DEMETALATION OF HYDROCARBON CHARGE STOCKS

Inventors: Paul B. Weisz, Yardley; Anthony J. Silvestri, Morrisville, both of Pa.

Assignee: Mobil Oil Corporation

Filed: Dec. 23, 1970

Appl. No.: 100,931

U.S. Cl.................208/211, 208/251 H, 252/454
Int. Cl........................C10g 23/02
Field of Search.....208/251, 253, 211, 208, 209, 208/213, 249, 295, 298, 299, 210, 110;
252/471, 454; 75/115

References Cited

UNITED STATES PATENTS


Primary Examiner—Paul M. Coughlan, Jr.
Assistant Examiner—G. J. Crasanakis
Attorney—Frederick E. Dumoulin, William J. Scherback, Oswald G. Hayes and Andrew L. Gaboriault

ABSTRACT

This specification discloses the demetalation of a hydrocarbon charge stock. The demetalation procedure involves contacting the hydrocarbon charge stock with hydrogen in the presence of, as a catalyst, a material derived from the naturally-occurring under-water deposit known as a manganese nodule. The manganese nodule may be employed without pretreatment or may be pretreated by sulfiding or by leaching to remove and recover one or more valuable metallic constituents. The manganese nodule catalyst, after it has become deactivated by use, may be processed to remove and recover one or more valuable metallic constituents.

23 Claims, 4 Drawing Figures
DEMETALATION OF HYDROCARBON CHARGE STOCKS

BACKGROUND OF THE INVENTION

1. Field of the Invention
This invention relates to the treatment of a hydrocarbon charge stock and relates more particularly to the treatment of a hydrocarbon charge stock to effect removal therefrom of organo-metallic compounds.

2. Description of the Prior Art
U.S. Pat. No. 3,214,236 discloses hydrogenation, desulfurization and denitrogenation as being conversion processes in which manganese nodules are catalytically useful. This patent also discloses that the manganese nodule catalyst can be a source of manganese and other valuable metals after being spent in effecting the desired catalytic conversion.

U.S. Pat. No. 3,509,041 discloses the use of manganese nodules, after pretreatment by base exchange to bond hydrogen ions thereto, in hydrocarbon conversion reactions, specifically cracking, hydrocracking, oxidation, olefin hydrogenation, and olefin isomerization.

U.S. Pat. No. 3,330,096 discloses the use of manganese nodules for removing sulfur compounds from gases.

U.S. Pat. No. 3,471,285 discloses the selective separation of manganese and iron from manganese nodules which also contain cobalt and nickel by reducing the nodules at elevated temperatures and then leaching with an aqueous solution of ammonium sulfate.

SUMMARY OF THE INVENTION

In accordance with the invention, a hydrocarbon charge stock is demetalized by contacting the charge stock with hydrogen, in the presence of, as a catalyst, a material derived from the naturally-occurring underwater deposit known as a manganese nodule. In accordance with a specific embodiment of the invention, the manganese nodule is employed without pretreatment. In accordance with other specific embodiments of the invention, the manganese nodule may be pretreated by sulfiding, or by leaching to remove one or more metallic constituents, or by any combination of the pretreating procedures. In accordance with still another embodiment of the invention, the catalyst, after becoming deactivated by use, is treated to remove and recover therefrom one or more metallic constituents.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 and 2 of the accompanying drawings are photomicrographs of the surfaces of the manganese nodules.

FIG. 3 is a flow diagram illustrating a procedure wherein demetalation of a hydrocarbon charge stock is carried out and the charge stock is then processed for sulfur and/or nitrogen removal.

FIG. 4 is a flow diagram illustrating a procedure wherein demetalation of a hydrocarbon charge stock is carried out and the charge stock is then subjected to catalytic cracking.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Various hydrocarbon charge stocks such as crude petroleum oils, topped crude oils, heavy vacuum gas oils, shale oils, oils from tar sands, and other heavy hydrocarbon fractions such as residual fractions and distillates contain varying amounts of non-metallic and metallic impurities. The non-metallic impurities include nitrogen, sulfur, and oxygen and these exist in the form of various compounds and are often in relatively large quantities. The most common metallic impurities include iron, nickel, and vanadium. However, other metallic impurities including copper, zinc, and sodium are often found in various hydrocarbon charge stocks and in widely varying amounts. The metallic impurities may occur in several different forms as metal oxides or sulfides which are easily removed by single processing techniques such as by filtration or by water washing. However, the metal contaminants also occur in the form of relatively thermally stable organo-metallic complexes such as metal porphyrins and derivatives thereof along with complexes which are not completely identifiable and which are not so readily removed.

The presence of the metallic impurities in the hydrocarbon charge stocks is a source of difficulty in the processing of the charge stocks. The processing of the charge stock, whether the process is desulfurizing, cracking, reforming, isomerizing, or otherwise, is usually carried out in the presence of a catalyst and the metallic impurities tend to foul and inactivate the catalyst to an extent that may not be reversible. Fouling and inactivation of the catalyst are particularly undesirable where the catalyst is relatively expensive, as, for example, where the active component of the catalyst is platinum. Regardless of the cost of the catalyst, fouling and inactivation add to the cost of the processing of the charge stock and therefore are desirably minimized.

Demetalation of the hydrocarbon charge stock can be effected by thermal processing of the charge stock. However, thermal processing results in conversion of an appreciable portion of the charge stock to coke and the portion of the charge stock converted to coke represents a loss of charge stock that desirably should be converted to a more economically valuable product or products. Moreover, by thermal processing, the metallic impurities tend to deposit in the coke with the result that the coke is less economically desirable than it would be in the absence of the metals.

Demetalation can also be effected by catalytic hydroprocessing of the charge stock. However, catalytic hydroprocessing results in the catalyst becoming fouled and inactivated by deposition of the metals on the catalyst. There is no convenient way of regenerating the catalyst and it ultimately must be discarded. Since these catalysts are relatively expensive, catalytic hydroprocessing to demetalize hydrocarbon charge stocks has suffered from adverse economics.

By the process of the invention, an economical and effective demetalation of a hydrocarbon charge stock is obtained. Manganese nodules are readily available in large quantities and are relatively inexpensive. Further, material derived from the nodules is capable of effectively removing the metallic impurities from a
hydrocarbon charge stock. Thus, whereas the material obtained from the manganese nodules becomes fouled and inactivated by the demetalizing process, the material is obtainable at such low cost that the fouled and inactivated material can be discarded without significant effect on the economics of the demetalizing process.

Manganese nodules, as is known, are naturally occurring deposits of manganese, along with other metals, including iron, cobalt, nickel, and copper, found on the floor of bodies of water. They are found in abundance on the floors of oceans and lakes. For example, they are found in abundance on the floor of the Atlantic and Pacific Oceans and on the floor of Lake Michigan. The nodules are characterized by a large surface area, i.e., in excess of 150 square meters per gram. The nodules have a wide variety of shapes but most often those from the oceans look like potatoes. Those from the floor of bodies of fresh water, such as the floor of Lake Michigan, tend to be smaller in size. Their color varies from earthy black to brown depending upon their relative manganese and iron content. The nodules are porous and light, having an average specific gravity of about 2.4. Generally, they range from one-eighth inch to 9 inches in diameter but may extend up to considerably larger sizes approximating 4 feet in length and 3 feet in diameter and weighing as much as 1,700 pounds. In addition to the metals mentioned above, the nodules contain silicon, aluminum, calcium and magnesium, and small amounts of molybdenum, zinc, lead, vanadium, and rare earth metals.

The chemical and physical properties of manganese nodules, as catalytic agents for the demetalation of hydrocarbon charge stocks, are, as compared with conventional catalytic agents for this purpose, considered to be somewhat unusual. The nodules have a high surface area, about 100-250 square meters per gram. They will, however, lose surface area by metal deposition during the demetalation reaction. Further, as shown by Roger G. Burns and D. W. Fuerstenau in American Mineralogist, Vol. 51, 1966, pages 895-902, "Electron-Probe Determination of Inter-Element Relationships in Manganese Nodules", the concentrations of the various metals contained in the nodules, i.e., the manganese, iron, cobalt, copper, and nickel, are not uniform throughout the crystalline structure of the nodule. Rather, a traverse across a section of a nodule will show marked differences in the concentrations of the various metals from point to point of the traverse. However, there appears to be a correlation between the concentrations of iron and cobalt. On the other hand, manufactured catalysts for demetalation are usually as uniform as the manufacturer can achieve.

The accompanying figures illustrate the structure of manganese nodules. These nodules were obtained from the Blake Plateau in the Atlantic Ocean. Each of FIGS. 1 and 2 is a photomicrograph of a surface of the nodules, FIG. 1 showing more of the pore system than FIG. 2. Magnifications in each figure are 150×. In each of the figures, the large dark areas are large pores. The light- and dark-banded regions are solid material. The nodules are formed by slow deposition of colloidal materials. The composition of the particles of the colloidal materials varies with time resulting in the microscopic stratification and inhomogeneity shown in the figures.

The manganese nodules can be employed as the catalyst for the demetalation of the hydrocarbon charge stock substantially as mined, or recovered, from the floor of the body of water in which they occurred. Thus, the nodules, as mined, possibly after washing to remove sea water or lake water therefrom and mud or other loose material from the surface of the nodules, may be employed for demetalation.

The demetalation reaction may also be carried out employing, as the catalyst, manganese nodules which have been subjected to a pretreatment. Pretreatments to which the manganese nodules may be subjected include sulfiding or leaching to remove therefrom one or more components of the nodules.

Sulfiding of the manganese nodules increases the extent of demetalization of the charge stock. It also increases the extent of desulfurization and Conradson Carbon Residue (CCR) reduction, each of which is desirable. This treatment is carried out by contacting the nodules with hydrogen sulfide. The hydrogen sulfide may be pure or may be mixed with other gases. However, the hydrogen sulfide should be substantially free of hydrogen. The temperature of sulfiding may be from about 300° F. to about 450° F. and the time of sulfiding may be from about 4 to about 8 hours. The sulfiding may be effected, for example, by passing the hydrogen sulfide over the manganese nodules continuously during the sulfiding reaction. The space velocity of the hydrogen sulfide is not critical and any space velocity compatible with the equipment and such that some hydrogen sulfide is continuously detected in the exit stream is suitable.

The manganese nodules may also be pretreated by being subjected to leaching to remove therefrom one or more components. As mentioned previously, the manganese nodules contain, in addition to manganese, copper, nickel, and molybdenum. They may be pretreated to leach therefrom the copper, nickel, or molybdenum, or any two, or all three, of these metals. The manganese nodules contain the copper, nickel, and molybdenum in sufficient quantities to provide a commercial source of these metals. Further, the removal, at least partially, of these metals and other of the metallic constituents of the nodules has apparently no effect on the catalytic activity of the nodules for demetalation of hydrocarbon charge stocks. Thus, by this embodiment of the invention, copper, nickel, and molybdenum, and other metals, may be recovered from the nodules for the economic advantage to be gained by such recovery and the remainder of the manganese nodules can then be employed as a catalyst for demetalation of hydrocarbon charge stocks.

Removal of the copper and the nickel may be effected by leaching the manganese nodules with an aqueous solution of a strong acid. By strong acid is meant such acids as hydrochloric, sulfuric, and nitric acids.

The molybdenum may be removed from the manganese nodules by leaching them with aqueous base solutions such as aqueous solutions of sodium hydroxide or sodium carbonate. These solutions should have a pH of at least 8 and preferably should have a pH of at least 10. The leaching with the aqueous base solutions can be carried out at ambient temperatures or at the boiling point of the solution.
The nodules, with or without pretreatment, may be crushed and sized to obtain a desired particle size depending upon the type of demetalation operation employed, for example, a fixed bed operation, an ebullition operation or otherwise.

The demetalation reaction is carried out by contacting the hydrocarbon charge stock simultaneously with the catalyst and with hydrogen. The temperatures at which the reaction is carried out can be from about 650°F. to about 850°F. At the higher temperatures, a greater degree of demetalation occurs. However, the temperatures employed should not be so high as to effect an undesirable degree of alteration of the charge stock. Preferably, the temperatures employed are in the range of 750°-850° F. The pressures at which the reaction is carried out can be from about 100 to about 3,000 pounds per square inch gage (psig). Preferably, the pressures employed are in the range of 500-2,000 psig. Where the reaction is carried out by passing the hydrocarbon charge stock through a bed of the catalyst, the liquid hourly space velocity (LHSV) of the charge stock can be from about 0.2 to 4, preferably 0.5 to 2, volumes of charge stock per volume of catalyst per hour. Hydrogen circulation is at rates of 2,000-15,000, preferably 5,000-10,000, standard cubic feet of hydrogen per barrel of hydrocarbon charge stock. The hydrocarbon charge stock along with the hydrogen may be passed upwardly through a fixed bed of the catalyst in an upflow reactor or may be passed downwardly through a fixed bed of the catalyst in a downflow trickle-bed reactor. The reaction may also be carried out by passing the charge stock and the hydrogen through an ebullient bed of the catalyst. The reaction may also be carried out by contacting the charge stock, the hydrogen, and the catalyst in a batch reactor.

The catalyst, after being employed in the demetalation reaction and having become catalytically deactivated, or spent, can be treated for the recovery therefrom of valuable metals. Thus, the catalyst, after becoming spent, may be treated to recover copper, nickel, molybdenum, or any two, or all three, of these metals. It may also be treated to recover therefrom any other component.

An advantage of the process of the invention resides in its economy with respect to hydrogen consumption. During the demetalation reaction, hydrogen is consumed and the consumption of the hydrogen adds to the cost of demetalation. Thus, reduction in the consumption of the hydrogen is economically desirable. Prior processes directed to demetalation have often required consumption of hydrogen in amounts between about 450 and 1,000 cubic feet per barrel of hydrocarbon charge stock. As compared to this, by the process of the invention, effective demetalation can be effected in many instances with consumption of 50 to 300 cubic feet of hydrogen per barrel of hydrocarbon charge stock.

While we do not wish to be limited to the consequences of any theory, it is believed that the reduced hydrogen consumption to a large extent is due to the sensitivity of the manganese nodules to the effects of sulfur. Manganese nodules, as well as other catalysts heretofore employed for the demetalation of hydrocarbon charge stocks, effect hydrogenation of molecules other than those containing metals. Thus, the manganese nodules, as well as other demetalation catalysts, will effect hydrogenation of benzene rings, for example. This hydrogenation of molecules other than those containing metals therefore results in consumption of the hydrogen in addition to that related to demetalation and, from the standpoint of the desired demetalation, represents a waste of hydrogen. However, as contrasted with other demetalation catalysts, the manganese nodules, in the presence of sulfur, have essentially no activity for hydrogenating benzene and other aromatic molecules. They will, however, hydrogenate olefins. Hydrocarbon charge stocks contain sulfur to a greater or lesser extent, and, regardless of whether the catalyst is subjected to a sulfiding pretreatment, the sulfur in the hydrocarbon charge stocks will effect a rapid sulfiding of the nodules. As a result, hydrogenation of the aromatic constituents of the charge stock is reduced with resulting reduction in the consumption of the hydrogen.

Whereas a rapid sulfiding of the nodules will occur from the sulfur in the hydrocarbon charge stocks, sulfiding pretreatment of the nodules, as previously described, is of value. It is believed that, under reducing conditions, a reduction of the metal oxides in the nodules can occur with consequent loss in surface area and diminished activity. The sulfides on the other hand are more stable to reduction. Thus, when the nodules are exposed to a reducing environment either before or during sulfiding as occurs when the sulfiding results from the sulfur in the charge stock, a prereduction or competitive reduction of the oxides can take place.

The process of the invention may be employed for the demetalation of any hydrocarbon charge stock containing organo-metallic compounds. Ordinarily, these will be hydrocarbon charge stocks containing sufficient metal to cause difficulty in the processing, or other subsequent use, of the charge stocks. Other subsequent use of the charge stocks can include burning of the charge stock as fuel wherein the metals cause corrosion problems. These charge stocks include whole crude petroleum oils, topped crude oils, residual oils, distillate fractions, heavy vacuum gas oils, shale oils, oils from tar sands, and other heavy hydrocarbon oils. Charge stocks derived from Mid-Continent and East Texas crude contain small amounts of metals. For example, some East Texas crude contain about 0.1 parts per million of vanadium and 2-4 parts per million of nickel. Charge stocks derived from West Texas crudes and foreign crudes, however, can contain larger amounts of metal. Kuwait crude can contain over 32 parts per million of vanadium and over 9 parts per million of nickel while Venezuelan crudes can contain 200-400 parts per million of vanadium and 17 to 59 parts per million of nickel.

The process of the invention can be carried out in conjunction with subsequent steps of processing of the hydrocarbon charge stock. For example, the hydrocarbon charge stock can be subsequently processed for removal of sulfur and/or nitrogen. Further, for example, the hydrocarbon charge stock can be subsequently processed by catalytic cracking.

Concerning processing of the hydrocarbon charge stock for removal of sulfur and/or nitrogen subsequent to demetalation employing manganese nodules, this
represents an operation in which economies are effected by employing an inexpensive catalyst in the first step to increase the life of a relatively expensive catalyst in the subsequent step. For sulfur and/or nitrogen removal, relatively expensive manufactured catalyst, particularly suited for this purpose, is employed. The prior removal of a significant fraction of the metals by the manganese nodules will reduce the deterioration of the more expensive manufactured catalyst by poisoning from the metals in the charge stock and lead to extended life of the more expensive catalyst. The processing sequence is unique in that the overall results are not mere additive results of the steps; catalyst life of the desulfurization catalyst is modified by the presence of the nodules, while the nodules perform a dual function of both demetalation and partial desulfurization.

The desulfurization catalyst suitable for use in such a combination process is broadly characterized as any hydrogenation catalyst which is tolerant of sulfur and nitrogen and which can be employed in an operating cycle or onstream life that is economically attractive. Thus, the desulfurization and/or denitrogenation catalyst may be any one of those known and used for such purposes in the prior art. Prominent catalysts used for this purpose include cobalt molybdate on alumina with or without small amounts of silica, nickel sulfide, tungsten sulfide, and nickel-tungsten sulfide alone or on a support material such as alumina which may or may not contain small amounts of combined silica. Other suitable and known desulfurization catalysts may also be employed.

To facilitate an understanding of the described combination process, reference will now be had to FIG. 3. In the arrangement of FIG. 3, a relatively heavy hydrocarbon feed such as a residual oil containing sulfur and metal contaminants is introduced to the process through line 10 to furnace 11 wherein the hydrocarbon feed is heated to an elevated temperature in the range of from about 650°F to about 850°F. The hydrocarbon feed may be heated either alone or in combination with hydrogen rich gas supplied through line 12, it being preferred to mix the hydrogen rich gas with the feed prior to being heated in the furnace. Therefore, the heated mixture is introduced through line 13 to demetalation reactor 14. Make-up fresh catalyst may be added with the hydrocarbon feed through line 15 or directly to the demetalation reactor. The demetalation reactor can be operated under liquid phase conditions wherein finely divided manganese nodules are added to and maintained in suspended motion by the liquid hydrocarbon flowing upwardly through the demetalation reactor. The rate of flow of the liquid feed upwardly through the demetalation reactor in this type of operation is sufficiently high to suspend the catalyst particles in a fairly random movement. The technique of causing random movement of particulate material by the upward flow of the liquid has been identified with the prior art as ebullition. The demetalation of the feed may also be accomplished in a dense fluid bed of solid particulate material, a moving bed operation, or other convenient means for effecting demetalation where the solid particulate material can be replaced as required after becoming spent.

The liquid hydrocarbon leaves the upper portion of the demetalation reactor through line 20. Hydrogen gas is purged from the upper portion of the demetalation reactor through line 21. A portion of this gas may be recycled to the demetalation reactor through line 22 provided with pump 23 and connected to line 12. Make-up hydrogen can be provided through line 24, also connected to line 12, if make-up hydrogen gas is required. At the level at which the hydrocarbon leaves the demetalation reactor, the hydrocarbon may contain catalyst fines and a fines separator 25 is provided. The fines separator may be a cyclone separator, filter arrangement, or any other convenient means for separating the entrained fines from the withdrawn liquid material. Liquid material is withdrawn from the fines separator through line 26 provided with pump 21 and passed on for further processing. If desired, intermediate fractionation, not shown, can be provided.

Spent fines, having relatively high concentrations of deposited metals therein of nickel, vanadium, copper and iron, may be withdrawn from the lower portion of the demetalation reactor through line 26.

Demetalation in the reactor will be carried out under the conditions previously mentioned, i.e., temperature within the range of from about 650°F to about 850°F, a pressure within the range of 100 to 3,000 psig, and a space velocity within the range of 0.2 to about 4. Some desulfurization of the charge will also be accomplished during demetalation but will be less effective than desired to be accomplished in the second step of the process.

In the second step of the process, the hydrocarbon charge recovered from the demetalation reactor, and in which the metals level has been significantly reduced, is then subjected to catalytic hydrodesulfurization. For this purpose, the hydrocarbon charge is passed to furnace 33 and thence through lines 34 and 35 to desulfurization reactor 36. Hydrogen make-up is provided through line 40. Catalytic hydrodesulfurization of sulfur-bearing hydrocarbon charge material has been known and practiced in the petroleum refining art for years. Generally speaking, satisfactory desulfurization results are obtained when operating at a temperature in the range of from about 650°F to about 850°F and a pressure in the range of about 500 to about 3,000 psig when employing a space velocity in the range of about 3. Suitable catalysts have already been described above.

In the desulfurization reactor, the desulfurization zone comprises a fixed catalyst bed through which the hydrocarbon charge is passed downwardly under desulfurizing conditions. Other types of desulfurization contact zones may be employed such as the trickle phase or an ebullating bed of catalyst. In the arrangement shown, the hydrocarbon charge, in admixture with hydrogen rich gas in suitable proportions, is caused to move, after suitable heating thereof in the furnace, downwardly through the bed of catalyst under desulfurizing conditions. The effluent is removed from the lower portion of the reactor through line 41 and passed to a separator 42. In the separator, a gasiform stream is separated from a normally liquid product stream. The gasiform stream comprising hydrogen, low boiling hydrocarbon, and compounds of sulfur and nitrogen is removed from the upper portion of the separator.
through line 43. This gasiform stream may be treated to produce a hydrogen rich stream by any one of a number of known techniques and the thus produced hydrogen rich stream recycled through line 35 for admixture with the hydrocarbon charge to be desulfurized. The remainder of the gasiform stream is purged from the system through line 45. Desulfurized product is removed from the separator through line 46.

It is contemplated having more than one desulfurization zone in sequence in which the latter zone or zones, depending on the number employed, will be employed to effect substantial denitrogenation of the hydrogen charge when required. Thus the process contemplates a third catalytic contact zone (not shown) for effecting more complete desulfurization and/or denitrogenation of the hydrocarbon charge in which case the third zone may be placed after the separator.

Concerning processing of hydrocarbon charge stock by catalytic cracking subsequent to demetalation, metal poisoning of the catalysts employed for cracking can lead to severe problems such as low gas density due to the formation of hydrogen, higher gas make, and lowered gasoline yields. This problem is generally circumvented by controlling the allowable metals content of the feed stock to the cracking unit. However, this restriction also limits the percentage of crude which can provide suitable feed stock to a cracking unit. Metals content of a catalytic cracking stock is often expressed in terms of a metals factor which is defined as parts per million (ppm) Fe + ppm V + 10 times the ppm Ni + 10 times the ppm Cu. In general, for satisfactory performance of a catalytic cracking unit, the metals factor of the feed stock should be limited to about 5. The invention allows the use of a process complex which includes demetalation which removes, for example, 90 percent of the metals; thus the metals factor of the feed stock to this catalytic processing complex can now be as high as 50. This in turn will significantly increase the percentage of crude which provides an acceptable feed stock for catalytic cracking. This processing combination is accomplished by distillation separation of a charge stock into a lighter and a heavier metals rich portion, demetalation of the heavier portion, and feeding the demetalized effluent to the catalytic cracking unit; all or part of the lighter portion would preferably be fed to the same catalytic cracking unit.

Reference will now be had to FIG. 4. The hydrocarbon charge stock, i.e., crude oil, is brought into an atmospheric pressure still 50 through line 51. Light gases are removed from the still through line 52 while the fraction boiling between the light gases and 400° F. is removed through line 53. The 400°-600° F. material from this still is used for catalytic cracking and is passed through lines 54 and 55 to catalytic cracking unit 60. The bottoms from the atmospheric still are passed through line 61 on to a vacuum still 62. The overhead from the vacuum still is passed through line 63 along with hydrogen to a demetallation reactor 64, while the bottoms will generally be passed through line 65 to thermal processing. The effluent from the demetalization reactor is then passed on to the catalytic cracking unit through line 55. The cut temperature of the vacuum still depends on the specific crude oil and the efficiency of the demetalation reactor, and is adjusted to yield an effluent from the demetallation reactor having a metals factor no greater than about 5. When the demetalization reactor is efficient enough, the vacuum tower can be completely circumvented and the bottoms from the atmospheric still passed directly to the demetalization unit.

Both the conversion and gasoline yield from catalytic cracking can often be improved by prior hydrogenation of the feed stock. Either the percentage of crude suitable as feed stock to such a conventional process or the life of the relatively expensive hydrogenation catalyst can be increased by providing a prior demetalization process using a relatively cheap disposable catalyst. Thus, the demetalization reactor 4 of FIG. 4 could be replaced by a complex consisting of both a demetalization reactor and a hydrogenation reactor (not shown).

For example, the system of demetalization plus desulfurization and/or denitrogenation, described in more detail in FIG. 3, could be used. The demetalization reactor now permits an increase in the cut temperature of the vacuum still or possibly direct use of the bottoms from the atmospheric still with an increase in the amount of catalytic cracking feed stock. The hydrogenation reactor, in turn, increases the hydrogen content of the feed stock leading to greater gasoline production from a given amount of feed stock. In the absence of the demetalization reactor, either increasing the cut temperature or completely bypassing the vacuum still would increase the amount of metals reaching the hydrogenation catalyst and would significantly curtail the life of this more expensive catalyst.

The following examples will be illustrative of the invention.

EXAMPLE 1

This example will illustrate the catalytic effect of manganese nodules on demetalation of a topped crude charge stock. The charge stock was Agha Jari topped crude and had the following physical characteristics and chemical composition:

Initial Boiling Point (IBP) 400°F.
Gravity, API 24.4
Sulfur, weight percent (wt. %) 2.20
Nitrogen, wt. % 0.20
Conradson Carbon Residue (CCR) wt. % 4.43
Nickel (Ni), parts per million (ppm) 13.3
Vanadium (V), ppm 45.8

The manganese nodules were obtained from the bottom of Sturgeon Bay in Lake Michigan. These nodules, after recovery from the lake bottom, were washed to remove salt, water, and mud. They were then crushed, leached with boiling water five times, dried to constant weight at 100° C., and sieved to 14-30 mesh (U.S. Standard Sieve Series). The nodules had the following physical characteristics and chemical composition:

Surface area, square meters per gram (m²g⁻¹) 200
Particle density, grams per cubic centimeter (g cm⁻³) 1.49
Pore diameter, Angstrom units (Å) 81
Pore volume, cubic centimeters per gram (cm³g⁻¹Å⁻¹) 0.409
Real density, g cm⁻³ 3.75
Manganese (Mn), wt. % 9.19
Iron (Fe), wt. % 35.4
Nickel (Ni), wt. % <0.01
Cobaltous oxide (CoO), wt. % 0.04
Molybdenum trioxide (MoO₃), wt. % 0.08
The nodules were placed in a downflow trickle-bed reactor, and hydrogen and the topped crude were passed through the reactor for 7 days. The reaction conditions and results are shown in Table I.

The hydrogen consumption in Table I, and in the subsequent tables, was a time-weighted average consumption over the course of the run.

**TABLE I**

<table>
<thead>
<tr>
<th>TIME ON STREAM, DAYS</th>
<th>% DESULFURIZATION</th>
<th>% CCR REDUCTION</th>
<th>% DEMETALATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>0.05</td>
<td>1.54</td>
<td>2.04</td>
</tr>
<tr>
<td>HYDROGEN CONSUMPTION, Standard Cubic Feet of Hydrogen per Barrel of Charge Stock (SCF/B)</td>
<td>12</td>
<td>0.06</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**TABLE II**

<table>
<thead>
<tr>
<th>TIME ON STREAM, DAYS</th>
<th>% DESULFURIZATION</th>
<th>% CCR REDUCTION</th>
<th>% DEMETALATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>0.05</td>
<td>1.54</td>
<td>2.04</td>
</tr>
<tr>
<td>HYDROGEN CONSUMPTION, Standard Cubic Feet of Hydrogen per Barrel of Charge Stock (SCF/B)</td>
<td>12</td>
<td>0.06</td>
<td>0.2</td>
</tr>
</tbody>
</table>

This example will illustrate the effect of temperature on the demetalation activity of sulfided manganese nodules.

The procedure set forth in Example 2 was continued for an additional period of 6.9 days. However, during this additional period, the temperatures employed were 800° and 850° F. The reaction conditions and results are given in Table III. In Table III, the hydrogen consumption is given only for the period that the reaction was carried out at 800° F. During the period at which the reaction was carried out at 850° F., difficulty was encountered in obtaining measurement of hydrogen consumption.

It will be noted from Tables II and III that, at 750° F., the demetalation at the beginning of operation was 98.9 percent. However, demetalation decreased as the operation continued and at the end of 10 days had declined to 75.8 percent. On the other hand, with the temperature being increased at this time to 800° F., demetalation rose to 96.4 percent and remained at this figure or higher for the entire 800° F. portion of the operation. At 850° F., the demetalation was over 99 percent complete.

**TABLE III**

<table>
<thead>
<tr>
<th>TIME ON STREAM, DAYS</th>
<th>% DESULFURIZATION</th>
<th>% CCR REDUCTION</th>
<th>% DEMETALATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>0.05</td>
<td>1.54</td>
<td>2.04</td>
</tr>
<tr>
<td>HYDROGEN CONSUMPTION, Standard Cubic Feet of Hydrogen per Barrel of Charge Stock (SCF/B)</td>
<td>12</td>
<td>0.06</td>
<td>0.2</td>
</tr>
</tbody>
</table>

This example will illustrate the catalytic effect of the manganese nodules for demetalation of a whole crude oil. The crude oil was Kuwait whole crude and had the following physical properties and chemical composition:

Gravity, °API | 31.1
The manganese nodules were the same as those employed in Example 1. They were packed into a downflow trickle-bed reactor and sulfided by passing 100 percent hydrogen sulfide through them at 450°F, and 1 atmosphere pressure for 8 hours at a space velocity of 480 volumes per volume of nodules per hour. After sulfiding, the crude oil and hydrogen were passed through the reactor. The reaction conditions and results are given in Table IV.

It will be seen that the demetalation activity of the catalyst was high throughout the period of the reaction. Demetalation was 96.9 percent after 2 hours of operation. Even after 5 days of operation, demetalation was still 82 percent.

### EXAMPLE 5

This example will illustrate the catalytic effect of manganese nodules on the demetalation of another topped crude oil. The nodules were the same as those employed in Example 1 except that they were sieved to 10–20 mesh. The nodules were packed into a downflow trickle-bed reactor and sulfided as described in Example 1. The charge stock was a Kuwait topped crude and had the following characteristics:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur, wt %</td>
<td>1.00</td>
</tr>
<tr>
<td>Nitrogen, wt %</td>
<td>0.06</td>
</tr>
<tr>
<td>CCR, wt %</td>
<td>2.10</td>
</tr>
<tr>
<td>Ni, ppm</td>
<td>7.23</td>
</tr>
<tr>
<td>V, ppm</td>
<td>3.93</td>
</tr>
</tbody>
</table>

This example will illustrate the catalytic effect of manganese nodules on the demetalation of petroleum residual oil. The petroleum residual oil was a Kuwait atmospheric residual oil and had the following characteristics:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur, wt %</td>
<td>3.74</td>
</tr>
<tr>
<td>Nitrogen, wt %</td>
<td>0.13</td>
</tr>
<tr>
<td>CCR, wt %</td>
<td>7.13</td>
</tr>
<tr>
<td>Ni, ppm</td>
<td>9.24</td>
</tr>
<tr>
<td>V, ppm</td>
<td>32.82</td>
</tr>
</tbody>
</table>

### TABLE VI

**Time on stream, days:**

- 45
- 59
- 72

**Percent demetalation:**

- 89.4
- 89.2
- 89.0

**Percent CCR reduction:**

- 42.8
- 42.6
- 42.4

**Example 6**

The nodules were the same as those employed in Example 1 except that they were sieved to 10–20 mesh and were sulfided. Sulfiding was effected by loading the nodules into an upflow reactor and passing hydrogen sulfide through them. Sulfiding was carried out under the same conditions as set forth in Example 2. Reaction conditions and results are given in Table VI.

It will be noted that, over the approximately 19-day run, the demetalation varied between 83.6 and 95.5 percent.
EXAMPLE 7

This example will illustrate the results obtained employing a conventional catalyst for demetalation of the same residual oil employed in Example 6. The catalyst employed was a molybdenum oxide-aluminum oxide catalyst and comprised 11.1 weight percent of MoO₃ on Al₂O₃. It is identified by the trade name "Harshaw Mo 1210 T". This catalyst was placed in a downflow reactor and the residual oil and hydrogen were passed through it at a variety of conditions. The conditions and results are given in Table VII. The conditions used between 4.79 and 9.42 days in this table were essentially the same as those employed in Example 6.

As shown in Table VII, the demetalation varied between 82.2 and 95.0 percent. This is comparable to the extent of demetalation obtained with the manganese nodules in Example 6. However, the hydrogen consumption in Example 7 was 563 SCF/B as compared to the lower hydrogen consumption in Example 6 of 222 SCF/B.

EXAMPLE 8

This example will illustrate the effect of the manganese nodules from the Atlantic Ocean on the demetalation of a residual oil. The example will also illustrate the effect of three other catalysts, the first of which is not considered to have hydrogenation activity and the other two of which contain metals or metal oxides which are used to impart hydrogenation activity in conventional hydrosulfurization catalysts. The oil was a West Texas Sour vacuum residue oil and had the following physical properties and chemical composition:

- Gravity, °API: 7.3
- Hydrogen, wt. %: 10.05
- Sulfur, wt. %: 4.02
- Nitrogen, wt. %: 0.36
- CCR, wt. %: 15.9
- Ni, ppm: 19
- V, ppm: 32

The manganese nodules were obtained from the Blake Plateau in the Atlantic Ocean and, after crushing and washing with hot water, had the following properties and chemical composition:

- Surface Area, m²/g: 225
- Pore Diameter, Å: 1.21
- Pore Volume (cc/g): 0.08
- Real density, g/cm³: 4.06
- Mn, wt. %: 20.9
- Fe, wt. %: 13.3
- Ni, wt. %: 0.92
- CoO, wt. %: 0.43
- MoO₃, wt. %: <0.1

These nodules were sieved to 14-30 mesh and were loaded into an upflow reactor, and a West Texas Sour vacuum gas oil which was relatively free of metallic constituents was passed over them along with hydrogen for a period of 3 days at 2,000 psig at 700°-750°F and a space velocity of 1.16 volumes of gas oil per volume of nodules per hour. Thereafter, the West Texas Sour vacuum residual oil was passed over the nodules along with the hydrogen at a temperature of 750°F. After a short time at 750°F, the temperature was raised to 800°F. Results obtained at 800°F are given in Table VIII.

The three other catalysts were, respectively, (I) an alumina (Al₂O₃) containing 6 percent by weight of silica (SiO₂), (II) an alumina base containing 6 percent by weight of silica and 0.5 percent by weight of nickel, and (III) an alumina base containing 6 percent by weight of silica, 3.10 percent by weight of cobalt oxide (CoO) and 17.3 percent by weight of molybdenum oxide (MoO₃). These catalysts were also loaded into upflow reactors and the West Texas Sour vacuum residual oil along with hydrogen was passed over the catalysts. Reaction conditions and results obtained are also given in Table VIII.

<table>
<thead>
<tr>
<th>EXAMPLE 7</th>
<th>EXAMPLE 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>This example will illustrate the results obtained employing a conventional catalyst for demetalation of the same residual oil employed in Example 6. The catalyst employed was a molybdenum oxide-aluminum oxide catalyst and comprised 11.1 weight percent of MoO₃ on Al₂O₃. It is identified by the trade name &quot;Harshaw Mo 1210 T&quot;. This catalyst was placed in a downflow reactor and the residual oil and hydrogen were passed through it at a variety of conditions. The conditions and results are given in Table VII. The conditions used between 4.79 and 9.42 days in this table were essentially the same as those employed in Example 6. As shown in Table VII, the demetalation varied between 82.2 and 95.0 percent. This is comparable to the extent of demetalation obtained with the manganese nodules in Example 6. However, the hydrogen consumption in Example 7 was 563 SCF/B as compared to the lower hydrogen consumption in Example 6 of 222 SCF/B.</td>
<td>This example will illustrate the effect of the manganese nodules from the Atlantic Ocean on the demetalation of a residual oil. The example will also illustrate the effect of three other catalysts, the first of which is not considered to have hydrogenation activity and the other two of which contain metals or metal oxides which are used to impart hydrogenation activity in conventional hydrosulfurization catalysts. The oil was a West Texas Sour vacuum residual oil and had the following physical properties and chemical composition: - Gravity, °API: 7.3 - Hydrogen, wt. %: 10.05 - Sulfur, wt. %: 4.02 - Nitrogen, wt. %: 0.36 - CCR, wt. %: 15.9 - Ni, ppm: 19 - V, ppm: 32</td>
</tr>
</tbody>
</table>
EXAMPLE 9

This example will illustrate the demetalation activity of a topped petroleum crude oil. The nodules employed were obtained from the Blake Plateau in the Atlantic Ocean. These nodules, after crushing and washing with hot water, had the following physical properties and chemical composition:

- **Surface Area**, m²/g: 226
- **Particle Density**, g cm⁻³: 1.43
- **Pore Diameter**, A: 73
- **Pore Volume**, cm³/g: 0.41
- **Real Density**, g cm⁻³: 3.33
- **Mn**, wt. %: 18.8
- **Fe**, wt. %: 12.3
- **Ni**, wt. %: 0.72
- **CoO**, wt. %: 0.46
- **MoO₃**, wt. %: 0.1

The topdressed petroleum crude oil was the same as that employed in Example 1. The reaction conditions and results obtained are given in Table XI.

As shown, the demetalation varied between 95.8 and 79.7 percent over the course of the run.

**TABLE XI**

<table>
<thead>
<tr>
<th>Temperature — 750°F.</th>
<th>Pressure — 2000 psig</th>
<th>H₂ Circ — 10,000 SCF/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time on Stream, Days</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.45</td>
<td>0.90</td>
</tr>
<tr>
<td>0.23</td>
<td>0.45</td>
<td>0.90</td>
</tr>
<tr>
<td>0.64</td>
<td>1.44</td>
<td>2.24</td>
</tr>
<tr>
<td>1.14</td>
<td>2.14</td>
<td>2.37</td>
</tr>
</tbody>
</table>

**HYDROGEN CONSUMPTION, SCF/B — 81**

**LIQUID PRODUCT PROPERTIES**

<table>
<thead>
<tr>
<th>Gravity, API</th>
<th>Sulfur, wt %</th>
<th>Nitrogen, wt %</th>
<th>CCR, wt %</th>
<th>Ni, ppm</th>
<th>V, ppm</th>
<th>% DESULFURIZATION</th>
<th>% CCR REDUCTION</th>
<th>% DEMETALATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.1</td>
<td>1.42</td>
<td>0.17</td>
<td>3.46</td>
<td>4.1</td>
<td>8.7</td>
<td>55.5</td>
<td>21.9</td>
<td>78.3</td>
</tr>
<tr>
<td>25.2</td>
<td>1.67</td>
<td>0.19</td>
<td>4.06</td>
<td>6.4</td>
<td>15.9</td>
<td>24.1</td>
<td>8.4</td>
<td>63.8</td>
</tr>
<tr>
<td>24.9</td>
<td>1.77</td>
<td>0.19</td>
<td>3.85</td>
<td>6.3</td>
<td>16.9</td>
<td>21.0</td>
<td>13.3</td>
<td>60.7</td>
</tr>
<tr>
<td>24.9</td>
<td>1.82</td>
<td>0.20</td>
<td>4.05</td>
<td>9.1</td>
<td>19.7</td>
<td>18.6</td>
<td>11.3</td>
<td>50.8</td>
</tr>
<tr>
<td>24.9</td>
<td>1.81</td>
<td>0.20</td>
<td>3.93</td>
<td>10.4</td>
<td>21.4</td>
<td>17.3</td>
<td>5.9</td>
<td>43.7</td>
</tr>
<tr>
<td>24.9</td>
<td>1.80</td>
<td>0.20</td>
<td>4.17</td>
<td>10.2</td>
<td>22.9</td>
<td>17.7</td>
<td>3.8</td>
<td>44.0</td>
</tr>
</tbody>
</table>

**EXAMPLE 10**

This example will illustrate the demetalation of a topped petroleum crude oil at a lower pressure and at a lower space velocity than in the previous example.

The manganese nodules and the topped petroleum crude oil were the same as those in the previous example. During the run, the temperature was increased from 750°F to 800°F. The reaction conditions and the results obtained are shown in Table X.

As shown, the percent demetalation varied between 93.1 and 59.2 percent over the course of the run.

**TABLE X**

<table>
<thead>
<tr>
<th>Temperature — 750°F—800°F.</th>
<th>Pressure — 560 psig</th>
<th>H₂ Circ — 10,000 SCF/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time on Stream, Days</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.11</td>
<td>0.25</td>
<td>0.64</td>
</tr>
<tr>
<td>0.64</td>
<td>1.14</td>
<td>1.64</td>
</tr>
<tr>
<td>1.64</td>
<td>2.14</td>
<td>2.43</td>
</tr>
<tr>
<td>2.63</td>
<td>3.09</td>
<td></td>
</tr>
<tr>
<td>HYDROGEN CONSUMPTION, SCF/B — 85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEMPERATURE, °F.</td>
<td>750 750 750 750 800 800 800</td>
<td></td>
</tr>
<tr>
<td>LIQUID PRODUCT PROPERTIES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gravity, API</td>
<td>Sulfur, wt %</td>
<td>Nitrogen, wt %</td>
</tr>
<tr>
<td>27.5</td>
<td>1.04</td>
<td>0.15</td>
</tr>
<tr>
<td>25.5</td>
<td>1.15</td>
<td>0.19</td>
</tr>
<tr>
<td>25.6</td>
<td>1.63</td>
<td>0.19</td>
</tr>
<tr>
<td>25.3</td>
<td>1.63</td>
<td>0.19</td>
</tr>
<tr>
<td>25.4</td>
<td>1.55</td>
<td>0.19</td>
</tr>
<tr>
<td>24.6</td>
<td>1.54</td>
<td>0.19</td>
</tr>
</tbody>
</table>

**EXAMPLE 11**

This example will illustrate the demetalation activity of manganese nodules obtained from the Atlantic Ocean on a topped petroleum crude oil.

The nodules employed were obtained from the Blake Plateau in the Atlantic Ocean. These nodules, after crushing and washing with hot water, had the following physical properties and chemical composition:

- **Surface Area**, m²/g: 226
- **Particle Density**, g cm⁻³: 1.43
- **Pore Diameter**, A: 73
- **Pore Volume**, cm³/g: 0.41
- **Real Density**, g cm⁻³: 3.33
- **Mn**, wt. %: 18.8
- **Fe**, wt. %: 12.3
- **Ni**, wt. %: 0.72
- **CoO**, wt. %: 0.46
- **MoO₃**, wt. %: 0.1

The topdressed petroleum crude oil was the same as that employed in Example 1. The reaction conditions and results obtained are given in Table XI.

As shown, the demetalation varied between 95.8 and 79.7 percent over the course of the run.

**EXAMPLE 12**

This example will illustrate the demetalation effect of manganese nodules from the Pacific Ocean on a topped petroleum crude oil.

The nodules employed were obtained from the Pacific Ocean and, after crushing and washing with hot water, had the following physical properties and chemical composition:

- **Surface Area**, m²/g: 230
- **Particle Density**, g cm⁻³: 1.52
- **Pore Diameter**, A: 69
- **Pore Volume**, cm³/g: 0.40
- **Real Density**, g cm⁻³: 3.80
- **Mn**, wt. %: 28.5
- **Fe**, wt. %: 13.9
- **Ni**, wt. %: 1.21
- **CoO**, wt. %: 0.23
- **MoO₃**, wt. %: 0.1

The nodules were sieved to 14–30 mesh and sulfided in accordance with the procedure described in Example 2. The reaction conditions and results obtained are given in Table XII.

As shown, the demetalation varied between 60.1 and 86.1 percent over the course of the run.
TABLE XII

Temperature — 750°F.
Pressure — 2000 psig
H₂ Circ. — 10,000 SCF/B

<table>
<thead>
<tr>
<th>TIME ON STREAM, DAYS</th>
<th>0.06</th>
<th>0.20</th>
<th>0.60</th>
<th>1.10</th>
<th>1.60</th>
<th>2.15</th>
<th>2.60</th>
</tr>
</thead>
<tbody>
<tr>
<td>HYDROGEN CONSUMPTION, SCF/B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LIQUID PRODUCT PROPERTIES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gravity, API</td>
<td>26.5</td>
<td>25.5</td>
<td>25.1</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Sulfur, wt %</td>
<td>1.20</td>
<td>1.39</td>
<td>1.49</td>
<td>1.50</td>
<td>1.52</td>
<td>1.47</td>
<td>1.53</td>
</tr>
<tr>
<td>Nitrogen, wt %</td>
<td>0.17</td>
<td>0.19</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>CCR, wt %</td>
<td>3.17</td>
<td>3.58</td>
<td>4.04</td>
<td>4.29</td>
<td>4.23</td>
<td>4.11</td>
<td>4.15</td>
</tr>
<tr>
<td>Ni, ppm</td>
<td>4.1</td>
<td>3.2</td>
<td>5.1</td>
<td>8.9</td>
<td>6.9</td>
<td>7.6</td>
<td>7.8</td>
</tr>
<tr>
<td>V, ppm</td>
<td>11.4</td>
<td>5.0</td>
<td>8.2</td>
<td>14.7</td>
<td>13.4</td>
<td>9.3</td>
<td>14.3</td>
</tr>
</tbody>
</table>

TABLE XIV

% DESULFURIZATION | 45.5 | 36.8 | 32.3 | 31.8 | 30.9 | 33.2 | 30.5 |
% CCR REDUCTION | 28.4 | 19.2 | 8.8 | 3.2 | 4.5 | 7.2 | 6.3 |
% DEMETALATION | 73.8 | 86.1 | 77.5 | 60.1 | 65.7 | 72.6 | 62.6 |

Example 13

This example will demonstrate the sensitivity of manganese nodules to the effect of sulfur with respect to the hydrogenation of aromatic compounds.

In this example, in the first portion thereof, benzene and hydrogen were passed over three different catalysts packed into a reactor. The first two catalysts were Atlantic Ocean nodules having the physical characteristics and chemical composition as given in Example 8, and Lake Michigan nodules having the physical properties and chemical composition given in Example 1. The third catalyst was the same type of conventional catalyst containing CoO/MoO₃ employed in Example 7. The reaction conditions were as follows:

Temperature | 700°F.
Pressure | 1,050 psig
HHSV | 4.0
Ratio of Hydrogen to Benzene | 2.68

At the end of two hours, the effluent stream from the reactors was analyzed for the proportion of cyclohexane contained therein. The results are given in Table XIII.

TABLE XIII

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mole Percent of Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atlantic Ocean Nodules</td>
<td>87.6</td>
</tr>
<tr>
<td>Lake Michigan Nodules</td>
<td>45.3</td>
</tr>
<tr>
<td>CoO/MoO₃</td>
<td>93.1</td>
</tr>
</tbody>
</table>

It will be observed from Table XIII that each of the catalysts had significant benzene hydrogenation activity, with the CoO/MoO₃ having the greatest activity.

In the second portion of this example, the procedure was repeated except that an olefin, i.e., hexene-1, and a sulfur-containing organic compound, i.e., 2-methyl thiophene, were mixed with the benzene. The mixture had the following composition in weight percent:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>79.4</td>
</tr>
<tr>
<td>Hexene-1</td>
<td>18.2</td>
</tr>
<tr>
<td>2-Methyl Thiophene</td>
<td>2.4</td>
</tr>
</tbody>
</table>

The reaction conditions were:

Temperature | 700°F.
Pressure | 1050 psig
HHSV | 4.0
Ratio of Hydrogen to other reactants | 10.0

After 22.5 hours on stream, the effluents from the reactors were analyzed to determine the extent of benzeno and hexene-1 hydrogenation and sulfur removal. The results are given in Table XIV.

Example 14

This example will illustrate the processing sequence, described in connection with FIG. 3, of demetallation followed by hydrotreating for sulfur and nitrogen removal. The Kuwait atmospheric residual oil described in Example 6 is fed to the demetallation reactor 14. The catalyst in the demetallation reactor is manganese nodules which have been cracked to small particle size. The effluting bed demetallation reactor is operated at 800°F., a LHSV of 1.0, a pressure of 2,000 psig, and a hydrogen circulation rate of 10,000 SCF/B. Ten percent of the catalyst in the demetallation reactor is withdrawn daily and an equivalent amount of fresh catalyst added daily.

The metals content of the liquid product from the demetallation reactor is significantly reduced relative to that of the feed to the demetallation reactor. The sulfur content is also reduced but to a lesser extent. The product from the demetallation reactor is passed on to the desulfurization reactor 36. The catalyst in the desulfurization reactor is cobalt molybdate on alumina. The desulfurization reactor is operated at a LHSV of 1.0, a temperature of 800°F., a pressure of 2,000 psig and a hydrogen circulation rate of 10,000 SCF/B. The sulfur content of the product from the desulfurization reactor is significantly reduced relative to the feed to the desulfurization reactor.

Example 15

This example will illustrate the processing sequence, described above in connection with FIG. 4, of demetallation prior to catalytic cracking. A Kuwait crude oil is fed to atmospheric still 50. The bottoms from the atmospheric still, which are very similar to the Kuwait atmospheric residual oil described in Example...
3,716,479

6. are passed to vacuum still 62. The cut temperature of the vacuum still is adjusted so that the overhead has a metals factor of about 50. This overhead is then passed on to demetallation reactor 64. The catalyst in the demetallation reactor is manganese nodules which have been crushed to small particle size. The ebulliating bed demetallation reactor is operated at a LHSV of 0.5, a pressure of 2,000 psig, and a hydrogen circulation rate of 10,000 SCF/B. Ten percent of the catalyst in the demetallation reactor is withdrawn daily and an equivalent amount of fresh catalyst added daily. The temperature of the demetallation reactor is controlled such that the product from this reactor has a metals factor of about 5. This product is then passed on to catalytic cracking unit 60.

EXAMPLE 16

This example will illustrate a processing sequence of demetallation and hydrogenation prior to catalytic cracking. A Kuwait crude oil is fed to atmospheric still 50 as illustrated in FIG. 4. The bottoms from the atmospheric still, which are very similar to the Kuwait atmospheric residual oil described in Example 6, are passed to vacuum still 62. The cut temperature of the vacuum still is adjusted so that the overhead has a metals factor of about 50. This overhead is then passed on to demetallation reactor 64 containing manganese nodules which have been crushed to small particle size. The ebulliating bed demetallation reactor is operated at a temperature of 800°F, a LHSV of 1.0, a pressure of 2,000 psig, and a hydrogen circulation rate of 10,000 SCF/B. Ten percent of the catalyst in the demetallation reactor is withdrawn daily and an equivalent of fresh catalyst added daily.

The product from the demetallation reactor, which has been significantly reduced in metals content relative to the feed to the demetallation reactor, is passed on to a hydrogenation reactor, i.e., the desulfurization reactor 36 illustrated in FIG. 3. The catalyst in the hydrogenation reactor is cobalt molybdate on alumina. The hydrogenation reactor is operated at a LHSV of 1.0, a temperature of 700°F, a pressure of 2,000 psig, and a hydrogen circulation rate of 7,500 SCF/B. The hydrogen content of the liquid effluent from the hydrogenation reactor is significantly increased relative to the feed to the hydrogenation reactor. This effluent is then passed on to the catalytic cracking unit 60.

The gasoline yield and conversion from this processing sequence are now far in excess of that obtainable by catalytic cracking alone; and a steady-state cracking operation is achieved with a charge stock metals input far in excess of that achieved by catalytic cracking.

We claim:

1. A process for the demetallation of a hydrocarbon charge stock containing metal impurities comprising contacting said hydrocarbon charge stock with hydrogen and with a catalyst comprising the naturally-occurring, underwater deposit known as manganese nodules.
2. The process of claim 1 wherein said catalyst is a manganese nodule which contains copper, nickel or molybdenum in its composition and which has had at least a portion of its copper, nickel or molybdenum content removed therefrom.

3. The process of claim 2 wherein said at least a portion of its copper or nickel content has been removed from said manganese nodule by leaching said manganese nodule with an aqueous solution of acid.
4. The process of claim 2 wherein said at least a portion of its molybdenum content has been removed from said manganese nodule by leaching said manganese nodule with an aqueous solution of base.
5. The process of claim 4 wherein said aqueous solution of a base has a pH of at least 8.
6. The process of claim 4 wherein said aqueous solution of a base has a pH of at least 10.
7. The process of claim 1 wherein said catalyst is obtained by contacting said manganese nodules with hydrogen sulfide.
8. The process of claim 7 wherein said manganese nodules are contacted with said hydrogen sulfide at a temperature from about 300°F. to about 450°F.
9. The process of claim 7 wherein said manganese nodules are contacted with said hydrogen sulfide for a time from about 4 hours to about 8 hours.
10. The process of claim 7 wherein said manganese nodules are contacted with said hydrogen sulfide at a temperature from about 300°F. to about 450°F. and for a time from about 4 hours to about 8 hours.
11. The process of claim 1 wherein said charge stock and said hydrogen are contacted with said catalyst at a temperature from about 650°F. to about 850°F.
12. The process of claim 1 wherein said charge stock and said hydrogen are contacted with said catalyst at a temperature of 750°F.-850°F.
13. The process of claim 1 wherein said charge stock and said hydrogen are contacted with said catalyst at a pressure from about 100 to about 3,000 pounds per square inch gage.
14. The process of claim 1 wherein said charge stock and said hydrogen are contacted with said catalyst at a pressure of 500-2,000 pounds per square inch gage.
15. The process of claim 1 wherein said charge stock and said hydrogen are contacted with said catalyst at a temperature from about 650°F. to about 850°F. and at a pressure from about 100 to about 1,000 pounds per square inch gage.
16. The process of claim 1 wherein said charge stock and said hydrogen are contacted with said catalyst by passing said charge stock through a bed of said catalyst.
17. The process of claim 16 wherein said charge stock is passed through said bed of catalyst at a rate from about 0.2 to about 4 volumes of charge stock per volume of catalyst per hour.
18. The process of claim 16 wherein said charge stock is passed through said bed of material at a rate from about 0.5 to about 2 volumes of charge stock per volume of material per hour.
19. The process of claim 16 wherein the circulation rate of said hydrogen is 2,000-15,000 standard cubic feet of hydrogen per barrel of charge stock.
20. The process of claim 16 wherein the circulation rate of said hydrogen is 5,000-10,000 standard cubic feet of hydrogen per barrel of charge stock.
21. The process of claim 16 wherein said charge stock is passed through said bed of catalyst at a rate from about 0.2 to about 4 volumes of charge stock per volume of catalyst per hour and the circulation rate of said hydrogen is 2,000-15,000 standard cubic feet of hydrogen per barrel of charge stock.
22. A process for the demetalation of a hydrocarbon charge stock containing metal impurities comprising contacting said hydrocarbon charge stock with hydrogen at a temperature from about 650°F. to about 850°F. and at a pressure from about 100 to about 3,000 pounds per square inch gage and with a catalyst comprising a manganese nodule which has been previously contacted with hydrogen sulfide at a temperature from about 300°F. to about 450°F. and for a time from about 4 hours to about 8 hours.

23. A process which comprises demetalizing a hydrocarbon charge stock containing metal impurities by contacting said hydrocarbon charge stock with hydrogen and with a catalyst comprising the naturally-occurring, underwater deposit known as manganese nodules and desulfurizing the demetalized hydrocarbon charge stock by contacting said demetalized hydrocarbon charge stock with hydrogen and with a desulfurizing catalyst under hydrodesulfurizing conditions.

* * * * *