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(54) Hydroconversion process.

(57) A heavy hydrocarbon is hydrotreated in the presence of a supported heterogeneous catalyst bearing IV-B, V-B, VI-B, VII-B, or VIII metal and (ii) a miscible/soluble IV-B, V-B, VI-B, VII-B, or VIII metal salt catalyst.

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FIELD OF THE INVENTION

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 1000°F+ charge to lower boiling products.

BACKGROUND OF THE INVENTION

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:

USP 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.

USP 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.

USP 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.

USP 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.

USP 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.

USP 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.

USP 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.

USP 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.

USP 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).

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

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

USP 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.

USP 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.

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

USP 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.

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

USP 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.

STATEMENT OF THE INVENTION

In accordance with certain of its aspects, this invention is directed to a method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling above about 1000°F to convert a substantial portion thereof to components boiling below 1000°F which comprises

passing said charge hydrocarbon oil containing a substantial quantity of components boiling above about 1000°F into contact with (i) a solid heterogeneous catalyst containing, as a hydrotreating component, a metal of Group IV-B, V-B, VI-B, VII-B, or VIII on a support and (ii) as an oil-soluble catalyst a compound of a metal of Group IV-B, V-B, VI-B, VII-B or VIII in a conversion zone;

maintaining said charge hydrocarbon oil containing a substantial quantity of components boiling above about 1000°F in said conversion zone at conversion conditions in the presence of hydrogen and mercaptan as a substantial portion of said components boiling above about 1000°F are converted to components boiling below 1000°F thereby forming product containing a substantial portion of components boiling below about 1000°F; and

recovering said product containing a substantial portion of components boiling below about 1000°F.

DESCRIPTION OF THE INVENTION

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 650°F. This process is particularly useful to treat charge hydrocarbons containing a substantial quantity of components boiling above about 1000°F to convert a substantial portion thereof to components boiling below 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
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 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 19.86%.

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 700°F-850°F, preferably about 750°F-810°F, say 800°F at hydrogen partial pressure of about 500-5000 psig, preferably about 1500-2500 psig, say 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 metal of Group IV-B, V-B, VI-B, VII-B or VIII of the Periodic Table.

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

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

When the metal is a Group VI metal, it may be chromium (Cr), molybdenum (Mo), or tungsten (W).

When the metal is a Group VII metal, it may be manganese (Mn) or rhenium (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).

Preferably the metal is a Group VI metal - most preferably molybdenum (Mo).

The compound of the metal is an oil-soluble compound 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
    iron 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
    iron xylene sulfonate
(vi) metal salts of sulfinic acids
    molybdenum benzene sulfinate
    iron benzene sulfinate
(vii) metal salts of phosphoric acids
    molybdenum phenyl phosphate
(viii) metal salts of mercaptans
    iron octyl mercaptide
    cobalt hexyl mercaptide
(ix) metal salts of phenols
    cobalt phenolate
    iron phenolate
(x) metal salts of polyhydroxy aromatic compounds
    iron catecholate
    molybdenum resorcinate
(xi) organo metallic compounds

molybdenum hexacarbonyl
iron hexacarbonyl
cyclopentadienyl molybdenum tricarbonyl

(xii) metal chelates
ethylene diamine tetra carboxylic acid-diferous salt

(xiii) metal salts of organic amines
cobalt salt of pyrrole

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

It is found that the impact of the oil-soluble compound may be augmented by use of compounds of more than one metal. For example if molybdenum (e.g. as the naphthenate) is employed, it is found desirable to add an additional quantity of cobalt (e.g. as the naphthenate). This 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 compound derived from a metal of Group IV-B, V-B, VI-B, VII-B, or VIII 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 60°F-300°F, say 200°F. The mixture is activated by heating to 400°F-835°F, typically 500°F-700°F, say 600°F at partial pressure of hydrogen of 500-5000 psig, typically 1000-3000 psig, say 2000 psig and at partial pressure of a gaseous mercaptan of 5-500 psig, typically 10-300 psig, say 50 psig. Total pressure may be 500-5500 psig, typically 1000-3300 psig, say 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, etc. aromatic mercaptans; dimethyl disulfide, carbon disulfide, etc.

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 700°F-850°F, preferably about 750°F-810°F, say 800°F at hydrogen partial pressure of about 500-5000 psig, preferably about 1500-2000 psig, say 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 rhenium (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 60°F-300°F, say 200°F for 1-24 hours, say 8 hours and calcining for 1-24 hours, say 3 hours at 750°F-1100°F, say 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 60°F-300°F, say 200°F for 1-24 hours, say 3 hours, and calcining at 570°F-1100°F, say 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 1000°F. Commonly the w% conversion of the 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.

DESCRIPTION OF SPECIFIC EMBODIMENTS

EXAMPLE I

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 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 160 ppm molybdenum metal. The catalyst is activated in situ during hydroconversion at 785°F and partial pressure of hydrogen of 2000 psig. Hydrogen Feed is 6300 SCFB. Charge LHSV is 0.4-1 hr^{-1}.

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

EXAMPLES II-V*

In this series of Examples, the procedure of Example I is duplicated except that the concentration of molybdenum (ppm) is varied. Temperature of operation is 785°F in Examples I-V*.

TABLE II

Molybdenum ppm	I 160	II 120	III 60	IV 30	V* 0
1000°F + Conv	62.0	59.5	51.4	49.3	44.7
HDS	71.4	67.0	66.2	64.5	61.0
HDV	84.4	82.2	80.2	78.1	73.9
HDNi	67.9	61.9	58.6	56.4	52.3
Cyclohexane Insol.	-	2.1	2.2	2.2	2.9

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

(i) In all cases, Examples I-IV, carried out in accordance with the method of this invention, show an improvement in 1000°F+ Conversion, hydrodesulfurization (HDS) Conversion, hydrodevanadiumizing (HDV) Conversion, hydrodenickelizing (HDNi) Conversion, and coke content as measured by Cyclohexane Insolubles.

(ii) The instant invention shows improvement in 1000°F+ Conversion of 10% to 39%;

(iii) the instant invention shows improvement in HDS Conversion of 5%-17%;

(iv) the instant invention shows improvement in HDV Conversion of 6%-14%; and

(v) the instant invention shows improvement in HDNi Conversion of 20%-47%;

(vi) the instant invention shows a decrease in coke content by about 20-50%.

EXAMPLES VI*-VII

In this series of runs, the procedure of Examples I-V is followed except:

(i) Temperature of operation is 800°F;

(ii) In Example VII, cobalt naphthenate is added in amount to give 160 ppm of cobalt metal (and no molybdenum naphthenate is present);

(iii) Example VI* otherwise duplicates Example V* except for the temperature of operation.

TABLE III

	Example	
Cobalt ppm	VI*	VII
	0	160
1000°F+ Conv	59.6	65.1
HDS	67.0	71.0
HDV	78.0	79.2
HDNi	56.3	66.4
Cyclohexane Insol.	6.3	4.1

From the above Table, it appears that cobalt naphthenate is an effective oil-miscible catalytic metal, although it appears to be less preferred than molybdenum.

EXAMPLE VIII

In this Example, the procedure of Example I is followed except that, in place of molybdenum naphthenate, there is added molybdenum hexacarbonyl to yield 100 ppm of molybdenum metal. Temperature of operation is 800°F.

TABLE IV

	Ex VI*	Ex VIII
$Mo(Co)_6$ (wppm)	0	100
1000°F+ Conv	59.6	72.2
HDS	67.0	69.2
HDV	78.0	83.2
HDNi	56.3	64.2
Cyclohexane Insol	6.3	3.7

From the above Table, it may be noted that:
(i) Example VIII, carried out in accordance with the method of the invention, shows significant improvement in 1000°F Conversion by 12.4%;
(ii) Removal of vanadium and nickel is shown by the HDV and HDNi values which increase respectively by 5.2% and 7.9%; and
(iii) Coke formation is reduced by 41% - from 6.3 down to 3.7 as is evidenced by Cyclohexane Insolubles.

EXAMPLE IX

In this Example IX, the procedure of Example I is followed except that the supported catalyst (Ni/Mo/Alumina in Example I) did not bear Ni or Mo i.e. it was only non-catalytic alumina.

TABLE V

	Example	
	III	IX
Mo (wppm)	60	60
Temp °F	785	785
Solid Catalyst	$Ni/Mo/Al_2O_3$	Al_2O_3
1000°F+Conv	51.4	41.7
HDS	66.2	34.9
HDV	80.2	48.6
HDNi	58.6	48.6
Cyclohexane Insol	2.2	4.1

From the above it is apparent that presence of the catalytic metals on the solid catalyst is necessary to attain improvements.

Example X

In this Example X, the procedure of Example III is followed except that 13 ppm cobalt (as cobalt naphthenate) is blended with 60 ppm molybdenum (as molybdenum naphthenate).

TABLE VI

	Example		
	V	III	X
Mo Conc (ppm)	0	60	60
Co CconC (ppm)	0	0	13
1000F+ 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 preferred molybdenum has a synergistic impact on hetero atom removal (HDS, HDV, HDNi).

(2) The addition of cobalt shows a further decrease in coke content.

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 invention.

Claims

1. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling above about 1000°F to convert a substantial portion thereof to components boiling below 1000°F which comprises

passing said charge hydrocarbon oil containing a substantial quantity of components boiling above about 1000°F into contact with (i) a solid heterogenous catalyst containing, as a hydrotreating component, a metal of Group IV-B, V-B, VI-B, VII-B, or VIII on a support and (ii) as an oil-soluble catalyst a compound of a metal of Group IV-B, V-B, VI-B, VII-B or VIII in a conversion zone;

maintaining said charge hydrocarbon oil containing a substantial quantity of components boiling above about 1000°F in said conversion zone at conversion conditions in the presence of hydrogen and mercaptan as a substantial portion of said components boiling above about 1000°F are converted to components boiling below 1000°F thereby forming product containing a substantial portion of components boiling below about 1000°F; and

recovering said product containing a substantial portion of components boiling below about 1000°F.

2. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling, above about 1000°F as claimed in Claim 1 wherein said oil-soluble catalyst is a salt of molybdenum.

3. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling, above about 1000°F as claimed in Claim 1 wherein said oil-soluble catalyst contains a salt of molybdenum and a salt of cobalt.

4. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling, above about 1000°F as claimed in Claim 1 wherein said oil-soluble catalyst contains molybdenum naphthenate and cobalt naphthenate.

5. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling, above about 1000°F as claimed in Claim 1 wherein said oil-soluble catalyst is soluble in the charge hydrocarbon in amount of at least 0.01 grams per 100 g of charge hydrocarbon.

6. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling, above about 1000°F as claimed in Claim 1 wherein said oil-soluble catalyst is activated prior to admission to said conversion zone.

7. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling, above about 1000°F as claimed in Claim 1 wherein said oil-soluble catalyst is activated prior to admission to said activation zone, by heating to 400°F-835°F at 500-5000 psig partial pressure of hydrogen in the presence of mercaptan.

8. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling, above about 1000°F as claimed in Claim 1 wherein said oil-soluble catalyst is activated prior to admission to said activation zone, by heating to 400°F-835°F at 500-5000 psig partial pressure of hydrogen in the presence of an oil which is miscible with said charge oil.

9. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling, above about 1000°F as claimed in Claim 1 wherein said oil-soluble catalyst is activated at conversion conditions.

10. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling, above about 1000°F as claimed in Claim 1 wherein said oil-soluble catalyst is activated during said conversion.

11. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling, above about 1000°F as claimed in Claim 1 wherein said heterogeneous 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.

12. The method of catalytically hydroconverting a charge hydrocarbon oil containing a substantial quantity of components boiling above about 1000°F to convert a substantial portion thereof to components boiling below 1000°F which comprises

passing said charge hydrocarbon oil containing a substantial quantity of components boiling above about 1000°F into contact with (i) a solid heterogeneous catalyst containing nickel and molybdenum on alumina and (ii) as an oil-soluble catalyst, molybdenum naphthenate, in a conversion zone;

maintaining said charge hydrocarbon oil containing a substantial quantity of comoponents boiling above about 1000°F in said conversion zone at conversion conditions including temperature of 700°F-850°F at hydrogen partial pressure of about 500-5000 psig in the presence of mercaptan, as a substantial portion of said components boiling above about 1000°F are converted to components boiling below 1000°F thereby forming product containing a substantial portion of components boiling below about 1000°F; and

recovering product containg a substantial portion of components boiling below about 1000°F.

13. A catalyst characterized by its ability to effect catalytic hydroconversion of a charge hydrocarbon containing a substantial quantity of components boiling above about 1000°F to a product containing a substantial portion of components boiling below about 1000°F which comprises

(i) a solid heterogeneous catalyst containing a metal of Group IV-B, V-B, VI-B, VII-B, or VIII on a support; and

(ii) an oil souble catalyst containing a component of a metal of Group IV-B, V-B, VI-B, VII-B, or VIII.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 4001

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-3 237 037 (CHEVRON) * claims 1,10,23 * * page 14, line 18 - line 35 * * page 16, line 27 - page 17, line 8 * ---	1,2,3,4, 5,11,13	C10G47/02
A	EP-A-0 064 429 (IFP) * claims 1,3 * -----	1,6,7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C10G B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 AUGUST 1992	OSWALD DE HERDT

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
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