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3,395,095 HYDROCRACKING OF HYDROCARBONS WITH THE CONSTANT ADDITION OF SULFUR TO THE REACTION ZONE

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This invention relates to the hydroconversion of hydrocarbons. More particularly, it is concerned with the conversion of heavy hydrocarbon liquids into lighter hydrocarbon liquids. In its more specific aspects it relates to the hydroconversion of hydrocracking of hydrocarbon liquids boiling above about 400° F. into hydrocarbon liquids boiling below about 400° F.

Hydrocracking, that is the cracking in the presence of hydrogen of petroleum hydrocarbons for the production of motor fuels and jet fuels, is well known. It is also known to carry out the reaction in the presence of a catalyst which is conventionally composed of two components, a cracking component which forms the major portion of the catalyst composite and a hydrogenating component which generally is supported on the cracking component. Suitable hydrogenating components comprise the metals of Group VI and Group VIII such as, for example, nickel, iron, tungsten, cobalt, palladium, platinum, molybdenum, their oxides or sulfides, and mixtures thereof. Particularly suitable hydrogenating components comprise nickel and palladium.

The hydrogenating component generally is present in the catalyst composite in an amount between about 0.1 and 40% by weight and is supported on a carrier having cracking activity. Supports such as natural cracking catalysts, synthetic silica alumina, synthetic silica magnesia, montmorillonite clay, alumina gel, silica gel and natural and synthetic zeolites are satisfactory. Advantageously the support is either naturally acidic or has had cracking activity imparted thereto by treatment with an acid such as hydrofluoric acid. A silica-alumina support containing between 80–90% silica and 10–20% alumina or a synthetic zeolite having a low alkali metal content has been found particularly suitable. The catalysts, depending on their composition and ruggedness, may be used in fixed, moving or fluidized beds.

In known hydrocracking processes it is customary to pass a feed having an initial boiling point higher than the end point of the desired products into contact with a fixed bed composed of particles of hydrocracking catalyst. The desired fractions are recovered from the reaction products and unconverted or insufficiently converted material may be withdrawn from the system or returned to the reaction zone. For the most part the desired reaction products of a hydrocracking process are motor fuels and jet fuels.

However, the hydrocracking processes of the prior art are relatively inflexible. By this is meant that when a plant is designed for the production of jet fuels it is equipped to produce only jet fuels economically and if it is designed for the production of gasoline, it is equipped to give good yields only of gasoline economically. As a result when a plant is designed to produce jet fuel it is inadvisable for the refiner to change to gasoline production despite what the marketing situation might be at that particular time. This means that a plant using a catalyst which is designed to produce jet fuel must continue to do so although there is an over supply of that commodity. The same hold true for gasoline. Plants designed to produce motor fuel are

not justified in changing to the production of jet fuel as the jet fuel so produced is of an inferior grade.

The problem is not merely a question of fractionating from the hydrocracked product a fraction boiling in the gasoline range or a fraction boiling in the jet fuel range as the case may be. The real problem lies in the production of these fuels having suitable properties. For example, when a hydrocracking plant is designed to produce jet fuels, the jet fuel product is of high quality but the motor fuel fraction is of low grade. Similarly when a hydrocracking plant is designed to produce high octane motor fuel then the jet fuel fraction produced simultaneously is unsatisfactory in that it does not meet jet fuel specifications.

It is an object of the present invention to provide a flexible hydrocracking process. Another object is to provide a process for the production of jet fuels and/or motor fuels of high quality without in effect changing the catalyst. These and other objects will be obvious to those skilled in the art from the following disclosure.

According to the present invention a hydrocarbon liquid fraction boiling above about 400° F. is converted into valuable products by contacting same under hydrocracking conditions with a hydrocracking catalyst containing a hydrogenating component comprising a Group VIII metal or metal oxide, recovering from the reaction product a fraction boiling in the motor fuel range, recycling to the hydrocracking zone a product fraction boiling above the motor fuel range, introducing sulfur compounds into the hydrocracking reaction zone, continuing said recycle until about 60–80% of the metal of the hydrogenating component has been converted to the sulfide and then recovering from the reaction product a hydrocarbon fraction boiling through the jet fuel range.

If it is intended to produce gasoline over an extended period of time then both the charge stock and the hydrogen should be substantially sulfur free to preserve the catalyst in its unsulfided form. This may be done by a preliminary desulfurization treatment of the charge stock in a well-known manner with a catalyst comprising nickel and/or cobalt and molybdenum in the presence of hydrogen. If hydrogen from the desulfurization step is used in the hydrocracking stage, it is advisable to treat the hydrogen for the removal of H₂S such as by scrubbing with ethanolamine or by contacting the hydrogen with a bed of zinc oxide.

When it is desired to produce jet fuel the preliminary desulfurization step can be eliminated and the sulfur containing charge stock can be introduced directly into the hydrocracking zone. The sulfur compounds present in the charge stock will gradually convert the catalyst to the sulfide form and the initial boiling point of the recycled product can then be increased from about 400° F. to about 550° F. However, it has been found advantageous to employ an initial or preliminary step to reduce nitrogen and sulfur levels regardless of the type of product fuel desired as certain other benefits are derived therefrom such as the saturation of olefins and polycyclic aromatics thus facilitating the subsequent hydrocracking reaction.

When the preliminary desulfurization step is employed and it is desired to start the production of jet fuel then the hydrocracking catalyst can be converted to the sulfide form either by using hydrogen sulfide containing off-gas from the desulfurization stage or in the alternative if hydrogen being used in the hydrocracking zone is substantially sulfur free, by adding sulfur containing compounds either to the hydrogen or to the hydrocarbon charge stock. Suitable sulfur containing compounds are H₂S, CS₂, and low molecular weight mercaptans or sulfides such as

butyl mercaptan and tertiary butyl sulfide. A particularly advantageous method of operation is to commence production of motor fuel using an unsulfided catalyst, charging hydrocarbon and scrubbed hydrogen from a desulfurization unit to the hydrocracking zone and permitting the residual sulfur present in the charge stock to gradually convert the catalyst to the sulfide form. In this way, motor fuel is produced while the catalyst is in the unsulfided state and product boiling above the motor fuel range is recycled to the hydrocracking zone until the catalyst becomes sulfided. Thereafter a jet fuel fraction boiling above the motor fuel fraction is also recovered as product. The recovered jet fuel fraction is superior to that obtained when the catalyst is in the unsulfided state and the gasoline produced when the catalyst is in the unsulfided form is superior to that produced with a sulfided catalyst.

The process of the present invention has its greatest application in the treatment of hydrocarbon fractions boiling above the motor fuel range for example boiling in the range of about 400° F. to about 900° F. although fractions having an initial boiling point as low as 200° F. may be satisfactorily treated. Suitable charge stocks include straight run gas oils, fluid catalytic cracking cycle gas oils, deasphalted oil, coker distillate gas oil and the like. Cycle oils and cycle oil extracts from catalytic cracking are particularly desirable. Suitable charge stocks are obtained from crude petroleum oils, shale oil, tar sand oil, oils derived from coal and the like.

As pointed out above if the charge stock contains sulfur compounds and it is desired to maintain the production of motor fuel over an extended period of time then the charge stock should be subjected to a preliminary desulfurization. This can be accomplished by a variety of methods known in the art, a preferred method comprising charging the hydrocarbon feed to a catalytic desulfurization zone containing a cobalt molybdate on alumina catalyst at a temperature of about 650° F., a pressure of about 500 p.s.i.g., a hydrogen recycle rate of about 5000–6000 s.c.f.b. and a liquid hourly space velocity between about 1 and 2. Such treatment will generally effect about a 70 to 80% reduction in the sulfur content of the charge. The remaining amount of sulfur is sufficient over a prolonged period of time to gradually convert the hydrocracking catalyst to the sulfide form after which the initial boiling point of the recycle product stream can be increased from about 400° F. to about 550° F. However, this period of time can be shortened or extended by varying the severity of the desulfurization reaction. The addition of sulfur containing compounds to the hydrocracker feed also results in a shorter period.

Hydrogen used in the process of the present invention may be obtained from any suitable source. The hydrogen need not be pure but may contain as much as 40% impurities. In this respect the term "hydrogen" as used in the specification and claims includes dilute hydrogen. The hydrogen need not be free from sulfur compounds but the presence of sulfur in the hydrogen should be controlled in accordance with the end product desired. If gasoline or motor fuel is the principal end product then the hydrogen should be relatively free from sulfur, but if it is desired to convert from the production of gasoline to jet fuel then advantageously the hydrogen will contain sulfur compounds the amount bearing directly on when the conversion is to take place. Suitable sources of hydrogen are catalytic reformer by-product gas, electrolytic hydrogen and hydrogen obtained from the partial oxidation of carbonaceous material followed by shift conversion and CO₂ removal.

The hydrocracking reaction is carried out at a temperature between about 500 and 850° F., preferably 550–800° F. Preferably the pressure is maintained within the range of 1000 to 3500 p.s.i.g. although pressures from 500 to 10,000 p.s.i.g. and higher may be used. Hydrogen rates from 1000 to 20,000 s.c.f.b. of charge stock are satis-

factory although hydrogen rates of 3000 to 8000 s.c.f.b. are preferred. Space velocities that is the volumes of liquid charge per volume of catalyst per hour may range between 0.1 and 10 but preferably are within the range of 0.5–2.

The catalysts used in the process of the present invention comprise two components, a hydrogenation component supported on a cracking component. As hydrogenating components the catalyst may contain from 0.5 to 40% preferably from about 5 to 20% by weight of a Group VI or Group VIII metal such as chromium, tungsten, cobalt, nickel or mixtures thereof. The hydrogenating component is supported on a cracking base such as a mixture of two or more difficultly reducible oxides such as silica-alumina, silica-magnesia, silica-titania, silica-zirconia and naturally occurring clays. The cracking properties of the base can be improved by treatment with an acidic material such as HF. A particularly suitable base of this type is a co-precipitated silica-alumina containing for example about 80–90% silica and 10–20% alumina.

Another type of support is a large pore zeolite, that is, a crystalline zeolite having uniform pore openings of about 6 to 15 Angstrom units. Zeolites of the X or Y type fall within this category. Advantageously these supports are prepared by subjecting a naturally occurring or synthetic zeolite to an ion exchange treatment to replace the alkali metals of the zeolite with hydrogen or divalent metal ions. Preferably the alkali metal content of the zeolite is reduced to less than 10% by weight. In the case of the divalent metal the ion exchange can be made directly using a solution containing ions of the desired metal or can go through an intermediate stage in which the zeolite is in the hydrogen ion form. The hydrogen ion form of the zeolite may be produced by treating the zeolite with an acidic solution having a pH no less than about 3 although preferably the acid form of the zeolite is produced by treating the zeolite with a solution of ammonia, drying and then heating to convert the ammonium ion form to the hydrogen ion form.

The hydrogenating component may be incorporated into the molecular sieve or zeolite support by means of impregnation or ion exchange or a combination of the two or into the conventional cracking catalyst support by impregnation using a solution of a compound of the hydrogenating metal or metals. The catalyst is then drained, dried and calcined to form the metal oxide. This form of the hydrogenating component may be charged as is to the hydrocracking zone or may be converted to the metal form by contact with hot hydrogen, in which case the reduction is preferably accomplished in the hydrocracking zone using the same reaction temperatures and pressures as are used during the hydrocracking reaction. Particularly suitable catalysts are a mixture of nickel and tungsten on silica-alumina or on a molecular sieve.

In the course of carrying out the hydrocracking process, the catalyst gradually loses its activity due to the formation of carbon thereon. By the time this happens, in a preferred embodiment of the invention, the catalyst has already become sulfided and the unit is on jet fuel production. To regenerate the catalyst by removal of the carbon an oxidizing gas containing a carefully regulated amount of oxygen for control of the catalyst temperature during the regenerative burning is introduced into the hydrocracking zone. After regeneration the catalyst will be for the most part in the oxide form. When the on-stream period is then begun, since the catalyst is in the oxide form, the product fraction boiling above the motor fuel range is recycled to the hydrocracking zone and the recycle of this fraction is continued until the catalyst is sulfided to such an extent that the operation is again converted to jet fuel production.

The following example is submitted for illustrative purposes only.

A charge stock fluid catalytic cracking cycle gas oil having the following characteristics:

Gravity, ° API	29.5
N, p.p.m.	67
S, p.p.m.	1700
Aromatics, vol. percent	32
ASTM distillation, ° F.:	
IBP-10%	416-508
20-40%	542-590
60-80%	630-668
90-EP (96%)	696-724

is subjected to a preliminary desulfurization by contact with a cobalt molybdate on alumina desulfurization catalyst at a temperature of 650° F., a pressure of 750 p.s.i.g., a hydrogen rate of 6000 s.c.f.b. and a space velocity of 1.0. The hydrogen off-gas is scrubbed with diethanolamine for removal of H₂S and combined with the desulfurized hydrocarbon liquid with which it is charged to a hydrocracking zone containing a hydrocracking catalyst composed of 6% Ni and 19% W on a silica-alumina (87% silica, 13% alumina) base. The sulfur content of the hydrocarbon charge is 150 p.p.m. Hydrocracking conditions and yields are tabulated below.

Temperature, ° F.	640
Pressure, p.s.i.g.	1500
Gas recycle rate, s.c.f.b.	6300
Space velocity (v./v./hr.)	1.0
Hydrogen consumption, s.c.f.b.	2300
115-200° F.:	
Vol. percent	33.15
RON (+3 cc. TEL)	94.7
200-400° F.:	
Vol. percent	63.70
RON (+3 cc. TEL)	82.4

The jet fuel product obtained from this operation is of low quality. The 350-550° F. fraction has a smoke point of only 17 mm. and an undesirably high aromatic content of 19 volume percent.

After the residual sulfur in the hydrocarbon charge has sulfided 85% of the metallic hydrogenation components of the catalyst, the yields and characteristics of the product are as follows:

115-200° F.:	
Vol. percent	19.6
RON (+3 cc. TEL)	91.2
200-400° F.:	
Vol. percent	79.5
RON (+3 cc. TEL)	68.5
350-550° F.:	
Smoke point mm.	31
Aromatics, vol. percent	1

No real problem is encountered in determining the sulfur content of the catalyst. It is easily calculated from the analysis of the sulfur present in the feed and the feed rate. The sulfur take-up by the metals of the hydrogenating component is practically quantitative. A substantial breakthrough of sulfur indicates that sulfiding of the catalyst is essentially complete. In the sulfided form, as can be seen from the above example, the catalyst produces a superior grade of jet fuel whereas, in the oxide form the catalyst produces a superior grade of gasoline.

Various 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 single-stage hydrocracking process for the conversion of a hydrocarbon liquid fraction into lighter hydrocarbons which comprises contacting in a single hydrocracking stage a sulfur-containing hydrocarbon fraction having an initial boiling point not less than about 400° F. in the presence of hydrogen under hydrocracking conditions with a hydrocracking catalyst comprising a hydrogenating component selected from the group consisting of (1) nickel and tungsten (2) their oxides and (3) mixtures thereof, recovering from the reaction product a motor fuel fraction having an end point of about 400° F., recycling to the hydrocracking zone a reaction product fraction boiling above the motor fuel range until at least 60% of the hydrogenation components of the catalysts are sulfided, recovering as product from the hydrocracking reaction a motor fuel fraction and a jet fuel fraction, and recycling to the hydrocracking zone that portion of the product boiling above the jet fuel range, the amount of sulfur introduced into the hydrocracking zone being maintained substantially constant throughout the process.

2. The process of claim 1 in which the hydrocarbon charge to the hydrocracking zone is subjected to a preliminary desulfurization.

3. The process of claim 1 in which at least 80% of the metal of the hydrogenating component is sulfided.

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