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EP 0 512 778 B1

Description

This invention relates to the hydroconversion of heavy hydrocarbon oils. More particularly it relates to a hydrotreating catalyst system which permits operation to yield increased conversion of 538 °C (1000 °F+) charge to lower boiling products.

As is well known to those skilled in the art, the petroleum refiner wishes to convert high boiling fractions such as vacuum resid to lower boiling fractions which are more readily handleable and/or marketable. Illustrative of the large body of prior art patents directed to this problem are the following:

US-A-4,579,646 discloses a bottoms visbreaking hydroconversion process wherein hydrocarbon charge is partially coked, and the coke is contacted within the charge stock with an oil-soluble metal compound of a metal of Group IV-B, V-B, VII-B, or VIII to yield a hydroconversion catalyst.

US-A-4,724,069 discloses hydrofining in the presence of a supported catalyst bearing a VI-B, VII-B, or VIII metal on alumina, silica, or silica-alumina. There is introduced with the charge oil, as additive, a naphthenate of Co or Fe.

US-A-4,567,156 discloses hydroconversion in the presence of a chromium catalyst prepared by adding a water-soluble aliphatic polyhydroxy compound (such as glycerol) to an aqueous solution of chromic acid, adding a hydrocarbon thereto, and heating the mixture in the presence of hydrogen sulfide to yield a slurry.

US-A-4,564,441 discloses hydrofining in the presence of a decomposable compound of a metal (Cu, Zn, III-B, IV-B, VI-B, VII-B, or VIII) mixed with a hydrocarbon-containing feed stream; and the mixture is then contacted with a "suitable refractory inorganic material" such as alumina.

US-A-4,557,823 discloses hydrofining in the presence of a decomposable compound of a IV-B metal and a supported catalyst containing a metal of VI-B, VII-B, or VIII.

US-A-4,557,824 discloses demetallization in the presence of a decomposable compound of a VI-B, VII-B, or VIII metal admitted with the charge and a heterogeneous catalyst containing a phosphate of Zr, Co, or Fe.

US-A-4,551,230 discloses demetallization in the presence of a decomposable compound of a IV-B, V-B, VI-B, VII-B, or VIII metal admitted with the charge and a heterogeneous catalyst containing $NiAs_x$ on alumina.

US-A-4,430,207 discloses demetallization in the presence of a decomposable compound of a V-B, VI-B, VII-B, or VIII metal admitted with the charge and a heterogeneous catalyst containing a phosphate of Zr or Cr.

US-A-4,389,301 discloses hydroprocessing in the presence of added dispersed hydrogenation catalyst (typically ammonium molybdate) and added porous contact particles (typically FCC catalyst fines, alumina, or naturally occurring clay).

US-A-4,352,729 discloses hydrotreating in the presence of a molybdenum blue solution in polar organic solvent introduced with the hydrocarbon charge.

US-A-4,338,183 discloses liquefaction of coal in the presence of unsupported finely divided metal catalyst.

US-A-4,298,454 discloses hydroconversion of a coal-oil mixture in the presence of a thermally decomposable compound of a IV-B, V-B, VI-B VII-B, or VIII metal, preferably Mo.

US-A-4,134,825 discloses hydroconversion of heavy hydrocarbons in the presence of an oil-soluble compound of IV-B, V-B, VI-B, VII-B, or VIII metal added to charge, the compound being converted to solid, non-colloidal form by heating in the presence of hydrogen.

US-A-4,125,455 discloses hydrotreating in the presence of a fatty acid salt of a VI-B metal, typically molybdenum octoate.

US-A 4,077,867 discloses hydroconversion of coal in the presence of oil-soluble compound of V-B, VI-B, VII-B, or VIII metal plus hydrogen donor solvent.

US-A-4,067,799 discloses hydroconversion in the presence of a metal phthalocyanine plus dispersed iron particles.

US-A-4,066,530 discloses hydroconversion in the presence of (i) an iron component and (ii) a catalytically active other metal component prepared by dissolving an oil-soluble metal compound in the oil and converting the metal compound in the oil to the corresponding catalytically active metal component.

It is an object of this invention to provide a novel process for hydroconversion particularly characterized by attainment of increased conversion. Other objects will be apparent to those skilled in the art.

According to the present invention, there is provided a method of catalytically hydroconverting a charge hydrocarbon oil containing from 50-98 weight percent of components boiling above 538 °C (1000 °F) to convert from 30-90 weight percent thereof to components boiling below 538 °C (1000 °F), which comprises passing said charge hydrocarbon oil containing from 50-98 weight percent of components boiling above

about 538 °C (1000 °F) into contact with (i) a solid heterogenous catalyst containing, as a hydrotreating component, a metal of Groups IV-B, V-B, VI-B, VII-B, or VIII on a support and (ii) as an oil-soluble catalyst a compound of molybdenum and a compound of cobalt; maintaining said charge hydrocarbon oil in said conversion zone at conversion conditions in the presence of hydrogen and mercaptan until from 30-90 weight percent of said components boiling above 538 °C (1000 °F) are converted to components boiling below 538 °C (1000 °F); and recovering said converted oil.

The charge which may be treated by the process of this invention may include high boiling hydrocarbons typically those having an initial boiling point (ibp) above about 343 °C (650 °F). This process is particularly useful to treat charge hydrocarbons containing a substantial quantity of components boiling above about 538 °C (1000 °F) to convert a substantial portion thereof to components boiling below 538 °C (1000 °F).

Typical of these streams are heavy crude oil, topped crude, vacuum resid, asphaltenes, tars, coal liquids, visbreaker bottoms, etc. Illustrative of such charge streams may be a vacuum resid obtained by blending vacuum resid fractions from Alaska North Slope Crude (59v%), Arabian Medium Crude (5v%), Arabian Heavy Crude (27%), and Bonny Light Crude (9v%) having the characteristics listed in Table I:

TABLE I

PROPERTY	Charge
API Gravity	5.8
538 °C (1000 °F) + (W%)	93.1
Composition (W%)	
C	84.8
H	10.09
N	0.52
S	3.64
Alcor Microcarbon Residue (McR) (%)	19.86
n-C_7 insolubles (%)	11.97
Metals content (wppm)	
Ni	52
V	131
Fe	9
Cr	0.7
Na	5.

It is a feature of these charge hydrocarbons that they contain undesirable components typified by nitrogen (in amount up to 1w%, typically 0.2-0.8w%, say about 0.52w%), sulfur (in amount up to 10w%, typically 2-6w%, say about 3.64w%), and metals including Ni, V, Fe, Cr, Na, etc. in amounts up to 900 wppm, typically 40-400 wppm, say 198 wppm). The undesirable asphaltene content of the charge hydrocarbon may be as high as 22w%, typically 8-16w%, say 11.97w% (analyzed as components insoluble in normal heptane).

The API gravity of the charge may be as low as minus 5, typically minus 5 - plus 35, say about 5.8. The content of components boiling above about 538 °C (1000 °F) may be as high as 100w%, typically 50-98 + w%, say 93.1w%. The Alcor MCR Carbon content may be as high as 30w%, typically 15-25w%, say 19.86w%.

In practice of the method of this invention, the charge hydrocarbon oil may be passed to a hydroconversion operation wherein conversion occurs in liquid phase at conversion conditions including 371 °C-454 °C (700 °F-850 °F), preferably about 399 °C-432 °C (750 °F-810 °F), say 426 °C (800 °F), at hydrogen partial pressure of about 3.5-34.6 MPa (500-5000 psig), preferably about 10.4-17.3 MPa (1500-2500 psig), say 13.9 MPa (2000 psig).

It is a feature of the method of this invention that there is added to the charge hydrocarbon oil (preferably prior to admission to hydroconversion) a catalytically effective amount of an oil-miscible, preferably an oil-soluble catalyst compound of a combination of a molybdenum salt and a cobalt salt.

The salts may be typified by

(i) metal salts of aliphatic carboxylic acids
molybdenum stearate
molybdenum palmitate
molybdenum myristate
molybdenum octoate
(ii) metal salts of naphthenic carboxylic acids
cobalt naphthenate
molybdenum naphthenate
(iii) metal salts of alicyclic carboxylic acids
molybdenum cyclohexane carboxylate
(iv) metal salts of aromatic carboxylic acids
cobalt benzoate
cobalt o-methyl benzoate
cobalt m-methyl benzoate
cobalt phthallate
molybdenum p-methy benzoate
(v) metal salts of sulfonic acids
molybdenum benzene sulfonate
cobalt p-toluene sulfonate
(vi) metal salts of sulfinic acids
molybdenum benzene sulfinate
(vii) metal salts of phosphoric acids
molybdenum phenyl phosphate
(viii) metal salts of mercaptans
cobalt hexyl mercaptide
(ix) metal salts of phenols
cobalt phenolate
(x) metal salts of polyhydroxy aromatic compounds
molybdenum resorcinate
(xi) organo metallic compounds
molybdenum hexacarbonyl
cyclopentadienyl molybdenum tricarbonyl
(xiii) metal salts of organic amines
cobalt salt of pyrrole

The preferred compounds may be cobalt naphthenate, molybdenum hexacarbonyl, molybdenum naphthenate, and molybdenum octoate.

According to the invention, the combined use of molybdenum (e.g. as the naphthenate) and cobalt (e.g. as the naphthenate) yields a positive synergistic promotional effect on catalytic desulfurization and demetallization. Typically cobalt may be added in amount of 0.2-2 moles, say 0.4 moles per mole of molybdenum.

The metal compounds to be employed are oil-miscible and preferably oil-soluble i.e. they are soluble in the charge hydrocarbon oil in amount of at least 0.01g/100g typically 0.025-0.25g/100g, say about 0.1g/100g or alternatively they are readily dispersable in the charge hydrocarbon oil in amount of at least those amounts. It is also a feature of these metal compounds that, when activated as hereinafter set forth, the activated compounds are also oil-miscible in the hydrocarbon oils with which they come into contact during practice of the method of this invention.

Activation of the oil-miscible compounds of molybdenum and cobalt in accordance with practice of the process of this invention may be effected either by pre-treatment (prior to hydroconversion) or in situ -(during hydroconversion). It is preferred to effect activation in situ in the presence of the hydrogenation catalyst to achieve a highly dispersed catalytic species.

Activation according to the preferred method may be carried out by adding 10-200 wppm, say 30 parts of metal compound to charge hydrocarbon at 15-149°C (60°F-300°F), say 94°C (200°F). The mixture is activated by heating to 204°-446°C (400°F-835°F), typically 260°-370°C (500°F-700°F), say 315°C (600°F) at partial pressure of hydrogen of 3.5-34.5 MPa (500-5000 psig), typically 7.0-20.8 MPa (1000-3000 psig), say 13.9 MPa (2000 psig) and at partial pressure of a gaseous mercaptan of 0.1-3.5 MPa (5-500 psig), typically 0.15-2.2 MPa (10-300) psig, say 0.4 MPa (50 psig). Total pressure may be 3.5-38.0 MPa (500-5500 psig), typically 7.0-22.8 MPa (1000-3300 psig), say 14.2 MPa (2050 psig). Commonly the gas may contain 40-99v%, typically 90-99v%, say 98v% hydrogen and 1-10v%, say 2v% mercaptan such as

hydrogen sulfide. Time of activation may be 1-12, typically 2-6, say 3 hrs.

In this embodiment, it will be noted that activation may occur at temperature which is lower than the temperature of conversion.

The mercaptans which may be employed may include hydrogen sulfide, aliphatic mercaptans, typified by methyl mercaptan, lauryl mercaptan, aromatic mercaptans; dimethyl disulfide, carbon disulfide.

These mercaptans apparently decompose during the activation process. It is not clear why this treatment activates the metal compound. It may be possible that the activity is generated as a result of metal sulfides formed during the treatment.

When the sulfur content of the charge hydrocarbon is above about 2w%, it may not be necessary to add a mercaptan during activation i.e. hydrodesulfurization of the charge may provide enough mercaptan to properly activate (i.e. sulfide) the oil-miscible decomposable catalyst.

In an alternative activation procedure, the oil-miscible metal compound may be activated in the presence of an oil which is compatible with the charge oil i.e. a separate portion of the charge oil or a different oil which is compatible with the charge oil. In this alternative the oil-miscible metal compound may be added to the oil in amount which is substantially greater (e.g. 2-20 times) than is the case when the compound is activated in the presence of the charge stream. After activation (at the same conditions as prevail when activation is carried out in the charge stream), the compatible oil containing the now activated metal may be admitted to the charge stream in amount sufficient to provide therein activated oil-miscible metal compound in desired amount.

In still another embodiment, activation may be carried out by subjecting the charge hydrocarbon oil containing the oil-miscible metal compound to hydroconversion conditions including temperature of 370°-462°C (700°F-850°F), preferably about 399°-432°C (750°F-810°F), say 427°C (800°F) at hydrogen partial pressure of about 3.5-34.5 MPa (500-5000 psig) preferably about 10.4-13.9 MPa (1500-2000 psig), say 13.9 MPa (2000 psig) - in the presence of a mercaptan but in the absence of heterogeneous hydroconversion catalyst.

In the preferred embodiment, activation may be carried out during hydroconversion i.e. in the presence of the heterogeneous, hydroconversion catalyst, hydrogen, and mercaptan.

Hydroconversion is carried out in the presence of solid heterogeneous catalyst containing, as a hydrogenating component, a metal of Group IV-B, V-B, VI-B, VII-B, or VIII on a support which may typically contain carbon or an oxide of aluminum, silicon, titanium, magnesium, or zirconium. Preferably the catalyst may contain a metal of Group VI-B and VIII - typically nickel and molybdenum.

When the metal is a Group IV-B metal, it may be titanium (Ti), zirconium (Zr), or hafnium (Hf).

When the metal is a Group V-B metal, it may be vanadium (V), niobium (Nb), or tantalum (Ta).

When the metal is a Group VI-B metal, it maybe chromium (Cr), molybdenum (Mo), or tungsten (W).

When the metal is a Group VII-B metal, it maybe manganese (Mn) or rheniun (Re).

When the metal is a Group VIII metal, it may be a non-noble metal such as iron (Fe), cobalt (Co), or nickel (Ni) or a noble metal such as ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), or platinum (Pt).

The solid heterogeneous catalyst may also contain, as a promoter, a metal of Groups I-A, I-B, II-A, II-B, or V-A.

When the promoter is a metal of Group I-A, it may preferably be sodium (Na) or potassium (K).

When the promoter is a metal of Group IB, it may preferably be copper (Cu).

When the promoter is a metal of Group II-A, it may be beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), or radium (Ra).

When the promoter is a metal of Group II-B, it may be zinc (Zn), cadmium (Cd), or mercury (Hg).

When the promoter is a metal of Group V-A, it may preferably be arsenic (As), antimony (Sb), or bismuth (Bi).

The hydrogenating metal may be loaded onto the solid heterogeneous catalyst by immersing the catalyst support in solution (e.g. ammonium heptamolybdate) for 2-24 hours, say 24 hours, followed by drying at 15.5°-149°C (60°F-300°F), say 93°C (200°F) for 1-24 hours, say 8 hours and calcining for 1-24 hours, say 3 hours at 399°-594°C (750°F-1100°F), say 499°C (930°F).

The promoter metal may preferably be loaded onto the solid heterogeneous catalyst by immersing the catalyst support (preferably bearing the calcined hydrogenating metal - although they may be added simultaneously or in any order) in solution (e.g. bismuth nitrate) for 2-24 hours, say 24 hours, followed by drying at 15.5°-149°C (60°F-300°F), say 93°C (200°F) for 1-24 hours, say 3 hours, and calcining at 299-594°C (570°F-1100°F), say 399°C (750°F) for 1-12 hours, say 3 hours.

The solid heterogenous catalyst employed in the method of this invention may be characterized by a Total Pore Volume of 0.2-1.2 cc/g, say 0.77 cc/g; a Surface Area of 50-500 m^2/g, say 280 m^2/g; and a Pore

Size Distribution as follows:

Pore Diameter Å	Volume cc/g
30-100	0.15-0.8, say 0.42
100-1000	0.10-0.50, say 0.19
1000-10,000	0.01-0.40, say 0.16

In another embodiment, it may have a pore size distribution as follows:

Pore Diameter Å	Pore Volume cc/g	Typical
>250	0.12-0.35	0.28
>500	0.11-0.29	0.21
>1500	0.08-0.26	0.19
>4000	0.04-0.18	0.11

The solid heterogeneous catalyst typically may contain 4-30w%, say 9.5w% Mo, 0-6w%, say 3.1w% Ni and 0-6w%, say 3.1w% of promoter metal e.g. bismuth. LHSV in the hydroconversion reactors may be 1-2, say 0.7. Preferably the heterogeneous catalyst may be employed in the form of extrudates of diameter of 0.7-6.5mm, say 1mm and of length of 0.2-25mm, say 5mm.

Hydroconversion may be carried out in a fixed bed, a moving bed, a fluidized bed, or preferably an ebullated bed.

It is a feature of the process of this invention that hydroconversion may be carried out in one or more beds. It is found that the active form of the catalyst is formed in or accumulates in the first of several reactors; and accordingly increases in conversion and heteroatom removal activities appear to occur in the first of several reactors.

Effluent from hydroconversion is typically characterized by an increase in the content of liquids boiling below 538°C (1000°F). Commonly the w% conversion of the 538°C (1000°F) + boiling material is 30%-90%, say 67% which is typically 5%-25%, say 12% better than is attained by the prior art techniques.

It is a feature of this invention that it permits attainment of improved removal of sulfur (HDS Conversion), of nitrogen (HDN Conversion), and of metals (HDNi and HDV Conversion). Typically HDS Conversion may be 30-90%, say 65% which is 1%-10%, say 4% higher than the control runs. Typically HDN Conversion may be 20%-60%, say 45% which is 1%-10%, say 4% higher than control runs. Typically HDNi plus HDV Conversion may be 70%-99%, say 90% which is 5%-20%, say 13% higher than control runs.

Practice of the method of this invention will be apparent to those skilled in the art from the following wherein, as elsewhere in this specification unless otherwise stated, all parts are parts by weight. An asterisk designates a control example.

EXAMPLE

In this Example which represents the best mode presently known of carrying out the method of this invention charge hydrocarbon is a blend of vacuum resid derived from Alaskan North Slope (59v%), Arabian Medium (5v%), Arabian Heavy (27v%), and Bonny Light (9v%).

The solid heterogeneous catalyst is commercially available hydrotreating catalyst (sold by Criterion Catalyst Company as HDS-1443B catalyt) containing 2.83w% nickel and 8.75w% molybdenum on alumina. This catalyst is 0.8 mm (1/32") diameter extrudates ~ 5mm long of Surface Area 285.2 m^2/g and Total Pore Volume of 0.78 cc/g. Pore Size Distribution is: 0.28 cc/g >250A; 0.21 cc/g >500A; 0.19 cc/g >1500A; 0.11 cc/g >4000A.

In this Example, there is added to the hydro carbon charge, molybdenum naphthenate in amount to provide 60 ppm molybdenum metal and cobalt napthenate to provide 13 ppm cobalt metal. The catalyst is activated in situ during hydroconversion at 418°C (785°F) and partial pressure of hydrogen of 13.9 MPa (2000 psig). Hydrogen Feed is 1061 Nm^3/m^3 (6300 SCFB). Charge LHSV is 0.4-1 hr^{-1}.

Results are set forth in the following Table which shows conversion of 538°C (1000°F), HDS Conversion, HDV Conversion, HDNi Conversion, and Cyclohexane Insolubles - all expressed in w%.

Comparative tests were made using no molybdenum or cobalt promoter, and using molybdenum promoter alone.

	Example		
	A*	B*	C
Mo Conc (ppm)	0	60	60
Co CconC (ppm)	0	0	13
538 °C + (1000 °F +) Conv.	44.7	51.4	51.2
HDS	61.0	66.2	67.9
HDV	73.9	80.2	84.2
HDNi	52.3	58.6	62.7
Cyclohexane Insol.	2.9	2.2	2.1

From the above Table, the following conclusion may be drawn:

(1) Addition of a small amount of cobalt with the molybdenum has a synergistic impact on hetero atom removal (HDS, HDV, HDNi).

(2) The addition of cobalt and molybdenum shows a further decrease in coke content compared to use of molybdenum alone.

Although this invention has been illustrated by reference to specific embodiments, it will be apparent to those skilled in the art that various charges and modifications may be made which clearly fall within the scope of the appended claims.

Claims

1. A method of catalytically hydroconverting a charge hydrocarbon oil containing from 50-98 weight percent of components boiling above 538 °C (1000 °F) to convert from 30-90 weight percent thereof to components boiling below 538 °C (1000 °F), which comprises

   passing said charge hydrocarbon oil containing from 50-98 weight percent of components boiling above about 538 °C (1000 °F) into contact with (i) a solid heterogenous catalyst containing, as a hydrotreating component, a metal of Groups IV-B, V-B, VI-B, VII-B, or VIII on a support and (ii) as an oil-soluble catalyst a compound of molybdenum and a compound of cobalt;

   maintaining said charge- hydrocarbon oil in said conversion zone at conversion conditions in the presence of hydrogen and mercaptan until from 30-90 weight percent of said components boiling above 538 °C (1000 °F) are converted to components boiling below 538 °C (1000 °F); and

   recovering said converted oil.

2. A method as claimed in Claim 1, wherein said oil-soluble catalyst contains molybdenum naphthenate and cobalt naphthenate.

3. A method as claimed in Claim 1 or Claim 2, wherein said oil-soluble catalyst is soluble in the charge hydrocarbon in an amount of at least 0.01 grams per 100 g of charge hydrocarbon.

4. A method as claimed in any one of Claims 1 to 3, wherein said oil-soluble catalyst is activated prior to admission to said conversion zone.

5. A method as claimed in Claim 4, wherein activation is effected by heating to 204-446 °C (400 °F-835 °F) at 3.5-34.5 MPa (500-5000 psig) partial pressure of hydrogen in the presence of mercaptan or in the presence of an oil which is miscible with said charge oil.

6. A method as claimed in any one of Claims 1 to 5, wherein said oil-soluble catalyst is activated during said conversion.

7. A method as claimed in any one of Claims 1 to 8, wherein said heterogenous catalyst contains (i) as hydrogenating component, a metal of Groups IV-B, V-B, VI-B, VII-B, or VIII and (ii) as a promoter a metal of Group I-A, I-B, II-A, II-B, or V-A.

8. A method as claimed in Claim 7, wherein said heterogenous catalyst contains nickel and molybdenum or alumina.

Patentansprüche

1. Ein Verfahren zur katalytischen Hydroumwandlung eines Chargen-Kohlenwasserstofföls, das 50-98 Gewichtsprozent Komponenten enthält, die oberhalb von 538 °C (1000 °F) sieden, um von 30-90 Gewichtsprozent davon in Komponenten umzuwandeln, die unterhalb von 538 °C (1000 °F) sieden, welches umfaßt, daß
   besagtes Chargen-Kohlenwasserstofföl, das von 50-98 Gewichtsprozent Komponenten enthält, die oberhalb von etwa 538 °C (1000 °F) sieden, in Kontakt mit (i) einem festen heterogenen Katalysator, der, als eine Hydrobehandlungskomponente, ein Metall der Gruppen IV-B, V-B, VI-B, VII-B oder VIII auf einem Träger enthält, und (ii), als einem öllöslichen Katalysator, einer Molybdänverbindung und eine Cobaltverbindung geleitet wird;
   besagtes Chargen-Kohlenwasserstofföl in besagter Umwandlungszone bei Umwandlungsbedingungen in der Gegenwart von Wasserstoff und Mercaptan gehalten wird, bis von 30-90 Gewichtsprozent besagter Komponenten, die oberhalb von 538 °C (1000 °F) sieden, in Komponenten umgewandelt sind, die unterhalb von 538 °C (1000 °F) sieden; und
   besagtes umgewandeltes Öl gewonnen wird.

2. Ein Verfahren nach Anspruch 1, wobei besagter öllöslicher Katalysator Molybdännaphthenat und Cobaltnaphthenat enthält.

3. Ein Verfahren nach Anspruch 1 oder Anspruch 2, wobei besagter öllöslicher Katalysator im Chargen-Kohlenwasserstoff in einer Menge von wenigstens 0,01 Gramm pro 100 g Chargen-Kohlenwasserstoff löslich ist.

4. Ein Verfahren nach einem der Ansprüche 1 bis 3, wobei besagter öllöslicher Katalysator vor der Zuführung zu besagter Umwandlungszone aktiviert wird.

5. Ein Verfahren nach Anspruch 4, wobei die Aktivierung durch Erhitzen auf 204-446 °C (400 °F-835 °F) bei 3,5-34,5 MPa (500-5.000 psig) Wasserstoffpartialdruck in der Gegenwart von Mercaptan oder in der Gegenwart eines Öls, das mit besagtem Chargenöl mischbar ist, bewirkt wird.

6. Ein Verfahren nach einem der Ansprüche 1 bis 5, wobei besagter öllöslicher Katalysator während besagter Umwandlung aktiviert wird.

7. Ein Verfahren nach einem der Ansprüche 1 bis 6, wobei besagter heterogener Katalysator (i), als Hydrierungskomponente, ein Metall der Gruppen IV-B, V-B, VI-B, VII-B oder VIII und (ii), als einen Beschleuniger, ein Metall der Gruppe I-A, I-B, II-A, II-B oder V-A enthält.

8. Ein Verfahren nach Anspruch 7, wobei besagter heterogener Katalysator Nickel und Molybdän auf Aluminiumoxid enthält.

Revendications

1. Procédé d'hydroconversion catalytique d'une huile d'hydrocarbure de charge contenant de 50 à 98 % en poids de constituants bouillant au-dessus de 538 °C (1000 °F) pour transformer de 30 à 90 % en poids de celle-ci en constituants bouillant au-dessous de 538 °C (1000 °F), qui comprend
   le fait d'amener cette huile d'hydrocarbure de charge contenant de 50 à 98 % en poids de constituants bouillant au-dessus d'environ 538 °C (1000 °F) en contact avec (i) un catalyseur hétérogène solide, contenant, comme constituant d'hydrotraitement, un métal des groupes IV-B, V-B, VI-B, VII-B, ou VIII sur un support et (ii) comme catalyseur oléosoluble, un composé du molybdène et un composé du cobalt ;
   le fait de maintenir cette huile d'hydrocarbure de charge dans cette zone de conversion, dans des conditions de conversion, en présence d'hydrogène et d'un mercaptan jusqu'à ce que de 30 à 90 % en poids de ces constituants bouillant au-dessus de 538 °C (1000 °F) soient transformés en constituants bouillant au-dessous de 538 °C (1000 °F) ; et

le fait de récupérer cette huile transformée.

2. Procédé selon la revendication 1, dans lequel le catalyseur oléosoluble contient du naphténate de molybdène et du naphténate de cobalt.

3. Procédé selon les revendications 1 ou 2, dans lequel ce catalyseur oléosoluble est soluble dans l'hydrocarbure de charge dans une quantité d'au moins 0,01 g pour 100 g d'hydrocarbure de charge.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel ce catalyseur oléosoluble est activé avant l'admission dans cette zone de conversion.

5. Procédé selon la revendication 4, dans lequel l'activation est effectuée par chauffage à 204-446 °C (400 °F-835 °F) sous 3,5-34,5 MPa (500-5 000 psig) de pression partielle d'hydrogène en présence de mercaptan ou en présence d'une huile qui est miscible à cette huile de charge.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel ce catalyseur oléosoluble est activé au cours de cette conversion.

7. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel ce catalyseur hétérogène contient (i) comme constituant d'hydrogénation, un métal des groupes IV-B, V-B, VI-B, VII-B ou VIII et (ii) comme promoteur, un métal des groupes I-A, I-B, II-A, II-B ou V-A.

8. Procédé selon la revendication 7, dans lequel ce catalyseur hétérogène contient du nickel et du molybdène ou de l'alumine.