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AUTO-REGENERATION OF HYDROFINING
CATALYSTS

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The invention described herein relates to the hydro-
refining of petroleum crude oils and other heavy hydro-
carbon fractions and/or distillates for the primary pur-
pose of eliminating, or reducing the concentration of
various contaminating influences contained therein. More
particularly, the present invention is directed toward an
auto-regenerative, single-stage catalytic hydrotreating
process for effecting the substantially complete removal
of various types of impurities from heavy hydrocarbon
charge stocks, and especially from petroleum crude oils.

Petroleum crude oils, topped or reduced crude oils,
and other heavy hydrocarbon fractions and/or distillates
including black oils, heavy cycle stocks, visbreaker liquid
effluent, etc., contain various non-metallic and metallic
impurities which detrimentally affect various processes to
which such heavy hydrocarbon fractions may be sub-
jected. Included among the non-metallic impurities are
large quantities of nitrogen, sulfur and oxygen which ex-
ist as heteroatomic compounds. Nitrogen is undesirable
because it very effectively poisons various catalytic com-
posites which may be employed in the conversion of a
variety of petroleum fractions; in particular, nitrogenous
compounds are known to be effective hydrocracking sup-
pressors, and, therefore, must necessarily be removed from
all catalytic hydrocracking charge stocks. Nitrogenous
and sulfurous compounds are also objectionable since
the combustion of fuels containing these impurities causes
the release of nitrogen and sulfur oxides which are nox-
ious, corrosive and present a serious problem with re-
spect to pollution of the atmosphere. Sulfur is detri-
mental with respect to motor fuels because of odor, gum
formation and a significantly lower lead susceptibility
than sulfur-free gasolines.

In addition to the foregoing described contaminating
influences, petroleum crude oils, and other heavy hydro-
carbonaceous material, contain high molecular weight
asphaltenic compounds. These are non-distillable, oil-
insoluble coke precursors which may be complexed with
sulfur, nitrogen, oxygen and various metals. They are
generally colloiddally dispersed within crude oil, and when
subjected to elevated temperature, as in a vacuum distil-
lation process, have the tendency to flocculate and polym-
erize, thereby making their conversion to more valuable
oil-soluble products extremely difficult. Thus, in the
heavy bottoms from a reduced crude vacuum distilla-
tion column, the polymerized asphaltenes exist as solid
material even at ambient temperatures; such a product is
useful only as road asphalt or as a low-grade fuel when
cut back with a middle-distillate hydrocarbons such as
kerosene, light gas oil, etc.

Of the metallic contaminants, those containing nickel
and vanadium are the most common, although other
metals, including iron, copper, lead, zinc, etc., are often
present. Such metals may occur as suspended metal
oxides or sulfides, or water-soluble salts which may be re-
moved, at least in part, by filtration, water washing, de-
salking or other relatively simple physical means; gen-
erally, however, the metals occur as thermally stable
organo-metallic complexes, such as metallic porphyrins
and the various derivatives thereof. A considerable
quantity of the organo-metallic complexes are linked with
the asphaltenes and become concentrated in residual frac-

tions; some of the remaining organo-metallic complexes
are volatile, oil-soluble and are, therefore, carried over
in the lighter distillate fractions. A reduction in the con-
centration of the organo-metallic complexes is not easily
achieved, and to the extent that the crude oil or other
heavy hydrocarbon charge stock becomes suitable for
further processing. Notwithstanding that the concen-
tration of these organo-metallic complexes may be rela-
tively small in distillate oils, for example, often less than
about 10 p.p.m. (calculated as if the complex existed as
the elemental metal), subsequent processing techniques
are often adversely affected thereby. For example, when
a hydrocarbon charge stock containing organo-metallic
compounds, such as metal porphyrins, in an amount above
about 3.0 p.p.m. is subjected to hydrocracking or catalytic
cracking for the purpose of producing lower-boiling com-
ponents, the metals become deposited upon the catalyst,
increasing in concentration as the process continues.
Since vanadium and the iron-group metals favor hydro-
genation activity, at cracking temperatures, the resulting
contaminated hydrocracking or cracking catalyst produces
increasingly excessive quantities of coke, hydrogen and
light hydrocarbon gases at the expense of more valuable
liquid product. Eventually, the catalyst must be sub-
jected to elaborate regenerative techniques, or more often
be replaced with fresh catalyst. The presence of ex-
cessive quantities of organo-metallic complexes adversely
affects other processes including catalytic reforming, isom-
erization, hydrodealkylation, etc. With respect to the
hydrotreating, or hydrotreating of hydrocarbon fractions
and/or distillates, the presence of large quantities of
asphaltenic compounds and organo-metallic complexes
as in topped or reduced crude oils, interferes considerably
with the activity of the catalytic composite with respect
to the destructive removal of the nitrogenous, sulfurous
and oxygenated compounds. Therefore, it is highly de-
sirable to produce a hydrocarbon mixture of reduced
sulfur and nitrogen concentration, however, being sub-
stantially free from asphaltenic material and organo-
metallic compounds. Such a mixture is then more readily
subject to fixed-bed hydrotreating at sufficiently severe
conditions required for a product virtually completely
free from sulfur and nitrogen.

The desirability of removing the foregoing described
contaminating influences from hydrocarbon mixtures is
well known within the art of petroleum refining. Here-
tofore, in the field of catalytic hydrotreating, two prin-
cipal approaches have been advanced: liquid phase hydro-
genation and vapor phase hydrocracking. In the former
type of process, the oil is passed upwardly in liquid phase
and in admixture with hydrogen through a fixed bed or
slurry of sub-divided catalyst. Although perhaps effec-
tive in removing oil-soluble, organo-metallic complexes,
this type of process is relatively ineffective with respect to
oil-insoluble asphaltenes, colloiddally dispersed within the
charge, with the consequence that the probability of
effecting simultaneous contact between catalyst particle
and asphaltene molecule is remote. Furthermore, since
the hydrogenation zone is at an elevated temperature, the
retention of unconverted asphaltenes, suspended in a free
liquid phase oil for an extended period of time will result
in flocculation causing conversion thereof to become sub-
stantially more difficult. The rate of diffusion of the
oil-insoluble asphaltenes is significantly lower than that of
dissolved molecules of the same molecular size; for this
reason, a fixed-bed process in which the oil and hydrogen
are passed in a downwardly direction, is virtually pre-
cluded. The asphaltenes, being neither volatile, nor dis-
solved in the crude, cannot move to the active catalyst
sites, the latter being obviously immovable. Further-
more, the efficiency of hydrogen to oil contact, obtained

by bubbling hydrogen through an extensive liquid body, is relatively low. On the other hand, vapor phase hydrocracking is carried out either with a fixed-bed, or an expanded-bed system at temperatures substantially above about 950° F. While this technique obviates to some extent the drawbacks of liquid phase hydrogenation, it is not well suited to treating crude oil and heavy hydrocarbon fractions due to the high production of coke and carbonaceous material with the result that the catalytic composite succumbs to a relatively rapid deactivation; this requires a large capacity catalyst regeneration system in order to implement the process on a continuous basis. Selective hydrocracking of a wide boiling range charge stock is not easily obtained, and excessive amounts of light gases are produced at the expense of the more valuable normally liquid hydrocarbons. Also, when charging a petroleum crude oil, a minimum limit on cracked gasoline production is unavoidable; this is not always desirable where the end result is to maximize the production of middle and heavy distillates such as jet fuel, diesel oils, furnace oils and gas oils.

A primary object of the present invention is to provide a process for the hydrotreating, or hydrorefining of petroleum crude oils and other heavy hydrocarbon fractions and/or distillates, which process may be conducted on a continuous basis without incurring the detrimental effects suffered by present-day methods. A further object of the present invention is to provide a hydrorefining process which, in and of itself, is autoregenerative.

Therefore, in a broad embodiment, the present invention relates to a process for hydrorefining an asphaltenic hydrocarbon charge stock containing organo-metallic contaminants, which process comprises the steps of: (a) reacting said charge stock and hydrogen in a reaction zone containing adsorptive hydrogenation catalyst particles, and at hydrorefining conditions including a temperature below that at which thermal cracking of asphaltenes is effected; (b) when said catalyst accumulates unreacted asphaltenes, increasing said temperature to a level above that at which thermal cracking of asphaltenes is effected; (c) when said unreacted asphaltenes are removed from said catalyst, decreasing said temperature to a level below that at which thermal cracking of asphaltenes is effected; and, (d) continually separating the reaction zone effluent to provide a normally liquid hydrocarbon fraction substantially free from asphaltenes and organo-metallic compounds.

Another broad embodiment of the present invention provides a process for hydrorefining an asphaltenic hydrocarbon charge stock containing organo-metallic contaminants, which process comprises the steps of: (a) reacting said charge stock and hydrogen in a reaction zone containing adsorptive hydrogenation catalyst particles disposed therein in a fluidized state, and at hydrorefining conditions including a temperature below that at which thermal cracking of asphaltenes is effected; (b) when said catalyst accumulates unreacted asphaltenes, ceasing the flow of said charge stock, maintaining the fluidized state of said catalyst by continuing the flow of hydrogen upwardly therethrough and increasing the temperature to a level above that at which thermal cracking of asphaltenes is effected; (c) when said unreacted asphaltenes are removed from said catalyst, decreasing the temperature to a level below that at which thermal cracking of asphaltenes is effected, reintroducing said charge stock and reacting the same with hydrogen as aforesaid; and, (d) continually separating the reaction zone effluent to provide a normally liquid hydrocarbon fraction substantially free from asphaltenes and organometallic compounds.

A more limited embodiment of the present invention encompasses a process for hydrorefining an asphaltenic hydrocarbon charge stock containing organo-metallic compounds, which process comprises the steps of: (a) reacting said charge stock and hydrogen in a reaction zone containing adsorptive hydrogenation catalyst particles in

a fluidized state and at hydrorefining conditions including a temperature within the range of about 725° F. to about 785° F. and below that at which thermal cracking of asphaltenes is effected; (b) when said catalyst accumulates unreacted asphaltenes, ceasing the flow of said charge stock, maintaining the fluidized state of said catalyst by continuing the flow of hydrogen upwardly therethrough, and increasing the temperature to a level above about 785° F. and at which thermal cracking of asphaltenes is effected; (c) when said unreacted asphaltenes are removed from said catalyst, decreasing said temperature to a level below that at which thermal cracking of asphaltenes is effected, and within the range of from about 725° F. to about 785° F., reintroducing said charge stock and reacting the same with hydrogen as aforesaid; and (d) continually separating the reaction zone effluent to provide a normally liquid hydrocarbon fraction substantially free from asphaltenes and organo-metallic compounds.

A specific embodiment of the present invention involves a process for hydrorefining an asphaltenic hydrocarbon charge stock containing organo-metallic compounds, which process comprises the steps of: (a) heating said charge stock, in admixture with hydrogen in an amount of about 5,000 to 500,000 standard cubic feet per barrel, to a temperature below that at which thermal cracking of asphaltenes is effected; (b) passing the heated mixture into a reaction zone upwardly through a fixed-fluidized bed of adsorptive hydrogenation catalyst particles; (c) reacting said mixture at a temperature below that at which thermal cracking of asphaltenes is effected and within the range of about 725° F. to about 785° F., and under an imposed pressure of from about 500 to 5,000 p.s.i.g.; (d) when said catalyst accumulates unreacted asphaltenes, ceasing the flow of said charge stock, increasing the temperature to a level at which thermal cracking of asphaltenes is effected and above about 785° F., and continuing the flow of hydrogen through said catalyst; (e) when said unreacted asphaltenes are removed from said catalyst, decreasing said temperature to a level below that at which thermal cracking of asphaltenes is effected, and within the range of from about 725° F. to about 785° F., reintroducing said charge stock into said reaction zone and reacting the same with hydrogen as aforesaid; and (f) continually separating the reaction zone effluent to provide a normally liquid hydrocarbon fraction substantially free from asphaltenes and organo-metallic compounds.

A wide variety of heavy hydrocarbon fractions and/or distillates may be treated effectively through the utilization of the process of the present invention. These heavy hydrocarbon oils include full boiling range crude oils, topped or reduced crude oils, atmospheric distillates, visbreaker bottoms product, heavy cycle oils from thermally or catalytically-cracked stock, light and heavy vacuum gas oils, etc. The present process is particularly well adapted for the hydrorefining of petroleum crude oil, and topped or reduced crude oil containing excessively large quantities of pentane-insoluble asphaltenic material and organo-metallic compounds. The full boiling range crude oil is a preferred stock since the oil-insoluble asphaltenes, being in their native environment, are colloiddally dispersed, and thus more readily converted to oil-soluble hydrocarbons, whereas the asphaltenic material in a reduced or topped crude have become agglomerated to some extent by reason of fractionation, and are, therefore, more difficult to convert. For example, a Wyoming sour crude having a gravity ° API at 60° F., of 23.2, contains about 2.8% by weight of sulfur, 2700 p.p.m. of total nitrogen, approximately 100 p.p.m. of organo-metallic compounds (calculated as if existing as the elemental metal), and contains about 8.4% by weight of pentane-insoluble asphaltenes. Similarly, a crude tower bottoms product, having a gravity ° API at 60° F., of 14.3, and contaminated by the pres-

ence of 3.1% by weight of sulfur, 3,830 p.p.m. of nitrogen and 85 p.p.m. of metals, consists of about 10.9% by weight of pentane-insoluble asphaltenes. Usually, the destructive removal of nitrogen and sulfur is more readily achieved than the conversion of asphaltenes and the removal of metallic contaminants. However, the activity of the catalytic composite with respect to the former, is severely hampered by the presence of excessive quantities of asphaltenic material and metals. Thus, it is of primary importance to remove substantially completely all of the latter contaminants, while at least partially reducing the concentration of sulfur and nitrogen.

In addition to the foregoing described contaminating influences, the heavier hydrocarbon fractions and/or distillates contain excessive quantities of unsaturated compounds consisting primarily of high molecular weight mono- and di-olefinic hydrocarbons. A successful, effective fixed-bed catalytic hydrotreating process is virtually precluded as a direct result of these various contaminants. At the operating conditions generally employed to effect successful hydrotreating, as well as hydrocracking, the mono- and di-olefinic hydrocarbons have the tendency to polymerize and co-polymerize, thereby causing deposition of high molecular weight, gummy polymerization products within the process equipment and onto the catalytic composite. Similarly, in processes for effecting the catalytic hydrocracking of such heavier hydrocarbon fractions into lower-boiling hydrocarbon products, the catalytic composite becomes deactivated through carbonization effected as a result of the deposition of the agglomerated pentane-insoluble asphaltenes, whereby the catalytically active centers and surfaces of the catalytic material are effectively shielded from the material being processed.

The difficulties encountered in a fixed-bed catalytic process are at least partially solved by employing a slurry operation wherein the finely-divided catalytic composite is intimately admixed with the hydrocarbon charge stock, the mixture being subjected to the desired operating conditions. However, the slurry-type of operation has the obvious disadvantage of relatively small amounts of catalyst being mixed with relatively large amounts of asphaltenic material, since it is difficult to suspend more than a small percentage of catalyst in the crude oil. In other words, too few active catalytic sites are made available for immediate reaction, with the result that the asphaltenic material undergoes thermal cracking resulting in large quantities of light gases and coke. In accordance with the process encompassed by the present invention, large quantities of catalyst are brought into contact with comparatively small amounts of asphaltenes through the utilization of a fixed-fluidized catalyst bed. This method permits the asphaltenes, which have relatively low rates of diffusion compared to other hydrocarbon molecules, to come into contact with the active catalytic sites. It has been found that a hydrogenation catalyst comprising a porous, refractory inorganic oxide carrier material, having a well-developed pore structure, has the ability to absorb a substantial quantity (up to about 50.0% by weight) of the high-boiling asphaltenes and yet continue to appear ostensibly dry and free-flowing. It has further been found that converted asphaltenes, that is, asphaltenes which have been hydrotreated under mild hydrogenative-cracking conditions to yield oil-soluble hydrocarbons comprise an excellent solvent for the untreated asphaltenes which are themselves pentane-insoluble, and colloiddally dispersed within the crude oil. The untreated asphaltenic material is much more readily converted when initially dissolved in such a solvent than one directly treated in a dispersed phase suspended in a liquid carrier. Thus, by maintaining the fixed catalyst bed in a fluidized state, through the utilization of fast flow hydrogen in an amount within the range of about 5,000 to about 500,000 standard cubic feet per barrel of liquid charge, the liquid-phase portion

of the feed, at a temperature within the range of about 725° F. to about 785° F., exists as a fine mist readily absorbed by the catalyst. This absorbed liquid, mostly asphaltenic in nature, will be converted by hydrogenation-hydrocracking reactions into soluble liquid which can act as a solvent for unconverted asphaltenes. Utilizing this principle permits the catalyst to function in an acceptable manner, and to remain free-flowing, for an extended period of time. However, the catalytic particles will eventually absorb more than about 50.0% by weight of asphaltenic material, and severe catalyst deactivation begins to take place. That the catalyst composite has absorbed asphaltenic material in an amount above about 50.0% by weight, is indicated, and can be determined by analyses performed on the normally liquid product effluent; that is, when the concentration of organometallic compounds, calculated as if the metal existed as the elements, approaches and exceeds 0.5 p.p.m. and/or when the residual pentane-insoluble asphaltenes approaches and exceeds a concentration above about 0.5% by weight. Since the rate at which unconverted asphaltenic material is absorbed by the catalytic composite increases as asphaltenes are absorbed by the catalytic composite, it is preferred to initiate the auto-regeneration procedure hereinafter set forth as the amount of absorbed asphaltenic material approaches and exceeds about 35.0% by weight. Another indication of rapid accumulation of unreacted asphaltenes by the catalytic composite is made available by the concentration of nitrogen and sulfur in the normally liquid product effluent. The present process will effectively eliminate the asphaltenes and metallic contaminants completely, and reduce nitrogen and sulfur about 60.0%, notwithstanding that the destructive removal of the latter is generally more easily performed. As unreacted asphaltenes are accumulated, the catalyst loses its capability to remove nitrogen and sulfur at an increasing rate.

As will be noted from the foregoing embodiments, the hydrotreating process of the present invention is effected at a temperature below that temperature at which thermal cracking of asphaltenes is effected. At such time as the catalyst accumulates unconverted asphaltenes, for example, above about 35.0% by weight, the operating temperature is increased to a level at which thermal cracking of asphaltenes is effected, and maintained at such elevated level until the unconverted asphaltenes are converted and removed from the catalytic composite. In order to minimize the cracking of hydrocarbonaceous material into light gaseous waste products, it is preferred to cut off the flow of hydrocarbons to the catalyst bed, continuing, however, the flow of hydrogen therethrough when the operating temperature is increased to a level above about 785° F.

As the asphaltenic material is being removed from the catalytic composite, by way of hydrogenation-cracking reactions, normally liquid hydrocarbonaceous material will appear in the effluent stream from the reaction zone. When normally liquid hydrocarbons no longer appear in the product effluent stream, it may be presumed that the catalytic composite is substantially completely free from absorbed unconverted asphaltenic material. At such time, fresh hydrocarbon charge stock may be re-introduced into the reaction zone in admixture with the fast-flowing hydrogen stream.

As above noted, this invention broadly involves contacting a mixed phase heavy oil charge with hydrogen in the presence of a finely-divided hydrogenation catalyst maintained in a fixed-fluidized state, and under conditions specifically designed to suppress or inhibit the thermal cracking of asphaltenic material. Thus, the catalytic composite is maintained at a temperature within the range of from about 725° F. to about 785° F., the mixture of hydrogen and hydrocarbons being initially heated to a temperature of about 725° F. to about 750° F. prior to contacting the catalytic composite. The operating pres-

sure should be in excess of about 500 p.s.i.g., having an upper economic limit of about 5,000 p.s.i.g., the preferred pressure range being from about 1,000 to about 3,000 p.s.i.g.

In carrying out this process, it is important to minimize cracking, and particularly the thermal cracking of the colloiddally dispersed asphaltenes in a petroleum crude oil, and the partially agglomerated asphaltenes in a reduced or topped crude oil. From the standpoint of maintaining the process equipment and various appurtenances in an operable condition, it is highly desirable to minimize cracking prior to introducing the heavy hydrocarbon charge stock into the hydrotreating zone, to contact the catalytic composite disposed therein. This is accomplished by preheating the heavy charge stock, in the absence of catalysts, however, in admixture with hydrogen in an amount of about 5,000 to about 500,000 standard cubic feet per barrel, to a temperature sufficiently high to partially vaporize the lower-boiling components, but which temperature is below that at which thermal cracking of asphaltenes is effected. Generally speaking the charge should be preheated to a temperature within the range of from about 500° F. to about 750° F., and preferably at a higher level within the range of about 725° F. to about 750° F. Although the hydrocarbon charge stock may be heated as above set forth in admixture with hydrogen, the two streams may be separately heated, the hydrogen stream being introduced into the reaction zone at a point below the charge stock introduction point, the hydrogen and charge stock flowing concurrently upwardly through the fixed-fluidized bed.

Maintaining a fluidized catalyst bed, which to all appearances is dry and free-flowing, and preventing the formation of free liquid phase oil within the hydrotreating reaction zone are necessary to the successful operation of the process embodied by the present invention. These elements assist in furnishing a high concentration of catalytically active sites in relation to asphaltenic and organo-metallic molecules, avoiding flocculation and agglomeration of the asphaltenes, and minimizing cracking and coke formation, the main contributors to rapid catalyst deactivation and subsequent loss of valuable liquid product. Thus, the object of the present invention is attained by the conjunctive effect of several factors: the partial vaporization of the charge stock at a temperature below that at which thermal cracking of asphaltenes is effected; the use of adsorptive hydrogenation catalyst particles; the utilization of a comparatively high catalyst to hydrocarbon weight ratio; and the use of an unusually high hydrogen to hydrocarbon ratio. The stream of hydrogen-containing gas, which, in a commercial process may contain up to about 50.0% of vapors other than hydrogen, is passed upwardly through the catalyst bed at a rate within the range of from about 5,000 to about 500,000 s.c.f./bbl. of total hydrocarbon charge, and preferably in the range of from about 50,000 to about 300,000 s.c.f./bbl. This hydrogen-containing stream, herein sometimes designated as "recycle hydrogen," since it is conveniently recycled externally of the hydrotreating zone, fulfills a number of various functions: it serves as a hydrogenating agent, a fluidizing medium, a heat carrier and a hydrocarbon stripping medium. The relatively high recycle hydrogen rate decreases the partial pressure of the oil vapor and increases vaporization of the oil at temperatures below that at which the thermal cracking of asphaltenes is effected. The weight hourly space velocity of the hydrocarbon charge stock, specified herein as the weight ratio of total oil charge to catalyst contained within the hydrotreating reaction per hour, is within the range of from about 0.25 to about 20 pounds of oil per pound of catalyst per hour, and preferably within the range of from about 1.0 to about 5.0. As the heated mixed phase hydrocarbon charge is initially contacted with the adsorptive hydrogenation catalyst particles, the heavier liquid phase portion of the charge is at least partially ad-

sorbed into the catalyst particles, and partly entrained as a very fine mist, in the fast-flowing hydrogen stream; the vaporized portion of the charge is swept upwardly through the catalyst bed by the hydrogen stream, while the lighter liquid phase portion of the charge is vaporized by contact with the hot catalyst particles and hydrogen. As a result of the combined effects of vaporization, gas stripping and absorption by the catalyst particles, free liquid phase oil cannot form within the hydrotreating zone. The non-volatilized oil is absorbed into the catalyst particles which, however, remain dry and free-flowing although having accumulated up to about 50.0% by weight of asphaltenic material. The heavy fraction, highly concentrated in impurities, is thus exposed to a large number of active catalyst sites and is subject to hydrogenation and/or hydrocracking under the most favorable conditions in order to yield lower-boiling hydrocarbons of substantially reduced impurity concentration. The upwardly flowing hydrogen stream strips off the hydrotreated oil from the catalyst particles as it is formed.

The effluent from the hydrotreating zone is passed through suitable separation means for the purpose of recovering any catalyst particles entrained by the fast-flowing hydrogen and hydrotreated oil vapors. Where desired, such separation means may be an integral part of the reaction zone whereby the separated catalyst is caused to settle into the lower portion of said zone, the catalyst-free vaporous stream comprising hydrogen, light hydrocarbon gases, oil vapors and some entrained liquid droplets, being removed from the upper portion of the reaction zone and passed into a suitable high-pressure separator. Hydrotreated oil is recovered from the separator, while the hydrogen-rich gaseous phase is returned to the hydrotreating zone in admixture with additional external hydrogen required to replenish and compensate for the net hydrogen consumption which may range from about 200 to about 3,000 s.c.f./bbl. of charge, the precise amount being dependent upon the physical and chemical characteristics of the charge stock.

The fluidized-fixed bed catalyst system is especially advantageous in processing those charge stocks containing excessive quantities of oil-insoluble asphaltenes and organo-metallic compounds, these impurities being effectively converted by the auto-solvent hydrotreating mechanism of this process. As hereinbefore set forth, asphaltenic material hydrotreated under mild hydrogenative conditions which preclude the thermal cracking thereof, to yield oil-soluble, high-boiling hydrocarbons, comprises an excellent solvent for untreated asphaltenic material which, in and of itself, is pentane-insoluble and colloiddally dispersed in the crude oil charge. Through the proper correlation of weight hourly space velocity and recycle hydrogen rate, not all of the hydrotreated oil is removed from the catalyst particles by hydrogen stripping, but a portion of the hydrotreated asphaltenic material is left absorbed within the catalyst particles to function as the solvent for incoming asphaltenes, and reaches an equilibrium level in a steady, lined-out operation. The heavier liquid phase portion of the raw charge stock, is absorbed into the catalyst particles dissolved in the particle-held solvent, thereby accelerating the conversion by a selective hydrocracking to additional asphaltene solvent. At least a portion of the solvent is stripped from the catalyst particles by the hydrogen stream, the remainder being left to dissolve additional incoming asphaltenes. The untreated asphaltenes in the heavy oil charge constitute, therefore, a continuous source of solvent by in situ auto-generation and preferential retention thereof by the adsorptive hydrogenation catalyst particles. This solvent auto-generation enables the process to be conducted for an extended period of time producing an acceptable liquid product effluent containing less than about 0.5 p.p.m. of organo-metallic compounds (calculated as the elemental metal) and less than about 0.5% by weight of pentane-insoluble asphaltenic material.

Eventually, however, the catalyst particles will have absorbed therein, or accumulated, unreacted asphaltenic material in an amount above about 35.0% by weight. As hereinbefore set forth, the catalyst will remain free flowing and ostensibly dry notwithstanding that up to about 50% by weight of asphaltenic material is absorbed therein. An indication that the catalytic particles have accumulated unreacted asphaltenic material within the range of from about 35.0% to about 50.0% by weight, is an increase in the concentration of pentane-insoluble asphaltenes and organo-metallic compounds remaining in the normally liquid product effluent removed from the high-pressure separator.

When the analyses on the normally liquid product effluent indicate that the catalytic composite has in fact accumulated asphaltenic material, the operating temperature is increased to a level above about 785° F., and at which the thermal cracking of asphaltenic material is effected. The preferred technique at this stage of the process is to cease the flow of fresh hydrocarbon charge stock, continuing, however, the flow of hydrogen through the catalyst bed. By this method, the absorbed asphaltenic material is subjected to thermal cracking, and to a certain extent hydrocracking, the products of the cracking reaction being stripped by the continued flow of hydrogen. As a result of the cracking operations, additional normally liquid product effluent will be removed from the high-pressure separator into which the reaction zone effluent normally flows. An indication that the catalytic composite is substantially, completely free from asphaltenic material in the absence of additional liquid product in the high-pressure separator, or when the composition of the hydrogen-rich gas stream is substantially identical to that being introduced at the bottom portion of the reaction zone. At such time, the temperature is decreased to the operating level within the range of about 725° F. to about 785° F., and below that temperature at which the thermal cracking of asphaltenes is effected; the fresh hydrocarbon charge stock is reintroduced into the reaction zone, and the process continued. By this method of processing and auto-regenerative techniques, the overall loss of charge stock and/or valuable liquid product to gaseous waste products, such as methane, ethane and other light paraffinic hydrocarbons, is minimized to the extent that the over-all operation is extremely economically feasible. Furthermore, an extended period of catalyst life is afforded prior to that time when the natural deterioration of the catalytically active metallic components require a total replacement of the catalyst disposed within the reaction zone.

The various non-metallic impurities, such as nitrogenous, sulfurous and oxygenated compounds, are converted by the present process to ammonia, hydrogen sulfide, water and hydrocarbons which are removed from the hydrotreating zone together with the hydrogen-rich gaseous phase. The various metallic impurities, including nickel, iron and vanadium are deposited upon the catalyst and gradually build up in concentration, or are, at least in part, converted into a volatile form and removed with the total reaction zone effluent. Although catalyst activity is not particularly impaired in the present process under the stated operating conditions, it may be desirable to withdraw, continuously or intermittently, a small slip stream of catalyst from the hydrotreating zone to chemically regenerate the same by suitable means including treatment with hydrogen chloride and/or chlorine to convert the deposited metals into a volatile form, returning the regenerated catalyst of reduced metal content into the hydrotreating zone.

The hydrogenation catalyst, for utilization in the present invention, can be characterized as comprising a metallic component having hydrogenation activity, which is composited with a refractory inorganic oxide carrier material of either synthetic, or natural origin, which carrier material has a medium to high surface area and a

well-developed pore structure. The composition and method of manufacturing the catalyst is not an essential feature of the present invention, with, however, the exception that it has the necessary absorptive capacity to retain substantial quantities of liquid phase material and unreacted asphaltenes within its pores. Suitable metallic components having hydrogenation activity by the metals of Groups V-B and VI-B and VIII of the Periodic Table, and compounds thereof. Thus, the catalytic composite may comprise one or more metals or compounds of metals from the group of vanadium, niobium, tantalum, molybdenum, tungsten, chromium, iron, cobalt, nickel, platinum, palladium, iridium, osmium, rhodium, ruthenium, and mixtures thereof. The catalyst may comprise any one or combination of any number of such metals, and may exist in the elemental state or as the oxide or sulfide in varying degrees of oxidation.

The concentration of the catalytically active metallic component, or components, combined with the refractory inorganic oxide carrier material, is primarily dependent upon the particular metal, or metals selected. For example, the metallic components from Groups V-B and VI-B, are preferably present in an amount within the range of about 1.0% to about 20.0% by weight, the iron-group metals in an amount within the range of about 0.2% to about 10.0% by weight and the platinum-group metals in an amount within the range of about 0.1% to about 5.0% by weight, all of which concentrations are calculated as if the metallic component existed as the elemental metal. The stated groups from the Periodic Table are those from Periodic Chart of the Elements, Fischer Scientific Company, 1953.

The refractory inorganic oxide carrier material may comprise alumina, silica, zirconia, magnesia, titania, boria, strontia, hafnia, and mixtures of two or more including silica-alumina, silica-zirconia, silica-magnesia, silica-titania, alumina-zirconia, alumina-magnesia, alumina-titania, magnesia-zirconia, titania-zirconia, magnesia-titania, silica-alumina-zirconia, silica-alumina-magnesia, silica-alumina-titania, silica-magnesia-zirconia, alumina-silica-magnesia-titania, etc. In particular instances, and where desired, the catalytic composite may comprise additional components including combined halogen, particularly fluorine and/or chlorine, boric and/or phosphoric acid, etc. The refractory inorganic oxide carrier material may be formed by any of the numerous techniques which are well defined in the prior art relating thereto. Such techniques include the acid-treating of a natural clay, sand, earth, or coprecipitation or successive precipitation from hydrosols, frequently coupled with one or more activating treatments including hot oil aging, steaming, drying, oxidizing, reducing, calcining, etc. The pore structure of the carrier, commonly defined in terms of surface area, pore diameter and pore volume, may be developed to specified limits; for example, by aging the hydrosol and/or hydrogel under controlled acidic or basic conditions at ambient or elevated temperature, by gelation at a critical pH, or by treating the carrier with various inorganic or organic reagents. The catalytically active metallic component or components may be composited with the carrier material by impregnating the freshly precipitated or finished carrier with a solution of a soluble metal compound, or by coprecipitating the metal with the carrier from an aqueous solution thereof. An absorptive hydrogenation catalyst, adaptable for utilization in the process of the present invention, will have a surface area of about 50 to about 700 square meters per gram, an average pore diameter of about 20 to about 300 angstroms, a pore volume of about 0.10 to 0.80 milliliter per gram and an apparent bulk density within the range of about 0.10 to about 0.80 gram per cubic centimeter. Measurement of surface area, pore diameter and pore volume of catalytic composites may be conducted according to the method set forth in *Catalysis*, volume I, pages 37-40, Reinhold Publishing Company (1954). In order to function as an acceptable fluidized bed, the catalyst particles themselves should have diam-

eters ranging from about 5 to about 1000 microns; in the case of non-spherical particles, the maximum dimension of such a particle should fall within the aforesaid range. Particle sizes of this magnitude may be readily achieved by spray-drying the carrier or by grinding the catalyst in a colloid mill. By way of specific example, a satisfactory hydrogenation catalyst, having the requisite surface area and pore characteristics, comprises about 2.0% by weight of nickel and about 16.0% by weight of molybdenum calculated as the elemental metals, on a equimolar alumina-silica carrier comprising 63.0% by weight of alumina, or 1.0% by weight of nickel and 8.0% by weight of molybdenum on a carrier material comprising 68.0% by weight of alumina, 10.0% by weight of silica and 22.0% by weight of boron phosphate.

The following examples are given for the purpose of illustrating the means by which the process encompassed by the present invention is effected. The charge stocks, temperatures, pressures, catalysts, rates, etc., are herein presented as being exemplary only, and are not intended to limit the invention to an extent greater than that defined by the scope and spirit of the appended claims.

Example I

The charge stock employed to illustrate the process of the present invention was a topped Wyoming sour crude oil. As received, this sour crude oil, having a gravity of 23.2° API at 60° F., was contaminated by the presence of 2.8% by weight of sulfur, 2700 p.p.m. of total nitrogen, 100 p.p.m. of metallic porphyrins (computed as elemental nickel and vanadium), and contained a high-boiling, pentane-insoluble asphaltenic fraction of about 8.39% by weight of the total crude oil. This sour Wyoming crude oil was "topped" having 5.0% of light-end removal, and indicated a gravity, degrees API at 60° F., of 19.5, and contained 3.0% by weight of sulfur, 2900 p.p.m. of total nitrogen, 105 p.p.m. of nickel and vanadium, the pentane-insoluble asphaltenic fraction being about 8.5% by weight.

The catalytic composite utilized a spray-dried, alumina-silica carrier material comprising 63.0% by weight of alumina. This carrier material was prepared by initially precipitating, at a pH above 8.0, a blend of acidified water glass and an aluminum chloride hydrosol with ammonium hydroxide. The hydrogel was washed free from sodium ions, chloride ions and ammonium ions, and spray-dried. An impregnating solution was prepared from molybdic acid (85.0% by weight of molybdenum trioxide) and nickel nitrate hexahydrate, the spray-dried carrier material being impregnated with an ammoniacal solution thereof. The impregnated composite was dried at a temperature of about 210° F., and finally oxidized in an atmosphere of air at a temperature of about 1100° F. for about one hour. The finished catalyst contained 2.0% by weight of nickel and 16.0% by weight of molybdenum existing as oxides, calculated, however, as if existing as the elemental metal, and indicated a particle size ranging from 20 to about 150 microns (approximately 99.0% by weight of the catalyst particles were of a size less than 150 microns).

A total of 220 grams of the nickel-molybdenum catalytic composite was supported in the reaction zone on a sintered metal disk. The reaction zone was fabricated from one and one-half inch, schedule 40, type 304 stainless steel pipe, equipped at the bottom portion thereof with a spiral preheater around which the oil entered from the bottom. By means of a short piece of tubing, the top of the preheater extended through the sintered plate, the end of the tubing being covered by an inverted cup which served to prevent the catalytic composite from falling into the preheater zone. After passing through the tube and under the cup, the partially vaporized charge stock contacts the catalyst and the hydrogen, the latter entering the reactor from the side, traveling upwardly around the oil-preheater section; the hydrogen passes through the sintered metal plate and ebulates the catalyst bed. The reaction products and excess hydrogen con-

tinue upward to a disengaging zone fabricated from two and one-half inch, schedule 40, type 136 stainless steel pipe. In this zone, the gas velocity is reduced to approximately one-half the velocity in the reaction zone itself in order that entrained catalyst particles will tend to fall back into the reaction zone. After leaving the reaction zone, the reaction products were passed through sintered metal filter elements to remove any catalyst fines that may have been entrained. The reaction products were cooled and passed into a high pressure separator from which the liquid hydrocarbon product was removed to a receiver, the hydrogen-rich gas being removed from the separator through a water scrubber and recycled back to the reactor. In order to compensate for the quantity of hydrogen consumed within the process and absorbed by the normally liquid product effluent, fresh hydrogen was added to the recycle gas as determined by the operating pressure within the reaction zone.

The above-described, fixed fluidized system was operated for a period of 204 hours, the first four of which constituted the start-up of the unit, the remaining 200 being divided into twenty-five, 8-hour individual test periods. The weight hourly space velocity throughout the entire test period was 0.86, based upon an average liquid charge to the reaction zone of 190 grams per hour (a low rate of 184 and a high rate of 194). The reaction zone pressure was maintained at about 2000 p.s.i.g., through compressive hydrogen recycle ranging from 52,300 to 56,000 s.c.f./bbl. of liquid charge; the hydrogen purity was, at all times, in excess of about 90.0% ranging from about 91.7% to 96.1% throughout the entire 204 hours.

In the following abbreviated table, data from seven of the 8-hour test periods are given as being representative of the overall operation:

TABULATED DATA

Hours on Stream.....	20	36	60	84	116	180	204
Gravity, °API at 60° F.....			31.4	31.1	30.6	30.3	-----
Sulfur, Wt. percent.....	0.32	-----	0.52	0.62	0.87	1.00	-----
Nitrogen, p.p.m.....	881	-----	1,290	1,490	1,710	1,790	-----
Pentane-insolubles, Wt. percent.....	0.27	0.18	0.17	0.11	0.02	0.08	0.09
Metals, p.p.m.....		0.14	0.10	-----	0.04	0.13	0.10

The operation was intentionally stopped at the termination of the twenty-fifth test period, or after 204 consecutive hours of operation. It will be noted that although the concentration of pentane-insoluble asphaltenic material is considerably below a level of 0.5% by weight, averaging approximately 0.13% throughout the entire operating period, and the concentration of organo-metallic compounds is well below the limit of 0.5 p.p.m., the operating temperature has been increased a total of about 25° F., and further that the gravity, °API at 60° F. of the normally liquid product effluent indicates a decline. In addition, the sulfurous and nitrogenous compounds remaining in the normally liquid product effluent have increased considerably from 0.32% by weight of sulfur and 881 p.p.m. of nitrogen. These four factors combine to indicate that the catalytic composite is accumulating unreacted asphaltenic material at an increased rate, and that the catalytic composite is slowly suffering a loss of its hydrogenation/hydrocracking activity. That is, as hereinbefore set forth, the capability of the catalyst to effect the destructive removal of nitrogenous and sulfurous compounds is hampered by the presence of excessive quantities of the pentane-insoluble asphaltenes as well as organo-metallic compounds. As the catalyst begins to lose activity as a result of the accumulation of unreacted asphaltenes, its capability to remove sulfur and nitrogen is initially affected, followed by an increasing inability to remove metals and convert the pentane-insolubles. Thus, it was decided to cease the operation, notwithstanding that the catalytic composite continued to

function acceptably with respect to the pentane-insoluble fraction and the removal of organo-metallic compounds.

Throughout the entire test period, 37,476 grams of the topped Wyoming sour crude oil were charged to the unit; of this amount, 36,183 grams of normally liquid product effluent were recovered. This amounts to a recovery, on a weight basis, of 96.5% indicating a loss to light gaseous hydrocarbons, hydrogen sulfide, coke, etc., of only 3.5% by weight of the total charge.

The catalyst was removed from the reaction zone, in an amount of 390 grams, indicating that the catalyst had absorbed therein about 170 grams of insoluble hydrocarbonaceous material. It is significant that this additional material amounts to a mere 0.5% by weight of the total charge to the unit.

Example II

The catalytic composite, removed from the reaction zone following the termination of the test period described in Example I, is disposed in the reaction zone as before, and hydrogen is circulated therethrough at a rate of about 50,000 s.c.f./bbl., under a compressive recycle pressure of about 2,000 p.s.i.g. The operating temperature is increased beyond the maximum desirable level when the charge stock is being processed, a temperature of 785° F., to a level of about 850° F. After a period of about one-half hour, normally liquid hydrocarbons appear in the high-pressure separator into which the total reaction zone effluent is passed. This indicates that the carbonaceous material absorbed into the catalytic composite is being removed by the fast-flowing hydrogen stream by being subjected to both thermal cracking and hydrocracking reactions. The temperature is slowly increased to a level of about 900° F., and maintained at this level until such time as additional normally liquid product no longer appears in the hydrogen pressure separator, or until an analysis on the exit-gas stream indicates a composition virtually identical to that being employed as the hydrogen-rich recycle stream. As such time, the hydrogen flow being continued, the temperature is lowered from a level of about 900° F. to about 750° F. prior to the reintroduction of the charge stock. The operation is then continued as described in Example I, and analyses indicate the substantially complete removal of pentane-insoluble asphaltenic material and organo-metallic compounds.

The foregoing examples illustrate the method by which the process of the present invention is effected. The normally liquid product effluent, recovered in a highly acceptable yield based upon charge stock, is virtually free from pentane-insoluble material and organo-metallic compounds. Therefore, it is extremely well suited as the charge stock to a process operating at significantly more severe conditions for the purpose of effecting the complete destructive removal of the remaining sulfurous and nitrogenous compounds. Thus, the method of the present invention is readily adapted to a multiple-stage process which, as will be recognized by those possessing skill within the art of petroleum refining, would lead directly to clean gasoline and diesel oil, the latter being sufficiently clean to be used immediately as diesel, jet or fuel oil.

We claim as our invention:

1. A process for regenerating an adsorptive hydrogenation catalyst containing asphaltenes in an amount of from about 35% to about 50% by weight, which comprises heating said catalyst to a temperature level above that at which thermal cracking of asphaltenes is effected and cracking said asphaltenes to produce normally liquid hydrocarbons therefrom and to regenerate the catalyst, maintaining the catalyst at said temperature level until the asphaltenes on the catalyst are converted and removed from the catalyst, and recovering the resultant regenerated asphaltene-free catalyst.

2. The process of claim 1 further characterized in that said catalyst comprises at least one metallic component selected from the metals of Groups V-B, VI-B and VIII of the Periodic Table.

3. The process of claim 2 further characterized in that said catalyst comprises a vanadium component.

4. The process of claim 1 further characterized in that said catalyst comprises a molybdenum component.

5. The process of claim 1 further characterized in that said catalyst comprises a nickel component.

6. The process of claim 1 further characterized in that said catalyst comprises a molybdenum component and a nickel component.

7. The process of claim 1 further characterized in that said temperature level is above about 785° F.

8. The process of claim 1 further characterized in that the products of cracking are stripped from the catalyst by the passage of hydrogen through the catalyst during the heating thereof.

9. A process for regenerating an adsorptive hydrogenation catalyst containing asphaltenes in an amount of from about 35% to about 50% by weight, which comprises heating said catalyst to a temperature level above that at which thermal cracking of asphaltenes is effected and cracking said asphaltenes to produce normally liquid hydrocarbons therefrom and to regenerate the catalyst, maintaining the catalyst at said temperature level until the asphaltenes on the catalyst are converted and removed from the catalyst while passing hydrogen upwardly through the catalyst to maintain the catalyst in a fluidized state, and recovering the resultant regenerated asphaltene-free catalyst.

10. The process of claim 9 further characterized in that said temperature level is above about 785° F.

References Cited by the Examiner

UNITED STATES PATENTS

2,737,477	3/1956	Hemminger	208—140
2,903,413	9/1959	Folkens et al.	208—57
2,985,580	5/1961	Heinemann	208—264
3,053,755	9/1962	Hansford et al.	208—110
3,113,097	12/1963	White	208—225
3,169,918	2/1965	Gleim	208—264
3,215,618	11/1965	Watkins	208—254

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