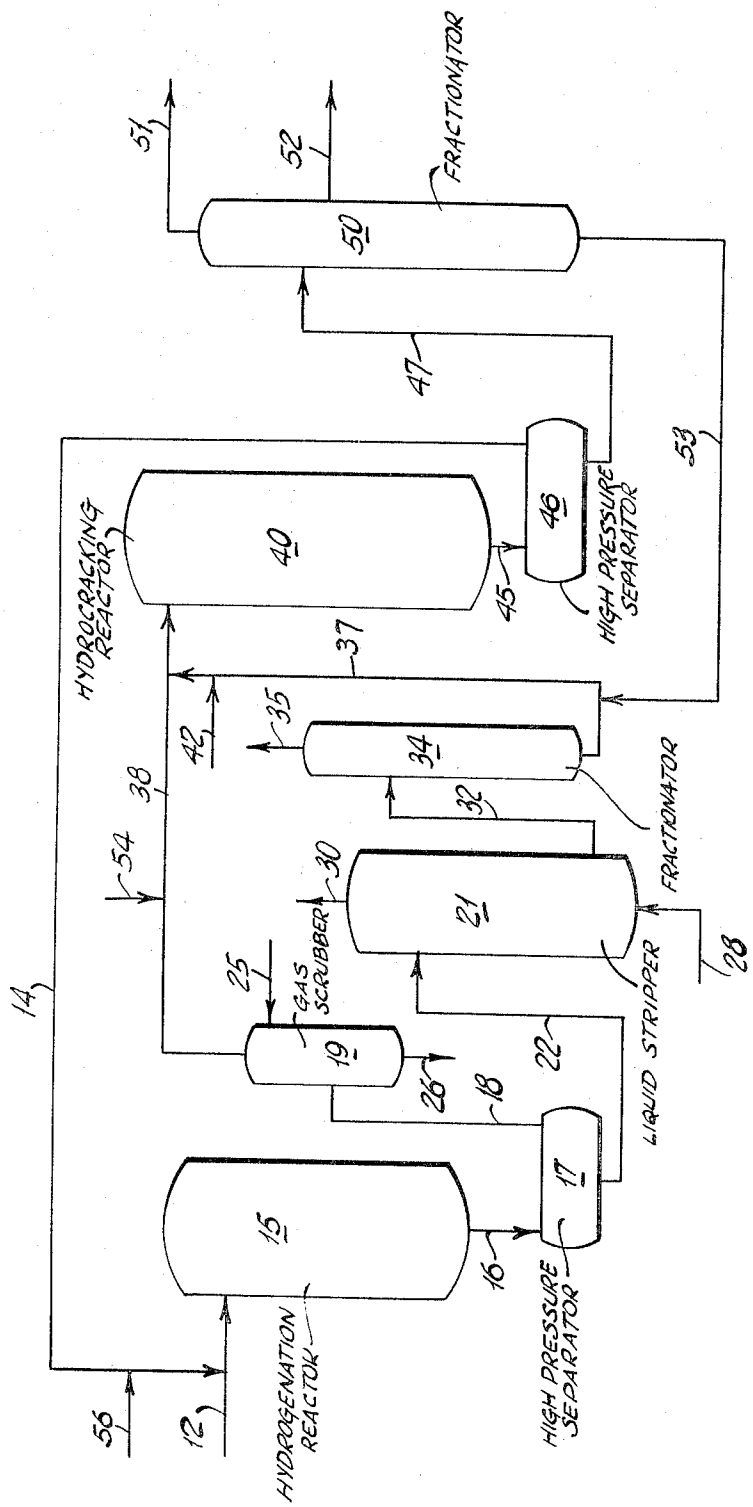
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HYDROCRACKING NITROGEN-CONTAINING FEED IN THE PRESENCE OF HALIDES

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HYDROCRACKING NITROGEN-CONTAINING FEED IN THE PRESENCE OF HALIDES

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This invention relates to the conversion of hydrocarbons. More particularly it is concerned with the conversion of hydrocarbons in the presence of hydrogen to lighter hydrocarbons. In its most specific aspects it is concerned with the conversion of a nitrogen containing hydrocarbon feed stock boiling approximately in the kerosine-gas oil range in the presence of hydrogen and a cracking catalyst into hydrocarbons boiling in the naphtha-kerosine range.

Hydrocracking, previously known as destructive hydrogenation, has become into prominence recently in the refining of petroleum hydrocarbons. In the hydrocracking process various reactions take place such as the cleaving of long straight carbon chains, the saturation of aromatic rings with subsequent rupture of cycloparaffinic structure, the isomerization of paraffinic chains into isoparaffinic chains and the dealkylation of alkyl aromatics. Ordinarily, the charge to a hydrocracking unit will comprise hydrocarbons boiling above the range of the desired product. For example, if a motor fuel is desired, the charge to the hydrocracking unit will have an initial boiling point of about 400–450° F. whereas if the desired products are motor fuels and jet fuels, then the charge to the hydrocracking unit will have an initial boiling point of 550–600° F. Advantageously, charge stocks such as straight run kerosine and gas oil stocks from catalytic cracking, vacuum gas oil and light distillates obtained from coal and shale may be charged to the hydrocracking unit. Ordinarily, product boiling above the desired end point is recycled to the hydrocracking unit.

Hydrocracking is preferably carried out in the presence of a catalyst which generally contains two components, a hydrogenating component and a cracking component. Numerous hydrogenating components have been disclosed in the prior art such as Group VIII metals for example platinum, palladium and nickel and the oxides and sulfides of molybdenum, nickel, copper, tungsten, and cobalt, and the like or mixtures thereof. The hydrogenating component is supported on a cracking base which advantageously is acidic in nature. Such bases comprise refractory oxides of two or more elements of Groups II, III, and IV of the periodic table. Suitable cracking supports include silica-magnesia, silica-alumina, silica-alumina-zirconia and the like. Preferably the cracking support is activated by treatment with an inorganic acid such as hydrofluoric acid or hydrochloric acid. The present invention is particularly concerned with the use of catalysts comprising as the hydrogenating component the oxide and/or sulfide of cobalt or nickel supported on a silica-alumina cracking base.

While these catalysts are eminently suitable for hydrocracking of various petroleum charge stocks, they are subject to an acute loss of catalyst activity when the charge stock contains even relatively small amounts of nitrogen. As a measure of the catalyst activity, it is customary to institute a hydrocracking reaction and conduct the process at certain conditions of temperature, pressure, space velocity and hydrogen rate to maintain a predetermined conversion of the charge into material having a particular end boiling point. As the reaction proceeds, the catalyst is subject to loss in activity and to compensate for the reduced activity the temperaure in the catalytic zone is increased to maintain a constant conversion rate. This increase in temperature necessary to maintain the desired conversion is called the aging rate. For example, it has been found that in a particular run when the charge contained 10 p.p.m. nitrogen, the aging rate was 24° F. per 100 hours. In the treatment of a similar charge containing only 3 p.p.m. nitrogen the aging rate was 7° F. per 100 hours and with a charge containing 1 p.p.m. nitrogen the aging rate was 2.4° F. per 100 hours. When hydrocracking to produce a high octane motor fuel, the reactions which result in the desired type of product are inhibited after the temperature in the hydrocracking unit has reached about 775° F. It therefore becomes apparent that a charge stock which contains even as much as 10 p.p.m. nitrogen produces an undesirably rapid decline in catalyst activity. As a result a charge stock destined for treatment in a hydrocracking unit either must be subjected to rather severe treatment or the process must pay an excessive economic penality in the way of frequent catalyst regeneration.

It has now been discovered that by the simple practice of subjecting the charge stock destined for the hydrocracking unit to a mild rather than severe hydrogenation thereby reducing the nitrogen content of the charge stock into the area of 5–20 p.p.m. nitrogen rather than the 0–2 p.p.m. of the prior art and adding an organic halide to the hydrogenation product, the life of the catalyst in the hydrocracking unit is extended considerably beyond the period that would normally be expected when charging a material of such a high nitrogen content. Alternatively the hydrocracking unit may be operated at a lower temperature for the same degree of conversion that would be obtained if the charge has been subjected to a severe denitrification treatment prior to being introduced into the hydrocracking unit.

It is an object of the present invention to provide a process for the hydrocracking of a hydrocarbon charge stock containing more than about 2 p.p.m. nitrogen.

It is a further object of this invention to prolong the life of a hydrocracking catalyst.

It is a still further object of this invention to provide a two-stage process in which a nitrogen containing charge stock is subjected to a mild denitrogenation treatment, an organic halide is added to the so-treated material and the mixture is subjected to the action of a hydrocracking catalyst comprising nickel or cobalt. These and other objects will be obvious to those skilled in the art from the following disclosure.

The catalysts used in the hydrocracking process of the present invention comprise a hydrogenating component such as an oxide and/or sulfide of cobalt and/or nickel supported on an acidic base such as silica alumina or silica magnesia. Optionally, the catalyst is treated with HF or HCL.

The hydrogen used in the present process may be suitably obtained as a by-product from catalytic reforming, by the electrolysis of water or by the partial combustion of carbonaceous or hydrocarbonaceous material to produce synthesis gas which is then subjected to shift conversion to produce relatively pure hydrogen. It is not necessary in the present process that the hydrogen be pure hydrogen. Ordinarily, a hydrogenating gas having only 40 volume percent hydrogen may be satisfactorily used although a gas containing 80–90 volume percent hydrogen is preferred. In this specification and in the appended claims the term "hydrogen" is intended to include dilute or impure hydrogen.

The reaction conditions within the hydrocracking unit generally include a temperature range from about 450–800° F. although a temperature from 500 to about 750–775° F. is preferred. Pressure will range from about 500–10,000 p.s.i.g. or higher although a pressure of from

about 1,000 to 3,000 p.s.i.g. is preferred. The hydrogen rate may range from 1,000 to about 20,000 s.c.f.b. (standard cubic feet per barrel) of normally liquid charge. Preferred hydrogen rates are from about 3,000–8,000 s.c.f.b. Preferably the space velocity, that is the volumes of liquid charge per volume of catalyst per hour, will be between 0.5 and 3 although rates ranging from 0.1–10 may be used.

If the charge stock to the hydrocracking unit contains not more than about 2–20 p.p.m. nitrogen it may be charged directly to the hydrocracking unit. Preferably as in the case of higher nitrogen containing stocks, the hydrocarbon feed is first charged to a denitrogenation zone where it is contacted with a catalyst such as a mixture of oxides of cobalt and molybdenum generally referred to as cobalt molybdate on a support such as magnesia or alumina. Suitable other catalysts comprise the oxides or sulfides or mixtures thereof of metals such as nickel, molybdenum, cobalt, tungsten and the like, for example sulfided nickel tungsten on alumina or a mixture of nickel and molybdenum in either the oxide or the sulfide form on alumina. Satisfactory denitrogenation temperatures include a range of 700–900° F., a pressure of 100–5,000 p.s.i.g., a space velocity of 0.1–10, and a hydrogen rate of from 500–10,000 s.c.f.b.

In the two-stage denitrogenation and hydrocracking operation each stage may have its own hydrogen circulation system or the hydrogen may circulate serially through both reaction zones. However, if the hydrogen from the denitrogenation zone is to be used in the hydrocracking zone, it is subjected to a basic nitrogen removal treatment as for example by washing with dilute acid. The charge to the hydrocracking unit after removal from the denitrogenation zone is advantageously stripped with an inert gas for the removal of nitrogen compounds such as ammonia therefrom. Apparently, the use of molecular nitrogen as a stripping gas, even though it is retained to the extent of 100 p.p.m. in the stripped hydrocracking unit charge stock, exerts no deleterious effect on the hydrocracking catalyst. The denitrogenation treatment also effectively removes oxygen containing compounds from the charge.

Halogen is added to the charge to the hydrocracking unit in the form of an organic halide such as an alkyl or aryl halide. Preferably those halides having a high halogen content as utilized although the invention is not limited thereto. Satisfactory results are obtained by the addition of dichloroethanes, carbon tetrachloride, tertiary butyl chloride and the like. The organic halide is added to the charge to the hydrocracking unit in an amount sufficient to proivde a halogen concentration of at least 1 atom of halogen per atom of nitrogen in the charge stock. Preferably at least 10 atoms of halogen are supplied per atom of nitrogen. Ordinarily, no apparent advantage is to be gained by supplying halogen in an atomic ratio in excess of about 300.

It is a feature of the present invention that when the hydrogenating component of the hydrocracking catalyst consists essentially of the oxide or sulfide of nickel or cobalt, no moisture or water need be added to the charge to the hydrocracking unit. In other words, the hydrocracking is carried out essentially under anhydrous conditions. Conventionally, the charge to the hydrocracking unit is subjected to a preliminary denitrogenation treatment or if its nitrogen content is sufficiently low is sent to the hydrocracking unit from a crude still or from a catalytic cracking unit, Under these circumstances the charge to the hydrocracking unit will be free from water or will contain water in the range of about 0–4 parts per million. Accordingly, in the absence of added water it will be appreciated that the hydrocracking process of the present invention is carried out under essentially anhydrous conditions.

For a better understanding of the process of the present invention reference is now made to the accompanying drawing which shows diagrammatically a flow scheme for the practice of a preferred embodiment of the invention.

The nitrogen containing hydrocarbon charge stock is introduced into the system through line **12** and with hydrogen from line **14** passes into hydrogenation reactor **15** where it is subjected to hydrodenitrogenation conditions. Effluent from hydrogenation reactor **15** is transferred by means of line **16** to high pressure separator **17** where a vapor liquid separation is made, the vapors being sent to gas scrubber **19** through line **18** and the liquid being sent to liquid stripper **21** through line **22**.

A scrubbing liquid such as for example, dilute sulfuric acid is introduced through line **25** into gas scrubber **19** and effectively removes impurities such as ammonia from the gas stream, the scrubbing liquid and impurities being withdrawn through line **26**. In liquid stripper **21** the liquid porton of the hydrogenation product is subjected to counter-current stripping with an inert gas such as nitrogen introduced through line **28** and removed through line **30**. This stripping operation serves to remove entrained gases such as low molecular weight hydrocarbons, ammonia and, if present, hydrogen sulfide. The stripped liquid then passes through line **32** to fractionator **34** from which naphtha is removed through line **35**. The heavier than naphtha liquid is then sent through line **37** and with purified hydrogen from line **38** is introduced into hydrocracking reactor **40**. Organic halide is injected into the hydrocarbon stream through line **42**. Effluent from hydrocracking reactor **40** flows through line **45** to high pressure separator **46** from which a hydrogen rich stream is recycled through lines **14** and **12** to hydrogenation reactor **15** and from which liquid product is sent through line **47** to fractionator **50**. Fractionator **50** may in actual practice include several vessels but is depicted here as a single unit which is used to separate the liquid product into various fractions which may be removed through lines **51** and **52**, respectively. Heavy hydrocarbons boiling above the desired product may be recycled to hydrocracking reactor **40** through lines **53**, **37** and **38**.

Make-up hydrogen as required may be introduced into the system depending on its purity either through line **54** or **56**. If the make-up hydrogen is of high purity advantageously it is introduced through line **54**. However if the make-up hydrogen is of low purity or contains undesirable components such as nitrogen then it is introduced into the system through line **56**. Although serial flow of hydrogen is shown, the hydrogen passing first through the hydrogenation reactor and then the hydrocracking reactor it is possible for each reactor to have its own hydrogen circulation system.

Obviously, various items of equipment such as heaters, valves, pumps, compressors and the like have been omitted from the drawing for the sake of simplicity.

The process of the present invention finds its most advantageous application in prolonging the life of a hydrocracking catalyst when the charge stock contains up to about 10 p.p.m. nitrogen. Referring back to the charges mentioned above having nitrogen contents of 10, 3 and 1 p.p.m. nitrogen respectively and corresponding aging rates of 24° F., 7° F. and 2.4° F. respectively per 100 hours, it is obvious that in conventional hydrocracking processes the catalyst life is indirectly proportional to the nitrogen content of the charge stock. The catalyst life ordinarily is measured in terms of the ΔT of the run, that is the difference between the starting temperature and the temperature at the end of the run. Over a ΔT of 200° F. hydrocracking at a constant conversion rate of the above essentially anhydrous (less than 10 p.p.m. H_2O) charge stocks results in catalyst lives of 1.15, 4 and 11.5 months respectively.

By way of example, an intermediate cycle gas oil obtained from a fluid catalytic cracking unit after being subjected to a mild denitrogenation and containing 8 p.p.m. H_2O and 4 p.p.m. nitrogen has an aging rate of 8.7° F. per 100 hours or a life of 3.2 months using a

catalyst comprising approximately 5% nickel on a base containing 11.4% alumina and 83.6% silica. When this same charge is hydrocracked under substantially the same operating and conversion conditions in the absence of added moisture but in the presence of 800 p.p.m. 1,1-dichloroethane, the aging rate is 3.4° F. per 100 hours which is translated into a catalyst life of 8.2 months.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for the hydrocracking of a hydrocarbon charge stock boiling within the range of about 400–800° F. and containing at least about 3 p.p.m. nitrogen which comprises contacting said charge stock with a catalyst comprising a hydrogenating component selected from the group consisting of oxides and sulfides of nickel and cobalt supported on an acidic cracking base at a temperature between about 450 and 800° F., a pressure between about 500 and 10,000 p.s.i.g. in the presence of between about 1,000 and 20,000 s.c.f. hydrogen per barrel of charge there being added to said charge an organic halide in an amount sufficient to provide at least 10 atoms of halogen per atom of nitrogen in said charge stock.

2. The process of claim 1 in which the hydrogenating component comprises nickel oxide.

3. The process of claim 1 in which the hydrogenating component comprises nickel sulfide.

4. The process of claim 1 in which the hydrogenating component comprises cobalt oxide.

5. The process of claim 1 in which the hydrogenating component comprises cobalt sulfide.

6. The process of claim 1 in which the hydrocracking is carried out in the absence of added water.

7. The process for the hydrocracking of an essentially anhydrous hydrocarbon charge stock boiling within the range of about 400–800° F. and containing between 3 and 10 p.p.m. nitrogen which comprises contacting said charge stock in the absence of added moisture with a catalyst comprising a hydrogenating component selected from the group consisting of oxides and sulfides of nickel and cobalt supported on an acidic cracking base at a temperature between about 450 and 800° F., a pressure between about 500 and 10,000 p.s.i.g. in the presence of between about 1,000 and 20,000 s.c.f. hydrogen per barrel of charge, there being added to the hydrocracking zone an organic halide in an amount sufficient to provide at least 10 atoms of halogen per atom of nitrogen in said charge stock.

8. The process of claim 7 in which the atomic ratio of halogen to nitrogen is between 10 and 300.

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