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## PROCESS

This invention concerns the catalytic hydrocracking of relatively high boiling hydrocarbon feedstocks to produce lighter or lower boiling components such as gasoline. More particularly, the invention is directed to an improved prehydrogenation-hydrocracking process for the conversion of distillate hydrocarbon feeds contaminated with organic nitrogen compounds wherein the prehydrogenation stage can, and preferably the hydrocracking stage also does, employ a hydrogen-containing recycle gas.

Since basic nitrogen compounds are known to poison hydrocracking catalysts, it has become common practice to first subject the feedstock to a catalytic prehydrogenation treatment or hydrotreating operation wherein the nitrogen content of the effluent which serves as the feed to the hydrocracking stage, is reduced. Unfortunately, this solution has not been entirely successful, particularly in cases where the hydrocarbon treated contains a significant amount of organic nitrogen contaminants and the system employs recycle gas. In this type of operation the conversion levels, especially at relatively low hydrocracking pressures, and the aging or deactivation rate of the catalyst, leave much to be desired. For instance, it has generally been considered necessary in the treatment of feedstocks having a nitrogen content of at least about 100 p.p.m. to conduct the hydrocracking operation in these systems at relatively high pressures, e.g., over 1,000 p.s.i.g., to effect the desired conversion. The improved process of the present invention enables the acquisition of the desired conversion at relative low hydrocracking pressures without experiencing the extent of catalyst aging normally associated with low-pressure hydrocracking operations.

In accordance with the present invention, a high-boiling mineral oil feedstock contaminated with organic nitrogen compounds to the extent that it has a nitrogen content of at least about 100 p.p.m. is subjected to a prehydrogenation treatment at a pressure of at least about 950 p.s.i.g. in the presence of a denitrogenation catalyst and molecular hydrogen to produce a normally liquid effluent having a lower nitrogen content. The normally liquid effluent of less than about 20 p.p.m., preferably less than about 10 p.p.m. nitrogen content is passed with molecular hydrogen to a hydrocracking zone where the hydrocarbon feed is cracked at a pressure up to about 800 p.s.i.g. in the presence of a catalyst comprising platinum group metal on a solid, acidic support to provide lower boiling hydrocarbons, usually part of which boil in the gasoline range, and a hydrogen-containing gas, at least a portion of which gas is usually recycled to the prehydrogenation zone, while maintaining the nitrogen content of the effluent from the hydrocracking zone at less than about 20 p.p.m., preferably less than about 10 p.p.m. It is a feature of this invention that all or at least a major portion of the makeup or fresh hydrogen is provided to the hydrocracker rather than to the pretreater. Apart of the hydrogen-containing gas from the hydrocracking zone can be recycled to this zone, in which control of the nitrogen content in the hydrocracking zone can be effected by removing ammonia from the hydrogen-containing gas recycled to the hydrocracking zone and/or by adding additional makeup hydrogen.

The amount of nitrogen in the hydrocracking zone can be affected by the extent, if any, of recycle to this zone of hydrocarbons boiling above the gasoline range. If the nitrogen content of the bottoms from distillation of the hydrocracking effluent is sufficiently low, e.g. less than about 20 p.p.m., preferably less than about 10 p.p.m., these residuals or other hydrocarbons of such low nitrogen content in the effluent, can be recycled to the hydrocracking zone. When the nitrogen in the hydrocracker effluent boiling higher than gasoline would be excessive for recycle to the hydrocracking zone, a distillate (whose nitrogen content is less than about 20 p.p.m., preferably less than about 10 p.p.m.) separated from the effluent and boiling above the gasoline range can be recycled to the hydrocracking zone. In such case the residual from the distillation would have a relatively high nitrogen content, for instance above about 10 p.p.m. or even above about 20 p.p.m.

in nitrogen, and, if desired, can be recycled to the prehydrogenation zone for further nitrogen removal and possibly hydrogenation of at least some of its aromatic constituents. By control or regulation of these various factors the nitrogen buildup which normally occurs in the hydrocracking zone of these systems is essentially prevented and hydrocracking at low pressures of below about 800 p.s.i.g. is feasible with its attendant advantages.

Amount such advantages is the suitability in accordance with this invention of using vessels with wall strength suitable for reforming for the hydrocracking reactors. Hydrocrackers in the past have generally consisted of single vessels constructed to withstand pressure of about 2,000 pounds or more, with the complications of required inner coolers and especially expensive high pressure header construction. In accordance with this invention, operation of the hydrocracking process with a series of 2,3 or more less expensive naphtha reforming type reactors suitable for pressures up to 700-800 pounds is contemplated and feasible, the heat exchange being handled by replacing the reforming heaters between reactors by coolers between reactors.

The feedstocks treated in accordance with the present invention include the normally liquid, mineral oil hydrocarbon distillate fractions boiling in or above the gas oil range and having a nitrogen content of at least about 100 p.p.m. more often over about 200 p.p.m. Preferably, the feeds are petroleum distillates boiling above the gasoline range, e.g. having a 5 percent distillation point above about 300° F. or above about 400° F.

The feed often boils over a range of at least about 150° F. and may have an end point of up to about 900° F. or more. Illustrative of suitable feedstocks are straight run gas oils, heavy and light cycle oils from catalytic and thermal cracking operations, coker oils and the like. Ordinarily, these feedstocks will also contain small, contaminating amounts of organic sulfur compounds.

The nitrogen content of the feedstocks as has been stated is essentially in the form of high-boiling organic compounds. All but a minor portion of such organic nitrogen compounds are hydrogenated in the hydrogenation zone to form ammonia. It has been found that the harmful effects of N-containing basic materials on hydrocracker performance vary with the compound. In general the heavy N-containing compounds have an order of magnitude or so more harmful poisoning effect on acid sites of the hydrocracking catalyst than the ammonia product of hydrogenation. If present, such organic nitrogen compounds will collect on the catalyst sites and essentially not desorb until hydrogenated, and, to maintain catalyst activity an increase in the partial pressure of hydrogen is needed. The rate of hydrogenation of such compounds increases more than linearly with an increase of hydrogen partial pressure. However, ammonia if present, also has a harmful effect due to its equilibrium adsorption on the acid sites of the catalyst. The amount of absorbed ammonia varies depending on the partial pressure of the ammonia. A decrease in ammonia partial pressure results in ammonia being displaced from acid sites, thereby increasing catalyst activity. Consequently, in accordance with some embodiments of this invention, a major portion of prehydrogenator or hydrocracker bottoms obtained in the distillation of the respective zone effluents, when significant nitrogen is still present, can be recycled to the hydrogenation zone, and, in addition, ammonia is prevented from recycling to the hydrocracker.

The process will now be described with reference to the attached DRAWING which is a diagrammatic flowsheet of preferred embodiments of the invention. In the DRAWING full lines with arrows indicate desired flow streams and dotted lines some optional flow streams. Fresh feed, such as gas oil, containing at least about 100 p.p.m. nitrogen is introduced by line 1 and hydrogen by line 4 into prehydrogenation zone 7. Prehydrogenation zone 7 is provided with a hydrogenation catalyst having denitrogenation activity which catalyst is generally sulfur insensitive or sulfactive. Suitable catalyst in-

clude, for example, catalytic amounts of one or more of the oxides or sulfides or metals selected from Groups VIII AND VI, preferably supported on a carrier such as alumina, Titania, silica and the like and mixtures thereof. The catalysts may be reduced with hydrogen if desired. Illustrative of particularly preferred catalysts are mixtures of cobalt or nickel and molybdenum oxides or sulfides and mixtures of nickel and tungsten oxides or sulfides on an alumina support or on alumina containing small amounts of silica. The catalytic metal oxide or sulfide components are usually present on the carrier in an amount of about 0.1 to 35 percent preferably 0.5 to 15 percent by weight.

As aforementioned, the prehydrogenation treatment in zone 7 is conducted under denitrogenation conditions, that is, conditions which reduce the nitrogen content of the normally liquid hydrocarbon feedstock to the hydrocracking zone to less than about 20, preferably less than about 10 p.p.m. by converting the nitrogen which is in the hydrogenation zone feed in the form of organic nitrogen compounds to ammonia. These reaction conditions may vary depending upon the particular feed and catalyst employed and are selected to effect the desired nitrogen reduction usually with no more than about 30 percent or 40 percent hydrocracking of the feedstock to materials boiling in the gasoline range. The reaction temperature employed is generally about 550° to 900° F., preferably about 600° to 850° F. A prehydrogenation zone pressure as low as will give the desired removal of nitrogen by conversion to ammonia can be selected, for example, at least about 950, preferably about 1,000 to say 2,000 p.s.i.g. or more. The weight hourly space velocity is generally about 0.5 to 20, preferably about 1 to 5, WHSV.

Affluent from prehydrogenation zone 7 is discharged by line 10 into separator 13. Most of the light gases including ammonia and hydrogen which have been carried from the prehydrogenation zone are removed overhead from separator 13 via line 16 to water scrubber 15. Water enter the scrubber via line 17 and leaves with dissolved soluble gases, particularly NH<sub>3</sub> and H<sub>2</sub>S, via line 18. The scrubbed gas, mainly H<sub>2</sub>, passes by line 2 to recycle pump 3 and thence to H<sub>2</sub> feed line 4 previously mentioned. A portion of such gas may be removed in a bleed stream if desired. The hydrogen gas to hydrocarbon ratio in the prehydrogenation zone 7 is usually about 1,000 to 15,000, preferably about 1,500 to 10,000, standard cubic feet per barrel of hydrocarbon.

Liquid product is removed from separator 13 and sent by line 19 through pressure reducing valve 11, at the outlet of which the pressure has been reduced to about 450 to 850 p.s.i.g. The valve outlet product then passes into separator-stripper 22, wherein light C<sub>4</sub> minus gases are stripped from the product. Distillate boiling in the gasoline range can be removed by line 25. Hydrotreated product as a distillate or as a residual from stripper-separator is sent via lines 28 and 31 to hydrocracking zone 37. If the stripper-separator bottoms product still contains a higher boiling portion of excessive nitrogen content, this may be separately removed via line 6 to prehydrogenation zone 7 for further nitrogen removal.

Hydrocracking zone 37 is provided with a platinum group metal hydrocracking catalyst. These catalysts comprise a platinum group metal on a suitable cracking base. Illustrative of suitable cracking bases are the acidic supports such as silica-alumina, silica-magnesia, silica-zirconia, alumina-boria, silica-titania, crystalline aluminosilicates and the like and mixtures thereof. The preferred supports are silica-aluminas containing over about 50 percent and up to about 90 percent silica, all or a part of which are crystalline aluminosilicates.

The crystalline aluminosilicates useful as supports for the platinum group metal component include the synthetic or naturally occurring materials having pore size of about 8-15 Å., preferably about 10-14 Å. Usually, with a given material, the pores are relatively uniform in size and often the crystalline aluminosilicate particles may have a size in the range of about 0.1 to 15 microns and a silica to alumina mole ratio of up to about 6:1, e.g., 2 to 6:1, preferably about 3.5 to 5.5:1. The

crystalline aluminosilicates may be admixed with minor or major amounts of other materials, e.g., silica, alumina, silica-alumina, etc., especially refractory metal oxides.

Crystalline aluminosilicates exist or are usually prepared in the sodium form and may be of the faujasite type. To convert the crystalline sodium aluminosilicates to active catalyst, the sodium cations can, if desired, be replaced in part or entirely by ion exchange with other monovalent, divalent or trivalent cations. Among the forms of the crystalline aluminosilicates which can be produced are those obtained by ion exchange such as, for example, with hydrogen, ammonium, magnesium, calcium, the rare earth metals, or their combinations. These forms may be obtained from the corresponding sodium aluminosilicates by ion exchange techniques. Thus, calcium ions, for example, may replace part or all of the sodium ions to produce the calcium form, or the sodium ions can also be exchanged, partially or completely, with ammonium ions to give the ammonium form or the ammonium crystalline aluminosilicate can be calcined to obtain the hydrogen form through ammonia release. Other techniques can be employed to produce the hydrogen form, but the ammonium exchange is the most common. The hydrogen form of the crystalline aluminosilicate is preferred. The amount of exchange of sodium ions by other ions, e.g., hydrogen and calcium ions, may vary between about 1 and 100 percent, preferably about 10 percent and 90 percent. The amount of exchange of sodium ions by hydrogen ions, for instance, is preferably about 10 percent to 40 percent for crystalline aluminosilicates with a silica to alumina mole ratio equal to or less than 3:1, and preferably about 70 percent to 90 percent for crystalline aluminosilicates with a silica to alumina mole ratio of greater than 3:1 and less than 12:1.

The platinum group metal (e.g., platinum, palladium, etc.) catalytic component of the invention is present on the cracking base in small catalytic amounts, usually about 0.05 to 5 percent, preferably about 0.3 to 1.5 percent by weight. Deposition of the platinum group metal on the cracking base support can be by methods known to the art, for instance, impregnation, coprecipitation, etc. The platinum group metal may be present in the oxide or sulfide form or reduced to the free metal state, for instance, by treatment with hydrogen. Also in the case of the crystalline aluminosilicates the platinum group metal can be introduced by ion exchange. The catalysts may be employed in any desired physical form, for instance, as a fluidized mass in which the catalyst particles are often in the size range of about 20 to 150 microns or as macrosized particles say of about one-sixtyfourth inch to one-half inch in diameter and about one-sixteenth to one inch or more in length. In the latter form the particles are frequently disposed as a fixed catalyst bed.

As aforementioned the pressure employed in hydrocracking zone 37 is up to about 800 p.s.i.g.; it is suitably between about 400 and 800 p.s.i.g. The weight hourly space velocity in the hydrocracking zone is often a minimum of about 2 and may be up to about 10 or more. The improved process of the invention permits the use with advantage of space velocities which are often about 1.5 to 3 times the weight hourly space velocity employed in the prehydrogenation zone. The hydrocracking temperature may vary but may generally be in the range of about 500° to 850° F., preferably about 550° to 850° F., preferably about 550° to 750° F., and the hydrogen to hydrocarbon ratio including the makeup hydrogen provided may ordinarily be about 6,000 to 30,000, preferably about 8,000 to 25,000, standard cubic feet per barrel of normally liquid hydrocarbon feed. Often at least about 50 percent hydrocracking to lower boiling materials can be effected in the hydrocracking zone.

The products from hydrocracking zone 37 are removed by means of line 40 and sent to separator 43. All or a substantial portion of the recycle gas stream from separator 43 including a major proportion of hydrogen, small amounts of ammonia, etc. is sent by line 46 and then line 58 to booster pump 39, line 2, recycle pump 3, and line 4 to prehydrogenation zone 7.

Often in accordance with the present invention, the hydrocracking zone is operated with a higher hydrogen to hydrocarbon mole ratio than the prehydrogenation zone, frequently a ratio at least about 1.5 or more times greater. The higher hydrogen to hydrocarbon mole ratio in the hydrocracking zone and the relatively high purity of the makeup hydrogen passing to this zone, contribute significantly to the maintenance of a low nitrogen content in the hydrocracking zone feed and successful operation at the low pressures employed. Low pressures permit the use of thinner reaction vessels and the charging of the major amount of makeup hydrogen to the reaction zone of lesser pressure reduces the booster compressor capacity which would be needed if this hydrogen were compressed to the prehydrogenation zone pressure.

Part, preferably the major part, of the recycle gas stream from separator 43 may be removed by means of line 46, recycled via line 49 to booster pump 45 and ammonia absorber 52 and then by line 55 to the hydrocracking zone 37. The ammonia absorber can be any means known to effectively remove ammonia from a gaseous stream. Two such purifiers in parallel, one in use and the other being regenerated, may be used. A particularly effective and convenient means comprises use of molecular sieve purifiers such as Linde 3A molecular sieves which are adapted to adsorb ammonia, water and fixed gases and permit the passage of hydrogen and hydrocarbons. If the hydrocracker feed has a relatively high sulfur content, e.g., over about 25 p.p.m., it may be desirable to also remove H<sub>2</sub>S from the hydrocracker recycle gas, for example; for this purpose molecular sieves of larger pore opening may be used. For maximum efficiency in removal of both H<sub>2</sub>S and NH<sub>3</sub>, sieves suitable for removal of H<sub>2</sub>S followed by preferred sieves for NH<sub>3</sub> removal are recommended. The mole ratio of hydrogen-containing gas to hydrocarbon in the hydrocracking zone can vary depending on the hydrogen concentration of the recycle gas stream, the carbon number of the hydrocracker feed, and the particular reaction condition used in the hydrocracking zone but in general will fall in the range of about 10 to 50 to 1, preferably 15 to 40:1. Ordinarily the gas to the hydrocracking zone will have a minimum hydrogen partial pressure of about 250 and a maximum total pressure of about 800 p.s.i.g.

Liquid product from separator 43 is delivered via line 61 to distillation zone 64, where light C<sub>4</sub> minus gases are stripped from the product and gasoline product drawn off. Depending on its nitrogen content as previously explained, bottoms product can be removed from the distillation column 64 and sent by line 67 to join hydrotreated product from line 28 and recycled via line 31 to the hydrocracking zone 37. If desired, all or a portion of such product may be conducted via lines 67 and 40 to the prehydrogenation zone 7. A lower boiling distillate from the hydrocracker effluent can be separated by line 68 and returned to the hydrocracking zone via line 31.

Fresh makeup hydrogen from a source not shown in delivered by way of pump 34 to line 5 and hydrocracking zone 37. The makeup hydrogen is usually of relatively high purity, e.g. greater than about 95 percent pure. A minor portion of the makeup hydrogen may also be delivered, if desired, to the prehydrogenation zone 7 via line 8 and connections to prehydrogenation zone 7. The makeup hydrogen accounts for hydrogen consumption in the operation as well as any mechanical losses, thereby maintaining the amount of hydrogen in the overall system, as well as in the hydrocracking zone, relatively constant for operations extending over prolonged periods of time. Operations as indicated with makeup hydrogen supplied mainly to the hydrocracker and with prevention of recycle nitrogen buildup in the hydrocracker, make possible lower pressure hydrocracker operation with satisfactory catalyst aging rate than has heretofore been possible.

The following examples are included to further illustrate the present invention as described above in connection with the drawing.

EXAMPLE I

The initial feedstock to the prehydrogenation zone was a gas oil having 10 percent boiling point of 538° F., a 50 percent boiling point of 628° F., and a 90 percent boiling point of 670° F., containing 234 p.p.m. nitrogen and having an API gravity of 32.5. The hydrotreating in a prehydrogenation zone was conducted at a temperature of 735° F., a pressure of 1,500 p.s.i.g., a space velocity of 2 WHSV and a hydrogen-containing gas to hydrocarbon ratio of about 2,500 SCF/B. The catalyst employed in the hydrogen pretreatment was nickel molybdate on alumina (4% Ni and 16% MoO<sub>3</sub>).

The hydrogen pretreated hydrocarbon liquid product after removal of light gases in a separator and C<sub>1</sub>-C<sub>4</sub> hydrocarbons and gasoline in a stripper-separator contained 3.2 p.p.m. nitrogen and 37 p.p.m. sulfur, and had an API gravity of 35.7. This C<sub>5</sub>+hydrotreated product was subjected to hydrocracking in a separate reaction zone at a temperature of approximately 575° F., to 625° F., and a pressure of 500 p.s.i.g. The space velocity during the run was 3 WHSV but for two short periods wherein space velocities of 1.5 WHSV and 6.0 WHSV, respectively, were used. The hydrocracking catalyst employed was a one-sixteenth inch extrudate containing 1 percent platinum on a support containing 90 percent of a composite of 85 percent silica-alumina and 15 percent faujasite, hydrogen-exchanged, crystalline aluminosilicate having a pore size of about 13 A. and a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio of about 4.5/1 the remaining 10 percent of the catalyst being activated alumina.

Hydrogen-containing gas from a separator was split with a lesser portion vented and the major portion being returned to the hydrocracking zone in a mole ratio of recycle gas to hydrocarbon feed of approximately 15:1. The hydrogen-containing recycle gas returned to the hydrocracking zone was passed through a molecular sieve purifier for removal of ammonia from the recycle gas stream. Makeup hydrogen was introduced into the hydrocracking zone in a mole ratio of hydrogen to hydrocarbon feed of 6:1. The total ratio of hydrogen to hydrocarbon feed, including recycle and makeup hydrogen, was about 8,500 SCF/B. The liquid product from the separator having a nitrogen content below 10 p.p.m., was distilled to obtain gasoline. The results of the run are shown in the table below:

Hrs. on oil	WHSV	Temp., ° F.	API gravity of C <sub>5</sub> + liquid product	Percent conversion
6/10.....	1.5	578	63.5	91
20/22.....	↓	574	72.3	100+
29/31.....	3.0	576	70.3	100+
35/37.....	↓	578	70.1	100+
43/45.....	6.0	576	61.3	55
45/46.....	↓	576	48.8	46
50/52.....	3.0	579	63.2	91
60/62.....	↓	580	62.8	90
70/72.....	↓	577	60.3	86
80/82.....	↓	578	58.3	82
86/88.....	↓	576	60.0	86
88/90.....	↓	577	64.1	92
110/112.....	↓	580	59.4	84
113/136.....	3.0	(1)	(1)	(1)
148/150.....	3.0	626	63.8	91
181/186.....	↓	625	57.8	80
5 hour H <sub>2</sub> purge				
195/197.....	3.0	601	64.3	92
213/215.....	↓	604	56.3	74
36 hour H <sub>2</sub> purge				
253/255.....	3.0	601	68.5	100+
257/259.....	↓	582	58.7	83
269/271.....	↓	576	53.0	62
287/289.....	↓	578	53.7	64
299/301.....	↓	582	60.1	51
313/315.....	↓	615	56.8	76
329/331.....	↓	↓	55.5	71
339/341.....	↓	↓	55.6	72
347/349.....	↓	614	54.0	66

<sup>1</sup> Operation with 36% H<sub>2</sub> and 64% CH<sub>4</sub> makeup gas gave no conversion at temperatures of 576 to 625.

Percent conversions as shown in the table were determined for the particular feed used by a correlation from the product A.P.I. values measured. One hundred percent conversion is a measure based on a complete disappearance by hydrocracking of material in the boiling range of the feed. Conversion as so defined has a maximum value of 100 percent. However, the product can be further cracked with a sufficiently active catalyst resulting in further lowering of product boiling range. Conversion beyond 100 percent actually occurred after 20/22 hours on oil, etc., as indicated in table.

Examination of the data in the table shows that the activity level of the catalyst was extremely high throughout the run. In fact, the catalyst activity actually increased during the initial period of operation. Compare, for instance, the conversion level for the 29/31-hour period which, despite twice as high a space velocity, actually surpassed the conversion level for the 6/10-hour period. A comparison of the 45/46-hour period with the 35/37- and 50/52-hour periods indicates that operation at low conversion levels is detrimental to maintenance of catalyst activity. After the 112th hour, the makeup gas was changed from pure hydrogen to a mixture of 36 percent hydrogen and 64 percent methane. The result was a nearly complete loss of conversion at the temperatures indicated with a product gravity being essentially the same as that of the feed. After 24 hours, pure hydrogen addition was resumed and a sample taken during the 148/150 hour period showed that catalyst performance was still exceedingly good in spite of the previous unfavorable conditions. The activity level remained about the same for the rest of the run. Two hydrogen purged periods with the feed off resulted only in slight improvement.

#### EXAMPLE II

Two feedstocks, A and B, were employed in a hydrocracking operation and were prepared by hydrogenation of petroleum gas oils. Feedstocks A was made by denitrogenation of a Mid-Continent, light, vacuum gas oil having an API gravity of 33.1, containing 189 parts per million nitrogen and having a boiling range of 492° F. (5 percent point) and 697° F. (95 percent point) according to the ASTM vacuum distillation procedure. This gas oil feed was hydrotreated in a prehydrogenation zone containing 2,000 grams (dry basis) of nickel-molybdena-alumina catalyst disposed in a 3-inch diameter reactor tube. The catalyst was an extrudate one-sixteenth inch in diameter and contained 2.30 percent weight nickel and 15.6 percent molybdena. Before being placed on stream the catalyst was purged with nitrogen at the rate of 10 standard cubic feet per hour for 30 minutes and the reactor was then pressured to 1,500 p.s.i.g. with hydrogen. The reactor was subsequently depressured and hydrogen sulfide was charged to bring the pressure to 200 p.s.i.g. and the temperature of the catalyst was raised to 650° F. over an eight hour period in a flow of hydrogen sulfide at the rate of 2 standard cubic feet per hour. The reactor was held at 600° F. and a 200 p.s.i.g. H<sub>2</sub>S pressure for 2 hours, and then cooled to 500° F. in a flowing hydrogen sulfide stream. The pressure of the system was then raised to 1,000 p.s.i.g. in an atmosphere of hydrogen and these conditions held for 28 hours.

The light, vacuum, Mid-Continent gas oil was hydrotreated over this catalyst during a 40-hour period at an average temperature of about 650° F., 2 WHSV, 3,000 standard cubic feet of hydrogen per barrel and 1,000 p.s.i.g. Similar conditions were maintained for a total on-stream time of 103 hours, except that for approximately the second 40 hours the temperature was about 665° F. and for the last 23 hours the temperature was about 660° F. The liquid product was stripped with nitrogen at a flow rate of 0.5 standard cubic feet per barrel and 150 to 180° F. A composite of the product, Feedstock A, has an API gravity of 35.4 and contained 7.4 p.p.m. nitrogen and 90 p.p.m. sulfur.

The second feedstock, i.e., Feedstock B, employed in the hydrocracking operation was prepared by hydrotreating a Mid-Continent, light cycle petroleum gas oil having a gravity

of 24.3 API, 0.851 percent sulfur and 347 p.p.m. nitrogen and exhibited a 5 to 95 percent boiling range (ASTM distillation) of 484° to 628° F. The hydrotreating reaction conditions were 695° F. (average), 4 WHSV, 1,000 p.s.i.g. and 3,000 standard cubic feet of hydrogen per barrel. The product had an API gravity of 29.5 and contained 410 p.p.m. sulfur and 12 p.p.m. nitrogen and exhibited a 5 to 95 percent boiling range (ASTM distillation) of 451° to 614° F. The catalyst employed was the nickel-molybdena-alumina catalyst used in preparing Feedstock A, and the product so obtained is designated Feedstock B.

Feedstocks A and B were hydrocracked by sequential treatment over a fresh portion of the same hydrocracking catalyst as employed in example I. The hydrocracking reaction conditions included temperatures of about 640° to 650° F., a pressure of 500 p.s.i.g. and a space velocity of 3 WHSV. When using Feedstock A and 11,000 standard cubic feet of hydrogen gas (makeup plus recycle) per barrel of feed, after about 700 hours on stream and at a temperature of 649° F. the liquid product has an API gravity of about 54 (about 65 percent conversion). For approximately the next 1,000 hours the gas rate was 18,000 standard cubic feet per barrel, and at the end of this period the liquid product had an API gravity of 56.5 representing about 75 percent conversion and the reactor temperature was 649° F. This demonstrated that increasing the hydrogen flow rates from 11,000 to 18,000 standard cubic feet of gas per barrel resulted in a substantially higher equilibrium activity for the catalyst. Such increase of hydrogen flow rate had the effect of decreasing nitrogen level on the catalyst.

Subsequently Feedstock B was hydrocracked at the same pressure, space velocity and 18,000 standard cubic feet of gas per barrel for approximately 350 hours at temperatures ranging from about 660° F. to 685° F. and the liquid product had an API gravity of from 47 to 44 (approximately 75 percent to 65 percent conversion); the latter product being that obtained after a total run of 2,042 hours.

#### EXAMPLE III

Operation in accordance with example II showed as stated that the prehydrogenation of light vacuum gas oil reduced the nitrogen to 7.4 p.p.m. For further reduction of the nitrogen content of the product passed to the hydrocracking reaction, a 20 percent bottoms fraction of the prehydrogenation liquid effluent is recycled to the prehydrogenator. The remaining 80 percent of the prehydrogenator liquid product is passed to the hydrocracker and contains 5.8 p.p.m. N. Use of this hydrocracker feed with reduced nitrogen makes possible longer stable life of the hydrocracker catalyst than with the entire prehydrogenated liquid product as feed, the most detrimental part of the latter hydrocracker feed being passed to the prehydrogenator for further processing. The heaviest fraction of any feed contains the most difficult contaminants to handle. Such contaminants are mostly fused ring heterocyclics. Nitrogen compounds of this sort have a serious poisoning effect if they reach the hydrocracker catalyst.

It is claimed:

1. A process for the production of hydrocarbons boiling over a lower temperature range than the feed which comprises subjecting a normally liquid hydrocarbon distillate boiling in or above the gas oil range having a nitrogen content of at least about 100 p.p.m. to a hydrogenation reaction under denitrogenation conditions including a pressure of at least about 950 p.s.i.g. and a reaction temperature of about 550°-900° F. in the presence of a catalyst having denitrogenation activity, and molecular hydrogen to produce a normally liquid effluent of lower nitrogen content and a hydrogen—and ammonia—containing gas, removing ammonia from and recycling said hydrogen-containing gas, removing ammonia from and recycling said hydrogen-containing to the hydrogenation zone, subjecting normally liquid effluent having less than about 20 p.p.m. nitrogen from said hydrogenation

tion reaction together with hydrogen including at least a major portion of the fresh hydrogen makeup used in the hydrogenation-hydrocracking system, to a catalytic hydrocracking reaction in the presence of a catalyst comprising a platinum group metal on an acidic support and under hydrocracking conditions including a temperature of about 500° F. to 850° F. and a pressure of up to about 800 p.s.i.g. to provide hydrocarbon effluent boiling over a lower temperature range than the feed and a hydrogen-containing gas, recycling at least part of the hydrogen-containing gas from the hydrocracking zone to the hydrogenation zone, said fresh hydrogen makeup, any nitrogen removal from any hydrogen-containing gas from the hydrocracking zone recycled to such zone, and any hydrocarbons recycled from the hydrocracking reaction liquid effluent to the hydrocracking zone being controlled to maintain the nitrogen content of the effluent from the hydrocracking zone at less than about 20 p.p.m.

2. The process of claim 1 wherein all of the fresh hydrogen makeup is provided to the hydrocracking zone.

3. The process of claim 1 wherein the normally liquid hydrocarbon distillate is a petroleum distillate boiling above about 300° F. to about 900° F. and having a nitrogen content of over about 200 p.p.m.

4. The process of claim 1 wherein the normally liquid effluent from the hydrogenation reaction passed to the hydrocracking reaction has a nitrogen content of less than about 10 p.p.m.

5. The process of claim 1 wherein the acidic support of the hydrocracking catalyst contains crystalline aluminosilicate.

6. The process of claim 1 wherein a portion of the hydrogen-containing gas from the hydrocracking zone is recycled to the hydrocracking zone and the nitrogen content of the gas is reduced before charging to the hydrocracking zone.

7. The process of claim 6 wherein the nitrogen content of the gas is reduced by absorption of ammonia through contact with a molecular sieve.

8. The process of claim 6 wherein fresh hydrogen makeup and hydrogen-containing recycle gas from the hydrocracking zone are supplied to the hydrocracking zone with a minimum hydrogen partial pressure of about 250 and a maximum total pressure of about 800 p.s.i.g. and the ratio of hydrogen to hydrocarbon in the hydrocracking reaction is about 6,000 to 30,000 standard cubic feet per barrel of normally liquid hydrocarbon feed, and the hydrocarbon space velocity in the hydrocracking zone is about 1.5 to 3 times that in the hydrogenation zone.

9. The process of claim 7 wherein the ammonia absorber additionally removes hydrogen sulfide.

10. The process of claim 1 wherein the hydrogenator effluent is distilled and resulting bottoms are recycled to the hydrogenation zone.

11. The process of claim 1 wherein the mole ratio of hydrogen to hydrocarbon in the hydrocracking zone is at least about 1.5 times that in the hydrogenation zone.

12. A process for the production of hydrocarbons boiling in the gasoline range which comprises subjecting a normally liquid hydrocarbon distillate boiling above the gasoline range

and in the range of about 300° to 900° F. and having a nitrogen content of at least about 100 p.p.m., to a hydrogenation reaction under denitrogenation conditions including a pressure of at least about 1,000 p.s.i.g. and a reaction temperature of about 550°-900° F. in the presence of a catalyst having denitrogenation activity, and molecular hydrogen to produce a normally liquid effluent having a nitrogen content of less than about 10 p.p.m. and a hydrogen and ammonia-containing gas, removing ammonia from and recycling such hydrogen-containing gas to the hydrogenation zone, subjecting normally liquid effluent reduced in nitrogen content from said hydrogenation reaction together with hydrogen in an amount of at least about 1.5 times the mole ratio of hydrogen to hydrocarbon in the hydrogenation zone, including at least a major portion of the fresh, high purity hydrogen makeup used in the hydrogenation-hydrocracking system, to a catalytic hydrocracking reaction in the presence of a catalyst comprising a platinum group metal on a crystalline aluminosilicate-containing acidic support and under hydrocracking conditions including a temperature of about 500° F. to 850° F. and a pressure of up to about 800 p.s.i.g. to provide hydrocarbon effluent containing gasoline and a hydrogen-containing gas, recycling portions of the hydrogen-containing gas from the hydrocracking zone to each of the hydrogenation zone and the hydrocracking zone, and removing nitrogen from the gas being recycled to the hydrocracking zone, said fresh hydrogen makeup, the nitrogen removal from the hydrogen-containing gas from the hydrocracking zone recycled to such zone, and any hydrocarbons recycled from the hydrocracking reaction liquid effluent to the hydrocracking zone being controlled to maintain the nitrogen content of the effluent from the hydrocracking zone at less than about 10 p.p.m., with the proviso that the hydrocarbon space velocity in the hydrocracking zone is about 1.5 to 3 times that in the hydrogenation zone.

13. The process of claim 12 in which the hydrogenation zone reaction conditions include temperatures of about 600° to 850° F. and pressures of about 1,000 to 2,000 p.s.i.g., and the hydrocracking zone reaction conditions include temperatures of about 550° to 750° F. and pressures of about 400 to 800 p.s.i.g.

14. The process of claim 13 in which all of the makeup hydrogen is added to the hydrocracking zone.

15. The process of claim 14 wherein the hydrogenator effluent is distilled and resulting bottoms are recycled to the hydrogenation zone.

16. The process of claim 15 in which a heavy portion of the hydrocracking zone liquid effluent is recycled to the hydrogenation zone for further reduction of the nitrogen content of such effluent portion.

17. The process of claim 1 in which the hydrocracking portion of the process is carried out by a plurality of reactors suitable for pressures up to about 800 pounds with no inner coolers in such reactors and with needed cooling provided by coolers in the flow system between such hydrocracking reactors.

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