United States Patent Office 2,902,429
Patented Sept. 1, 1959

2,902,429

DEMETALLIZATION OF HYDROCARBON FRACTIONS

John W. Scott, San Anselmo, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

No Drawing. Application June 17, 1955
Serial No. 516,321

7 Claims. (Cl. 208—89)

This invention relates to a process for the demetallization of hydrocarbon fractions. More particularly, it relates to the catalytic treatment of petroleum hydrocarbons heavier than gasoline in order to remove organo-metallic compounds contained therein.

In the petroleum industry, the most important product is gasoline, and the primary aim of the refiner is to produce the maximum quantity of gasoline of the highest quality from a barrel of petroleum at the lowest possible cost. With the advent of the catalytic cracking process, improved yields of excellent quality gasoline were realized over those obtained prior to the development of this process. The best feed to a catalytic cracking unit has been found to be a straight-run distillate of the nature of gas oil obtained by the simple distillation of crude petroleum. However, the amount of feed stock of this nature is limited and the amount of residue fraction is large. Consequently, various methods have been devised for cutting more deeply into the residue in order to obtain greater quantities of catalytic cracking charging stock.

One major problem encountered in the preparation of catalytic cracking feed from residue fractions is that the feed must be relatively free of organo-metallic compounds, such as vanadium, nickel, copper, chromium, and iron combined within organic molecular structures. These metallic compounds, if present in the catalytic cracking process feed, will poison the cracking catalyst (e.g., silica-alumina, or the like) and thereby effect an undesirable increase in gas and coke production at the expense of desired liquid products. It has been found that in order to prevent this catalyst poisoning, the metals content of the cracking feed must desirably be kept below about 4 parts per million (p.p.m.), and preferably below about 2 p.p.m. Since the organo-metallic compounds generally boil in the same range as the heavier gas oils, it is often required when treating metal-containing crudes to reduce the upper limit of the boiling range of the gas oil catalytic cracker feed so as to exclude these undesired compounds. As a result, portions of the heavier gas oils, though excellent catalytic cracking charging stocks, cannot be employed as such due to the high metals content and must, instead, be included within the residuum from the crude distillation column at a considerable economic loss.

Accordingly, it is an object of the present invention to provide a process for the demetallization of hydrocarbon fractions which does not require cutting back on the end point of the distillate. A further object is to provide a process for the catalytic treatment of petroleum fractions, prior to catalytically cracking said fractions, to remove organo-metallic and some sulfur compounds therefrom if the latter are present in the feed. Other objects will be apparent from a consideration of the following description of the subject invention.

The present invention is based on the discovery that the substantial demetallization of hydrocarbon fractions containing organo-metallic compounds can be effected by contacting the fractions in the presence of hydrogen under superatmospheric pressure and at elevated temperatures with a catalyst having a relatively small amount of a sulfur-resistant hydrogenating-dehydrogenating component disposed upon a low surface area carrier. It has been found that when the process of the present invention is followed in treating a heavy gas oil petroleum fraction, the effluent from the contacting step is an excellent catalytic cracking unit feed stock containing less than 4 p.p.m. metals.

The catalyst employed in the contacting zone is one wherein a material having sulfur-resistant hydrogenating-dehydrogenating activity is deposited or otherwise disposed on a low surface area support or carrier. The hydrogenating-dehydrogenating component of the catalyst can be selected from one or more of the various group VI and group VIII metals, as well as the oxides and sulfides thereof, representative materials being the oxides of molybdenum, cobalt, tungsten, and nickel. If desired, more than one hydrogenating-dehydrogenating material can be present, and particularly good results have been obtained with catalysts containing molybdenum oxide along with cobalt oxide. Preferred components are molybdenum oxide and a mixture of 3–6 parts molybdenum oxide with about 1 part cobalt oxide. This latter mixture, which gives a catalyst which is particularly effective for sulfur removal if such is desired, can readily be disposed on the carrier by soaking it in a solution of ammonium molybdate, drying the catalyst for 24 hours at 220° F., calcining the dried material for 10 hours at 1000° F., and then depositing the cobalt on the calcined carrier in a similar manner.

Two major features of the subject catalyst distinguish it from the conventional hydrodesulfurization catalysts currently being employed in the petroleum refining industry. The first distinguishing feature is that, whereas the hydrogenating-dehydrogenating component of the conventional catalyst comprises of the order of 5 or more weight percent of the total weight of the component and carrier, the present catalyst effects substantial demetallization with a catalytic component of from 0.1 to 1.0, and preferably from 0.25 to 0.75, weight percent. This represents a considerable economic advantage, particularly in view of the fact that in the catalytic demetallization of petroleum fractions, the metals removed from the feed are deposited upon the catalyst, thereby causing a gradual but definite decline of catalyst activity, and requiring its ultimate replacement due to accumulation of metals within and upon the catalyst particles. Since there is no convenient way of regenerating such deactivated catalyst when simple combustion is no longer effective, the fact that excellent demetallization can be accomplished with a comparatively small, and therefore less expensive, amount of hydrogenating-dehydrogenating component is an unexpected and desirable result.

The second distinguishing feature of the present catalyst is that the carrier or support upon which is deposited the hydrogenating-dehydrogenating component is one having a low surface area. This means that it, too, can be significantly cheaper than is employed in conventional catalyst supports. In conventional hydrodesulfurization catalysts the catalytic-promoting agent is disposed upon high surface area supports ranging from bauxite with a surface area of about 50 m.²/gm. (square meters per gram) to synthetic gels such as alumina or silica-alumina with a surface area on the order of 400 m.²/gm. In the present invention, carriers with a surface area of not more than 15, and preferably not more than about 3, m.²/gm. are employed. It has been found that if high surface area supports are used, that the demetallization of hydrocarbon fractions, particularly of fractions containing both sulfur and organo-metallic compounds, is not realized to the degree that can be obtained by the catalyst of the present process. It has also been

found that the amount of hydrogen consumed in the contacting operation in accomplishing a given reduction in metal content, is considerably less when employing the present process than in the case of the high surface area catalyst. This reduction in hydrogen consumption not only reflects a considerable economic saving, but also indicates that the present demetallization process is one of high efficiency. Thus, the practice of the subject process not only provides a higher degree of metals removal than previous processes, but also reduces the amount of unnecessary hydrogenation of molecules other than those containing metals. Although the mechanism of the subject reaction is not completely understood, it is believed that the low surface area catalyst carrier of the present invention provides a support in which the pore diameter is considerably in excess of 100 Angstroms, and probably ranges upward from 500 A. in some cases, thereby allowing the relatively large organo-metallic molecules to have access to the catalytic agent. (These pore diameters are characterized through use of the usual ratio between pore volume and area: pore diameter=4×pore volume/surface areas with these values being determined in accordance with the methods of Brunauer, Emmett and Teller.) According to the present theory, if the support is one of large surface area, as, for example, silica-alumina with an area of 400 m.²/gm., that large area can be attained only with an average pore diameter appreciably below 100 A., usually in the range of from 25 to 50 A., and in such a case the large metal-containing molecules cannot contact the catalytic component effectively. Instead, smaller molecules, such as those containing sulfur compounds and the like, are able to pass into the pores and contact the catalytic agent with the result that the smaller molecules are selectively hydrogenated in preference to the large organo-metallic ones which can only reach catalytic surfaces only at the exterior of the catalyst pellet. The use of the present carrier, with its large pore structure, allows the organo-metallic compounds to contact the catalyst at least equally with, and possibly in preference to, the smaller molecules. I have found that low surface area supports (below 15 m.²/gm.), such as diatomaceous earth, natural clays, and Alundum are particularly suitable for the practice of the present process. However, it must be understood that any low-surface area carrier having the characteristics described above is within the scope of the present invention. The general rule is to give the large organo-metallic molecules the same opportunity to contact catalytic surface as is given the smaller molecular species in the feed by using a catalyst support containing a minimum of small pores. Results with an impervious Alundum support give eloquent proof of this rule, for such a support is substantially devoid of small pores and shows high selectivity for hydrogenation of organo-metallic compounds in the presence of such readily hydrogenated species as sulfur compounds.

The contacting step of the subject process is carried out at a temperature of from about 650° to 900° F., a preferred range being from about 700° to 800° F., and at a pressure of from about 500 to 1500 p.s.i.g., with the preferred range being from about 700 to 1000 p.s.i.g. Of course, both optimum temperature and pressure conditions depend upon the type, boiling range, etc., of the feed stock to be demetallized, but, in general, these conditions fall within the above-noted ranges. The reaction is one in which hydrogen is consumed and it is, therefore, conducted in the presence of from about 1000 to 10,000 s.c.f./b. (standard cubic feet per barrel of feed) of hydrogen, comprising gas recycle plus makeup hydrogen. The hydrocarbon feed is passed into contact with the catalyst at a space velocity of from about 0.25 to 5.0 v./v./hr. (volumes of feed per volume of catalyst per hour).

The invention can be advantageously carried out by any method of reacting a liquid, vapor, or mixed phase feed with hydrogen in the presence of a solid catalyst, either in a fixed bed, moving bed, or a fluid-solid contacting system. High-boiling stocks, which are substantially liquid-phase in the reaction system, are advantageously passed upflow through the catalyst to obtain good contacting of stock and catalyst in large vessels.

The following experimental runs were made upon conventional high surface area, high metals content hydrogenation-dehydrogenation catalyst (Run No. 5–1091A), and the catalyst of the present invention (Run No. 5–1042). In both runs the hydrocarbon fraction employed as a feed had the following characteristics:

Southern California heavy gas oil:

Gravity	°API	20.6
Initial boiling point	°F	385
End point	°F	1050
Sulfur content, wt. percent		1.42
Metals content, p.p.m.—		
Copper		0.67
Nickel		10.5
Vanadium		0.85
Total		12.0

Tabulated below (Table I) are the reaction conditions and results of both of these runs.

Table I

Run No.	5–1042	5–1091A
Temperature, °F	800	800.
Pressure, p.s.i.g.	800	810.
Catalyst Carrier	Norton Alundum.	Alumina.
Surface Area to N², m.²/gm.	0.1	140.
Metallic Components	Molybdenum and Cobalt Oxide.	Molybdenum and Cobalt Oxide.
Metals Ratio	3:1	3:1.
Total Metals Content, Wt. % Oxide	0.1	15.8.
Hydrogen Consumption, s.c.f./b.	308	400.
Results:		
Gravity, Degrees API	23.8	25.4.
Aniline Point	155	148.
Sulfur Content, Wt. %	0.80	0.50.
Metals Content, p.p.m.:		
Copper	0.11	0.08.
Nickel	1.7	2.1.
Vanadium	0.12	0.23.
Total Metals Content, p.p.m.	1.9	2.4.

A comparison of the two runs shows that when employing the catalyst of the subject invention, the reduction in metals content is greater than that obtained by the conventional catalyst, and that this effect is realized with a catalyst having a catalyst metals content of only 0.6% that of the conventional one. The economic advantage realized by this catalyst metals content is obvious. Further, the fact that better demetallization is accomplished by the subject catalyst using only three-quarters of the amount of hydrogen used in Run No. 5–1091A indicates that the present method is considerably more selective in hydrogenating the organo-metallic compounds.

While the above example shows the demetallization of the entire heavy gas oil charging stock (boiling range 385°–1050° F.) suitable for employment in a catalytic cracking unit, equally good results can be obtained by treating fractions of said charging stock such as the heavier ends which contain the bulk of the organo-metallic compounds. Accordingly, a preferred modification of the present process is to split the feed to a catalytic cracking unit into two fractions, a lighter fraction containing essentially no organo-metallic compounds and a heavy fraction containing virtually all of said compounds. This latter fraction can then be demetallized by employing the catalyst and operating conditions of the present process (as illustrated above, for example), with

the demetallized heavy fraction then being mixed with the lighter fraction for passage into the cracking zone. In this manner, demetallization can be effected to the degree heretofore noted (e.g., 4 p.p.m. or below) while only treating a small portion of the overall feed to the catalytic cracking unit. Various other modifications of the process will suggest themselves to those skilled in the art.

The following advantages are also obtained by employing the present process:

(1) The subject catalyst can be regenerated for reuse by combustion.

(2) The metals lay down as an ash on the exterior of the catalyst particles and are in themselves effective as a catalytic agent.

(3) Extensive accumulations of ash between the catalyst particles have been observed; this ash can be blown, flushed, or sifted out periodically in order to recover the valuable metals concentrate.

(4) While desulfurization of the feed is not a primary object of the present invention, the high desulfurization activity of the cheap, low area supports is an unexpected benefit.

I claim:

1. A process for the demetallization of a metals-containing hydrocarbon fraction which comprises contacting said fraction in the presence of hydrogen at a temperature of from about 650° to 900° F. and at a superatmospheric pressure with a catalyst comprising a carrier having a surface area of not more than 15 m.²/gm., and a sulfur-resistant hydrogenating component disposed thereon in an amount from 0.25–0.75 percent by weight of the total catalyst.

2. The process of claim 1, wherein the carrier has a surface area of not more than about 3 m.²/gm.

3. The process of claim 1, wherein the component disposed upon the carrier is molybdenum oxide.

4. The process of claim 1, wherein the component disposed upon the carrier comprises about 1 part cobalt oxide and about 3–6 parts molybdenum oxide.

5. A process for the demetallization of a metals-containing hydrocarbon fraction, which comprises contacting said fraction in the presence of hydrogen at a temperature of from about 650° to 900° F. and at a pressure of from about 500 to 1500 p.s.i.g. with a catalyst comprising from about 0.1 to 1.0% by weight of cobalt and molybdenum oxides disposed in a ratio of about one part of cobalt oxide to about 3–6 parts of molybdenum oxide upon a carrier having a surface area of not more than 3 m.²/gm.

6. The process of claim 5, wherein the catalyst comprises from 0.25 to 0.75% by weight of cobalt and molybdenum oxides.

7. In a catalytic cracking process wherein a hydrocarbon feed is contacted in a catalytic cracking zone with a cracking catalyst under cracking conditions, the method of treating said feed prior to cracking to remove metal-containing compounds therefrom, which comprises: separating said feed into two fractions, one being higher boiling and richer in said compounds than the other; removing metal-containing compounds from said higher boiling fraction by passing said higher boiling fraction into contact with a catalyst in the presence of from about 1000–10,000 s.c.f./b. of hydrogen at a temperature of from about 650° F. to 900° F. and superatmospheric pressure, said catalyst comprising a support having a surface area of not more than 15 m.²/gm. and a sulfur-resistant hydrogenating-dehydrogenating component disposed on said support in an amount from 0.25–0.75 percent by weight of the total catalyst; and passing the fraction so demetallized and the other fraction to said cracking zone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,440,236	Stirton	Apr. 27, 1948
2,697,683	Engel et al.	Dec. 21, 1954
2,698,305	Plank et al.	Dec. 28, 1954
2,700,015	Joyce	Jan. 18, 1955
2,769,756	Porter et al.	Nov. 6, 1956

FOREIGN PATENTS

682,387	Great Britain	Nov. 12, 1952