



HYDROCARBON CONVERSION PROCESS AND CATALYSTS USED THEREIN

BACKGROUND OF THE INVENTION

5 Hydrocracking continues to be an important refinery process for producing modern fuels, and much attention has been devoted to the development of hydrocracking catalysts. In particular, hydrocracking is useful in the production of middle distillate fractions, those petroleum fractions boiling in the range of about 250°-700°F. (121°-371°C.) as determined by the appropriate ASTM test procedure.

10 These middle distillate fractions are particularly desirable as valuable fuels products. The term "middle distillate" is intended to include the diesel, jet fuel and kerosene boiling range fractions. The kerosene or jet fuel boiling point range is intended to refer to a temperature range of about 280°-525°F. (138°-274°C.) and the term "diesel boiling range" is intended to refer to hydrocarbon boiling points of about 250°-700°F.

15 (121°-371°C.). Gasoline or naphtha is normally the C₅ to 400°F. (204°C.) boiling point fraction of available hydrocarbons. The boiling point ranges of the various product fractions recovered in any particular refinery will vary with such factors as the characteristics of the crude oil source, refinery local markets, product prices, etc. Reference is made to ASTM standards D-975 and D-3699-83 for further details on

20 kerosene and diesel fuel properties.

Processes for hydrocracking heavy petroleum feedstocks to middle distillates generally involve successive hydrocracking steps or "stages". Successive hydrocracking stages are usually performed in separate reaction vessels, though this is not required. Initial stages are operated at conditions and with catalysts which are

25 active for sulfur and nitrogen removal, for aromatic saturation, and for other hydrotreating reactions. First stage hydrocracking catalysts are designed for high conversion activity in the presence of feeds having high sulfur and nitrogen contents, and often with high aromatic contents. Typical first stage hydrocracking catalysts comprise a cracking component, a binder and a non-noble metal hydrogenation

30 component such as nickel, molybdenum, cobalt, and/or tungsten. The cracking



component is generally an amorphous material such as silica-alumina, though a zeolite may be included.

Hydrocracking stages after the first stage are operated at hydrocracking conditions, using catalysts while are intended for high cracking rates. Such second stage catalysts may contain either base metal hydrogenation components, such as nickel, molybdenum, cobalt, and/or tungsten, or noble metal hydrogenation components, such as platinum or palladium. While catalysts comprising a noble metal hydrogenation component are more active in certain situations than those having a base metal as the hydrogenation component, they are also susceptible to sulfur contamination, which deactivates the catalysts and shortens their useful lives. For these reasons noble metal catalysts have been typically used in second-stage hydrocracking units, or units wherein the feed comprises relatively small amounts of sulfur and nitrogen.

Traditionally, palladium has been the popular choice as the hydrogenation component of second-stage hydrocracking catalysts because of its relatively high selectivity and substantially lower cost than platinum. However, continual development of refinery processes has generated new requirements for second stage hydroprocessing. The common practice of feeding high sulfur feeds to the two-stage hydrocracker has increased the amount of sulfur fed into the second-stage. Upsets in the sulfur control processes between the first and second stage also occasionally result in high sulfur loads in the second stage feed. Under these conditions, noble metal catalysts containing palladium are unacceptable, since the palladium catalysts are particularly sensitive to sulfur compounds, even relatively small amounts contained in some first stage effluents. Processes wherein substantially all the sulfur is not removed from the feed before introduction into the second-stage hydrotreater readily fouls the palladium catalyst decreasing both its selectivity and activity.

A number of noble metal catalysts have been proposed. U.S. Patent No. 5,393,408 discloses a process for stabilizing a lubricating oil base stock. Catalysts taught for this process contain a hydrogenation component independently selected from the group consisting of the platinum group metals, nickel, cobalt, chromium, molybdenum, tungsten and tin. A combination of metals containing both platinum

and palladium are also taught, but there is no suggestion of any possible benefit for using a particular range of platinum and palladium.

U.S. Patent No. 4,387,258 teaches a selective hydrogenation process to convert alkynes and dienes to alkene containing an olefinic double bond using a catalyst
5 comprising platinum or palladium on a crystalline silica polymorph.

U.S. Patent No. 3,852,207 teaches a two stage process for producing a lubricating aid having good UV stability. Catalysts taught for the hydrogenation step contain a hydrogenation component, including platinum or palladium. The silica-
alumina support of the preferred hydrogenation catalyst has an aluminum content of
10 from 40 to 95 wt % and or alumina/silica weight ratio between 40/60 and 95/5.

T. Lin, et al., Ind. Eng. Chem. Res. 1995, 34, 4284-4289 and J. Chiou, et al., Ind. Eng. Chem. Res. 1995, 34, 4277-4283 disclose methods of improving the sulfur tolerance of supported platinum catalysts by adding a second metal, such as
palladium, to the supported catalyst.

U.S. Patent No. 3,962,071 to Itoh et al., claims a process which includes
15 hydrocracking, fractionation, and hydrogenation for enhancing lubricating oil photostability. In Itoh et al., the hydrogenation catalyst includes palladium on a silica containing refractory inorganic oxide carrier having 5-40 weight percent silica, a surface area of 100-500 m²/g, a pore volume of 0.5-1.2 ml/g, an average pore diameter
20 of 30-120 Angstroms, and a bulk density of 0.5-0.7 g/ml.

U.S. Patent No. 3,637,484, U.S. Patent No. 3,637,878, and U.S. Patent No. 3,703,461, all to Hansford, disclose a process for hydrogenating an aromatic hydrocarbon feedstock with a catalyst having a support composed of a silica-alumina
cogel in a large pore alumina gel matrix and containing a platinum group metal. The
25 catalyst composition of Hansford has a pore volume of 0.8-2.0 ml/g with about 0.3-1.0 ml/g of the pore volume in pores of diameter greater than about 500 Angstroms. In Hansford, the support employs a relatively high ratio of alumina to silica, always in excess of 60 weight percent of alumina as compared to silica. Conversely, supports having high ratios of silica to alumina have been disclosed in U.S. Patent Nos.
30 4,139,493; 4,325,805; and 4,601,996. However, catalysts containing higher ratios of

silica to alumina generally contain a hydrogenation component other than a platinum group metal, commonly nickel, tin, molybdenum, or cobalt.

Clark, et al., in U.S. Patent No. 5,346,874 disclose a hydrogenation process and a catalyst comprising from about 0.1% to about 2.0% by weight of palladium and
5 from about 0.1% to about 2.0% by weight of platinum on a support comprising borosilicate.

EP 0 519 573 discloses a catalyst composition for the hydrogenation of hydrocarbon feedstocks.

Noble metal catalysts, primarily comprising platinum and/or palladium, are
10 known for hydrogenation reactions such as olefin or aromatic hydrogenation. To minimize yield losses, such hydrogenation catalysts contain little or no cracking activity, generally comprising alumina supports with no amorphous or crystalline (e.g. zeolitic) silica-alumina components. Conversions in these hydrogenation processes are low. While noble metal catalysts are also desirable for cracking reactions, with
15 larger amounts of cracking leading to molecular weight reduction, they tend to be vulnerable to sulfur components in the feedstock, and can only be used for cracking very low sulfur feeds. Even upsets in an otherwise low sulfur process, which may dump large quantities of sulfur on a hydrocracking catalyst, fouls the conventional noble metal catalyst. It is desirable to have a process and a catalyst for cracking a
20 hydrocarbonaceous oil with the performance advantages of a noble metal catalyst but with improved sulfur tolerance.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process for hydrocracking low sulfur containing feeds while reducing the deleterious effect of sulfur on
25 catalyst performance and life. Another object of the present invention is to provide a process for increased middle distillate production. Still another object of the present invention is to decrease hydrogen consumption.

The present invention provides a process for converting a hydrocarbonaceous oil into a product of lower average molecular weight and lower average boiling point comprising contacting a hydrocarbonaceous oil, under hydrocracking conditions sufficient to convert at least about 30% of the hydrocarbonaceous oil which boils

- 5 above 288°C(550°F) to middle distillate components having a boiling point of less than 288°C(550°F) with a catalyst comprising a cracking component, a binder, and a

hydrogenation component comprising platinum and palladium in a molar ratio of between 10:1 and 1:10.

The present invention is directed to a hydrocracking process for hydrocracking a high sulfur feed, including a feed containing greater than 20 ppm sulfur, up to sulfur levels of 100 ppm or higher. The present invention is further directed to a hydrocracking process, such that at least about 30 vol%, preferably at least about 50 vol%, of a hydrocarbonaceous oil which boils above 288°C(550°F) is converted to a cracked product having a boiling point of less than 288°C(550°F). At least about 75 vol% of the preferred hydrocarbonaceous oil of this process has a normal boiling point above about 288°C(550°F).

More preferably, at least about 75 vol% of the hydrocarbonaceous oil has a normal boiling point above about 371°C(700°F). The preferred catalyst of this process comprises a cracking component, such as an amorphous and/or zeolitic silica-alumina component, and a hydrogenation component comprising platinum and palladium in a molar ratio of between 10:1 and 1:10, preferably in the molar ratio of between 4:1 and 1:4.

Among other factors, the present invention is based on the discovery of a hydrocracking catalyst, containing both platinum and palladium in a particular ratio on a single catalyst particle, which shows high tolerance to sulfur contained in a hydrocracking feed. Furthermore, while the catalyst of this invention has considerably more activity than the base metal catalysts, even in the presence of sulfur, the catalyst is also significantly and surprisingly more selective for producing middle distillate fuels than is either conventional base metal catalysts or conventional catalysts which contain palladium alone.

DETAILED DESCRIPTION OF THE INVENTION

The present process is directed to hydrocracking reactions for the production of middle distillate fuels. Such hydrocracking reactions include removing sulfur and nitrogen from hydrocarbonaceous oils and converting components of the oils to products of an average lower molecular weight and an average lower boiling point. While cracking of the petroleum components is desirable, it is preferable to minimize cracking to light products boiling below 121°C(250°F).

The catalyst useful in the present process comprises a cracking component, a binder, and a palladium-platinum hydrogenation component having a palladium to platinum molar ratio of between 10:1 and 1:10, preferably between about 4.0:1 to 1:4.0 and most preferably between about 2:1 and 1:2.

5 The cracking component includes an amorphous cracking component, which generally is the base material for the catalyst. The preferred amorphous cracking component is silica-alumina, containing typically between 10 and 90 weight percent silica, preferably between 15 and 65 weight percent silica, and more preferably between about 20 and 60 weight percent silica, the remainder being alumina. Base
10 materials suitable for preparing the catalysts used in the process of this invention are commercially available, for example, from Condea Chemie, GmbH of Hamburg, Germany, and base materials from Condea Chemie designated as "Siral 40[®]" have been found to be particularly suitable to prepare catalysts employed in the present invention. Alternatively, the silica-alumina base materials are prepared using known
15 coprecipitation, cogelation, and/or comull procedures. Crystalline silica-alumina materials such as zeolites may also be included as part of the support of the hydrogenation catalysts to increase catalyst acidity.

The base material may further comprise in the range of 0-85 wt % of a zeolite cracking component, preferably a Y-type zeolite. The preferred catalyst contains up to
20 25% zeolite and preferably in the range of 1-20% zeolite. One of the zeolites which is considered to be a good starting material for the manufacture of hydrocracking catalysts is the well-known synthetic zeolite Y as described in U.S. Patent No. 3,130,007, issued April 21, 1964. A number of modifications to this material have been reported, one of which is ultrastable Y zeolite as described in U.S. Patent No.
25 3,536,605, issued Oct. 27, 1970. To further enhance the utility of synthetic Y zeolite, additional components can be added. For example, U.S. Patent No. 3,835,027, issued on Sept. 10, 1974 to Ward, et al., describes a hydrocracking catalyst containing at least one amorphous refractory oxide, a crystalline zeolitic aluminosilicate and a hydrogenation component selected from the Group VI and Group VIII metals and
30 their sulfides and their oxides. Zeolites having small unit cell sizes are described in U.S. Patent Nos. 5,059,567 and 5,246,677, the disclosures of which are incorporated herein by reference for all purposes. The zeolite-containing catalyst particles may be

prepared using conventional methods. One such method is described in U.S. Application Serial No. 07/870,011, filed by M.M. Habib et al. on April 15, 1992, and now abandoned, the disclosure of which is incorporated herein by reference for all purposes. Also, so-called x-ray amorphous zeolites (i.e., zeolites having crystallite
5 sizes too small to be detected by standard x-ray techniques) can be suitably applied as cracking components.

The preferred catalysts employed in the present invention contain a catalyst support that is generally prepared from these base materials. The distribution of silica and alumina in the support may be either homogeneous or heterogeneous, but is
10 preferably heterogeneous. A homogeneous distribution is ordinarily obtained when the silica-alumina ratio is uniform throughout the support, resulting for example from conventional coprecipitation or cogelation techniques. These homogeneous supports, wherein the necessary silica content is uniformly distributed, are difficult to prepare in the large-pore forms required herein. Pure alumina, on the other hand, can readily be
15 prepared in these forms, preferably using acid or base peptization methods. A preferred form of the support consists of an alumina gel in which is dispersed the silica-alumina base material, which form is referred to herein as the "heterogeneous" support. The alumina gel is also referred to herein as the "oxide binder." The support may also contain refractory materials other than alumina or silica, such as for example
20 other inorganic oxides or clay particles, provided that such material does not adversely affect the hydrogenation activity of the final catalyst. Other inorganic oxides that may be present in the support may include, but are not necessarily limited to, titania, magnesia and zirconia or combinations thereof. Generally, silica-alumina will make up at least 90 weight percent of the entire support, and most preferably the support
25 will be substantially all silica-alumina.

As stated above, the support is preferably prepared by mixing the base material with a peptized oxide binder, such as alumina, which has been treated with an acid, generally a strong acid such as nitric, acetic, or hydrochloric acids. Generally, the weight ratio of base material to oxide binder is in the range from 95/5 to 30/70 and
30 preferably 65 base material/35 binder. Pore size is in part controlled in supports prepared as described herein by the length of time that the oxide binder is exposed to the acid during the peptizing step, and by the amount of acid used. To prepare the

particulate refractory inorganic support for the catalyst. the base material is mixed with an oxide binder which has been treated with acid, preferably with less than about 3 weight percent of 100% pure acid (based on the weight of total calcined solids). A 4-12% acid is used to make a mesoporous catalyst. The proportion of acid will vary depending on the type of acid, the reactivity of the raw material powders, the type of mixing equipment, and the mixing time, temperature, etc.

The support used in the practice of the present invention is a particulate support. The exact size and shape of the catalyst support particles will vary depending on the particular method that will be used to hydrogenate the lubricating oil base stock. The effective diameter of the zeolite catalyst particles are in the range of from about 0.079cm(1/32 inch) to about 0.635cm(1/4 inch), preferably from about 0.127cm(1/20 inch) to about 0.318cm(1/8 inch). The catalyst particles may have any shape known to be useful for catalytic materials, including spheres, cylinders, fluted cylinders, prills, granules and the like. For non-spherical shapes, the effective diameter can be taken as the diameter of a representative cross section of the catalyst particles. The zeolite catalyst particles will further have a surface area in the range of from about 50 to about 500 m²/gram. When the support is to be extruded in the preparation of the catalyst materials, mixing the base material with the peptized oxide binder enhances the extrusion process and improves the strength of the completed catalyst pellets. The extrudate is usually dried and calcined in an oven to produce the support. After calcining, the support is ready for the addition of the hydrogenation component of the catalyst.

The amount of palladium-platinum hydrogenation component on the catalyst must be sufficient to act as an effective catalyst to hydrocrack the petroleum feed. Generally, the amount of alloy on the support used to catalyze a hydrogenation process within the scope of the present invention will be within the range of from about 0.01 weight percent to about 5 weight percent, preferably the range is from about 0.1 weight percent to about 1 weight percent. Generally, adding greater than about 1 weight percent of the alloy does not significantly improve on the activity of the catalyst and is therefore economically disadvantageous. However, amounts in excess of 1 weight percent are usually not harmful to the performance of the catalyst. The preferred catalyst comprises from about 0.1 to 0.5 wt% palladium and from about 0.1 to 0.4 wt% platinum, and more preferably from about 0.1 to 0.25 wt% palladium

and from about 0.1 to 0.25 wt% platinum. The ratio of palladium to platinum useful as the hydrogenation component is 10:1 to 1:10. A more preferred ratio is 2.5:1 to 1:2.5. Most preferably, the palladium to platinum molar ratio is 2:1 to 1:2.

5 A number of methods are known in the art to deposit platinum and palladium metal or their compounds onto the support, such as, for example, by ion exchange, impregnation, coprecipitation, etc. It has been found that depositing platinum and palladium on the supports used in the catalyst of the present invention is particularly advantageous when using a contacting solution containing active compounds of both platinum and palladium under a controlled pH. The contacting solution preferably will
10 be buffered to maintain a pH within the range of from about 9 to about 10. Values outside of this pH range may be used to deposit platinum and palladium jointly on the support, but the final distribution of the alloy on the support may not be as favorable as those obtained within this pH range.

When depositing platinum and palladium by impregnation, the metals are
15 usually added to the impregnating solution as a metal salt, generally as an organic amine complex salt of a mineral acid. Ammonium salts have been found to be particularly useful in preparing the impregnating solution. Representative of the ammonium salts that may be used are nitrates, carbonates, bicarbonates and lower carboxylic acid salts such as acetates and formates. In the case of palladium, an
20 ammonium nitrate salt or an ammonium chloride salt have been found to give satisfactory results. However, other salts of the metals are also operable and could be used to impregnate the support. In such case, it may be useful to determine the optimal pH to use during impregnation for the particular salt selected in order to obtain the best distribution of metals on the support. It has been found that excellent
25 distribution of palladium will be obtained using the present support if an impregnating solution containing tetraamine palladium nitrate is buffered to a pH of from between about 9.6 and about 10.

Following impregnation, the impregnated support should be allowed to stand before drying for a period of time sufficient for it to attain equilibration with the
30 impregnating solution. For an extrudate, this period usually is at least 2 hours, and periods of up to 24 hours are not detrimental to the finished catalyst. A suitable time

for a given support may be readily determined by one skilled in the art having regard to this disclosure by, for example, drying at various times after impregnation and measuring the metal distribution. Following impregnation and standing, the catalyst is again dried and/or calcined. The prepared catalyst may be reduced with hydrogen as is
5 conventional in the art and placed into service.

The hydrocracking reaction takes place in the presence of hydrogen, preferably at hydrogen pressures in the range of between about 3.45×10^6 Pa (500 psia) and 20.7×10^6 Pa (3000 psia), more preferably in the range of about 6.21×10^6 Pa (900 psia) to about 20.7×10^6 Pa (3000 psia). The feed rate to the hydrogenation catalyst system is in the range of from about 0.2 to about 1.5 LHSV, preferably
10 in the range of about 0.2 to about 1.0 LHSV. The hydrogen supply (makeup and recycle) is in the range of from about 500 to about 20,000 standard cubic feet per barrel of lubricating oil base stock (89.0 to about 3560 l/l), preferably in the range of from about 2000 to about 10,000 standard cubic feet per barrel (356 to about 1781 l/l).

The hydrocarbonaceous feed to the hydrocracker is generally a distillate stream
15 from a vacuum distillation process. The feed may be derived from a crude stream or from a refinery process such as an FCC process, a coker process, a residuum demetallization and/or hydrotreating process, a synthetic fuel process, a deasphalting process, a hydrocracking or hydrotreating process or the like. The feed may have been processed, e.g. by hydrotreating, prior to the present hydrocracking process to reduce
20 or substantially eliminate its heteroatom content. The preferred feed has a boiling point range starting at a temperature above 500°F. (260°C.), and more preferably a boiling point range between 500°-1050°F. (260-566°C.) Preferred feedstocks to the reaction zone therefore include gas oils having at least 70 vol% of their components boiling above 650°F. (343°C.) and at least 90 vol% of their components boiling below
25 950°F. (510°C.). The hydrocracking feedstock may contain nitrogen, usually present as organonitrogen compounds in amounts greater than 1 ppm. It is a feature of the present invention that high nitrogen feeds, e.g. containing up to 100 ppm of organonitrogen may be treated in the present process. The feed will normally also contain sulfur containing compounds sufficient to provide a sulfur content of greater
30 than 1 ppm. and up to 250 ppm.

The preferred process is a downflowing reaction process. The hydrocracking reaction zone is operated at hydrocracking reaction conditions, including a reaction temperature in the range of from about 250°C to about 500°C, pressures up to about 300 bar (30.5 MPa) and a feed rate (vol oil/vol cat hr) from about 0.1 to about 10 hr⁻¹.
5 Hydrogen circulation rates are generally in the range from about 350 std liters H₂/kg oil to 1780 std liters H₂/kg oil. Preferred reaction temperatures range from about 340°C to about 455°C. Preferred total reaction pressures range from about 500 pounds per square inch absolute (psia) to about 3,500 psia (about 3.5 MPa - about 24.2 MPa), preferably from about 1,000 psia to about 3,000 psia (about 7.0 MPa -
10 about 20.8 MPa). With the preferred catalyst system described above, it has been found that preferred process conditions include contacting a hydrocarbonaceous feed with hydrogen in the presence of the layered catalyst system under hydrocracking conditions comprising a pressure of about 16.0 MPa (2,300 psia), a gas to oil ratio at from about 606-908 std liters H₂/kg oil (4,000 scf/bbl to about 6,000 scf/bbl), a LHSV
15 of about 1.0 hr⁻¹, and a temperature in the range of 360°C. to 427°C (680°F. - 800°F.).

The hydrocracked oil product exiting the hydrocracking reaction zone includes normally liquid phase components, which comprise reaction products and unreacted components of the VGO, and normally gaseous phase components, which comprise gaseous reaction products and unreacted hydrogen. The reaction products include
20 cracked products having a boiling point below that of the feed to the hydrocracking process, such that at least 5%, more preferably at least about 10% by volume and still more preferably at least about 30% by volume of the components in the VGO which boil above 550°F are converted in the reaction zone to components which boil below about 550°F. The hydrocracker effluent is further decreased in nitrogen and sulfur
25 content. Preferably the normally liquid products present in the hydrocracker reaction zone effluent contain less than about 20 ppm sulfur and less than about 10 ppm nitrogen, more preferably less than about 10 ppm sulfur and about 5 ppm nitrogen.

EXAMPLES

Example 1

30 Several base metal catalysts, a palladium catalyst and the platinum-palladium catalyst of this invention were tested in a pilot plant for middle distillate selectivity.

Catalyst A is a catalyst of this invention, containing 0.16 Wt% Palladium, 0.2 Wt% Platinum, 80% silica-alumina, 16% alumina with 4% ultra-stable Y zeolite.

Catalyst A was prepared by impregnating the $\text{SiO}_2\text{-Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ /zeolite base with a solution containing platinum and palladium salts, drying the impregnated catalyst and
5 calcining at 842°F in air for 30 minutes.

Catalyst B and Catalyst C were from two catalyst preparations containing 10 wt% NiO and 24 wt% WO_3 on a silica-alumina support.

Catalyst D was prepared like Catalyst B but with 4% ultra-stable Y zeolite

Catalyst E contained 0.5 Wt% Pd on silica-alumina with 4% zeolite

10 A vacuum gas oil from commercial refinery production was fed through a two stage pilot-plant unit. The first stage comprised a Ni-W-Ti on silica-alumina catalyst and was run under such conditions as to target approximately 40% conversion to components boiling below 288°C(550°F). The effluent from the first stage was subjected to vacuum distillation and the residuum was fed to the second stage. The second-stage
15 contained the subject catalysts and targeted an approximately 60% per pass conversion to products boiling below 288°C(550°F). Feed to the second-stage contained less than 6ppm sulfur in each case. The results shown in Table 1 demonstrate the catalyst of this invention is more selective for middle distillate than the base metal and palladium catalysts. It also demonstrates that the catalyst of this invention is more active than
20 the base metal catalysts. The results further demonstrate that less hydrogen is consumed using the catalyst of the present invention.

Table 1

Second Stage Catalyst	B	C	D	E	A
Catalyst Temp, °F	716	718	701	604	671
	Overall, Two-Stage Yields, Wt% (zero bleed basis)				
C ₄ -	6.8	6.2	6.1	5.2	5.2
Naphtha (C ₅ -125°C(250°F))	25.0	25.0	26.6	25.6	22.8
Light Distillate (121-204°C(250-400°F))	35.8	35.4	36.5	37.7	37.3
Middle Distillate (204-288°C(400-550°F))	34.8	35.5	33.0	34.1	36.7
Total Distillate (121-288°C(250-550°F))	70.6	70.9	69.5	71.8	74.0
H ₂ Consumption, l/l (SCF/B)	287(1610)	289(1620)	285(1600)	280(1570)	272(1530)

Example 2

In this example, a palladium catalyst (catalyst E from example 1) and a platinum-palladium catalyst of this invention (catalyst A from example 1) were tested under high sulfur conditions. The conditions of this experiment were substantially the same as those in example 1 except the feed to the second stage of the pilot-plant unit was spiked with sulfur compounds to achieve a second-stage feed containing 20 ppm sulfur. The results in Table 2 show that the platinum-palladium catalyst of this invention is more selective for middle distillate production than the palladium catalyst.

Table 2

Second-Stage Catalyst	E	A
	Overall Yield, Wt%	
C ₄ -	5.8	5.1
Naphtha (C ₅ -121°C(250°F))	27.5	24.1
Middle distillate (121-288°C(250-550°F))	69.3	72.8

Example 3

In this example, a base metal catalyst (catalyst B of example 1) and a platinum-palladium catalyst of this invention (catalyst A of example 1) were tested under substantially the same conditions as in Example 1. The middle distillate products were further analyzed for smoke point and freeze point and distilled to compare 5, 50 and 95% cuts. The results in Table 3 indicate that the platinum-palladium catalyst of this invention is more selective for the middle distillate products than is the base metal catalyst. The results also show that less hydrogen is consumed in the process using the platinum-palladium catalyst of this invention. The results further indicate that the properties of the middle distillate made with a platinum-palladium catalyst of this invention are virtually the same as those made with the base metal catalyst.

Table 3

Second-Stage Catalyst	B	A
	Overall Yield, Wt%	
C ₄ -	6.7	4.9
Naphtha (C ₅ -121°C(250°F))	27.0	24.1
Middle distillate (121-288°C(250-550°F))	69.2	73.2
H ₂ Consumption, l/l (SCF/B)	278(1560)	263(1480)
Middle Distillate Product Quality		
Smoke Point, mm	31	34
Freeze Point, °C	-61	-59
5% cut, °C(°F)	126(259)	126(259)
50% cut, °C(°F)	205(401)	204(400)
95% cut, °C(°F)	284(543)	285(545)

Example 4

This example was run under substantially the same conditions as that of example 3 except the feed to the second stage was spiked with sulfur compounds to achieve 30 ppm sulfur and a 14°C(25°F) ascending temperature profile was practiced in the first stage and an 8.3°C(15°F) ascending profile was practiced in the second stage to model typical commercial conditions. The results summarized in table 4 indicate that the even under the ascending profile and high sulfur conditions the platinum-palladium catalyst of this invention was more selective for the middle distillate products than the base metal catalyst and consumed less hydrogen. Comparison with the results obtained in example 3 revealed that the base metal catalyst was more susceptible to catalyst aging (with a 3.2% decline in selectivity) than the platinum-palladium catalyst of this invention (1.1% decline in selectivity). Analysis products indicates that the middle distillate product made with a platinum-palladium catalyst of this invention were virtually the same as those made with the base metal catalyst.

Table 4

Second-Stage Catalyst	B	A
	Overall Yield, Wt%	
C ₄ -	8.0	5.1
Naphtha (C ₅ -121°C(250°F))	27.8	24.8
Middle Distillate (121-288°C(250-550°F))	67.0	72.4
H ₂ Consumption, scf/bbl (lH ₂ /kgoil)	1560(240)	1480(223)
Middle Distillate Product Quality		
Smoke Point, mm	30	30
Freeze Point, °C	-62	-57
5% cut, °C(°F)	126(259)	126(259)
50% cut, °C(°F)	204(400)	204(400)
95% cut, °C(°F)	284(543)	288(550)

Example 5

The sulfur tolerance of a palladium catalyst, Catalyst F. (Catalyst F is Catalyst A without Platinum) and the platinum-palladium catalyst of this invention (Catalyst A of example 1) were tested. Each catalyst was tested over an extended period with feed containing high amounts of sulfur, and for short intervals with feed containing at least 100 ppm sulfur. Test conditions were substantially the same as in Example 1.

Catalyst F was contacted for short intervals with feed containing first 50 ppm sulfur and then 100 ppm sulfur, followed by extended runs using feed containing 20 ppm sulfur. Table 5 shows that Catalyst F suffered significant loss in performance (measured by jet fuel yield loss) when contacted with the high sulfur feed. At the end of the test, the catalyst produced 10.7% less jet fuel yield than near the beginning of the test. By contrast, Catalyst A was contacted with 200 ppm sulfur feed, followed by an extended period with 20 ppm feed. In this test, Catalyst A produced 1.6% less jet fuel at the end of the test as near the beginning of the test. In a second test, Catalyst A was contacted with 700 ppm sulfur feed, followed by an extended period with 30 ppm feed. In this second test, Catalyst A produced 3.0% less jet fuel at the end of the test, compared to near the beginning of the test. These results show that the palladium containing catalyst was significantly more susceptible to sulfur poisoning that was the catalyst of the invention, which contained a platinum/palladium alloy.

Table 5

Catalyst	Test	Sulfur in Feed, ppm	Contact Time, hrs	Jet Fuel Yield, wt%	Relative Yield Loss, %
Catalyst F	T1	2	800	71.3	
		50	180	66.2	7.2
		100	132	64.3	9.8
		2	220	69.6	2.4
		10	350		
		2	400	69	3.2
		20	470	63.7	10.7
Catalyst A	T2	<6	300	74.0	
		200	8		
		20	170	72.8	1.6
	T3	<6	500	73.2	
		30	840	72.4	1.1
		700	4		
		30	3000	71.0	3.0

WHAT IS CLAIMED IS:

1. A process for converting a hydrocarbonaceous oil into a product of lower average molecular weight and lower average boiling point comprising contacting a hydrocarbonaceous oil, under hydrocracking conditions sufficient to convert at least about 30% of the hydrocarbonaceous oil which boils above 550°F(288°C) to middle distillate components having a boiling point of less than 550°F(288°C), with a catalyst comprising a cracking component, a binder, and a hydrogenation component comprising palladium and platinum in a molar ratio of between 10:1 and 1:10.
2. The process according to claim 1 wherein the molar ratio of palladium to platinum in the alloy is between about 4.0:1 and about 1:4.0.
3. The process according to Claim 1 wherein the hydrogenation component comprises from about 0.10 to 0.25 wt% palladium and from about 0.10 to 0.25 wt% platinum.
4. The process according to Claim 1 wherein the cracking component comprises silica-alumina.
5. The process according to Claim 4, wherein the cracking component further comprises an ultra-stable Y-type zeolite.
6. The process according to Claim 1 wherein the binder is alumina.
7. The process according to Claim 1 wherein the hydrocarbonaceous feed is a denitrified VGO containing less than about 200 ppm nitrogen.
8. The process according to Claim 1 wherein at least about 70 vol% of the hydrocarbonaceous oil has a boiling point above about 650°F(343°C).
9. The process according to Claim 8 wherein at least about 75 vol% of the hydrocarbonaceous oil has a normal boiling point above about 700°F(371°C).
10. The process according to Claim 1 conducted at hydrocracking conditions sufficient to convert at least about 50% of the hydrocarbonaceous oil which boils

above 550°F(288°C) to middle distillate components having a boiling point of less than 550°F(288°C).

11. A process for converting a hydrocarbonaceous oil into a product of lower average molecular weight and lower average boiling point comprising contacting a hydrocarbonaceous oil, under hydrocracking conditions sufficient to convert at least about 30% of the hydrocarbonaceous oils which boils above 700°F(371°C) to middle distillate components having a boiling point of less than 700°F(371°C), with a catalyst comprising a cracking component, a binder, and a hydrogenation component comprising platinum and palladium in a molar ratio of between 10:1 and 1:10.