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JET FUEL AND MOTOR FUEL PRODUCTION BY HYDROFINING AND TWO-STAGE HYDROCRACKING

Edward T. Child, Fishkill, Donald A. Messing and Robert M. Suggitt, Wappingers Falls, and Thomas M. Liden, Beacon, N.Y., assignors to Texaco Inc., New York, N.Y.

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ABSTRACT OF THE DISCLOSURE

High quality jet and motor fuels are prepared by hydrotreating a hydrocarbon oil charge stock, passing the effluent from the hydrotreating zone into contact with a hydrocracking catalyst comprising a Group VIII metal supported on a modified zeolite and at least one amorphous inorganic oxide, recovering a motor and a jet fuel fraction and contacting that portion of the product boiling above the jet fuel range with a nickel hydrocracking catalyst.

This application is a continuation of Ser. No. 739,140 filed June 24, 1968, now abandoned.

This invention is concerned with the conversion of hydrocarbon oils. More particularly, it is concerned with the hydrocracking of heavy hydrocarbon oils into lighter products. In a more specific aspect, it is concerned with the production of high octane motor fuel and high quality jet fuel simultaneously from higher boiling hydrocarbon oils.

The hydrocracking of petroleum oils has been known for many years and was practiced, although not too successfully in Europe several decades ago. However with the development of new catalysts and new operating techniques, it has been improved to the stage where it has attained commercial significance and is now being used in many refineries. In the early days of its commercial use, hydrocracking was designed exclusively for the production of motor fuel or gasoline. Currently with the increased demand for jet fuel, which can no longer be met by the supply of straight run kerosene, attempts have been made to adapt hydrocracking of heavy oils to the production of jet fuel as well as the production of motor fuel. Unfortunately, the sophisticated present day jet engine requires specific characteristics in a jet fuel just as the spark ignition engine requires specific characteristics in a motor fuel.

The characteristics of high quality jet fuel are entirely different from those of high octane motor fuel, the prime difference being that aromatics are a desirable component of motor fuel because of their high octane rating whereas such materials are extremely undesirable in a jet fuel as they contribute to a low luminometer number indicating that the jet fuel will burn with a radiant flame. It is therefore hardly possible to subject a heavy oil such as a gas oil to hydrocracking and to recover from the product a low aromatic jet fuel having a high luminometer number and also to recover from the same product a highly aromatic motor fuel having a high octane number. If a hydrocracking unit is designed and operated to produce high octane gasoline then the jet fuel fraction of the product is of inferior quality and similarly if the hydrocracking unit is designed and operated to produce high luminometer number jet fuel then the gasoline fraction is not of high quality.

Several attempts have been made recently to produce jet fuels and motor fuels simultaneously in a two-stage

type of hydrocracking process but on the whole they have been unsatisfactory in that an undesirably large volume of fixed gases has been produced in the first stage, and the feed stock sent to the second stage has been of poor quality for second stage conversion.

It is therefore an object of the present invention to provide a novel hydrocracking process. Another object is to provide a process for the simultaneous production of motor fuel and jet fuel in a hydrocracking unit. Still another object of the invention is to provide a novel two-stage hydrocracking process in which different catalysts are used in each stage. Another object of the invention is to provide a two-stage hydrocracking process in which relatively small amounts of fixed gases are produced in the first stage and a suitable charge stock is sent to the second stage. These and other objects will be obvious to those skilled in the art from the following disclosure.

In accordance with the above objects, our invention provides a process for the simultaneous production of a high quality jet fuel and high octane motor fuel which comprises passing a hydrocarbon oil into contact with a hydrotreating catalyst under hydrotreating conditions, passing the entire effluent from the hydrotreating zone into contact in a first stage with a hydrocracking catalyst comprising a Group VIII metal on a support comprising a modified zeolite and at least one amorphous inorganic oxide under hydrocracking conditions, separating a motor fuel and a jet fuel from the first stage effluent, passing that portion of the effluent boiling above the jet fuel range into contact in a second stage with a hydrocracking catalyst comprising nickel on a cracking support under hydrocracking conditions and recovering a motor fuel fraction from the second stage effluent.

The charge stocks suitable for processing include heavy petroleum hydrocarbon oils such as straight run gas oil, fluid catalytically cracked cycle gas oil, atmospheric residuum, shale oil, tar sand oil, delayed coker gas oil, crude oil, mixtures thereof and the like.

The hydrogen used in the process of our invention need not necessarily be pure. The hydrogen content of the hydrogenating gas should be at least about 60% and is preferably at least about 75% by volume. Particularly suitable sources of hydrogen are catalytic reformer by-product hydrogen and hydrogen produced by the partial combustion of a carbonaceous material followed by shift conversion and CO_2 removal. Hydrogen rates are expressed in terms of standard cubic feet per barrel of charge to the reactor, viz. s.c.f.b.

The catalyst used in the hydrotreating reactor should have good hydrotreating activity but little, if any, cracking activity. Suitable catalysts comprise a hydrogenating component as for example the oxide or sulfide of cobalt, nickel, iron, molybdenum, tungsten, chromium, vanadium and mixtures thereof on a support such as silica, alumina, zirconia, magnesia and mixtures thereof used as such or in conjunction with zeolites not necessarily of reduced alkali metal content. Preferred catalysts comprise nickel tungsten on boria promoted alumina and nickel molybdenum on activated alumina. The hydrogenating component should be present in an amount between about 5% and 40% by weight based on the catalyst composite. Catalysts containing about 6% nickel and 20% tungsten or 5% nickel oxide and 15% molybdenum oxide have been found satisfactory. When the charge is a heavy hydrocarbon oil containing for example at least 1% Conradson carbon residue then advantageously the catalyst support will contain at least 2% silica and will have a minimum surface area of 250 square meters per gram and a minimum pore volume of 0.6 cc. per gram.

The charge together with hydrogen is introduced into the hydrotreating zone which is maintained at a temper-

ature between about 550 and 900° F. and a pressure between 200 and 10,000 p.s.i.g. The hydrocarbon charge is introduced at a liquid hourly space velocity between 0.2 and 10 volumes of oil per volume of catalyst per hour and the hydrogen is introduced at a rate of between 1000 and 50,000 s.c.f.b. Preferred conditions include a temperature of 650–800° F., a pressure of 500–2000 p.s.i.g., a space velocity of 0.5–2.0 v./v./hr. and a hydrogen rate of 3000–10,000 s.c.f.b. The entire effluent from the hydrotreating zone is passed to the first stage of the hydrocracking zone although in some instances it may be advantageous to cool the effluent to a suitable hydrocracking temperature.

The first stage hydrocracking zone is maintained at a temperature of 550–900° F., preferably 650–800° F. and the catalyst bed is of a size sufficient to provide a space velocity of between 0.2 and 10 v./v./hr., preferably 0.52–2 v./v./hr. The pressure within the first stage hydrocracking zone is substantially the same as the pressure in the hydrotreating zone, sufficient pressure drop being taken to maintain the flow of reactants through the system.

The catalyst used in the first stage hydrocracking zone contains two components, a hydrogenating component supported on a cracking component. Suitable hydrogenating components comprise metals and compounds of metals of Group VIII, e.g. the noble metals particularly platinum and palladium, and the iron group metals, particularly cobalt and nickel. Advantageously the catalyst may also contain a Group VI metal, e.g. molybdenum or tungsten used in conjunction with the iron group metal. The hydrogenating component may be used either in the metallic form or in the form of a compound, e.g. the oxide, sulfide or telluride.

The cracking component of the catalyst comprises a modified crystalline zeolite and at least one amorphous inorganic oxide, the modified zeolite being present in an amount between about 15 and 60% by weight. Suitable amorphous inorganic oxides are those displaying cracking activity such as silica, alumina, magnesia, zirconia and beryllia which if necessary has been treated with an acidic agent such as hydrofluoric acid to impart cracking activity thereto. A preferred mixture of amorphous inorganic oxides comprises silica-alumina in a proportion ranging from 60–90% silica and 10–40% alumina.

The modified zeolite portion of the cracking component has uniform pore openings of from 6–15 angstrom units, has a silica-alumina ratio of at least 2.5, e.g. 3–10, and has a reduced alkali metal content. The modified zeolite is prepared by subjecting synthetic zeolite Y to ion exchange by contacting the zeolite several times with fresh solutions of an ammonium compound at temperatures ranging between about 100 and 250° F. until it appears that the ion exchange is substantially complete. The ion exchanged zeolite is then washed to remove solubilized alkali metal and dried at a temperature sufficiently high to drive off ammonia. This treatment converts the zeolite Y to the hydrogen form and reduces the alkali metal content to about 2–4 weight percent. The ion exchanged zeolite is then calcined at a temperature of about 1000° F. for several hours. After cooling, the ion-exchanged, calcined zeolite is subjected to additional ion exchange by contact several times with fresh solutions of an ammonium compound and again washed and dried. This treatment results in a further reduction in the alkali metal content of the zeolite to less than 1% usually to about 0.5% or less. It would appear that after the first calcination, it is possible to engage in further ion exchange with the removal of additional alkali-metal ions not removable in the initial ion exchange. Calcination at e.g. 1000–1500° F. may take place here or may be postponed until after the incorporation of the inorganic oxide and impregnation with the hydrogenating component at which time the composite should be calcined. Whether the calcination is postponed or repeated, the final calcination temperature should not exceed 1200° F.

Hydrocracking catalysts containing a hydrogenating component supported on a cracking component composed of at least one amorphous inorganic oxide and the twice ion exchanged, twice calcined zeolite have superior hydrocracking activity and additionally are more resistant to deactivation when brought into contact with nitrogen compounds and polycyclic aromatics. They also show good stability to steam. The hydrocracking catalyst should also be substantially free from rare earth metals and should have a rare earth metal content below 0.5 weight percent, preferably below 0.2 weight percent. It has been found that although rare earth metals are reputed to enhance the activity and stability characteristics of cracking catalysts, their presence in a hydrocracking catalyst has been found to be undesirable.

When the hydrogenating component of the hydrocracking catalyst is a noble metal it should be present in an amount between about 0.2 and 5.0% by weight based on the total catalyst composite. Preferably the noble metal is present in an amount between 0.5 and 2%. When the hydrogenating component comprises a Group VIII metal it should be present in an amount between about 1 and 40% by weight based on the total catalyst composite. If the iron group metal is the sole hydrogenating component, it may be present in an amount between about 5 and 10%. When a Group VI metal is used in conjunction with a Group VIII metal, the Group VI metal may be present in an amount preferably between about 5 and 30%. Particularly suitable catalysts are those containing between 0.5 and 1.0 weight percent noble metal and those containing between 5 and 10% iron group metal and between 15 and 30% Group VI metal. Specific examples of suitable catalysts are those containing 0.6–0.75 weight percent palladium or containing about 6% nickel and 20% tungsten on a support made up of about 25% modified zeolite Y, 55% silica and 20% alumina. The hydrogenating component may be deposited on the cracking component by impregnating the latter with a solution of a compound of the hydrogenating component, drying and forming e.g. into pellets or extrudates. Such techniques are well known in the art and require no description here.

The effluent from the first stage hydrocracking zone is passed to a high pressure separation zone from which a gas rich in hydrogen is removed and recycled to the hydrotreating zone. Advantageously, a hydrogen bleed stream is taken from the recycle stream to prevent the build-up of gaseous hydrocarbons therein. Desirably, the recycle stream is also subjected to a purification treatment for the removal of H_2S and NH_3. A make-up stream of hydrogen is introduced into the recycle stream to replenish that portion drawn off and the hydrogen consumed in the hydrotreating zone and the first stage hydrocracking zone.

The remainder of the effluent removed from the high pressure separator is fractionated to separate therefrom a gasoline fraction and a jet fuel fraction. That portion of the effluent boiling above the jet fuel range is introduced into the second stage hydrocracking zone with additional hydrogen.

In the second stage hydrocracking zone the pressure is maintained between about 200 and 10,000 p.s.i.g., preferably between 500 and 2000 p.s.i.g. The temperature range in the second stage hydrocracking zone is 500–900° F., preferably 550–800° F., hydrogen is introduced at a rate of between 1000 and 50,000 s.c.f.b., a preferred rate being between 3000 and 10,000 s.c.f.b. and the space velocity is between 0.2 and 10 v./v./hr., preferably 0.5–2.0 v./v./hr.

The catalyst in the second stage hydrocracking zone also contains a hydrogenating component supported on a cracking component. The hydrogenating component is nickel, preferably in oxide form, in an amount between 4 and 20% by weight of the catalyst composite and preferably between 5 and 10%. Advantageously the feed both

hydrocarbon and hydrogen should be substantially sulfur free to avoid conversion of the hydrogenation component to the sulfide as the gasoline product obtained when the catalyst is in the sulfide form is somewhat inferior to the gasoline obtained when the hydrogenating component is in the oxide form.

The cracking component may be a low alkali metal crystalline zeolite, a mixture of amorphous inorganic oxides or a combination thereof. Advantageously the support may be of the same composition as the support used in the catalyst of the first stage hydrocracking zone.

The effluent from the second stage hydrocracking zone is then separated into a normally liquid hydrocarbon portion and a hydrogen-rich stream which latter may be recycled to the second stage hydrocracking zone or may be introduced into a common recycle stream which supplies hydrogen to both the hydrotreating zone and the second stage hydrocracking zone. In the case of a common recycle stream, care should be taken to ensure that the hydrogen fed to the second stage hydrocracking zone is essentially sulfur free, i.e. containing less than 100 p.p.m. sulfur. The normally liquid hydrocarbon portion of the effluent is separated into a gasoline fraction which is withdrawn as product and that portion of the effluent boiling above the gasoline fraction including the jet fuel and heavier hydrocarbons is recycled to the second stage hydrocracking zone.

The following examples are given for illustrative purposes only and are not to be construed as limiting the invention in any manner.

EXAMPLE I

This example shows a typical conventional process for the production of gasoline.

Charge

Gravity, ° API	28.3
ASTM distillation, ° F.:	
IBP–5	392–466
10–20	508–553
30–40	578–604
50	626
60–70	646–665
80–90	686–718
95–EP	750–760
Sulfur, wt. percent	0.18
Total nitrogen, p.p.m.	102

The hydrotreating zone catalyst is composed of 3% nickel oxide and 15% molybdena on alumina. Both the first and second stage hydrocracking catalysts contain 0.7% palladium on a decationized zeolite Y containing 2.5% Na_2O. The entire effluent of the hydrotreating zone is sent directly to the first stage hydrocracking zone.

Reaction conditions and other data are as follows:

Reaction conditions:	Hydrotreating zone
Temperature, ° F.	690
Pressure, p.s.i.g.	1500
LHSV, v./v./hr.	1.0
Hydrogen rate, s.c.f.b.	6000

Hydrocracking zone	1	2
Temperature, ° F	695	590
Pressure, p.s.i.g	1,500	1,500
LHSV, v./v./hr	0.9	1.5
Hydrogen rate, s.c.f.b	6,000	6,000
Yields:		
C_1–C_3, weight percent	4.2	
i-C_4, volume percent	7.6	15.0
n-C_4, volume percent	4.7	6.0
i-C_5, volume percent	11.2	14.3
n-C_5, volume percent	1.5	1.6
C_6–215° F., volume percent	14.5	23.4
215–400° F. volume percent	33.1	59.5
400° F. + to stage 2	46.6	
Total C_4+	118.9	119.8
Research Octane No. (+3 cc. TEL):		
IBP–215° F	96.9	93.3
215–400° F	87.5	75.3
Hydrocarbon analysis, volume percent:		
Paraffins	32.9	36.7
Cycloparaffins	45.6	58.6
Aromatics	21.4	4.8

EXAMPLE II

This example shows the superiority of our processing scheme over that of Example I for the production of gasoline. The charge, hydrotreating catalyst and reaction conditions here are the same as those for Example I but the first stage hydrocracking catalyst contains 6% nickel and 19% tungsten on a support composed of 26% alumina, 52% silica and 22% modified zeolite prepared by subjecting a synthetic zeolite Y to ion exchange with ammonium chloride, washing, drying and calcining at 1000° F., subjecting the treated zeolite to a second ion-exchange with ammonium chloride, washing, drying and calcining at 1000° F. to yield a modified zeolite containing 0.16% Na_2O, incorporating the silica-alumina into the modified zeolite, impregnating the support with a solution of nickel nitrate and after drying with a solution of ammonium metatungstate, drying, calcining at 1000° F. and then sulfiding. The second stage hydrocracking catalyst contains 6% nickel oxide on a support composed of 73% silica and 27% alumina.

Hydrocracking zone	1	
Temperature, ° F	695	650
Pressure, p.s.i.g	1,550	1,500
LHSV, v./v./hr	0.9	1.5
Hydrogen rate, s.c.f.b	6,000	6,000
Yields:		
C_1–C_3, weight percent	0.8	
i-C_4, volume percent	5.7	16.0
n-C_4, volume percent	4.2	8.0
i-C_5, volume percent	8.4	15.0
n-C_5, volume percent	2.5	1.1
C_6–215° F., volume percent	19.9	19.2
215–400° F., volume percent	28.8	57.9
400° F. + to stage 2	51.3	
Total C_4+	120.8	117.2
Research Octane No. (+3 cc. TEL):		
IBP–215° F	95.8	95.6
215–400° F	88.1	81.6
Hydrocarbon analysis, volume percent:		
Paraffins	28.4	39.1
Cycloparaffins	56.7	45.8
Aromatics	15.0	15.2

EXAMPLE III

When the process of Example II is operated to produce jet fuel and gasoline, the operating data and yield figures appear in the table below.

Hydrocracking zone	1	2
Temperature, ° F	675	645
Pressure, p.s.i.g	1,500	1,500
LHSV, v./v./hr	0.75	1.5
Hydrogen rate, s.c.f.b	6,000	6,000
Yields:		
C_1–C_3, weight percent	0.7	
i-C_4, volume percent	2.2	14.8
n-C_4, volume percent	1.3	7.3
i-C_5, volume percent	2.6	14.3
n-C_5, volume percent	1.0	1.0
115–235° F., volume percent	10.4	[1] 20.1
235–295° F., volume percent	8.2	[2] 58.7
295–525° F., volume percent	42.1	
525° F. + to stage 2	49.5	
Motor fuel; Research Octane No. (+3 cc. TEL):		
115–235° F	94.1	[1] 95.9
235–295° F	86.1	[2] 81.8
Hydrocarbon Analysis, volume percent:		
Paraffins	35.2	37.8
Cycloparaffins	58.8	46.1
Aromatics	6.0	16.1
Jet fuel:		
Smoke point, mm	23	
Freezing point, ° F	−59	
Aromatics, volume percent	11	
ASTM distillation, ° F:		
IBP–10%	333–361	
20–50%	376–425	
70–90%	452–488	
EP	517	

[1] 115–215° F.
[2] 215–400° F.

In Examples II and III, the total amount of sulfur introduced into stage 2 from both hydrocarbon and hydrogen sources is less than 100 p.p.m. based by weight on the hydrocarbon charge.

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 process for the simultaneous production of a high quality jet fuel and high octane motor fuel which comprises contacting a petroleum hydrocarbon oil in a hydrofining zone with hydrogen and with a hydrofining catalyst under hydrofining conditions to convert sulfur and nitrogen impurities in said oil into hydrogen sulfide and ammonium gas, passing the entire effluent from said hydrofining zone into a first hydrocracking stage and contacting said effluent therein with hydrogen, and with a hydrocracking catalyst comprising an iron group metal sulfide and a Group VI metal sulfide on a support comprising a hydrogen zeolite having an alkali metal content of less than 0.5 wt./percent, a rare earth metal content not exceeding 0.2 wt./percent, a silica-alumina ratio of at least 2.5 and uniform pore openings of 6–15 A. prepared from an alkali metal zeolite by an alternating sequence of at least two ion exchanges with a solution of an ammonium compound and two calcinations, said support also including at least one amorphous inorganic oxide selected from the group consisting of silica, alumina, magnesia, zirconia, beryllia and mixtures thereof, separating a motor fuel and a jet fuel from the first hydrocracking stage effluent as products of the process, passing that portion of said effluent boiling above the jet fuel range into a second hydrocracking stage and contacting therein said effluent boiling above the jet fuel range with hydrogen and with a hydrocracking catalyst comprising a hydrogenating component consisting essentially of nickel or nickel oxide on a cracking support under hydrocracking conditions and recovering from the second hydrocracking stage effluent a motor fuel as product of the process.

2. The process of claim 1 in which said nickel of the second hydrocracking stage catalyst is supported on a base comprising silica and alumina.

3. The process of claim 1 in which the nickel of said second hydrocracking stage catalyst is supported on a base comprising a hydrogen zeolite having an alkali metal content of less than 1%, a silica-alumina ratio of at least 2.5 and uniform pore openings of 6–15A.

4. The process of claim 1 in which the effluent passed to the second stage hydrocracking zone contains not more than 100 p.p.m. sulfur based on the weight of the hydrocarbon charge.

5. The process of claim 1 in which the first stage hydrocracking catalyst support contains between 15 and 60% zeolite having an alkali metal content of less than 0.5%, a silica-alumina ratio of at least 2.5 and uniform pore openings of 6–15A.

6. The process of claim 1 in which the hydrogenating component of the first stage hydrocracking catalyst comprises nickel sulfide and tungsten sulfide.

7. The process of claim 1 in which the initial charge stock contains at least 1% Conradson carbon residue and the hydrofining catalyst support contains at least 2% silica and has a surface area of at least 250 sq. meters per gram and a pore volume of at least 0.6 cc. per gram.

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DELBERT E. GANTZ, Primary Examiner

G. J. CRASANAKIS, Assistant Examiner