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CATALYTIC HYDROCRACKING PROCESS EMPLOYING WATER AS A PROMOTER

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This invention relates to the catalytic hydrocracking of substantially nitrogen-free, high boiling hydrocarbons to produce therefrom lower boiling hydrocarbons, boiling for example in the gasoline range. The invention is directed specifically to methods for improving the activity of the catalyst and prolonging its active life, improving the selectivity of conversion, and for decreasing the overall hydrogen consumption. Briefly, the basic novel aspect of the invention comprises carrying out the hydrocracking in the presence of certain small amounts of steam. It is found that the addition of steam in small amounts has a desirable effect in reducing the rate of catalyst deactivation, reducing hydrogen consumption, and decreasing the proportion of feed which is converted to light hydrocarbons in the C_1 to C_4 range, as compared to hydrocarbons in the gasoline range. At the same time, the intrinsic activity of the catalyst is improved in many cases, and in any event is not harmfully affected.

As a result of the increasing demand for light motor fuels, and the decreasing demand for heavier petroleum products such as fuel oil and the like, there is much current interest in more efficient methods for converting the heavier products of refining into gasoline. The conventional methods of accomplishing this, such as catalytic cracking, coking, thermal cracking and the like, always result in the production of a more highly refractory unconverted oil, or cycle oil, which cannot be economically converted to gasoline. It is known that such refractory materials can be converted to gasoline by catalytic hydrocracking. However, the application of the hydrocracking technique has in the past been fairly limited because of several interrelated problems.

The basic problem revolves about the difficulty in keeping the catalyst free of deactivating deposits such as coke, tars and the like. This problem can be minimized by operating at high hydrogen pressures, i.e., above about 3,000 p.s.i.g. However, the use of high pressures requires expensive equipment, and utility costs are also higher. There is also a problem common to all hydrocracking processes involving conversion of the feed to light hydrocarbons. Conversion of feed to dry gases, i.e., methane, ethane, propane and butanes, represents a considerable waste of feedstock as well as hydrogen. By using controlled amounts of steam, as described herein, all of these problems are mitigated to a considerable extent,

It is therefore a principal object of this invention to improve the selectivity of conversion to gasoline in catalytic hydrocracking processes. A further object is to decrease the rate of catalyst deactivation. Another object is to decrease the amount of hydrogen consumed per barrel of gasoline produced. Still another object is to improved the intrinsic activity of hydrocracking catalysts. Other objects will be apparent from the more detailed description which follows.

Feedstocks which may be treated herein comprise any mineral oil fraction boiling above the conventional gasoline range, i.e., above about 300° F., and usually above about 400° F., and having an end-boiling-point up to about 1,000° F., but preferably not greater than about 850° F. This includes straight-run gas oils and heavy naphthas, coker distillate gas oils and heavy naphthas, deasphalted crude oils, cycle oils derived from catalytic or thermal cracking operations, and the like. These fractions may be derived from petroleum crude oils, shale oils, tar sand oils, coal hydrogenation products and the like. Specifically, it is preferred to employ oils conforming to the following specifications:

End-boiling-point	400–750° F.
API gravity (60° F.)	20–35°.
Acid solubles (aromatics+olefins)	30% minimum.

Feedstocks of the above character may contain before hydrofining from about 0.01% up to about 4% or more by weight of sulfur, and from about 0.01% up to about 2% or more of nitrogen in the form of organic compounds thereof. They are also characterized by a high content of fused-ring polycyclic aromatic hydrocarbons, which largely accounts for their refractory nature.

In the hydrocracking of the foregoing feedstocks, it is found that any small amount of water up to about 2% by weight, based on feed, will give some beneficial results. Larger amounts are usually undesirable in that the hydrocracking activity of the catalyst is impaired. It is specifically contemplated to use water in amounts between about 0.0075% and 1.5% by weight (0.001–0.2 moles thereof per mole of feed having an average molecular weight of 240), and preferably between about 0.04% and 0.5% by weight, based on feed.

The water may be added as steam to the feed or the hydrogen, or it may be added in the form of any suitable precursor from which water is formed during the hydrocracking reaction. Examples of suitable water precursors include, for example, carbon dioxide, carbon monoxide, alcohols, ketones, aldehydes, esters and the like.

Conventional hydrocracking conditions are contemplated for use herein, i.e., pressures between about 3,000 and 10,000 p.s.i.g., temperatures between about 650° and 1,000° F., space velocities between about 0.5 and 8, and hydrogen/oil ratios between about 1,000 and 12,000 s.c.f./barrel of feed. However, an important aspect of the invention resides in the fact that the steam, by virtue of its effect in reducing the coking rate of the catalyst, permits the use of lower pressures than have generally been considered optimum. Specifically, it is found that pressures below 3,000 p.s.i.g., and ranging down to about 500 p.s.i.g., may be employed without encountering excessive coking rates, provided that the conversion per pass is suitably limited to e.g., about 20–70% per pass. It is preferred to use temperatures of about 500° to 850° F., space velocities between about 0.5 and 5, and hydrogen/oil ratios between about 5,000 and 15,000 s.c.f. per barrel of feed.

According to a preferred modification of the process, the hydrocracking operation is divided into two separate stages, with the unconverted oil from each cracking stage being treated exclusively in the second stage. It is further preferred to subject the raw feed to a prehydrogenation, or hydrofining, treatment prior to the first hydrocracking stage.

The catalyst to be used in the hydrofining treatment may comprise any of the oxides and/or sulfides of the transitional metals, and especially an oxide or sulfide of a Group VIII metal (particularly iron, cobalt or nickel) mixed with an oxide or sulfide of a Group VIB metal (preferably molybdenum or tungsten). Such catalysts may be employed in undiluted form, but preferably are supported on an adsorbent carrier in proportions ranging between about 2% and 25% by weight. Suitable carriers include in general the difficultly reducible inorganic oxides, e.g., alumina, silica, zirconia, titania, clays such as bauxite, bentonite, etc. The preferred carrier is activated alumina, and especially activated alumina containing about 3–15% by weight of coprecipitated silica gel.

The preferred hydrofining catalyst consists of cobalt

oxide or sulfide plus molybdenum oxide or sulfide supported on silica-stabilized alumina. Compositions containing between about 2% and 8% of CoO, 4% and 20% of MoO_3, 3% and 15% of SiO_2, and the balance Al_2O_3, are specifically contemplated.

Suitable hydrofining conditions are as follows:

	Operative	Preferred
Avg. bed Temp., ° F	500–850	700–825
Pressure, p.s.i.g.	500–5,000	800–3,000
Liquid hourly space velocity	0.5–50	1–10
Hydrogen ratio, s.c.f./b.	500–12,000	800–8,000

The effluent from the hydrofining treatment may be passed directly to the hydrocracking zone, or it may be treated, as by condensation and water washing, to remove ammonia, hydrogen sulfide and other contaminants prior to contacting the hydrocracking catalysts. From the standpoint of maintaining maximum catalyst efficiency in the hydrocracking zone, it is normally preferable to remove most or all of the ammonia and sulfur compounds. However, this entails considerable added expense, and it has been found that substantial benefits of the prehydrofining treatment are obtained even when the total products of hydrofining are passed directly to the hydrocracking zones.

When employing multiple stages of hydrocracking, it is contemplated that water vapor may be used in any one or more stages. Water vapor may also be present in the hydrofining zone without deleteriously affecting the hydrofining efficiency.

When employing multiple stages of hydrocracking, it is normally preferable to provide at least one terminal stage wherein the feed is contacted with the catalyst in the substantial absence of ammonia and basic nitrogen compounds. By removing the basic nitrogen compounds, substantially higher conversion levels may be maintained at the same rate of catalyst deactivation.

The rate of coking or catalyst deactivation in the hydrocracking process may be conveniently expressed from an operating standpoint in terms of the "Temperature Increase Requirement" (TIR), which is the average daily temperature increase required to maintain a given conversion level at a constant feed rate. This factor determines the run length between regenerations. For example, starting with a fresh catalyst, and after the initial "wild" activity has been dissipated over a 1–3 day induction period, a 60% conversion per pass may be obtained at 650° F. It is found that, to maintain the 60% conversion, it is necessary to increase the temperature in the hydrocracking zone about 1° F. per day until the temperature reaches 775° F. This provides an operating period of 125 days, after which regeneration of the catalyst is required. It is a notable fact that over this temperature range of at least 100° F., the TIR appears to be substantially a linear function of time, and only when high temperatures are reached, above about 800° F., does the TIR relationship become exponential. It is preferred to discontinue the hydrocracking operation as soon as the TIR curve begins to indicate that excessive temperature increments, e.g., of more than about 2° to 4° F. per day, are being required in order to maintain conversion, for this indicates the transition to non-selective cracking, accompanied by high gas make, a rapid coking rate and a substantially deactivated catalyst. It should be noted, however, that it is unnecessary actually to carry out a daily temperature rise in this mode of operation; TIR refers to the average increase per day, and from an operational standpoint, it may be more desirable to adjust the temperature periodically, e.g., every 2 to 7 days, to provide the average daily increase.

By operating in accordance with the foregoing, run lengths of at least about 2 months and up to one year or more, are readily obtainable. Specifically, it is contemplated that hydrocracking runs be initiated at temperatures between about 500° and 700° F., and continued for at least about 2 months with periodic temperature increases to give an average TIR of about 0.2–3° F. per day.

The hydrocracking catalysts employed herein may comprise any desired combination of a solid, refractory cracking base with a suitable hydrogenating component. Suitable cracking bases include for example mixtures of two or more refractory oxides such as silica-alumina, silica-magnesia, silica-zirconia, alumina-boria, silica-titania, silica-zirconia-titania, acid treated clays and the like. Acidic metal phosphates such as aluminum phosphate may also be used. The preferred cracking bases comprise composites of silica and alumina containing about 50–90% silica; coprecipitated composites of silica, titania, and zirconia containing between 5% and 75% of each component; partially dehydrated, zeolitic, crystalline molecular sieves, e.g., of the "X" or "Y" crystal types, having relatively uniform pore diameters of about 8 to 14 Angstroms, and comprising silica, alumina and one or more exchangeable zeolitic cations. Any of these cracking bases may be further promoted by the addition of small amounts, e.g., 1 to 10% by weight, of halogen or halides such as fluorine, boron trifluoride or silicon tetrafluoride.

The molecular sieve type cracking bases, when compounded with a noble metal hydrogenating component, are particularly useful for hydrocracking at relatively low temperatures of 500–700° F., and low pressures of 500–2,000 p.s.i.g. Such catalysts retain their activity for long periods of time under the conditions prescribed. It is preferred to employ molecular sieves having a relatively high SiO_2/Al_2O_3 ratio, e.g., between about 2.5 and 6.0. The most active forms are those wherein the exchangeable zeolitic cations are hydrogen or a divalent metal such as magnesium, calcium or zinc. In particular, the "Y" molecular sieves, wherein the SiO_2/Al_2O_3 ratio is about 5, are preferred, either in their hydrogen form, or a divalent metal form, preferably magnesium. Normally, such molecular sieves are prepared first in the sodium or potassium form, and the monovalent metal is ion-exchanged out with a divalent metal, or where the hydrogen form is desired, with an ammonium salt followed by heating to decompose the zeolitic ammonium ion and leave a hydrogen ion. It is not necessary to exchange out all of the monovalent metal; the final compositions may contain up to about 6% by weight of NaO, or equivalent amounts of other monovalent metals. Catalysts of this nature are more particularly described in Belgian Patents Nos. 598,582, 598,682, 598,683 and 598,686.

As in the case of the X molecular sieves, the Y sieves also contain pores of relatively uniform diameter in the individual crystals. In the case of X sieves, the pore diameters may range between about 6 and 14 A., depending upon the metal ions present, and this is likewise the case in the Y sieves, although the latter usually are found to have crystal pores of about 9 to 10 A. in diameter.

The foregoin cracking bases are compounded, as by impregnation, with from about 0.5% to 25% (based on free metal) of a Group VIB or Group VIII metal hydrogenating component, e.g., an oxide or sulfide of chromium, tungsten, cobalt, nickel, or the corresponding free metals, or any combination thereof. Alternatively, even smaller proportions, between about 0.05% and 2% of the metals platinum, palladium, rhodium or iridium may be employed. The oxides and sulfides of other transitional metals may also be used, but to less advantage than the foregoing.

In the case of the zeolitic type cracking bases, it is preferable to distribute the hydrogenating metal thereon by ion-exchange. This can be accomplished by digesting the zeolite with an aqueous solution of a suitable compound of the desired hydrogenating metal wherein the metal is present in a cationic form, and then reducing to form the free metal, as described for example in Belgian Patent No. 598,686.

The following examples are cited to illustrate the in-

vention and the results obtainable, but are not to be construed as limiting in scope:

Example I

An experimental run employing two stages of hydrocracking with one stage of prehydrofining was carried out as follows, in the absence of added water:

The feedstock was a gas oil blend mainly composed of coker distillate gas oils. Its principal characteristics were:

End-boiling-point, ° F.	600
Gravity, ° API	30.3
Sulfur content, wt. percent	2.1
Nitrogen content, wt. percent	0.15
Acid-solubles, vol. percent	51

This feed oil was passed first over a hydrofining catalyst consisting of 3% cobalt oxide and 9% molybdenum oxide supported on an alumina carrier which was stabilized by the addition of about 5% SiO_2. The hydrofining conditions were:

Temperature, ° F.	725
Pressure, p.s.i.g.	1,575
Space velocity, v./v./hr.	2.0
Hydrogen/oil, s.c.f./b.	5,000

The total hydrofining effluent was then passed continuously into a first-stage hydrocracking reactor filled with a nickel oxide-promoted silica-zirconia-titania catalyst, containing about 19% silica, 48% zirconia, 28% titania and 4.5% nickel oxide by weight. This catalyst was prepared by co-precipitating all four components in one step at a pH between 6 and 12, i.e., by mixing a stream of acidic zirconium sulfate, titanium sulfate, and nickel sulfate solution with a stream of alkaline sodium silicate solution, followed by washing, drying and calcining of the resulting gel.

The effluent from the first stage of hydrocracking was then blended with the effluent from the second stage of hydrocracking, described hereinafter, and the blend was condensed while simultaneously washing with water to remove ammonia. Hydrogen-rich recycle gas was recovered and recycled in part to the hydrofining step and in part to the second hydrocracking stage. The total liquid condensate was fractionated to recover the gasoline product boiling up to about 385° F. The residue of oil boiling above 385° F. was then fractionated to recover a 10% bottoms fraction which was removed from the process. Remaining recycle oil was passed continuously through the second hydrocracking reactor, which was filled with the same hydrocracking catalyst. Average conditions in the respective hydrocracking zones during this operation were as follows:

	First Hydrocracking Zone	Second Hydrocracking Zone
Temperature, ° F	785	760
Pressure, p.s.i.g	1,575	1,575
Space Velocity, v./v./hr	2	2
H_2/oil ratio, s.c.f./b	8,000	8,000
Conversion per pass to 385° F. end-point products, vol. percent of reactor charge	33	42

Under the above conditions, the efficiency of conversion to C_5-385° F. end-point gasoline was about 104%, i.e., the volume of C_5-385° F. gasoline recovered is 104% of the volume of fresh feed which was converted to all products. However, about 8 weight-percent of the fresh feed was converted to C_1–C_4 hydrocarbons, indicating a substantial conversion of feed to undesired products with concomitant waste of hydrogen. By periodically increasing the temperature in the first hydrocracking zone by an average of about 0.7° F. per day, and 1.2° F. per day in the second hydrocracking zone, the same conversion levels can be maintained for over 30 days of continuous operation.

The foregoing results are substantially improved by carrying out the operation in the presence of added water. Specifically, by carrying out the same operation while maintaining about 0.2 part by weight of water per 100 parts of feed (about 0.028 mole-percent) in each hydrocracking zone and in the hydrofining zone, it is found that the temperature need be increased only about 0.5–0.6° F. per day in each hydrocracking reactor to maintain the same conversion levels. Moreover, the conversion to total C_1–C_4 hydrocarbons is reduced to about 6% by weight of the feed. Hydrogen consumption is about 100 s.c.f. per barrel of 385° F. end-point gasoline less than in the operation conducted in the absence of water vapor.

Example II

To illustrate the effect of steam in low-temperature hydrocracking with a molecular sieve catalyst, two comparative runs were carried out using as feed a hydrofined California coker distillate gas oil boiling over the range of 380–800° F. and containing about 10 p.p.m. of nitrogen and 19 p.p.m. sulfur. The catalyst in each run was a 50/50 copelleted mixture of (1) powdered Linde MB–5390 isomerization catalyst (a "decationized," or hydrogen form of Y molecular sieve loaded with 0.5% Pd), and (2) a powdered activated alumina upon which was distended 25% by weight of nickel oxide. In each run, the conditions were:

Pressure, p.s.i.g.	1,500.
LHSV	1.0.
H_2/oil ratio, s.c.f./b.	8,000.
Temperature	Gradually raised from 600° F. to maintain 50% conversion to 400° F. end-point products.

In run A, no water was added to the feed, while in run B, 0.2% by weight of water was added as butanol to the feed. In run A, at the end of 104 hours on-stream, a temperature of 623° F. was required to maintain a 50.1% conversion to 400° F. end-point product. In run B however, at the end of 110 hours, the temperature was only 617° F. to maintain a conversion of 50.2%. This difference of 6° F. represents a susbtantial difference in catalyst activity, equivalent to an absolute conversion difference of about 7%. In other words, if the temperature in run A were lowered to 617° F. at 104 hours, the conversion would be only about 43%.

It is thus apparent that the addition of water had a substantial effect in maintaining catalyst activity. This is further reflected in TIR differences, for in run A, when the hydrocracking temperature was 617° F., the TIR was about 7° F., while in run B, when the temperature reached 617° F., the TIR was only about 3° F.

When conventional hydrocracking catalysts such as nickel oxide supported on silica-alumina, are substituted in the foregoing examples, generally similar differential results are obtained, with respect to the presence or absence of steam.

This application is a continuation-in-part of application Serial No. 4,198, filed January 25, 1960, and now abandoned.

It is not intended that the invention should be limited to the details described above since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. In a hydrocracking process wherein a feedstock boiling above the gasoline range and originally containing organic nitrogen compounds, is first treated for the removal of said nitrogen compounds, the improvement which comprises subjecting said treated feedstock to catalytic hydrocracking at a temperature between about 500° and 850° F. and a pressure between about 500 and 3,000 p.s.i.g., while introducing into the hydrocracking zone a

substantial amount, between about 0.0075% and 1.5%, based on feed, of an activity promoting agent consisting essentially of water vapor, and in the presence of a hydrocracking catalyst comprising a solid refractory cracking base upon which is deposited a hydrogenating component selected from the class consisting of the Group VIB and Group VIII metals and their oxides and sulfides, and recovering gasoline boiling range hydrocarbons from said hydrocracking.

2. A process as defined in claim 1 wherein said hydrocracking catalyst is a coprecipitated composite of silica gel, zirconia gel and titania gel, and incorporated therein a small proportion of a hydrogenating component selected from the class consisting of the Group VIB and Group VIII metals, and the oxides and sulfides of said metals.

3. A process as defined in claim 1 wherein said hydrocracking catalyst comprises a dehydrated, zeolitic molecular sieve of the Y crystal type, containing zeolitic hydrogen ions, upon which is deposited a Group VIII noble metal hydrogenating component.

4. A process for converting a substantially nitrogen-free mineral oil feedstock boiling above the gasoline range to lower boiling hydrocarbons, which comprises subjecting said feedstock to catalytic hydrocracking at a temperature between about 500° and 850° F. and a pressure between about 500 and 3,000 p.s.i.g., in the presence of added hydrogen and a hydrocracking catalyst while introducing into the hydrocracking zone a substantial amount, between about 0.0075% and 1.5% by weight based on feed, of an activity promoting agent consisting essentially of water vapor, and recovering lower boiling hydrocarbons.

5. A process as defined in claim 4 wherein the concentration of water in said hydrocracking zone is maintained at between about 0.04% and 0.5% by weight, based on feed.

6. A process as defined in claim 4 wherein said hydrocracking catalyst comprises a dehydrated, zeolitic molecular sieve of the Y crystal type, containing zeolitic hydrogen ions, upon which is deposited a Group VIII noble metal hydrogenating component.

7. A process as defined in claim 4 wherein said hydrocracking is initiated at a temperature between about 500° and 700° F. and is continued for at least about 2 months while periodically raising the temperature by an average of about 0.2° to 3° F. per day to maintain a substantially constant conversion per pass.

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