the charge. Preferably the mixture of hydrogen and charge is introduced into the upper end of a reactor containing a fixed bed of pelletized catalyst and is passed downwardly through the bed. Advantageously, hydrogen may be introduced at various points in the bed to control the reactant temperature.

The catalyst used in the hydrocracking zone comprises a Group VI metal, a Group VIII metal, mixtures thereof and compounds thereof on an amorphous inorganic oxide support.

Suitable metals include iron, cobalt, nickel, chromium, vanadium, tungsten and molybdenum. Preferred catalysts contain from about 2–8% of a Group VIII metal and 5–30% of a Group VI metal. Preferred combinations are cobalt and molybdenum, nickel and molybdenum and nickel and tungsten. The metals are presently in the form of the oxide when prepared but may be converted to the sulfide prior to inaugurating the onstream period. The sulfiding may take place either prior to the introduction of the catalyst in the reactor vessel or may be carried out in situ after the catalyst has been loaded to the reactor.

The hydrocracking catalyst also comprises an amorphous support such as alumina advantageously having acidic properties produced by the addition of activated silica or boron oxide or by treatment of the alumina with a halogen acid such as hydrofluoric acid. The support should have a surface area of at least 250 m.^{2}/g. preferably 275 to 350 m.^{2}/g. and should have a pore volume of at least 0.6 cc./g., preferably between 0.7 and 1.0 cc./g. The support should also have an average pore diameter of less than 100 preferably 75–100 Angstrom units. The average pore diameter is represented by the formula $4V/A$ where V is the pore volume and A is the surface area. The pore volume is ordinarily expressed as cc./g. and the surface area as m.^{2}/g.

The reaction conditions of the first or hydrocracking zone include a temperature between about 750 and 950° F., a pressure between about 500 and 5000 p.s.i.g., a space velocity between about 0.1 and 10 volumes of liquid charge per volume of catalyst per hour with a hydrogen rate of between about 1000 and 30,000 s.c.f.b. per barrel of charge. Preferred conditions are a temperature of 750–900° F., a pressure between 1500 and 3000 p.s.i.g., a space velocity between 0.25 and 1.5 and a hydrogen rate between 3000 and 10,000 s.c.f.b.

The effluent from the hydrocracking zone is then cooled to a suitable temperature prior to introduction into the second or desulfurization zone. The cooling may be effected by direct or indirect heat exchange, the former being preferred. Since some light hydrocarbons are formed in the hydrocracking step, there may be a tendency when certain charge stocks are used for asphalt to precipitate as a result of the temperature reduction and the presence of these lighter hydrocarbons. To avoid such precipitation and the concomitant plugging of the apparatus, advantageously the cooling is accomplished by the addition of an aromatic-rich fraction which is introduced at a temperature sufficient to effect the desired reduction in the temperature of the first stage effluent. By aromatic-rich fraction is meant a fraction having at least 50 vol. percent aromatics. Although any aromatic-rich fraction may be used, a particularly suitable coolant in this respect is a heavy cycle gas oil withdrawn from a fluid catalytic cracking unit. The hydrocracking effluent may be separated into hydrogen and various fractions and the hydrogen purified if desired and recycled to the first zone with only a fraction or portion of the effluent being introduced into the desulfurization zone. However, in a preferred embodiment the entire effluent from the first or hydrocracking zone is introduced into the second or desulfurization zone.

The catalyst used in the desulfurization zone is to a large extent similar to the catalyst used in the first zone in that it comprises a Group VI metal, a Group VII metal, compounds or mixtures thereof. The Group VI metal may be present in an amount between about 5 and 30 weight percent preferably 8–25% and the Group VIII metal in an amount between about 2 and 10 weight percent, preferably 2–8%. As in the case of the first stage catalyst, the metals are generally in the form of the oxide or sulfide.

The desulfurization catalyst also comprises an amorphous inorganic oxide support which need not necessarily have cracking activity such as alumina, zirconia, silica and magnesia. However, it is possible to use a catalyst having the same composition and characteristics as the hydrocracking catalyst in the desulfurization zone.

As pointed out above, two separate reactions are involved in the process of this invention, hydrocracking and desulfurization. We have also found that the same catalyst may have a different deactivation rate for each reaction. It is for this reason that the conversion in the hydrocracking zone should be maintained relatively constant and the desulfurization should also be maintained constant.

The hydrocracking unit should be operated to obtain 25–70% conversion of the 100° F.+ portion of the charge to materials boiling below 1000° F. If the conversion is less than 25%, the charge to the desulfurization zone behaves more like vacuum residuum such that low desulfurization levels and high deactivation rates are experienced in the second zone. If the conversion of the 1000° F.+ fraction is greater than 70% the quality of the unconverted 1000° F.+ residuum becomes worse than the charge stock.

The following examples are presented for illustrative purposes only.

EXAMPLE I

In this example, the charge is an Arabian vacuum residuum having the following characteristics:

TABLE 1

Gravity, ° API	10.3
Sulfur, wt. percent	3.8
Conradson Carbon Residue, wt. percent	23.4
Metals, p.p.m.:	
Ni	24
V	64
1000° F.+vol. percent	100

The composition and properties of the catalyst are as follows:

TABLE 2

Cobalt, wt. percent	2.1
Moldbdenum, wt. percent	11.0
Silica, wt. percent	2.5
Alumina, wt. percent	Balance
Surface area, m.^{2}/g.	312
Pore volume, cc./g.	0.66
Average pore diameter, A.	82.5

The reaction zone is maintained at the following conditions:

TABLE 3

Hydrogen partial pressure, p.s.i.a.	1800
Space velocity, v./v./hr.	0.25
Hydrogen feed rate, s.c.f.b.	10,000
Hydrogen purity, vol. percent	90.0

After the initial edge is removed, an average catalyst bed temperature of 745° F. is required to provide a liquid product having a sulfur content of 1.0 wt. percent. After

45 days of maintaining a 1.0% sulfur level in the product the average catalyst bed temperature is 800° F. showing a catalyst deactivation rate of 1.2° F./day.

EXAMPLE II

This example is similar to Example I, the difference being that a product containing 0.5 wt. percent sulfur is produced. After the initial edge has been removed the average catalyst bed temperature required to produce the desired product is 780° F. After 48 days of operation, the temperature is 825° F. but due to the conversion of more than 70% of the 1000° F.+ material in the charge and the resulting asphaltene precipitation in the reactor outlet line, the run is terminated. The 1000° F.+ portion of the product is found to contain a higher Conradson Carbon Residue than the charge stock. The catalyst deactivation rate is 0.94° F./day.

EXAMPLE III

This example represents the process of our invention. The same catalyst used in Example I is loaded into two reactors. The reaction conditions in the first hydrocracking reactor A and the second desulfurization reactor B are tabulated below:

TABLE 4

	A	B
Hydrogen partial pressure	1,800	1,800
Space velocity, v./v./hr.	0.5	0.5
Hydrogen rate, SCFB	10,000	10,000
Hydrogen purity, vol. percent	90	90

In this run, the same overall space velocity, 0.25, as in Examples I and II is used. After the initial edge is worn on the catalyst in reactor A, an average catalyst bed temperature of 800° F. is required to obtain a 45% conversion of the 1000° F.+ portion of the charge. Similarly, the temperature in the second reactor is maintained at 740° F. to obtain a product having 0.5 wt. percent sulfur. After 159 days of operation maintaining a 1000° F.+ conversion between 45 and 50%, the hydrocracking catalyst average bed temperature is 818° F. and for a product constantly having a sulfur content of about 0.5 wt. percent, the average desulfurization catalyst bed temperature is 775° F. These results represent catalyst deactivation rates of 0.106° F./day for the hydrocracking and 0.23° F./day for the desulfurization with an average deactivation rate of 0.17° F./day. During the run, the product from the first reactor increased in sulfur content from 0.9 to 2.2 wt. percent, indicating that the deactivation rate of the catalyst for desulfurization was much higher than its deactivation rate for hydrocracking. To maintain a constant 0.5 wt. percent sulfur in the second stage product, it was necessary to increase the desulfurization in the second stage from 45 wt. percent at the start of the run to 77 wt. percent yet this was accomplished with a deactivation rate of only 0.23° F./day. The overall conversion of 1000° F.+ across both reactors was relatively constant at about 55 vol. percent. The quality of the 1000° F.+ residuum in the product was substantially the same as the quality of the 1000° F.+ portion of the charge except for the reduced sulfur content.

The aromatic-rich fraction mixed with the effluent from the hydrocracking zone need not be low in sulfur and actually may have a high sulfur content so that in its passage through the desulfurization zone, its sulfur content is reduced.

It is also possible, in the alternative, to add the aromatic-rich fraction to the effluent from the desulfurization zone, particularly if it is of low sulfur content, as it does not need to be subjected to desulfurization and in some instances it can be used to greater advantage as the effluent from the desulfurization zone is cooled to lower temperatures than is the effluent from the hydrocracking zone.

Obviously, various modifications of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for the production of petroleum hydrocarbon fractions of reduced sulfur content which comprises contacting a residue-containing petroleum fraction in the presence of hydrogen with a supported catalyst comprising a member selected from the group consisting of Group VI metals, Group VIII metals, their compounds and mixtures thereof under hydrocracking conditions comprising a temperature between about 750 and 950° F., a pressure between about 500 and 5000 p.s.i.g., a space velocity of 0.1–10 and a hydrogen rate between about 1000 and 30,00 s.c.f.b., cooling the effluent by the addition thereto of an aromatic-rich fraction and passing the resulting mixture into contact with a supported catalyst comprising a member selected from the group consisting of Group VI metals, Group VIII metals, their compounds, and mixtures thereof under desulfurization conditions comprising a temperature between about 60 and 850° F., a pressure between about 500 and 5000 p.s.i.g., a space velocity of between about 0.1 and 10 and a hydrogen rate between about 1,000 and 30,000 s.c.f.b. and recovering from the effluent a fraction of reduced sulfur content.

2. The process of Claim 1 in which the entire effluent of the hydrocracking zone is introduced into the desulfurization zone.

3. The process of Claim 1 in which the hydrocracking temperature is gradually increased throughout the on-stream period to maintain the hydrocracking conversion substantially constant.

4. The process of Claim 1 in which the hydrocracking catalyst comprises cobalt and molybdenum.

5. The process of Claim 1 in which the hydrocracking catalyst comprises nickel and molybdenum.

6. The process of Claim 1 in which the hydrocracking catalyst comprises nickel and tungsten.

7. The process of Claim 1 in which in the hydrocracking zone the conversion of 1000° F.+ material in the charge to 1000° F.— material is within the range of 25 to 70 volume percent.

8. The process of Claim 7 in which the conversion is within the range of 40 to 70 volume percent.

9. The process of Claim 1 in which the effluent from the desulfurization zone is cooled by addition thereto of an aromatic-rich fraction.

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CERTIFICATE OF CORRECTION

Patent No. 3,825,485 Dated July 23, 1974

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

COLUMN 1, line 48, "mercaptants" should read -- mercaptans =-

COLUMN 1, lines 54-55 "howeven" should read --however--

COLUMN 6, line 30 "60" should read --600--

Signed and sealed this 8th day of October 1974.

(SEAL)
Attest:

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