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COMPLETE SPECIFICATION

Process of Hydrocracking Hydrocarbon Oils

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the Laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for hydrocracking hydrocarbon oils with refining of the hydrocarbon fractions intended for use as charge stock to the hydrocracking step whereby a major proportion of the total nitrogen content of the stock is removed therefrom prior to the hydrocracking conversion. More specifically, the present invention is directed to a hydrocracking treatment in combination with a hydrotreating treatment in which the feed stock is subjected to hydrotreating at relatively severe conditions in order to convert the organically bound nitrogen compounds present in the feed stock into a form readily removable from the hydrocarbons prior to the hydrocracking stage, thereby enhancing the hydrocracking conversion, maintaining the catalyst utilized in the hydrocracking stage in a highly active state and eliminating the necessity for increasing the severity of the hydrocracking reaction conditions as the hydrocracking catalyst is used for increasingly longer conversion periods.

The purpose of the present method of pretreating the hydrocracking charge stock is to convert the naturally-occurring nitrogen-containing compounds present in these feed stocks into a form which may be readily removed therefrom following the pretreatment and to accomplish such conversion of the nitrogen-containing compounds to such an extent that substantially all of the organically bound nitrogenous compounds originally present in the feed stock are converted to a form which may be readily

removed from the stock prior to the hydrocracking stage of the process. Another object of the pretreatment stage of the present combination process is to enable the hydrocracking stage of the process to be operated for extended periods of time at conditions of relatively low severity which is essential if the conversion of the feed stock into the desired lower boiling or gasoline boiling range products is to be maintained at a high level. The pretreatment of the hydrocracking charge stock to reduce its nitrogen content also enables the hydrocracking catalyst to maintain its initially high level of activity without resort to reactivation or regeneration procedures.

In accordance with this invention a petroleum hydrocarbon charge contaminated with naturally-occurring, organic nitrogenous compounds detrimental to the hydrocracking catalyst is contacted at a temperature of from 315° to 482° C. in the presence of hydrogen at a pressure of from 34 to 204 atmospheres with a catalyst comprising a Group VI metal and an iron group metal of the elements of Group VIII of the Periodic Table supported on a refractory metal oxide base and at a space velocity of the charge relative to the catalyst at which substantially all of the nitrogen in said nitrogenous compound is converted to ammonia and the nitrogen content of said charge is reduced to less than one part per million parts by weight of said charge, the ammonia is separated from the reaction product and thereafter the normally liquid portion of said reaction product is contacted at a temperature of from 260° to 538° C. in the presence of hydrogen at a pressure of from 34 to 204 atmospheres with a hydrocracking catalyst comprising a metal selected from the elements of Group VIII of the Periodic Table on an acidic cracking catalyst support.

More specific embodiments of the present invention concern the use of specific catalyst compositions in each of the hydrotreating and

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hydrocracking stages of the process, specific feed stocks peculiarly adapted to the hydro-refining treatment and conversion in the hydrocracking process and preferred ranges of reaction conditions whereby the desired effects realized by the present combination process are especially evident and pronounced.

Hydrocracking is a functionally descriptive term applied to the conversion of hydrocarbons, usually of petroleum origin and usually of high molecular weight, such as that of the middle distillate and higher boiling range fractions of petroleum. The process is effected in the presence of hydrogen at a superatmospheric pressure and at a temperature sufficient to crack the large hydrocarbon molecules comprising the feed stock into lower boiling range hydrocarbons and usually to more highly branched chain structure which provide a motor fuel of greater anti-knock rating. The best processes from the standpoint of economy of operation in producing a higher yield of gasoline boiling range product from a given volume of feed stock are effected in the presence of a catalyst which enhances the cracking phase of the conversion into hydrocarbons boiling within the gasoline range and simultaneously hydrogenates any olefinic or aromatic fragments formed by virtue of the cracking operation into their saturated paraffinic and naphthenic analogs. The most advantageous catalysts are those which crack the feed stock into hydrocarbon fragments containing from about 5 to about 12 carbon atoms and produce a minimum of light gaseous hydrocarbons, such as methane, ethane, propane and C_4 paraffins and olefins which reduce the yield of the desired gasoline boiling range product. The hydrocracking catalyst is thus composed of at least two functional components, one of which accomplishes the cracking phase of the operation and the other of which accomplishes the hydrogenation phase of the reaction occurring substantially simultaneously with the cracking reaction. The cracking component of the catalyst is an acid-acting material, herein referred to as an "acidic component", which may be supplied by a metal halide of one of the iron group metals of the Periodic Table or by any other non-volatile (at the particular hydrocracking conditions), halide salt of a metal other than an alkali or an alkaline earth metal. The acidic component of the hydrocracking catalyst may also be supplied as an acidic composite of refractory metal oxides such as alumina-silica, zirconia-silica, zirconia-alumina-silica, magnesia-silica, or alumina-boron oxide composite, or a naturally-occurring silicate, such as clay. The hydrogenation component of the catalyst is generally a metal selected from one of the elements of Group VIII of the Periodic Table in the form of a free metal or as the oxide or sulfide thereof, preferably

of such metals as cobalt, nickel, platinum, palladium and ruthenium on a refractory support, such as alumina, containing from 0.01 to about 3.0 percent by weight of combined halogen selected from fluorine and chlorine. In the presence of such catalysts and at hydrocracking reaction conditions, that is, at hydrocracking temperatures and in the presence of hydrogen at a superatmospheric pressure, the olefinic fragments formed by cracking the paraffinic component of the feed stock are simultaneously hydrogenated to the paraffin analog containing the same number of carbon atoms and any aromatic components present in the charge stock or formed by virtue of the hydrocracking reaction become saturated with hydrogen to form the corresponding naphthene analog.

It has been found, however, based upon the results of many experimental runs in which a variety of feed stocks and various reaction conditions were utilized that the presence of nitrogen-containing compounds in the feed stock, such as the organic nitrogenous compounds which occur naturally in hydrocarbons of petroleum origin, such as the pyrroles, amines, indoles and others rapidly deactivate both the acidic cracking component and the hydrogenation catalyst component of all known hydrocracking catalysts. The deactivation presumably occurs by reaction of the nitrogen-containing compounds with the catalyst components, forming a nitride or other chemical compound with the catalyst components. Deactivation occurs precipitously at the hydrocracking process conditions and the catalyst does not recover activity at the same process conditions when the feed stock supplied to the process is decontaminated. Although a factor in the deactivation, the basicity of the nitrogenous contaminant and its reaction with the cracking catalyst component resulting in neutralization of its acidity, is not the predominating factor involved in the deactivation. Rather, the formation of addition complexes of the nitrogenous contaminant with the catalyst components, covering up the active centers of catalytic activity available to the hydrocarbon stock charged to the hydrocracking operation is believed to be the predominant factor in the deactivation of the catalyst. The deactivation is not a simple, reversible phenomenon, rectified by mere heating of the catalyst in the presence of hydrogen; instead, the deactivation is a deep-seated change in the chemical make-up of the catalyst and reactivation is accomplished only by heating the catalyst at high temperatures in the presence of free oxygen which removes the deactivating factor by oxidation.

Numerous experimental runs also establish the fact that catalyst deactivation proceeds at a rate directly proportional to the total nitrogen content of the feed stock. It is there-

fore essential, and the experimental runs upon which the present process is based will bear this out, that the nitrogen content of the feed stock to the hydrocracking stage of the process must be reduced to an almost negligible concentration in order to maintain the activity of the hydrocracking catalyst at an economical, commercially feasible level. The objectives of the present pretreatment stage of the process is to convert the nitrogen contained in the nitrogenous compounds present in the feed stock into a form which may be readily removed from the resultant treated charge stock prior to contact of the charge stock with the hydrocracking catalyst. The present invention is based upon the discovery that through a deep-seated hydrorefining treatment in the presence of certain hydrogenating catalysts, hereinafter referred to, the total nitrogen content of the hydrocarbon feed stock may be reduced through such hydrorefining treatment to less than 1 part per million parts (ppm.) by weight of feed stock. The direct, tangible effect of such pretreatment is the fact that deactivation of the hydrocracking catalyst does not occur to any substantial degree; the hydrocracking reaction may be effected at relatively mild conditions, at which the conversion to gasoline boiling range product is at an optimum level, yielding only a small proportion of the undesired light hydrocarbon gases; the life of the catalyst on stream is markedly prolonged; and the necessity for continual revision upward of the process temperature, resulting in more severe hydrocracking conditions and the production of greater yields of undesirable light gases is eliminated.

The present hydrocracking process is primarily directed to charge stocks boiling above the gasoline range, although any hydrocarbon feed stock within a wide range of molecular weights is subject to cracking and can be employed in the present combination process. Hydrocracking is advantageously applied to petroleum-derived feed stocks of the middle distillate boiling range and above, such as kerosene fractions, gas oil fractions, lubricating oil and white oil stocks, the high boiling bottoms recovered from the fractionators accompanying catalytic cracking operations and referred to as heavy recycle stock, fuel oil stocks and other sources of hydrocarbons having a depreciated market demand because of the high boiling points of these hydrocarbons and the presence of asphalt and tarry residues in these stocks. In general, each of the above sources of feed stock contains high boiling nitrogen-containing compounds as contaminants, compounds which make their appearance in the asphaltic residues present in these fractions. These stocks, which frequently contain from 1200 to 5000 ppm. nitrogen, accordingly, constitute a source of feed stock which may be

treated herein with the greatest evident advantage.

The first stage of the present combination process, referred to herein as a hydrorefining pretreatment stage, is effected in the presence of a catalyst and at reaction conditions which convert the nitrogenous, organically-bound components into ammonia and a hydrocarbon residue. At the hydrorefining conditions and in the presence of the catalyst, the organically-bound nitrogen compounds are hydrogenated at the nitrogen-carbon bonds to form ammonia which is released in a free form from the reaction media. Suitable catalysts for effecting the hydrorefining reaction, are the supported iron group metals of the elements of Group VIII of the Periodic Table, their oxides or sulfides, composited with a Group VI metal, metal oxide or compound of the metal, such as tungsten oxide or chromium oxide. The preferred Group VI metal is molybdenum in the form of a compound thereof, such as the molybdate or thiomolybdate derivative of the Group VIII metal. The essential catalytic components of the hydrorefining catalyst are composited with a refractory support which may be selected from a large number of non-reactive metal oxides, such as zirconia, magnesia, titanium oxide, silica, cerium oxide, thorium oxide and preferably alumina or a mixture of alumina with zirconia or magnesia. The Group VIII metals, which in combination with molybdenum or the oxides or sulfides thereof composited with the support and which in combination produce the present hydrorefining catalyst are cobalt, nickel and iron, collectively referred to as the "iron group" metals of Group VIII of the Periodic Table. These metals may be present, together with the Group VI metal, such as molybdenum on the support as the oxides or sulfides of the metals and may also be present on the refractory support as a compound, such as a cobalt molybdate or iron group metal thiomolybdate. The preferred composites contain from 2 to about 30, and more preferably, from about 5 to about 20 percent of the iron group metal and from 1 to about 20 percent of the molybdenum metal or molybdenum compound supported on the refractory metal oxide. Of the other Group VI elements, these are preferably on the refractory base as the oxides, such as chromia and tungsten oxide.

The hydrorefining pretreatment of the charge stock to the hydrocracking stage of the present process is effected at temperatures of from about 315° to about 482° C. and more preferably, of from about 343° to about 427° C., in the presence of hydrogen supplied at a pressure of from about 34 to about 204 atmospheres and more preferably at a pressure of from about 68 to about 136 atmospheres. A particularly significant reaction variable which is believed to account for the substan-

5 tially complete conversion of the organic
nitrogen-containing compounds present in the
feed stock to ammonia is the rate at which
the charge stock is passed over the catalyst
at the hydrorefining conditions; that is, the
residence time of the charge stock with the
catalyst. In order to realize the deep-reaching
conversion of the organic nitrogenous com-
pounds into ammonia, in which form the
nitrogen is readily removed from the hydro-
refined product as a readily recoverable gas,
the time of contact of the feed stock with the
hydrorefining catalyst should at least be suffi-
cient to provide a liquid hourly space velocity
of not greater than about 2.0 volumes of
feed stock per volume of catalyst per hour
and more preferably, less than 1.5, and down
to about 0.5, the ammonia product resulting
from such conversion partially dissolving in
the liquid portion of the treated charge stock
and partially occupying the gas phase com-
prising hydrogen.

20 The conversion of the nitrogenous com-
pounds present in the feed stock to ammonia
is a necessary, preliminary step to the re-
moval of the nitrogen compound from the
feed stock. Since ammonia itself also has a
decidedly deleterious effect on the hydro-
cracking catalyst, its removal from the pro-
duct of the hydrorefining stage is an essential
phase of the present combination process.
For this purpose, the liquid portion of the
effluent product of the hydrorefining stage
may be washed with an aqueous acid, such
as dilute hydrochloric acid or sulfuric acid,
for example, in a countercurrent wash tower
to dissolve the ammonia product from the
hydrocarbon stock. In a preferred method of
removal, the ammonia gas is stripped from
the liquid portion of the hydrocarbon stock
by counter-currently passing a light, non-
condensable inert gas through the stock at a
velocity sufficient to completely vaporize the
ammonia from the liquid hydrocarbons. A
convenient stripping gas for this purpose is
the hydrogen supplied to the process, gen-
erally in relatively pure form from extraneous
sources which may be bubbled upwardly, in
the form of finely divided gas bubbles through
the hydrorefined liquid product flowing
counter-currently downwardly through a ver-
tical tower, into the bottom of which the
hydrogen gas is charged. Instead of hydro-
gen, the stripping gas may be natural gas,
carbon monoxide, nitrogen, or a flue gas from
a hydrocarbon burner. Ammonia is readily
removed from the stripping gas by scrubbing
with an aqueous acid solution or by passing
the gas mixture comprising ammonia through
a cation exchange resin. The counter-current
contact of the stripping gas against the down-
wardly flowing hydrorefined liquid product
is enhanced by providing a suitable packing
material in the contacting tower, such as for
example quartz chips, or Berl saddles, or by

allowing the liquid product to flow down-
wardly through a bubble cap and tray con-
tactor. Various methods are known in the art
for removal of ammonia from hydrocarbon
liquids and any method which will free the
hydrorefined liquid product of the ammonia
formed during the hydrorefining stage may
be utilized in the present process.

The hydrogen charged to the hydrorefining
stage is supplied in excess of that consumed
by the hydrorefining process, the excess after
removal of ammonia therefrom being avail-
able for recycling to the inlet and of the
hydrorefining stage, if desired.

The hydrocracking stage of the present
combination process is a conversion reaction
effected in the presence of a catalyst con-
taining components which are sensitive to
nitrogen compounds, the hydrocracking acti-
vity of the catalyst being substantially reduced
when even small quantities of organic
nitrogen-containing compounds are present in
the feed stock. In order to compensate for
the loss in the activity of the catalyst during
the hydrocracking conversion because of the
presence of nitrogen contaminants in a feed
stock which has not been pretreated to re-
move nitrogenous contaminants, the process-
ing conditions must be made progressively
more severe by raising the temperature and/
or pressure conditions and increasing the
residence time of the charge stock with the
catalyst to thereby compensate for such loss
in catalyst activity. Although the quantity of
charge stock converted at the more severe
hydrocracking conditions increases, the higher
rate of conversion substantially increases, the
proportion of the undesired light gaseous
components in the product, and the propor-
tion of desirable normally liquid components
in the product is correspondingly substan-
tially reduced. Utilizing a charge stock which
has been previously hydrorefined in accord-
ance with the present process to reduce the
total nitrogen content to a level not greater
than 1 ppm., the hydrocracking activity of
the catalyst is maintained at a higher level at
mild operating conditions and the conver-
sion to the more useful normally liquid pro-
duct is maintained at a level above about 80
percent. Furthermore, the hydrocracking
catalyst may be utilized for more extended
periods of time without reactivation and
without increasing the temperature, pressure
and/or residence time of the charge stock
with the catalyst. The effect of nitrogen in
the charge stock to the hydrocracking stage
of the process will be illustrated in the
examples which follow.

Hydrocracking of the previously hydro-
refined charge stock is effected at tempera-
tures of from about 260° to about 538° C.
and more preferably from about 315° to
about 399° C. in the presence of hydrogen
at a pressure within the range of from about



34 to about 204 atmospheres. The quantity of hydrogen supplied to the reactor is directly dependent upon the type of charge stock employed in the process, but generally, hydrogen supplied at a rate of from about 89 to about 534 normal liters per liter of hydrocarbon charge stock will generally be sufficient to form a non-olefinic product. Part of this hydrogen may be made up of recycle separated from the light gaseous overhead of the effluent product.

The hydrocracking catalyst is a multi-component composite comprising a hydrogenating component and a cracking component composited into a uniform blend and supplied to the hydrocracking process either as a powdered material for suspension in the liquid hydrocarbon stock in the form of pellets for use in a stationary bed of the process. The catalyst base having cracking activity is a material having acid-acting properties which normally characterizes a cracking catalyst. One of the preferred acidic supports which functions as the cracking component in the hydrocracking catalyst composition is a mixture of silica with another refractory metal oxide, such as alumina, zirconia, magnesia, thorium oxide or cerium oxide in which the silica comprises from 5 percent to about 20 percent by weight of the resulting composite. One of the preferred cracking catalyst supports providing a base for the hydrogenating catalyst component is a composite of silica and alumina, coprecipitated as the gel oxides from their salts by addition of a base to an aqueous solution of the salts. The gel composite, after drying is desirably calcined at temperatures of from about 400° to about 550° C. prior to incorporation of the hydrogenating component in the cracking catalyst base. Another suitable acid-acting base for the hydrogenating component of the hydrocracking catalyst is a refractory metal oxide, such as alumina or zirconia containing a non-volatile metal halide, such as a portion of the support converted to its halide salt, also referred to as "combined halogen". The halides for this purpose may be selected from the fluorides and chlorides and may be present in amounts of the halogen on the support of from about 0.01 percent to about 5 percent by weight of the combined composite. Thus, alumina may be treated with a hydrogen halide such as hydrogen chloride and/or hydrogen fluoride to incorporate thereby a combined halogen with the alumina support. Alternatively, the hydrogenating component may be added to the metal oxide support in the form of a halide, the halogen of which combines with the support to form an acid-acting combined halogen. Thus, for example, when the hydrogenating component is a platinum group metal, such as platinum itself or palladium, the latter is composited with the refractory

metal oxide support in the form of a halide, such as platinum or palladium chloride. Other platinum group metals, such as ruthenium, rhodium, iridium, and osmium may also be composited in amounts, preferably from about 0.01 to about 1.0 percent by weight, with the refractory metal oxide support as the hydrogenating component of the resulting hydrocracking catalyst. These metals may also be composited with the cracking catalyst support such as a silica-alumina composite in the form of the metal itself or as the oxide or sulfide thereof, being rapidly reduced to the free metal at the reaction conditions and in the presence of hydrogen maintained in the reactor during the hydrocracking process. Other hydrogenating components which may suitably be used in the formulation of the hydrocracking catalyst include the iron group metals (iron, cobalt and nickel) of Group VIII of the Periodic Table as free metals or in the form of their oxides or sulfides composited with the cracking catalyst component. Mixtures of one or more of the metals in the composite, such as a mixture of nickel and cobalt, are also contemplated herein for use as the hydrogenating component of the catalyst.

When utilizing an iron group metal in the formulation of a hydrocracking catalyst, it is preferred that the catalyst also contains from 0.1 to about 10 percent by weight of molybdenum in the form of the free metal, oxide or other compound thereof, such as a molybdate or thiomolybdate.

Both the hydrorefining and hydrocracking stages of the present process may be effected by contacting the charge stock in liquid phase with a stationary bed of the catalyst, for example, by passing a mixture of the hydrocarbon feed stock and hydrogen through the catalyst at the particular conversion conditions required in each of the stages. For this type of operation, the catalyst is usually supplied in the form of pellets or gelled spheres. In an alternative type of operation the catalyst, in the form of finely divided particles, may be suspended in the liquid hydrocarbon charge maintained at the conversion temperature and in the presence of hydrogen at the required conversion pressure, although preferably, some form of agitation of the hydrocarbon slurry of the catalyst is provided in order to expose both the hydrocarbon stock and the catalyst to the action of hydrogen at the conversion temperature.

The results of laboratory test runs, herein-after presented in the form of examples, conclusively establish the effect of temperature and pressure in both the hydrorefining and hydrocracking stages of the present combined process. In both instances, an increase of either the temperature or pressure produces an increase in the degree of conversion obtained. These results further indicate that

although the detrimental effect of nitrogen in the feed stock can be partially compensated for by increasing the temperature at which the process is carried out, the resulting increase in the severity of the process conditions results in an undesirable shift toward the production of low molecular weight cracked products, predominantly the normally gaseous light hydrocarbons and hydrogen; stated otherwise, the proportion of desired higher molecular weight products of the hydrocracking reaction, preferably the normally liquid products boiling in the gasoline range, are increased as the temperature of the hydrocracking reaction is reduced and the proportion of undesirable gaseous products is increased as the conversion temperature is increased. These quantitative and qualitative factors will be referred to in greater detail in the following examples.

EXAMPLE I

Various hydrocracking catalysts were evaluated in a series of runs in which a white oil boiling in the range of from 366° to 468° C. (comprising a mixture of C_{20} to about C_{32} paraffinic and naphthenic hydrocarbons) was utilized as feed stock to a hydrocracking process for the conversion of the stock into products boiling in the gasoline range, comprising hydrocarbons containing from about 5 to about 12 carbon atoms per molecule. The white oil charge stock has a specific gravity at 15.6° C. of 0.8838. The oil charge of these runs contains a mere trace (less than 1 ppm.) of nitrogen. In each of the runs the white oil and hydrogen were charged into the bottom of a tubular reactor packed with one of a variety of catalysts, hereinafter specified, the liquid portion of the feed being charged at a liquid hourly space velocity of 1.0 (that is, 1 volume of liquid per volume of catalyst per hour). The tubular reactor, surrounded

by a circulating, heated salt bath, maintains the temperature of the reactor constant and uniform, at from about 274° to about 371° C., depending upon the run. Hydrogen was supplied along with the charge stock at a rate of 534 normal liters per liter of white oil charge and at a pressure of 102 atmospheres.

In run No. 1, the catalyst was a composite of 2 percent nickel and 6 percent molybdenum on a cracking catalyst base consisting of a precalcined composite of alumina and silica containing 63 percent alumina and 37 percent of silica.

In run No. 2 the catalyst consisted of a composite of 2 percent of cobalt and 6 percent of molybdenum on a precalcined composite of a silica-alumina base containing 63 percent alumina and 37 percent silica.

In run No. 3 the catalyst consisted of a composite of 0.4 percent palladium deposited on a precalcined alumina-silica base containing 63 percent alumina and 37 percent silica.

In run No. 4 the catalyst consisted of a composite of platinum, alumina and combined halogen containing 0.35 percent platinum, 0.3 percent by weight of chlorine and 0.3 percent by weight of fluorine on an alumina base.

In each of the runs the products of the reaction were cooled at the pressure existing in the hydrocracking reaction, the non-condensed gases, consisting essentially of hydrogen, were separated from the liquid product and recycled to the hydrocracking reactor. The liquid product is thereafter reduced in pressure to atmospheric and stripped to remove components of the overhead condensing at room temperature (about 25° C.). The remaining liquid residue was recovered as the desired liquid product of the hydrocracking reaction. The following tables present the observed data for the runs utilizing the above catalysts:

RUN No. 1

(Catalyst: Nickel-Molybdenum on Silica-Alumina Base)

Reactor Temp., °C.	315	329	343	357	371
Charge:					
Oil, grms.	1004	1042	1040	1028	609
Hydrogen, grms.	19.1	23.9	25.8	33.6	20.0
Cumulative Hours on Stream	18	36	54	72	90
Product:					
Liquid, grms.	905	937	923	880	526
Gas, norm. liters	11.3	23.2	51.5	68.3	46.2
Liquid Properties					
Specific Gravity, at 15.6° C.	.8388	.8212	.7985	.7728	.7678
Distillation:					
Initial boiling point, °C.	59	70	60	49	49
% up to 204° C.	20	32.5	49.0	64.5	68.5
% up to 274° C.	27.0	40.5	48.0	73.0	78.0
% up to 300° C.	29.0	43.0	61.5	76.0	80.0
% up to 343° C.	34.0	48.0	65.0	79.0	83.0

RUN No. 2

(Catalyst: Cobalt-Molybdenum on Silica-Alumina Base)

Reactor Temp., °C.	315	329	343	357	371
Charge:					
Oil, grms.	1080	1069	1070	1046	1047
Hydrogen, grms.	9.2	11.9	16.7	24.5	26.1
Cumulative Hours on Stream	18	36	54	72	90
Product:					
Liquid, grms.	1082	1006	941	832	810
Gas, norm. liters	18.4	38.1	67.2	109	111.3
Liquid Properties					
Specific Gravity, at 15.6° C.	.8519	.8236	.7972	.7732	.7591
Distillation:					
Initial boiling point, °C.	81	82	68	76	61
% up to 204° C.	17	36	54	70	81
% up to 274° C.	22	42	62	79	85
% up to 300° C.	24	44	65	82	90
% up to 343° C.	27	48	68	84	93

- 5 In the runs utilizing both the nickel and cobalt catalysts (both sulfided and free metal), the conversion of the high boiling stock remains at a high level and increases as the temperature is increased. Only an extremely small proportion of the charge stock is lost to gaseous product (C_2 and lower hydrocarbons), particularly at relatively low conversion levels.

RUN No. 3

(Catalyst: 0.4% Pd on Silica-Alumina Base)

Reactor Temp., °C.	315	329	343	357	371
Charge:					
Oil, grms.	1076	1047	1036	1053	1029
Hydrogen, grms.	20.4	24.5	33.0	27.6	26.7
Cumulative Hours on Stream	18	36	54	72	90
Product:					
Liquid, grms.	1046	955	812	758	796
Gas, norm. liters	31.1	34.0	76.5	90.6	90.6
Liquid Properties					
Specific Gravity, at 15.6° C.	.7936	.7636	.7515	.7487	.7511
Distillation					
Initial boiling point, °C.	57	54	66	72	67
% up to 204° C.	43	65.0	81	86	83
% up to 274° C.	62.5	83.5	92	95	92
% up to 300° C.	68.0	87.0	94	97	94
% up to 343° C.	76.0	92.0	100	100	96

- 15 Palladium on a silica-alumina base provides one of the preferred catalysts for the present hydrocracking process, yielding an unusually high proportion of liquid, converted product and an exceptional yield of gasoline boiling range material, accompanied by a relatively low gas yield. The catalyst is also capable of providing a process which consumes large quantities of hydrogen to form non-olefinic hydrocarbon product: 20 accompanying the large conversion of stock to product is a low yield of carbon deposited on the surface of the catalyst.

RUN NO. 4

(Catalyst, Pt. on Alumina-Halogen Base)

Reactor Temp., °C.	315	329	343	357	371
Charge:					
Oil, grms.	960	1030	1015	1040	1010
Hydrogen, grms.	21	23.2	26.1	30.1	26.5
Cumulative Hours on Stream	18	39	57	78	101
Product:					
Liquid, grms.	970	1028	960	910	940
Gas, norm. liters	28.3	36.8	59.5	73.6	82.2
Liquid Properties:					
Specific Gravity, at 15.6° C.		.8676		.8100	.7818
Distillation:					
Initial boiling point, °C.		152		113	78
% up to 204° C.		5.5		35.0	59.0
% up to 274° C.		11.0		63.0	87.5
% up to 300° C.		14.0		71.5	93.0
% up to 343° C.		22.0		83.0	97.1

Of the foregoing catalysts tested for hydrocracking activity, the catalyst consisting of palladium deposited on a silica-alumina base was not only the most active in yielding the desired gasoline boiling range product (204° C. end point conversion), but was also the most desirable catalyst from the standpoint of gas yield, hydrogen consumption and product distribution. The aforementioned palladium catalyst, therefore, constitutes one of the preferred catalytic agents for the hydrocracking stage of the process.

EXAMPLE II

A white oil having a specific gravity of 0.8762 at 15.6° C., boiling between 338° and 466° C. and which has been treated to reduce the total nitrogen content to less than 1 ppm. was utilized as initial feed stock in an upflow hydrocracking reactor similar to the apparatus specified in Example I above. The catalyst packed in the tubular reactor was a composite of 0.4 percent of palladium deposited on a precalcined alumina-silica base containing 63 percent alumina and 37 percent silica, that is the catalyst indicated by the results in Example I above as being the most effective catalyst in the group tested. The white oil feed stock at a temperature of 302° C., together with hydrogen at 102 atmospheres was charged into the reactor at a rate equal to a liquid hourly space velocity

of 1.0. The effluent products of the reaction from the hydrocracking reactor were separated in a manner similar to that described in Example I above. During the first twenty hours of operation, at the above conditions, the conversion of liquid feed stock to gasoline boiling range product (that is, liquid product boiling up to 204° C.) was maintained substantially constant at a rate of about 56 percent conversion.

During the next twenty hours on stream charging the white oil feed stock the effect of introducing 0.003 weight percent sulfur into the reaction by mixing carbon disulfide with the white oil charge stock was determined. During the addition of the carbon disulfide to the charge stock the conversion to 204° C. end point gasoline boiling range product increased from 56 percent by weight to 73 percent by weight of the total product. However, butane production increased from 4.8 percent to 17.9 percent and pentanes in the exit gas increased from 0.02 percent to 7.7 percent by weight; it is believed that the crystal structure of the palladium on the catalyst support has been changed by the presence of a hydrogen sulfide-producing additive to the feed stock.

During the next period of operation, from 40 hours to 125 hours, the carbon disulfide was withdrawn from the feed stock and a

treated Mid-Continent gas oil containing 1 ppm. of total nitrogen and having a boiling range from 280° to 401° C. was mixed with the white oil charge stock in equal volume proportions. Processing of this mixed charge stock thereafter continued at 302° C. during the next period of conversion up to 125 hours. During this period, conversion of the mixed feed stock dropped from a high of 73 percent to a level of 34 percent, based on the net production of the desired 204° C. end point gasoline boiling range fraction.

During the next period of conversion from a total of 125 hours on stream to a total of 325 hours on stream, a feed stock consisting exclusively of white oil charge stock was fed into the hydrocracking reactor. The conversion of charge stock to 204° C. end point gasoline boiling range product gradually increased during the period up to 200 hours on stream to 45 percent conversion to 204° C. end point product. After 250 hours on stream, carbon disulfide was again added to the white oil charge stock in an amount sufficient to provide 0.03 weight percent sulfur, and the rate of conversion of the white oil feed stock to 204° C. end point gasoline product again increased to approximately 50 percent, but the recovery of conversion to the 56 percent level realized prior to the addition of the nitrogen-containing gas oil feed stock was not evident, apparently because of the retention of a portion of the nitrogen-containing compounds which deactivate the palladium-alumina-silica hydrocracking catalyst composite.

After approximately 325 hours on stream, the white oil charge stock was mixed with 10 percent by weight of a vacuum distilled gas oil obtained from Wyoming and West Texas crude oils. This blended feed stock had a specific gravity at 15.6° C. of 0.8822. The mixed feed stock had an initial boiling point of 296° C. and an end boiling point of 498° C. and contained 139 ppm. of total nitrogen. This feed stock was processed at the same reaction conditions as previously maintained and with the same catalyst as initially supplied to the hydrocracking reactor. The percent conversion of feed stock to the desired 204° C. end point gasoline boiling range product dropped from 50 percent to nil at the indicated processing conditions within a period of 3 hours on stream. The temperature of the reaction mixture was thereafter increased in 28° C. increments to 413° C. over the ensuing 50 hours. At 329° C., 357° C. and 385° C. the conversion was still insignificant. At 413° C., the conversion of the mixed feed stock to product boiling within the gasoline boiling range increased to about 41 percent, and thereafter remained substantially steady at 40 percent conversion until the reactor had been on stream a total of 450 hours. Nitrogen analysis of the pro-

duct indicated that at 413° C. the catalyst, previously contaminated with the nitrogen-containing compounds, was now decomposing these compounds, since the nitrogen content of the product decreased to 0.7 ppm. The percent of isobutane in the C₄ fraction of the hydrocracked product was 71 percent, compared to about 93 percent for the product formed at the lower temperature hydrocracking in the absence of the nitrogen-containing catalyst contaminant. Although the higher conversion temperature produced only a slightly lower yield of 204° C. end point gasoline product, the proportion of C₅ to 82° C. fraction in the higher temperature conversion product was much greater than in the low temperature conversion product. It is evident, therefore, that substantially less isomerization takes place in the conversion at the higher versus the low reaction temperature and the proportion of relatively volatile components in the product is substantially greater in the case of the high temperature conversion.

The foregoing results with respect to the conversion of feed stock to 204° C. end point gasoline product (lower curve) and to 343° end boiling point product (upper curve) are illustrated in the accompanying diagram in which the hours on stream of the test are plotted along the abscissa and the conversion products in volume percent of the charge are plotted along the ordinate, and which depicts graphically the dependency of conversion on the reaction temperature and the particular charge stock involved in the process.

EXAMPLE III

In the following series of runs a gas oil charging stock having the properties enumerated below and having a high nitrogen content was subjected to hydrorefining at various reaction conditions and at different degrees of severity to reduce the nitrogen content of the treated stock to various levels. The resulting treated stock was thereafter subjected to hydrocracking in order to determine the effect of reducing the nitrogen content of the feed stock on the life and activity of the hydrocracking catalyst. In these runs the nitrogen content of the hydrorefined stock was reduced in stages with relatively small increments between stages to thereby indicate with a high degree of specificity the level of nitrogen content at which hydrocracking becomes inoperable or inefficient.

The charge stock in these runs having the properties indicated in the following Table II, was a mixture of light and heavy vacuum gas oils derived from Wyoming and West Texas crude oils. In the initial hydrorefining stage of the process the charge stock was passed over a hydrorefining catalyst containing 2.2 percent nickel and 6.5 percent molybdenum deposited on a calcined alumina base.

TABLE II
Properties of Vacuum Gas Oil Blend

Specific Gravity at 15.6° C.	0.9440
Initial Boiling Point, °C.	318
10% over	415
30% „	459
50% „	487
70% „	517
90% „	526
End Boiling Point, °C.	532
Total Nitrogen, ppm.	1810
Basic Nitrogen, ppm.	625

5 The mixed gas oil feed stock was passed in an upflow direction through a tubular reactor packed with the catalyst and surrounded by a salt bath maintained at the desired con-

version temperature (shown in the following Table III) to effect the hydrorefining reaction. The reaction conditions and the properties of the product are tabulated as follows:

TABLE III
Hydrorefining Mixed Gas Oils at Various Conditions
Using A Nickel-Molybdenum-Alumina Catalyst

Run No.	1	2	3	4	4
Temperature, °C.	399	399	399	399	399
Pressure, atm.	102	204	102	170	204
Hydrogen flow rate, nom. l/l	890	890	890	89	890
Space Velocity, liquid hourly	1.0	1.0	0.25	0.25	0.25
Properties of Liquid Product					
Initial B.P., °C.	196	199	160	151	143
End. B.P., °C.	354	357	343	337	333
Nitrogen Content, ppm.	108	11	5.3	0.9	0.2
Yield of Liquid Product, % of C ₆ +	99	98.5	99	98.5	98

The results indicated in the above Table III establish the fact that the nitrogen content of the liquid product formed in the hydrorefining reaction may be reduced to nil without sacrifice in the yield of liquid product and also establishes the fact that the nitrogen content of the hydrorefined product depends upon the severity of the hydrorefining reaction conditions. Thus, the nitrogen content of the product may be reduced to less than 1 ppm. by the indicated hydrorefining pretreatment of the charge stock at a conversion temperature of 399° C. by either increasing the hydrogen pressure or the residence time of the charge stock with the catalyst undergoing conversion. The interchangeability of space velocity and reaction pressure on the conversion of the charge stock and the resulting reduction of the nitro-

gen content of the product is also illustrated by the fact that a product containing 10 ppm. of ultimate nitrogen content utilizing the feed stock specified above can also be formed at 102 atmospheres pressure and at a space velocity of 0.5, the product being essentially similar to that obtained by hydrorefining the above feed stock at a pressure of 204 atmospheres and at 1.0 space velocity.

Using the same feed stock as that specified in the foregoing runs, the effect of the hydrorefining conversion temperatures on the nitrogen content of the liquid product formed in the reaction, while maintaining the pressure (204 atmospheres) and space velocity (1.0 LHSV) reaction conditions essentially constant, is demonstrated in the following Table IV:

TABLE IV

Effect of Temperature on Nitrogen Removal from Gas Oil Containing 1680 ppm. Nitrogen at Constant Pressure and Space Velocity, Using a Nickel-Molybdena-Alumina Catalyst

Run No.	6	7	8	9	10
Temperature, °C.	329	343	371	399	427
Pressure, atm.	204				
Space Velocity, LHSV	0.5				
Hydrogen Flow Rate, Normal liter/liter	534				
Properties of Liquid Product					
Total Nitrogen Content, ppm.	380	209	140	10	1

The ammonia formed by the hydrorefining conversion of the gas oil charging stock in the presence of the hydrorefining catalyst at the reaction conditions indicated in the above runs was removed from the liquid portion of the product by bubbling an inert gas through the liquid product at a temperature of about 30° C. until the effluent gas stream was free of ammonia. Various inert gases were tested and each was found to remove the ammonia to a satisfactory degree. Thus, hydrogen, methane, or carbon monoxide bubbled through a tower containing the liquid, hydrorefined product, were very effective gases for this purpose. Generally, the liquid product was free of ammonia after bubbling hydrogen through the liquid for a period of from 15 to 20 minutes at room temperature, although this period may be reduced by increasing the temperature and/or allowing the liquid to flow downwardly through a packed column against a rising stream of the inert gas.

Each of the hydrorefined gas oil products of the above runs 1 to 5 inclusive, after removal of dissolved ammonia therefrom, was subjected to hydrocracking in the presence of hydrogen at a superatmospheric pressure and in the presence of a hydrocracking catalyst, which in the following runs was selected as the catalyst most effective in the series of hydrocracking experiments of Example I, above; that is, a silica-alumina cracking catalyst base consisting of a calcined composite of 63 percent alumina and 37 percent by weight of silica impregnated with a palladium salt and subsequently calcined to yield a composite containing 0.4 percent palladium. The catalyst was packed in a vertical tubular reactor surrounded by a salt bath maintained at the desired reaction temperature. In each of the following runs, the same reaction conditions were maintained in each of the runs in order to determine the independent effect of the nitrogen content of

the feed stock on the extent of conversion during the processing period. Reaction temperature was maintained at 357° C. and the hydrorefined gas oil was charged at a rate sufficient to provide a liquid hourly space velocity of 1.5 volumes of liquid feed stock per volume of catalyst per hour and hydrogen was charged along with the feed stock at a rate of 267 normal liters per liter of charge stock and at a pressure of 204 atmospheres gauge. The products were removed from the top of the reactor and passed into a high pressure separator wherein the gaseous portion of the product was separated at the reaction pressure from the liquid portion which was drained from the bottom of the separator and passed into a distillation column operated at atmospheric pressure wherein the light gases boiling below isopentane (approximately 30° C.) were distilled from the remaining liquid portion of the product. The residue was thereafter distilled to separate a fraction having an end point of 204° C. upon which the percentage conversion was based and upon which the evaluation of the charge stock for producing gasoline boiling range material was based. The following Table V presents the observed data:

TABLE V
Hydrocracking Hydrorefined Gas Oils, Effect of Nitrogen Content of Charge Stock

Charge Stock, Run No.	1	2	3	4	5
Nitrogen Content, ppm.	108	11	5.3	0.9	0.2
Conversion Period, Hours on Stream	10	24	30	100	100
Conversion ⁽¹⁾ at Beginning of Run	⁽²⁾	⁽²⁾	75	75	76
Conversion ⁽¹⁾ at End of Period	nil	28	41	67	74

Notes: ⁽¹⁾ Conversion is measured by the volume percent of the charge stock converted to liquid product boiling in the gasoline range (21° C. initial to 204° C. end boiling point).

⁽²⁾ Activity of catalyst declined too rapidly to obtain ~~measurement~~ *measurement* of conversion.



It will be noted from the above runs that as the nitrogen content of the hydrorefined gas oil feed stock increases, the hydrocracking conversion drops off rapidly with time. Thus, in the case of the feed stock containing 180 ppm. of nitrogen the catalyst was rapidly deactivated and did not maintain a sufficient degree of activity for a sufficient period of time to permit measurement of the conversion to 204° C. end point product. In the case of the hydrorefined charge stock containing 5.3 ppm. of nitrogen the catalyst was also rapidly deactivated. Thus, although the catalyst was capable of converting 75 percent of the charge stock to 204° C. end point product in the initial period of conversion, after only 30 hours on stream, the activity had decreased to a level at which the catalyst would convert only 41 percent of the hydrorefined charge stock to 204° C. end point product. Even when the nitrogen content of the hydrorefined product was reduced to only 0.9 ppm., the activity gradually declined from the initial conversion level of 75 percent to 67 percent over a processing period of 100 hours on stream. However, when the nitrogen content of the hydrorefined charge stock was reduced to 0.2 ppm., the activity of the catalyst declined only slightly over a 100 hours processing period, having an activity level capable of converting 76 percent of the charge to 204° C. end point product at the beginning of the period to 74 percent conversion at the end of 100 hours. The foregoing results, therefore, strikingly demonstrate the adverse effect of nitrogen contamination of the feed stock on the hydrocracking activity of the catalyst and dramatically demonstrate the desirability of removing the nitrogen contamination as completely as possible from the feed stock to the hydrocracking process.

Following the above processing periods, the temperature in each case was raised in order to bring the activity of the hydrocracking catalyst to its initial activity of 75 percent conversion. In the case of the charge stock containing 108 ppm of nitrogen, it was

necessary to increase the conversion temperature to a level of 399° C. and the activity once again rapidly declined with continued use of a charge stock having the above nitrogen content. In the case of the charge stock sufficiently hydrorefined to a nitrogen content of only 0.2 ppm., the hydrocracking activity of the catalyst was increased to a conversion level of 76 percent from its activity after 100 hours on stream of 74 percent by merely increasing the temperature of the reaction an additional 5.8° C.

Other hydrocracking catalysts of the type specified in Example I above, that is, catalysts containing cobalt and/or nickel or their sulfides in combination with molybdenum on a cracking catalyst base such as a silica-alumina composite or a catalyst comprising a platinum group metal such as palladium on a composite of alumina and a combined halogen such as fluorine and/or chlorine also demonstrate the same sensitivity to the nitrogen-containing compounds in the feed stock charged to the hydrocracking process. In each case it was necessary to increase the conversion temperature of the hydrocracking reaction to a level at which an excessive degree of gaseous products were formed, as the catalyst remained on stream during the hydrocracking conversion process.

WHAT WE CLAIM IS:—

1. A process for catalytically hydrocracking a petroleum hydrocarbon charge contaminated with a naturally-occurring, organic nitrogenous compound detrimental to the hydrocracking catalyst which comprises contacting said charge at a temperature of from 315° C. to 482° C. in the presence of an excess of hydrogen at a pressure of substantially from 34 to 204 atmospheres with a hydrorefining catalyst comprising a Group VI metal and an iron group metal of the elements of Group VIII of the Periodic Table supported on an inert refractory metal oxide base and at a space velocity of the charge relative to the catalyst at which substantially all of the nitrogen in said nitrogenous compound is converted to ammonia and the nitrogen content of said charge is reduced to less than one part per million parts by weight of

said charge, separating said ammonia from the reaction product and thereafter contacting the normally liquid portion of said reaction product at a temperature of from 260° to 538° C. in the presence of hydrogen at a pressure of from 34 to 204 atmospheres with a hydrocracking catalyst comprising a metal selected from the elements of Group VIII of the Periodic Table on an acidic cracking catalyst support.

2. The process of Claim 1, characterized in that the acidic cracking catalyst support in the hydrocracking catalyst is a calcined composite of silica and alumina, and the element of Group VIII for the hydrocracking catalyst is selected from palladium and nickel.

3. The process of Claim 1, characterized in that the hydrocarbon charge containing the nitrogenous compound is contacted with a hydrorefining catalyst in which the inert refractory metal oxide is alumina and which contains nickel and molybdenum.

4. The process according to one of the Claims 1 to 3, characterized in that a petroleum hydrocarbon charge boiling above the gasoline boiling range and containing the harmful nitrogenous compound is contacted with the hydrorefining catalyst in the presence of the excess hydrogen at a temperature in the range of from 343° to 427° C. and at a space velocity of less than 1.5 liquid volumes of the charge per hour per volume of catalyst and the normally liquid hydrocarbon portion of the resultant reaction product containing less than 1 part nitrogen per million parts by weight is converted into a lower boiling liquid non-olefinic product by contacting the same with the hydrocracking catalyst at a temperature in the range of from 315° to 427° C. together with from 89 to 534 normal liters of hydrogen per liter of said liquid hydrocarbon portion.

5. The process of hydrocracking hydrocarbon oils initially containing combined nitrogen substantially as described.

J. Y. & G. W. JOHNSON,
Furnival House,

14—18, High Holborn, London, W.C.1,
Chartered Patent Agents,
Agents for the Applicants.

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