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DEMETALATION OF HYDROCARBON FRACTIONS BY HYDROGENATION PRIOR TO CATALYTIC CRACKING

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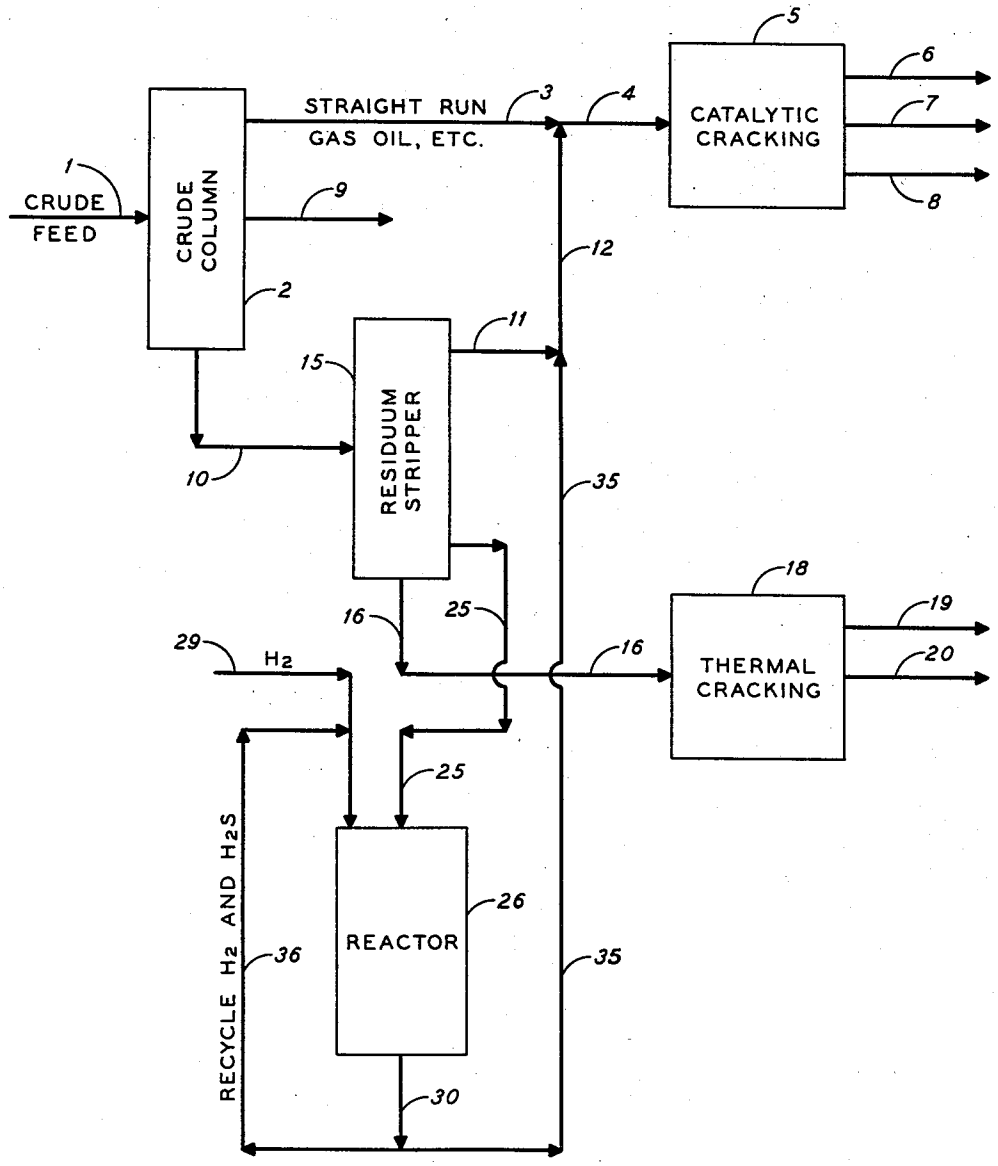

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DEMETALATION OF HYDROCARBON FRACTIONS BY HYDROGENATION PRIOR TO CATALYTIC CRACKING

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1 Claim. (Cl. 208—89)

This invention relates to the catalytic cracking of petroleum hydrocarbons, more particularly to the treatment of petroleum hydrocarbons heavier than gasoline that are unsuitable as feeds to a catalytic cracking unit to convert them to suitable catalytic cracking feeds, and still more particularly to the reduction of the metals content of said heavier petroleum hydrocarbons.

Gasoline is the most important product obtained from crude petroleum stocks, from the standpoint of the petroleum refiner, who desires to produce from each barrel of crude the maximum amount of high quality gasoline at the minimum cost. This objective has been greatly aided by the catalytic cracking process, which has resulted in improved yields of gasoline of excellent quality. It has been found that the best feed to a catalytic cracking unit is a straight-run distillate oil of the nature of gas oil resulting from a simple distillation of crude petroleum. However, the amount of feed stock of this nature is limited, and the remaining residue fraction is large. Consequently, in order to increase the total available satisfactory catalytic cracking feed stock, various methods have been developed for cutting into the residue fraction and preparing catalytic cracking feed stock therefrom.

In preparing catalytic cracking feed stock from portions of the residue fraction by treating those portions, the refiner must overcome various problems, the solutions to which involve changing certain characteristics of the treated portions. Those portions frequently contain excessive amounts of sulfur, metals (particularly in the form of organo metallic compounds or complexes), and other contaminants. Excessive amounts of sulfur in the feed to a catalytic cracking unit will appear in the gasoline and other products from the unit, which is undesirable. However, excessive metals content in the feed to a catalytic cracking unit frequently is much more serious and intolerable, particularly because the metallic impurities tend to poison the cracking catalysts, thereby decreasing useful catalyst life and increasing operating costs. Heretofore, it has been the practice, when cutting into the residue fraction and treating a portion thereof to prepare it as feed to a catalytic cracking unit, to remove both sulfur and metallic impurities, an operation which has often been unnecessarily expensive for reasons which will be developed later. One of the objects of the present invention is to provide a process which will reduce the metals content of a portion of a residue fraction already having a sulfur content that is tolerable for a feed to a catalytic cracking unit, and which is considerably more attractive economically than prior art processes.

Because the refiner must strike a balance between a number of factors in order to achieve maximum economic benefit from crude petroleum, it may be seen that a process for demetalating portions of a residue fraction more cheaply than formerly will allow him in many cases to treat greater quantities of the residue fraction to convert them to satisfactory catalytic cracker feeds. Generally, a large portion of the residue fraction is thermally cracked, blended with cutter stock, and sold as fuel oil. Because fuel oil commands a smaller price than gasoline, the refiner generally will desire to increase the amount

of residue fraction prepared for catalytic cracker feed to the point where the cost of treating further amounts makes it more economical from an overall standpoint to send those further amounts to thermal cracking. It is one of the objects of the present invention to provide a process by which the refiner in many cases may prepare greater amounts of the residue fraction for catalytic cracking than formerly possible, without reducing the attractiveness of the overall economics.

It has been found that the foregoing objects may be obtained by a process wherein a substantial amount of the metals content is removed from a heavy hydrocarbon stock having a substantial metals content, for example, a portion of the residue fraction from a crude distillation unit, by contacting said stock with hydrogen in the presence of a sulfided hydrogenation catalyst at a pressure of from about 300–3000 p.s.i.g., preferably about 600–1000 p.s.i.g., and a temperature of from about 350–600° F., preferably about 400–550° F. In contrast with previous demetalating processes operated at severer conditions, the present process results in substantial demetalation of the hydrocarbon stock without appreciable desulfurization, and without the necessity for the large hydrogen consumption required to both demetalate and desulfurize. Thus, the process uses less hydrogen, which is often difficult to obtain in large amounts, and reduces the cost of the operating equipment required to handle larger amounts of hydrogen.

Further objects and advantages of the invention will become apparent from the following detailed description thereof, when considered in connection with the accompanying drawing, in which the single figure there shown is a diagrammatic illustration including apparatus and flow paths applicable in carrying out the invention.

Referring now to the drawing, a crude feed having a substantial metals content is passed through line 1 into crude column 2, where it is separated according to conventional practice into various fractions. Also in accordance with conventional practice, a fraction, which may comprise straight run gas oil, may be passed through lines 3 and 4 to catalytic cracking unit 5, from which various products may be withdrawn, for example, through lines 6, 7 and 8. Still in accordance with conventional practice, other fractions may be withdrawn from column 2, for example, through line 9, and a residue or bottoms fraction is withdrawn through line 10 and passed to residuum stripper 15. From residuum stripper 15 a gas oil friction may be passed to catalytic cracking zone 5 through lines 11, 12 and 4. Still in accordance with conventional practice, a bottoms fraction from residuum stripper 15 would be unsuitable for a feed to catalytic cracking unit 5 because of its substantial metals content. Therefore, it would be passed through line 16 to thermal cracking zone 18, particularly when the metals content of the bottoms fraction and the overall economics indicated that the treating costs, including hydrogen costs, involved in demetalating any portion of the fraction would not be warranted. From thermal cracking zone 18, various products, including fuel oils, would be withdrawn, for example, through lines 19 and 20. However, if it were possible to reduce the conventional costs of demetalating a portion of the bottoms fraction from stripper 15 enough so that the overall economics of the operation would not suffer, it would be desirable to demetalate this portion and send it to catalytic cracking zone 5 in order to increase gasoline production, instead of passing it through line 16 to thermal cracking zone 18. According to the present invention, such a demetalating treatment is possible, and is accomplished in the following manner.

Instead of passing the entire bottoms fraction from residuum stripper 15 through line 16 to thermal cracking zone 18, a cut from that fraction is withdrawn through

line 25 and passed into hydrogenation reactor 26, which may be heated to a desired temperature by conventional means. Reactor 26 contains a hydrogenation catalyst. Such catalysts are well known in the art, and normally comprise from about 1–20% of sulfides of metals from groups VI–VIII, on a suitable support, for example, activated alumina or clay. However, particularly good results have been obtained with molybdenum sulfide on alumina, and with mixtures of molybdenum sulfide and cobalt sulfide on alumina. The following characteristics are typical of a satisfactory catalyst comprising molybdenum sulfide and cobalt sulfide on alumina, and, minus the cobalt oxide, are also typical of a satisfactory catalyst consisting essentially of molybdenum sulfide on alumina.

A. CHEMICAL COMPOSITION, PRIOR TO SULFIDING (MOISTURE FREE)

Ingredient:	Weight percent
CoO	3.7
MoO_3	12.1
Cl	0.05
Fe_2O_3	0.11
Na_2O	0.04
C (graphite)	1–2

B. PHYSICAL PROPERTIES

Pellet size, inches	3/16
Surface area $(N_2)M^2/g$	143
Bulk density, gm./ml	1.02
Crushing strength, pounds	30

The catalyst may be used in the 3/16-inch pellet form if the size of the reactor permits, or may be crushed to smaller size, e.g., 8–14 mesh or 14–20 mesh. Catalysts of the foregoing characteristics are commonly sold for desulfurizing operations. Other catalysts which may be used with a small sacrifice in results obtained include molybdenum oxide plus nickel oxide on alumina, and cobalt oxide plus molybdenum oxide plus nickel oxide on alumina.

In accordance with the invention, the catalyst in reactor 26 is sulfided. Desirably, the sulfiding is accomplished in reactor 26 prior to the introduction into reactor 26 of the feed to be demetalated. The catalyst may be sulfided, for example, by reducing it at from 700° F. to 900° F., preferably about 800° F., and from 900 to 1200 p.s.i.g., preferably around 1000 p.s.i.g., with a mixture containing H_2 and H_2S, the H_2S partial pressure being about 15 to 250 p.s.i.g., for about 2 hours, during which sulfide forms on the catalyst. At the end of the sulfiding pre-treatment period, reactor 26 is cooled to operating temperature, i.e., to about 350° F. to 600° F., and the demetalating operation is begun.

The fraction to be demetalated is passed into reactor 26 through line 25 at a space velocity of about 0.25 to 6 v./v./hr., and preferably 0.5 to 2 v./v./hr. Reactor 26 is maintained at a total pressure (including partial pressures of H_2 and H_2S) of from about 300–3000 p.s.i.g., preferably 600–1000 p.s.i.g., and at a temperature of from about 350° F. to 600° F., preferably 400° F. to 550° F. Hydrogen is passed into reactor 26 through line 29 at a rate of from about 50–300 cu. ft., preferably 100–200 cu. ft. per barrel of feed, it having been found that under the above conditions the hydrogen consumption will be not more than about 200 cu. ft. per barrel of feed.

The hydrogen under the above conditions reacts in the presence of the sulfided catalyst with the organometallic compounds to liberate the metals from the complexes which bind them, upon which liberation the metals deposit onto the catalyst. The hydrogen also serves to keep the catalyst clean, destroy color bodies in the feed, and reduce Conradson carbon, which is a measure of potential coking on the catalyst of a catalytic cracking unit. The Conradson carbon content may be reduced by the process of the present invention by around 50% by weight, reductions having been noted of an original content of around 3.7 weight percent down to a final content of around 1.9 weight percent. The hydrogen also results in a minor amount of hydrocracking in reactor 26.

From reactor 26 the demetalated stock is passed through lines 30, 35, 12 and 4 to catalytic cracking unit 5, where it serves as a valuable addition to the feed to that unit. From reactor 26 hydrogen and H_2S are recycled at a rate of 500 to 10,000 standard cubic feet per barrel, preferably 3000 to 6000 standard cubic feet per barrel, to line 29 through line 36, the H_2S being desirable to maintain catalyst sulfiding; in contrast with many prior art processes in which sulfiding deliberately is avoided, the sulfiding performs an essential and critical function in the present invention. It has been found that the demetalating results achieved under the operating conditions of the process are only possible with sulfiding, and desirably heavy sulfiding, of the catalyst. The sulfiding is maintained during process operation, for example, by H_2S recycle with additional sulfur being added as necessary to replace sulfur lost from the system. The added sulfur may be introduced into the hydrogenation reactor during catalyst reactivation or, for example, by introducing into the system during operation a sulfur-containing material which will be converted to H_2S under process operating conditions. In this manner the demetalating can be accomplished at milder conditions than used in the prior art, and therefore little desulfurization will occur, with a resulting large decrease in hydrogen consumption. In further contrast with many prior art processes, at about 500° F., very little sulfur is removed. At around 600° F. and 1000 p.s.i.g., only about 10% of the sulfur is removed. At around 800° F. under prior art conditions, most of the sulfur would be removed, with attendant high hydrogen consumption. It is thus surprising to find that temperatures can be reduced to a range where little sulfur is removed, while at the same time demetalation to a practical extent can continue to be accomplished. Under the mild conditions of the process, denitrification does not occur, although many prior art demetalating processes are operated under such severe conditions, particularly higher temperatures of at least 700° F., that denitrification as well as desulfurization and demetalation occur.

According to the present invention, it has also been found that the catalyst in the hydrogenation reactor may be regenerated efficiently and easily by stopping the flow of feed to the reactor, withdrawing feed remaining therein, and proceeding exactly as described above in connection with the sulfiding pre-treatment of the catalyst.

The feed to the hydrogenation reactor of the present invention is an incremental gas oil, which for purposes of this invention is defined as a heavy petroleum fraction that because of a substantial metals content cannot be used as a feed to a catalytic cracking unit, and which, if not demetalated, would have to be sent to a thermal cracking unit. By substantial metals content is meant, for example:

Metal:	Parts per million in feed
Copper	0.2 to 5.
Nickel	0.2 to several thousand.
Vanadium	0.2 to several thousand.

Such feeds will generally have a blackish color, and it has been found that after being treated according to the process of the present invention the resulting demetalated product has an orange color. Further, after being so treated, the metals content is reduced to well within the maximum permissible limits for a feed to a catalytic cracking unit, which should not have a nickel plus vanadium content of over 0.5 p.p.m. Higher contents excessively poison the catalytic cracking catalyst by causing excessive fouling and coke laydown, thereby reducing catalyst life by an intolerable amount.

The process of the present invention may be used by feeding to the hydrogenation reactor a bottoms cut or other cuts from a residuum stripper, as described above. or by feeding heavier petroleum fractions having a substantial metals content and derived from other sources.

The incremental gas oil to be demetalated may be derived from Boscan crude, which may have the following exemplary characteristics:

Gravity	(Asphaltic).
Vanadium content	About 1700 p.p.m.
Ni content	About 150 p.p.m.

This crude can be processed in accordance with the present invention by first diluting it with a cutter stock.

The following examples will serve to further illustrate the process of the present invention. In each of the examples the feed used was an incremental gas oil obtained from the bottoms of a residuum stripper by taking a deep distillation cut having the following characteristics:

Gravity, ° A.P.I	14.1
Viscosity at 130° F., SSU	5916
Viscosity at 210° F., SSU	208
Total N, wt. percent	0.73
Basic N, p.p.m	1680
S, wt. percent	1.96
Cu, p.p.m	2.7
Ni, p.p.m	12.6
V, p.p.m	1.5

Example I

The feed was diluted with methylcyclohexane in the ratio of 4 parts feed to 1 part methylcyclohexane. The diluted feed was passed continuously for 29 hours at a liquid hourly space velocity of 0.5 (based on undiluted feed) over a sulfided cobalt oxide and molybdenum oxide on Al_2O_3 catalyst at 550° F., 1000 p.s.i.g. and an H_2 recycle rate of 6000 s.c.f./bbl. feed. After separating gases from the effluent from the catalyst bed, the metals content of the resulting product at various times during the 29-hour run, based on the undiluted feed, ranged as follows:

Ni	0.00–0.24 p.p.m.
V	Less than 0.1 p.p.m.
Cu	0.00–0.3 p.p.m.

Example II

The feed was diluted with methylcyclohexane in the ratio of 4 parts feed to 1 part methylcyclohexane. The diluted feed was passed continuously for 36 hours at a liquid space velocity of 0.5 v./v./hr. over a sulfided cobalt oxide and molybdenum oxide on Al_2O_3 catalyst at 600° F., 1000 p.s.i.g. and an H_2 recycle rate of 6000 s.c.f./bbl. of feed. After separating gases from the effluent from the catalyst bed, the metals content of the resulting product at various times during the 36-hour run, based on the undiluted feed, ranged as follows:

Ni	Less than 0.1 p.p.m.
V	About 0.1 p.p.m.
Cu	Less than 0.1 p.p.m.

Example III

The feed was introduced into the hydrogenation reactor in undiluted form, and was passed continuously for 14 hours at a liquid hourly space velocity of 0.5 over a sulfided molybdenum oxide on Al_2O_3 catalyst at 600° F., 1000 p.s.i.g., and an H_2 recycle rate of 6000 s.c.f./bbl. feed. During the 14 hours the average Ni content of the product ranged from 0.1 to 0.2 p.p.m. The hydrogen consumption was less than 180 cu. ft./bbl.

Example IV

The run in Example III was continued by dropping the temperature to 550° F., maintaining the other conditions

the same, and operating for an additional 11 hours. During the additional 11 hours, the average Ni content of the product ranged from 0.1 to 0.2 p.p.m. The hydrogen consumption was less than 180 cu. ft./bbl.

Example V

The feed was introduced into the hydrogenation reactor in undiluted form, and was passed continuously for 50 hours at a liquid hourly space velocity of 0.5 over a sulfided cobalt oxide and molybdenum oxide on Al_2O_3 catalyst at 600° F., 1000 p.s.i.g., and a H_2 recycle rate of 6000 s.c.f./bbl. feed. Throughout the 50 hours the concentration of Ni in the product remained below 0.3 p.p.m., averaging less than about 0.21 p.p.m., and the concentration of V in the product remained below about 0.04 p.p.m.

The process of the present invention may be seen to differ markedly from conventional hydrofining processes. Those processes use large amounts of hydrogen to produce H_2S, which is withdrawn to effect removal of a large part of the feed sulfur, and their conditions generally are such that considerable cracking is accomplished. With the process of the present invention, demetalation is accomplished with little or no desulfurization, little or no cracking, a considerable reduction in catalytic cracking coke-forming materials, and with a considerable reduction in hydrogen consumption. The hydrogen sulfide for the process of the present invention may be supplied from an external source instead of relying upon its production from sulfur in the feed, and in this manner hydrogen consumption may be reduced even further. However, the hydrogen consumption even when relying upon the feed sulfur is considerably lower than in conventional hydrofining, because at the operating conditions of the process a small part at most of the sulfur present is converted to hydrogen sulfide, whereas in conventional hydrofining a large part of the sulfur present is converted, with attendant high hydrogen consumption.

Although only certain specific arrangements and modes of construction and operation of the present invention have been described and illustrated, numerous changes could be made in those arrangements and modes without departing from the spirit of the invention, and all such changes that fall within the scope of the appended claim are intended to be embraced thereby.

I claim:

In an integrated catalytic cracking process which comprises separating a crude feed into components comprising at least one fraction suitable as feed to a catalytic cracking unit, and at least one fraction not so suitable because of excessive metals content, the improvement which comprises passing the suitable fraction to a catalytic cracking unit, passing the unsuitable fraction to a residuum stripper, separating said unsuitable fraction in said stripper into fractions including a fraction unsuitable because of excessive metals content as feed to a catalytic cracking unit, demetalating said unsuitable stripper fraction by contacting it with hydrogen in the presence of a sulfided hydrogenation catalyst at a hydrogen supply rate of about 50 to 300 cubic feet of hydrogen per barrel of feed, a pressure of from about 300–3000 p.s.i.g. and a temperature of from about 350° F. to 600° F. whereby a substantial amount of the metals content of said unsuitable stripper fraction is removed therefrom, and passing said demetalated stripper fraction to said catalytic cracking unit.

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