

## PROCESS FOR TREATING A HYDROCARBON-CONTAINING FEED

### Field of the Invention

The present invention is directed to a process for treating a hydrocarbon-containing feedstock.

### Background of the Invention

Increasingly, resources such as heavy crude oils, bitumen, tar sands, shale oils, and hydrocarbons derived from liquefying coal are being utilized as hydrocarbon sources due to decreasing availability of easily accessed light sweet crude oil reservoirs. These resources are disadvantaged relative to light sweet crude oils, containing significant amounts of heavy hydrocarbon fractions such as residue and asphaltenes, and often containing significant amounts of sulfur, nitrogen, metals, poly-aromatic hydrocarbon compounds, and/or naphthenic acids. The disadvantaged crudes typically require a considerable amount of upgrading, for example by cracking, hydrotreating, and fluidized catalytic cracking (FCC), in order to obtain more valuable hydrocarbon products. Cracking other than FCC is generally effected by treating a crude or a heavy fraction of a crude at a temperature ranging from 375°C to 500°C, optionally in the presence of a catalyst (catalytic cracking) and optionally in the presence of hydrogen (hydrocracking), and results in the decomposition of larger and heavier molecular weight constituents to smaller, lighter molecular weight compounds by cleavage of carbon-carbon linkages. Hydrotreating is generally effected by treating a crude or a fraction of a crude at a temperature ranging from 260°C to 400°C in the presence of hydrogen, and optionally in the presence of a catalyst, and results in reduction of sulfur, nitrogen, oxygen, and metals in the crude. FCC is generally effected by treating a heavy hydrotreated, cracked crude fraction having a boiling point of at least 343°C (650°F) at a temperature of at least 500°C with a fluidized cracking catalyst to further crack the hydrocarbons to produce naphtha, kereone, and diesel hydrocarbon fractions.

In conventional processes for upgrading disadvantaged heavy crude oil and bitumen feedstocks, the feedstocks are fractionated by distillation to separate the lightest distillate fractions, containing lower-boiling hydrocarbons, by atmospheric pressure distillation. Heavier fractions containing higher boiling fractions, called vacuum gas oils, are separated by subsequent vacuum distillation. The heaviest fraction called residue or pitch containing the highest boiling, non-distillable hydrocarbons is produced as the bottoms fraction from the vacuum distillation. Lighter hydrocarbons may be recovered from the vacuum gas oils

and residue fractions by fluid catalytic cracking or coking. Typically, vacuum gas oils are catalytically cracked in a Fluidized Catalytic Cracker (FCC) to produce lighter hydrocarbons, non-condensable hydrocarbon gases, and coke, where the lighter hydrocarbons may be blended with other distillate fractions to make fuel products.

- 5 Residue may be cracked in a coker or hydrocracked in a residue hydrocracker to produce lighter hydrocarbon fractions, heavier residue fluid, non-condensable gases, and coke, where the lighter hydrocarbon fractions may be blended with other distillate fractions to make fuel products, and the residue fluid may be further cracked in a Residue Fluidized Catalytic Cracker (RFCC) to produce more light hydrocarbons. The separated fractions
- 10 may be hydrotreated after atmospheric or vacuum distillation to reduce sulfur, nitrogen, and metals content of the fractions since heteroatoms and metals are undesirable in fuel products produced from the light distillate fractions, and act as hydrocracking catalyst poisons in the vacuum gas oil fraction and residue fraction.

- Typically in a conventional process for upgrading a disadvantaged heavy crude
- 15 feed or bitumen a maximum of about 70%-75% of the carbon content of the disadvantaged crude feed material is captured as non-residue, non-asphaltenic hydrocarbons that are liquid at standard temperature and pressure (STP—25°C, 0.101 MPa), the remainder of the carbon content being produced as gaseous hydrocarbons and carbonaceous solids such as coke. Furthermore, in a conventional process a large percentage of the sulfur is
- 20 concentrated in high molecular weight refractory heteroatomic hydrocarbons after hydrocracking the hydrotreated heavy fractions, requiring a deep hydrotreatment step to remove of most or all of the sulfur prior to further cracking by FCC so that the sulfur does not poison the FCC catalyst, where a “deep” hydrotreatment step involves hydrotreating at a hydrogen partial pressure of at least 10.3 MPa (1500 psi).

- 25 Alternatively, disadvantaged heavy crude oil and bitumen feedstocks may be hydrotreated and catalytically hydrocracked to produce an upgraded hydrocarbon product without initially separating the feedstock into fractions. Current “whole crude” heavy oil or bitumen feedstock upgrading processes also suffer from the production of excess coke and gas, and typically a maximum of about 70%-75% of the carbon content of the
- 30 disadvantaged crude feed material is captured as non-residue, non-asphaltenic hydrocarbons that are liquid at STP. Current “whole crude” heavy oil or bitumen feedstock upgrading processes also create substantial quantities of refractory sulfur and nitrogen heteroatomic hydrocarbon compounds, which must be removed by deep hydrotreating if the heavy hydrocarbons of the product are to be further cracked by FCC.

Formation of coke and refractory sulfur compounds is a particular problem in upgrading and refining heavy crudes and bitumen, whether as “whole crude” feedstocks or as fractions of a heavy crude or bitumen, that has limited the yield of desirable liquid hydrocarbons from such feedstocks. Cracking or hydrocracking, either thermal or catalytic, is required to obtain a high yield of hydrocarbons that are liquid at STP from a heavy crude or bitumen due to the large quantity of high molecular weight, heavy hydrocarbons such as residue and asphaltenes that are present in such feedstocks. Cracking hydrocarbons involves breaking bonds of the hydrocarbons, particularly carbon-carbon bonds, thereby forming two hydrocarbon radicals for each carbon-carbon bond that is cracked in a hydrocarbon molecule. Numerous reaction paths are available to the cracked hydrocarbon radicals, the most important being: 1) reaction with a hydrogen donor to form a stable hydrocarbon molecule that is smaller in terms of molecular weight than the original hydrocarbon from which it was derived; and 2) reaction with another hydrocarbon or another hydrocarbon radical to form a hydrocarbon molecule larger in terms of molecular weight than the cracked hydrocarbon radical—a process called annealation. The first reaction is desired, it produces hydrocarbons of lower molecular weight than the heavy hydrocarbons contained in the feedstock— and preferably produces naphtha, distillate, or gas oil hydrocarbons. The second reaction is undesired and leads to the production of coke and refractory sulfur-containing heteroatomic hydrocarbons. Furthermore, the second reaction is autocatalytic since the cracked hydrocarbon radicals are reactive with the growing coke particles.

Furthermore, sulfur tends to be concentrated in high molecular weight heteroatomic hydrocarbons in heavy crude oil and bitumen feedstocks. These molecules are also particularly susceptible to annealation due to the large quantity of large, high molecular weight sulfur-containing heteroatomic hydrocarbons in heavy oil and bitumen feedstocks. As a result, significant quantities of large, high molecular weight refractory sulfur-containing heteroatomic hydrocarbons are formed in conventional cracking processes when utilizing a heavy crude oil or bitumen as a feedstock. These sulfur compounds typically poison FCC catalysts that are utilized to further crack heavy hydrocarbons into more desirable light hydrocarbons.

Therefore, hydrocarbon-containing feedstocks having a relatively high concentration of heavy hydrocarbon molecules therein are particularly susceptible to coking and the formation of refractory high molecular weight sulfur-containing heteroatomic hydrocarbons due to the presence of a large quantity of high molecular

weight hydrocarbons and heteroatoms in the feedstock with which cracked hydrocarbon radicals may combine to form coke or refractory sulfur-containing hydrocarbons. As a result, yields of non-residue, non-asphaltenic hydrocarbons that are liquid at STP from heavy crude oils and bitumen have been limited by coke formation induced by the cracking reaction itself. A desirable characteristic of coking is that it tends to concentrate large aromatic ring structures, sulfur, nitrogen, and metals in the coke—leaving cracked, lighter hydrocarbon fragments of improved quality relative to the residue fraction of the feedstock—but this concentration effect is obtained at considerable expense in liquid product yield (at STP).

Numerous catalysts have been developed for use in processes for hydroprocessing disadvantaged hydrocarbon feedstocks, either as “whole crude” feeds or as heavy fractions of a heavy crude oil or bitumen, however, such catalysts have not eliminated problems associated with coking and production of refractory sulfur compounds, and catalyst activity may be significantly reduced over time by accumulation of coke on the catalyst.

Conventional hydrocracking catalysts are generally selected to possess acidic properties that catalytically facilitate cracking by promoting the formation of cracked radical carbocation hydrocarbon species from hydrocarbons in the feedstock. Such catalysts typically include an acidic support, usually formed of alumina, silica, titania, or alumina-silica, on which a Group VIB metal or metal compound and/or a Group VIII metal or metal compound is deposited or interspersed to catalyze hydrogenation of the cracked radical hydrocarbon species. These catalysts likely promote the formation of coke and refractory sulfur compounds since they induce the formation of highly unstable and highly reactive carbocation radical hydrocarbon species without concomitantly hydrogenating the highly reactive carbocation radical hydrocarbon species as they are formed, thereby permitting a portion of the highly reactive radical hydrocarbon species to react with other hydrocarbons, heteroatomic hydrocarbons, or hydrocarbon radicals to form proto-coke or coke, and/or refractory heteroatomic sulfur-containing hydrocarbons.

Improved processes for processing heavy hydrocarbon-containing feedstocks to produce a lighter hydrocarbon-containing crude product are desirable, particularly in which coke formation is significantly reduced or eliminated, the yield of non-residue, non-asphaltenic hydrocarbons that are liquid at STP is increased so that at least 80% --and more preferably at least 90%--of the carbon content in the feed is captured in non-residue, non-asphaltenic hydrocarbons that are liquid at STP, and in which FCC may be conducted upon a heavy hydrocarbon fraction without the necessity of a deep hydrotreating step.

### **Summary of the Invention**

The present invention is directed to a process comprising providing a first hydrocarbon-containing composition comprising, per gram of the first hydrocarbon-containing composition, at least 0.05 grams of hydrocarbons having a boiling point in the range from 25°C up to 204°C, at least 0.1 gram of hydrocarbons having a boiling point in the range from 204°C up to 260°C, at least 0.25 gram of hydrocarbons having a boiling point in the range from 260°C up to 343°C, at least 0.3 gram of hydrocarbons having a boiling point in the range from 343°C to 538°C, at most 0.03 gram of hydrocarbons having a boiling point of greater than 538°C, where the boiling point ranges of the first hydrocarbon-containing composition are as determined by ASTM Method D5307, and from 0.001 to 0.05 gram of sulfur on an atomic basis as determined by ASTM Method D4294, wherein at least 40 wt.% of the sulfur, on an atomic sulfur basis as determined by ASTM Method D4294, is contained in hydrocarbon compounds having a boiling point of less than 343°C as determined by ASTM Method D5307, and at least 40 wt. % of the sulfur contained in hydrocarbon compounds having a boiling point of less than 343°C in the first hydrocarbon-containing composition is contained in benzothiophenic compounds as determined by GC-GC sulfur chemiluminescence;

contacting the first hydrocarbon-containing composition with hydrogen and a catalyst comprising a Column 6 metal of the Periodic Table or a compound thereof at a temperature of from 260°C to 425°C and a pressure of from 3.4 MPa to 27.5 MPa to produce a second hydrocarbon-containing composition;

separating the second hydrocarbon-containing composition into fractions wherein one fraction is comprised of hydrocarbons having a boiling point of from 343°C to 538°C as determined in accordance with ASTM Method D5307; and

contacting the fraction comprised of hydrocarbons having a boiling point of from 343°C to 538°C with a fluidized catalytic cracking catalyst at a temperature of at least 500°C to produce a third hydrocarbon-containing product.

### **Brief Description of the Drawings**

Fig. 1 is a schematic of a system useful for practicing the process of the present invention.

Fig. 2 is a schematic of a system useful for practicing the process of the present invention.

### **Detailed Description of the Invention**

The present invention is directed to a process for treating a hydrocarbon-containing composition having a unique sulfur profile. The hydrocarbon-containing composition (the “first” hydrocarbon-containing composition) is provided by hydrocracking a hydrocarbon-

containing feedstock, particularly a heavy hydrocarbon-containing feedstock such as a heavy crude oil or bitumen that contains at least 20 wt.% of hydrocarbons having a boiling point of greater than 538°C, as determined in accordance with ASTM Method D5307, to produce a liquid hydrocarbon product. The hydrocarbon-containing feedstock is mixed with hydrogen and a metal-containing catalyst having little or no acidity, where the metal-containing catalyst is preferably a Lewis base, at a temperature of from 375°C to 500°C at a pressure of from 6.9 MPa to 27.5MPa to catalytically hydrocrack the hydrocarbon-containing feedstock. Hydrocarbons in the mixture that vaporize at the temperature and pressure of the hydrocracking reaction, including lower molecular weight hydrocarbons initially in the hydrocarbon-containing feedstock and hydrocracked hydrocarbons generated by catalytically hydrocracking hydrocarbons in the hydrocarbon-containing feedstock, are separated from the mixture as a vapor. A hydrocarbon-depleted feed residuum comprising hydrocarbons that are liquid at the temperature and pressure at which the mixing is effected is retained in the mixture, preferably along with the metal-containing catalyst, while the vapor is separated from the mixture. The vapor comprises hydrogen, hydrocarbons that are gaseous at STP, and the first hydrocarbon-containing composition, which is comprised of one or more hydrocarbon compounds that are liquid at STP. Apart from the mixture, the first hydrocarbon-containing composition is hydrotreated to produce a second hydrocarbon-containing composition by contacting the first hydrocarbon-containing composition with a catalyst comprising a Column 6 metal of the Periodic Table, or a compound thereof, at a temperature of from 260°C to 425°C and a pressure of from 3.4 MPa to 27.5 MPa and preferably at most 10.5 MPa. The first hydrocarbon-containing composition may be condensed and separated from the hydrocarbons that are gaseous at STP and hydrogen in the vapor prior to hydrotreating, or the entire vapor containing the first hydrocarbon-containing product may be hydrotreated without separating the first hydrocarbon-containing composition. The hydrotreating step is effective to substantially reduce the sulfur content of the second hydrocarbon-containing composition relative to the first hydrocarbon-containing composition. The second hydrocarbon-containing composition is then separated into fractions, where one of the fractions is a heavy hydrocarbon fraction comprising hydrocarbons having a boiling point of from 343°C (650°F) to 538°C (1000°F). The heavy hydrocarbon fraction is contacted with a fluidized catalytic cracking catalyst at a temperature of at least 500°C to produce a hydrocarbon-containing product. The hydrocarbon-containing product comprises naphtha and distillate (diesel and kerosene) hydrocarbons and hydrocarbons that are gaseous at STP.

The process of the present invention may be effective to substantially reduce the sulfur content of the first hydrocarbon-containing composition. Due to the process for providing the first hydrocarbon-containing composition, the first hydrocarbon-containing composition may have a unique sulfur-containing compound composition. The base-catalyzed hydrocracking step utilized on a heavy hydrocarbon feedstock to provide the first hydrocarbon-containing composition may preferentially convert high molecular weight heteroatomic hydrocarbon compounds to easily hydrotreated sulfur and nitrogen compounds which are subsequently removed by a mild catalytic hydrotreating step.

Certain terms that are used herein are defined as follows:

"Anaerobic conditions" means "conditions in which less than 0.5 vol.% oxygen as a gas is present". For example, a process that occurs under anaerobic conditions, as used herein, is a process that occurs in the presence of less than 0.5 vol.% oxygen in a gaseous form. Anaerobic conditions may be such that no detectable oxygen gas is present.

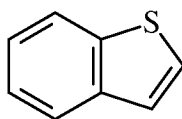
"Aqueous" as used herein is defined as containing more than 50 vol.% water. For example, an aqueous solution or aqueous mixture, as used herein, contains more than 50 vol.% water.

"ASTM" refers to American Standard Testing and Materials.

"Atomic hydrogen percentage" and "atomic carbon percentage" of a hydrocarbon-containing material—including crude oils, crude products such as syncrudes, bitumen, tar sands hydrocarbons, shale oil, crude oil atmospheric residues, crude oil vacuum residues, naphtha, kerosene, diesel, VGO, and hydrocarbons derived from liquefying coal—are as determined by ASTM Method D5291.

"API Gravity" refers to API Gravity at 15.5°C, and as determined by ASTM Method D6822.

"Benzothiophenic compound" refers to a hydrocarbon compound including the structure:



As used in the present application, a benzothiophenic compound includes any hydrocarbon compound containing the above structure, including di-benzothiophenes, naphthenic-benzothiophenes, naphthenic-di-benzothiophenes, benzo-naphtho-thiophenes, naphthenic-benzo-naphthothiophenes, and dinaphtho-thiophenes, in addition to benzothiophene.

"BET surface area" refers to a surface area of a material as determined by ASTM Method D3663.

"Blending" as used herein is defined to mean contact of two or more substances by intimately admixing the two or more substances.

Boiling range distributions for a hydrocarbon-containing material may be as determined by ASTM Methods D5307.

- 5 "Bond" as used herein with reference to atoms in a molecule may refer to a covalent bond, a dative bond, or an ionic bond, dependent on the context.

"Carbon number" refers to the total number of carbon atoms in a molecule.

- "Catalyst" refers to a substance that increases the rate of a chemical process and/or that modifies the selectivity of a chemical process as between potential products of the  
10 chemical process, where the substance is not consumed by the process. A catalyst, as used herein, may increase the rate of a chemical process by reducing the activation energy required to effect the chemical process. Alternatively, a catalyst, as used herein, may increase the rate of a chemical process by modifying the selectivity of the process between potential products of the chemical process, which may increase the rate of the chemical  
15 process by affecting the equilibrium balance of the process. Further, a catalyst, as used herein, may not increase the rate of reactivity of a chemical process but merely may modify the selectivity of the process as between potential products.

- "Catalyst acidity by ammonia chemisorption" refers to the acidity of a catalyst substrate as measured by volume of ammonia adsorbed by the catalyst substrate and subsequently  
20 desorbed from the catalyst substrate as determined by ammonia temperature programmed desorption between a temperature of 120°C and 550°C. For clarity, a catalyst that is decomposed in the measurement of acidity by ammonia temperature programmed desorption to a temperature of 550°C, e.g. a salt, and/or a catalyst for which a measurement of acidity may not be determined by ammonia temperature programmed desorption, e.g. a  
25 liquid, is defined for purposes of the present invention to have an indefinite acidity as measured by ammonia chemisorption. Ammonia temperature programmed desorption measurement of the acidity of a catalyst is effected by placing a catalyst sample that has not been exposed to oxygen or moisture in a sample container such as a quartz cell; transferring the sample container containing the sample to a temperature programmed  
30 desorption analyzer such as a Micrometrics TPD/TPR 2900 analyzer; in the analyzer, raising the temperature of the sample in helium to 550°C at a rate of 10°C per minute; cooling the sample in helium to 120°C; alternately flushing the sample with ammonia for 10 minutes and with helium for 25 minutes a total of 3 times, then measuring the amount of

ammonia desorbed from the sample in the temperature range from 120°C to 550°C while raising the temperature at a rate of 10°C per minute.

"Coke" is a solid carbonaceous material that is formed primarily of a hydrocarbonaceous material and that is insoluble in toluene as determined by ASTM Method D4072.

- 5 "Cracking" as used herein with reference to a hydrocarbon-containing material refers to breaking hydrocarbon molecules in the hydrocarbon-containing material into hydrocarbon fragments, where the hydrocarbon fragments have a lower molecular weight than the hydrocarbon molecule from which they are derived. Cracking conducted in the presence of an atomic hydrogen donor may be referred to as hydrocracking. Cracking effected by
- 10 temperature in the absence of a catalyst may be referred to a thermal cracking. Cracking may also produce some of the effects of hydrotreating such as sulfur reduction, metal reduction, nitrogen reduction, and reduction of TAN.

- "Diesel" refers to hydrocarbons with a boiling range distribution from 260°C up to 343°C (500°F up to 650°F) as determined in accordance with ASTM Method D5307. Diesel
- 15 content may be determined by the quantity of hydrocarbons having a boiling range of from 260°C to 343°C relative to a total quantity of hydrocarbons as measured by boiling range distribution in accordance with ASTM Method D5307.

- "Dispersible" as used herein with respect to mixing a solid, such as a salt, in a liquid is defined to mean that the components that form the solid, upon being mixed with the liquid,
- 20 are retained in the liquid at STP for a period of at least 24 hours upon cessation of mixing the solid with the liquid. A solid material is dispersible in a liquid if the solid or its components are soluble in the liquid. A solid material is also dispersible in a liquid if the solid or its components form a colloidal dispersion or a suspension in the liquid.

- "Distillate" or "middle distillate" refers to hydrocarbons with a boiling range distribution
- 25 from 204°C up to 343°C (400°F up to 650°F). Distillate content is as determined by ASTM Method D5307. Distillate may include diesel and kerosene.

"Hydrogen" as used herein refers to molecular hydrogen unless specified as atomic hydrogen.

- "Insoluble" as used herein refers to a substance a majority (at least 50 wt.%) of which does
- 30 not dissolve in a liquid upon being mixed with the liquid at a specified temperature and pressure, where the undissolved portion of the substance can be recovered from the liquid by physical means. For example, a fine particulate material dispersed in a liquid is

insoluble in the liquid if 50 wt.% or more of the material may be recovered from the liquid by centrifugation and filtration.

"IP" refers to the Institute of Petroleum, now the Energy Institute of London, United Kingdom.

- 5 "Kerosene" refers to hydrocarbons with a boiling range distribution from 204°C up to 260°C (400°F up to 500°F) at a pressure of 0.101 MPa. Kerosene content may be determined by the quantity of hydrocarbons having a boiling range of from 204°C to 260°C at a pressure of 0.101 MPa relative to a total quantity of hydrocarbons as measured by boiling range distribution in accordance with ASTM Method D5307.
- 10 "Lewis base" refers to a compound and/or material with the ability to donate one or more electrons to another compound.
- "Ligand" as used herein is defined as a molecule, compound, atom, or ion bonded to, or capable of bonding with, a metal ion in a coordination complex.
- "Light hydrocarbons" refers to hydrocarbons having carbon numbers in a range from 1 to
- 15 4.
- "Mixing" as used herein is defined as contacting two or more substances by intermingling the two or more substances. Blending, as used herein, is a subclass of mixing, where blending requires intimately admixing or intimately intermingling the two or more substances, for example into a homogenous dispersion.
- 20 "Monomer" as used herein is defined as a molecular compound or portion of a molecular compound that may be reactively joined with itself or another monomer in repeated linked units to form a polymer.
- "Naphtha" refers to hydrocarbon components with a boiling range distribution from 38°C up to 204°C (100°F up to 400°F). Naphtha content may be determined by the quantity of
- 25 hydrocarbons having a boiling range of from 38°C to 204°C at a pressure of 0.101 MPa relative to a total quantity of hydrocarbons as measured by boiling range distribution in accordance with ASTM Method D5307. Content of hydrocarbon components, for example, paraffins, iso-paraffins, olefins, naphthenes and aromatics in naphtha are as determined by ASTM Method D6730.
- 30 "Non-condensable gas" refers to components and/or a mixture of components that are gases at STP.

When two or more elements are described as "operatively connected", the elements are defined to be directly or indirectly connected to allow direct or indirect fluid flow between the elements.

5 "Periodic Table" refers to the Periodic Table as specified by the International Union of Pure and Applied Chemistry (IUPAC), November 2003. As used herein, an element of the Periodic Table of Elements may be referred to by its symbol in the Periodic Table. For example, Cu may be used to refer to copper, Ag may be used to refer to silver, W may be used to refer to tungsten etc.

"Polyaromatic compounds" refer to compounds that include three or more aromatic rings.  
10 Examples of polyaromatic compounds include, but are not limited to anthracene and phenanthrene.

"Polymer" as used herein is defined as a compound comprised of repetitively linked monomers.

"Pore size distribution" refers a distribution of pore size diameters of a material as  
15 measured by ASTM Method D4641 unless specified as being determined by mercury porosimetry, in which case the distribution of pore size diameters of the material is measured by ASTM Method D4284.

"SCFB" refers to standard cubic feet of a gas per barrel of crude feed.

"STP" as used herein refers to Standard Temperature and Pressure, which is 25°C and  
20 0.101 MPa.

"TAN" refers to a total acid number expressed as milligrams ("mg") of KOH per gram ("g") of sample. TAN is as determined by ASTM Method D664.

"VGO" refers to hydrocarbons with a boiling range distribution of from 343°C up to 538°C (650°F up to 1000°F) at 0.101 MPa. VGO content may be determined by the quantity of  
25 hydrocarbons having a boiling range of from 343°C to 538°C at a pressure of 0.101 MPa relative to a total quantity of hydrocarbons as measured by boiling range distribution in accordance with ASTM Method D5307.

"wppm" as used herein refers to parts per million, by weight.

The present invention is directed to a process in which a first hydrocarbon-  
30 containing composition having a unique sulfur profile that is highly susceptible to hydrodesulfurization is hydrotreated, preferably mildly, to produce a second hydrocarbon-containing composition containing little sulfur, fractionating the second hydrocarbon-containing composition to produce a light hydrocarbon fraction and a heavy hydrocarbon

fraction comprising hydrocarbons having a boiling point of from 343°C to 538°C, and subsequently fluid catalytically cracking the heavy hydrocarbon fraction. The first hydrocarbon-containing composition is provided by catalytically hydrocracking a hydrocarbon-containing feedstock utilizing a non-acidic, preferably Lewis basic, catalyst.

5

### **Providing a First Hydrocarbon-Containing Composition**

#### *Hydrocarbon-containing feedstock*

The hydrocarbon-containing feedstock that is hydrocracked to provide the first hydrocarbon-containing composition used in the process of the present invention contains heavy hydrocarbons that are subject to being cracked. The hydrocarbon-containing feedstock may be selected to contain at least 20 wt.% hydrocarbons having a boiling point of greater than 538°C. The amount of hydrocarbons having a boiling point of greater than 538°C in a hydrocarbon-containing material may be determined in accordance with ASTM Method D5307. The hydrocarbon-containing feedstock may be selected to contain at least 25 wt.%, or at least 30 wt.%, or at least 35 wt.%, or at least 40 wt.%, or at least 45 wt.%, or at least 50 wt.% hydrocarbons having a boiling point of greater than 538°C. The hydrocarbon-containing feedstock may be selected to contain at least 20 wt.% residue, or at least 25 wt.% residue, or at least 30 wt.% residue, or at least 35 wt.% residue, or at least 40 wt.% residue, or at least 45 wt.% residue, or at least 50 wt.% residue.

The hydrocarbon-containing feedstock may contain significant quantities of lighter hydrocarbons as well as the heavy hydrocarbons. The hydrocarbon-containing feedstock may contain at least 30 wt.%, or at least 35 wt.%, or at least 40 wt.%, or at least 45 wt.%, or at least 50 wt.% of hydrocarbons having a boiling point of 538°C or less. The amount of hydrocarbons having a boiling point of 538°C or less in a hydrocarbon-containing material may be determined in accordance with ASTM Method D5307. The hydrocarbon-containing feedstock may contain at least 20 wt.%, or at least 25 wt.%, or at least 30 wt.%, or at least 35 wt.%, or at least 40 wt.%, or at least 45 wt.% of distillate and VGO hydrocarbons. The hydrocarbon-containing feedstock may be a whole crude oil, or may be a topped crude oil.

The hydrocarbon-containing feedstock may also contain significant quantities of sulfur and nitrogen. The hydrocarbon-containing feedstock may contain at least 2 wt.% sulfur, or at least 3 wt.%, or at least 5 wt.% sulfur as determined in accordance with ASTM

Method D4294; and the hydrocarbon-containing feedstock may contain at least 0.25 wt.% nitrogen, or at least 0.4 wt.% nitrogen.

The hydrocarbon-containing feedstock may be a heavy or an extra-heavy crude oil containing significant quantities of residue or pitch; a topped heavy or topped extra-heavy crude oil containing significant quantities of residue or pitch; bitumen; hydrocarbons derived from tar sands; shale oil; crude oil atmospheric residues; crude oil vacuum residues; and asphalts.

### *Hydrogen*

The hydrogen that is mixed with the hydrocarbon-containing feedstock and the catalyst in the catalytic hydrocracking step to produce the first hydrocarbon-containing composition utilized in the process of the present invention may be derived from a hydrogen source. The hydrogen source may be hydrogen gas obtained from any conventional sources or methods for producing hydrogen gas.

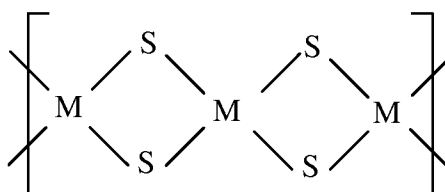
### *Non-acidic Hydrocracking Catalyst*

A metal-containing catalyst utilized to catalytically hydrocrack the hydrocarbon-containing feedstock to produce the first hydrocarbon-containing composition may be substantially non-acidic and may contain a transition metal sulfide. The substantially non-acidic metal-containing catalyst may have an acidity as measured by ammonia chemisorption of at most 500  $\mu\text{mol}$  ammonia desorbed from the catalyst per gram of catalyst. More preferably a non-acidic transition metal sulfide catalyst utilized in the catalytic hydrocracking has an acidity as measured by ammonia chemisorption of at most 200, or at most 100, or at most 50, or at most 25, or at most 10  $\mu\text{mol}$  ammonia desorbed from the catalyst per gram of catalyst, and most preferably has an acidity as measured by ammonia chemisorption of 0  $\mu\text{mol}$  ammonia desorbed from the catalyst per gram of catalyst. Any metal-containing catalyst utilized in the catalytic hydrocracking may comprise at most 0.1 wt.%, or at most 0.01 wt.%, or at most 0.001 wt.% of alumina, alumina-silica, zeolite, or silica, and, preferably, the one or more catalysts contain no detectable alumina, alumina-silica, zeolite, or silica. The metal-containing catalyst utilized in the catalytic hydrocracking preferably has little or no acidity to avoid catalyzing the formation of hydrocarbon radical cations and thereby avoid catalyzing the formation of coke and refractory sulfur and nitrogen compounds in the course of hydrocracking the hydrocarbon-containing feedstock.

The metal-containing catalyst is preferably a Lewis base. It is believed that a Lewis base catalyst donates electrons or electron density to promote cracking of hydrocarbons in the hydrocarbon feedstock and/or to stabilize cracked hydrocarbon radicals to inhibit the formation of coke and refractory sulfur and nitrogen compounds.

The non-acidic catalyst utilized in hydrocracking the hydrocarbon feedstock to provide the first hydrocarbon-containing composition may be a thiometallate catalyst that is a material comprised of a first metal, a second metal, and sulfur; where the first metal is selected from the group consisting of copper (Cu), nickel (Ni), cobalt (Co), iron (Fe), bismuth (Bi), silver (Ag), manganese (Mn), zinc (Zn), tin (Sn), ruthenium (Ru), lanthanum (La), praseodymium (Pr), samarium (Sm), europium (Eu), ytterbium (Yb), lutetium (Lu), dysprosium (Dy), lead (Pb), and antimony (Sb), and where the second metal is selected from the group consisting of molybdenum (Mo), tungsten (W), tin (Sn), and antimony (Sb), where the second metal is not the same as the first metal. The thiometallate catalyst may comprise a tetrathiometallate material.

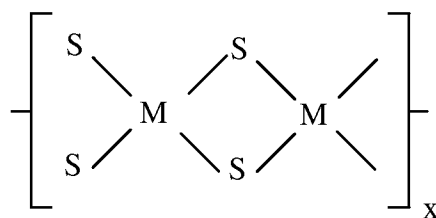
The thiometallate catalyst may have a structure wherein at least a portion of the material of the catalyst is comprised of the first metal and the second metal having a structure according to formula (I)



(I)

where M is either the first metal or the second metal, and at least one M is the first metal and at least one M is the second metal. The material of the catalyst as shown in formula (I) may include a third metal selected from the group consisting of Cu, Fe, Bi, Ag, Mn, Zn, Ni, Co, Sn, Re, Rh, Pd, Ir, Pt, Ce, La, Pr, Sm, Eu, Yb, Lu, Dy, Pb, Cd, Sb, and In, where the third metal is not the same as the first metal or the second metal, and where M is either the first metal, or the second metal, or the third metal, and at least one M is the first metal, at least one M is the second metal, and at least one M is the third metal.

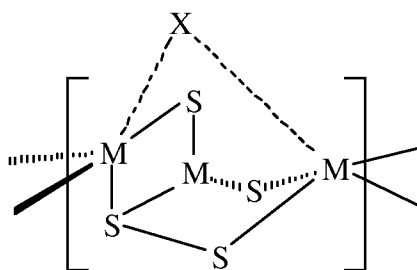
The material of the thiometallate catalyst may be a polythiometallate polymer formed of repeating monomeric units having the structure (II):



(II)

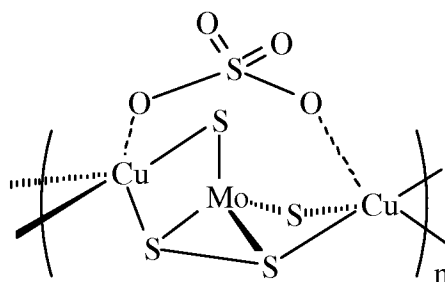
where M is either the first metal or the second metal, at least one M is the first metal, at least one M is the second metal, and where x is at least 2.

- 5           At least a portion of the material of the metal-containing non-acidic catalyst may be comprised of the first metal, the second metal, and sulfur having a structure according to formula (III):



(III)

where M is either the first metal or the second metal, at least one M is the first metal and at least one M is the second metal, and X is selected from the group consisting of  $\text{SO}_4$ ,  $\text{PO}_4$ , oxalate ( $\text{C}_2\text{O}_4$ ), acetylacetonate, acetate, citrate, tartrate, Cl, Br, I,  $\text{ClO}_4$ , and  $\text{NO}_3$ . For example, the material of the catalyst may contain copper thiometallate-sulfate having the structure shown in formula (IV):

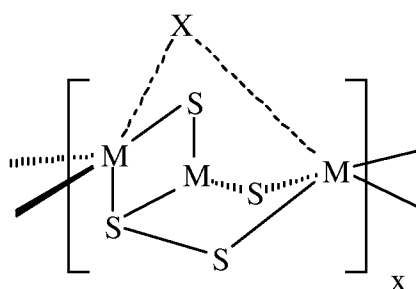


(IV)

- where n may be an integer greater than or equal to 1. The material of the catalyst as shown in formula (III) may include a third metal selected from the group consisting of Cu, Fe, Bi, Ag, Mn, Zn, Ni, Co, Sn, Re, Rh, Pd, Ir, Pt, Ce, La, Pr, Sm, Eu, Yb, Lu, Dy, Pb, Cd, Sb, and

In, where the third metal is not the same as the first metal or the second metal, where M is either the first metal, or the second metal, or the third metal, and at least one M is the first metal, at least one M is the second metal, and at least one M is the third metal. The portion of the material of the catalyst comprised of the first metal, the second metal, and sulfur

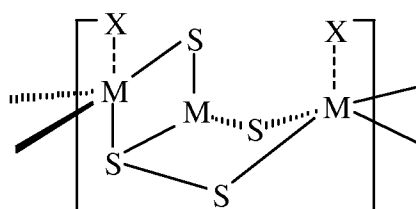
5 may also have a polymeric structure according to formula (V):



(V)

where M is either the first metal or the second metal, at least one M is the first metal and at least one M is the second metal, X is selected from the group consisting of SO<sub>4</sub>, PO<sub>4</sub>, oxalate (C<sub>2</sub>O<sub>4</sub>), acetylacetonate, acetate, citrate, tartrate, Cl, Br, I, ClO<sub>4</sub>, and NO<sub>3</sub>, and x is at least 2 and preferably is at least 5;

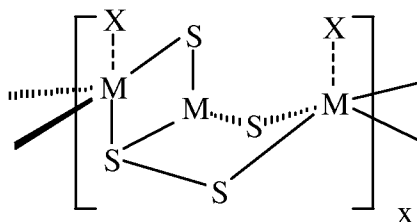
At least a portion of the catalyst material may be comprised of the first metal, the second metal, and sulfur having a structure according to formula (VI):



(VI)

where M is either the first metal or the second metal, at least one M is the first metal and at least one M is the second metal, and X is selected from the group consisting of SO<sub>4</sub>, PO<sub>4</sub>, oxalate (C<sub>2</sub>O<sub>4</sub>), acetylacetonate, acetate, citrate, tartrate, Cl, Br, I, ClO<sub>4</sub>, and NO<sub>3</sub>. The material of the catalyst as shown in formula (VI) may include a third metal selected from the group consisting of Cu, Fe, Bi, Ag, Mn, Zn, Ni, Co, Sn, Re, Rh, Pd, Ir, Pt, Ce, La, Pr, Sm, Eu, Yb, Lu, Dy, Pb, Cd, Sb, and In, where the third metal is not the same as the first metal or the second metal, and where M is either the first metal, or the second metal, or the third metal, and at least one M is the first metal, at least one M is the second metal, and at

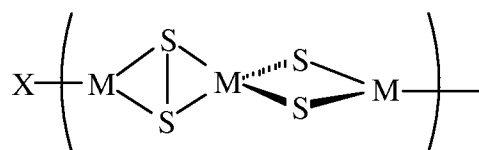
least one M is the third metal. The portion of the catalyst material comprised of the first metal, the second metal, and sulfur may also have a polymeric structure according to formula (VII):



(VII)

where M is either the first metal or the second metal, and at least one M is the first metal and at least one M is the second metal, X is selected from the group consisting of SO<sub>4</sub>, PO<sub>4</sub>, oxalate (C<sub>2</sub>O<sub>4</sub>), acetylacetonate, acetate, citrate, tartrate, Cl, Br, I, ClO<sub>4</sub>, and NO<sub>3</sub>, and x is at least 2 and preferably is at least 5.

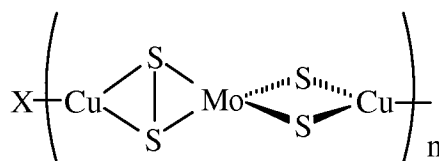
At least a portion of the catalyst material may be comprised of the first metal, the second metal, and sulfur having a structure according to formula (VIII):



(VIII)

where M is either the first metal or the second metal, at least one M is the first metal and at least one M is the second metal, and X is selected from the group consisting of SO<sub>4</sub>, PO<sub>4</sub>, oxalate (C<sub>2</sub>O<sub>4</sub>), acetylacetonate, acetate, citrate, tartrate, Cl, Br, I, ClO<sub>4</sub>, and NO<sub>3</sub>.

For example, at least a portion of the catalyst material may have a structure in accordance with formula (IX):

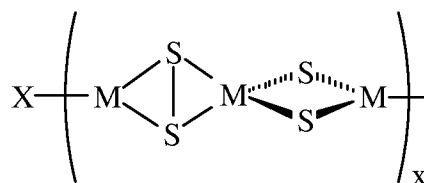


(IX)

where X is selected from the group consisting of SO<sub>4</sub>, PO<sub>4</sub>, oxalate (C<sub>2</sub>O<sub>4</sub>), acetylacetonate, acetate, citrate, tartrate, Cl, Br, I, ClO<sub>4</sub>, and NO<sub>3</sub>, and n is an integer equal to or greater

than 1. The catalyst material as shown in formula (VIII) may include a third metal selected from the group consisting of Cu, Fe, Bi, Ag, Mn, Zn, Ni, Co, Sn, Re, Rh, Pd, Ir, Pt, Ce, La,

Pr, Sm, Eu, Yb, Lu, Dy, Pb, Cd, Sb, and In, where the third metal is not the same as the first metal or the second metal, and where M is either the first metal, or the second metal, or the third metal, and at least one M is the first metal, at least one M is the second metal, and at least one M is the third metal. The portion of the catalyst material comprised of the first metal, the second metal, and sulfur may also have a polymeric structure according to formula (X):



(X)

where M is either the first metal or the second metal, at least one M is the first metal and at least one M is the second metal, X is selected from the group consisting of  $\text{SO}_4$ ,  $\text{PO}_4$ , oxalate ( $\text{C}_2\text{O}_4$ ), acetylacetonate, acetate, citrate, tartrate, Cl, Br, I,  $\text{ClO}_4$ , and  $\text{NO}_3$ , and x is at least 2 and preferably is at least 5.

The material of a preferred thiometallate catalyst may contain less than 0.5 wt.% of ligands other than the sulfur-metal bonded complexes between sulfur and the first metal and between sulfur and the second metal. Ligands, other than the sulfur-metal bonded complexes with the first metal and the second metal, may not be present in significant quantities in the material since they may limit the particle size of the material of the catalyst to less than 50 nm, for example, by inhibiting the first metal and the second metal from forming sulfur-bridged chains.

The material of the thiometallate catalyst may be tetrathiometallate material comprised of alternating  $\text{M}^1\text{S}_4$  and  $\text{M}^2\text{S}_4$  tetrahedral formations located adjacent to each other, where  $\text{M}^1$  is the first metal and  $\text{M}^2$  is the second metal as described above, and where the metal of each tetrahedral formation is bonded to at least two sulfur atoms that are also bonded to the metal of an adjacent tetrahedral formation. The tetrathiometallate material may have a polymeric structure wherein a portion of the first metal is located within interstices or holes in the polymeric structure, where the portion of the first metal located within interstices or holes in the polymeric structure is not bonded with a sulfur atom or second metal atom included in the polymeric structure.

A preferred thiometallate catalyst for use in hydrocracking the hydrocarbon feedstock to provide the first hydrocarbon-containing composition preferably is formed

primarily of a material comprised of the first metal, second metal, and sulfur as described above, and the material of the preferred catalyst is formed primarily of the first metal, second metal, and sulfur as described above. The first metal, second metal, and sulfur may comprise at least 75 wt.%, or at least 80 wt.%, or at least 85 wt.%, or at least 90 wt.%, or at least 95 wt.%, or at least 99 wt.% or 100 wt.% of the material of the thiometallate catalyst structured as described above, where the material of the catalyst comprises at least 50 wt.% or at least 60 wt.%, or at least 70 wt.%, or at least 75 wt.%, or at least 80 wt.%, or at least 90 wt.%, or at least 95 wt.%, or at least 99 wt.% or 100 wt.% of the thiometallate catalyst.

The first metal may be present in the material of a preferred thiometallate catalyst in an atomic ratio relative to the second metal of at least 1:2. The atomic ratio of the first metal to the second metal in the material of the thiometallate catalyst, and/or in the thiometallate catalyst, may be greater than 1:2, or at least 2:3, or at least 1:1, or at least 2:1, or at least 3:1, or at least 5:1. It is believed that the first metal contributes significantly to the catalytic activity of the thiometallate catalyst in hydrocracking the hydrocarbon feedstock when the first metal is present in the material of the catalyst, and/or in the catalyst, in an amount relative to the second metal ranging from slightly less of the first metal to the second metal to significantly more of the first metal to the second metal. Therefore, the first metal may be incorporated in the material of the thiometallate catalyst, and/or in the catalyst, in an amount, relative to the second metal, such that the atomic ratio of the first metal to the second metal ranges from one half to significantly greater than one, such that the first metal is not merely a promoter of the second metal in the catalyst.

It is believed that the thiometallate catalyst is particularly effective for use in hydrocracking a heavy hydrocarbon-containing feedstock due, in part, to the molecular structure of the catalyst, which facilitates donation or sharing of electrons as a Lewis base from the catalyst to a hydrocarbon or a hydrocarbon anion radical. The sulfur atoms linking the first and second metals in the catalyst may facilitate the electron donating/sharing activity of the catalyst, acting to enable charge transfer from the first metal to the second metal or from the second metal to the first metal across the molecular orbitals of the sulfur atoms, as well as potentially acting to directly share electrons from the sulfur atoms in the catalyst with the hydrocarbon or hydrocarbon anion radical. The sulfur atoms may further facilitate donation/sharing of electrons from the catalyst to a hydrocarbon or hydrocarbon anion radical by charge stabilization of the catalyst as the catalyst donates/shares electrons with a hydrocarbon or hydrocarbon anion radical. It is believed that the structure of the catalyst is particularly effective in facilitating donation or

sharing of electrons from the catalyst to a hydrocarbon or hydrocarbon anion radical when the catalyst has a polythiometallate polymeric structure such as set forth in formula (II) above, particularly when x is at least 5, since any charge induced in the catalyst by sharing or donation of electrons to the hydrocarbon or hydrocarbon anion radical may be spread  
5 over a large number of sulfur atoms and first and second metals that form the polymeric structure of the catalyst.

A preferred thiometallate catalyst may be particularly effective in hydrocracking a heavy hydrocarbon-containing material since the molecular structure of the tetrathiometallate material may have sulfided electron-rich metals incorporated therein  
10 while inhibiting reduction of such electron-rich metals to a zero-oxidation state during the hydrocracking process. Use of sulfided electron-rich metals is typically avoided in hydrocarbon cracking processes since the metal of typical electron-rich metal compounds may be easily desulfided and reduced to its zero-oxidation state in the presence of hydrogen, and zero-oxidation state electron-rich metals catalyze the production of coke in a  
15 cracking process. For example, copper sulfide is an electron-rich metal that is not typically utilized in cracking processes due to its propensity be desulfurized and thereafter to catalyze coke formation. The molecular structure of a thiometallate catalyst useful in hydrocracking a heavy hydrocarbon feedstock to produce the first hydrocarbon-containing composition, however, enables the use of an electron-rich metal such as copper or bismuth  
20 in the thiometallate catalyst, where electron-rich metals such as copper or bismuth are preferred for use as the first metal in the catalyst. The electron-rich metal may be bound in the catalyst by two sulfur atoms, inhibiting or preventing the reduction of the electron-rich metal to its zero-oxidation state, and thereby inhibiting or preventing the formation of coke by the zero-oxidation state electron-rich metal. Inclusion of an electron-rich metal,  
25 particularly copper, in the thiometallate catalyst material promotes the electron donation/sharing characteristics of the thiometallate catalyst material by increasing the electron density of the thiometallate catalyst material available to be donated or shared.

A preferred non-acidic metal-containing catalyst used in the catalytic hydrocracking of a hydrocarbon feedstock to produce the first hydrocarbon-containing  
30 composition may contain little or no oxygen. The catalytic activity of the catalyst(s) in hydrocracking is, in part, believed to be due to the availability of electrons from the catalyst(s). Due to its electronegativity, oxygen tends to reduce the availability of electrons from a hydrocracking catalyst when it is present in the catalyst in appreciable quantities, therefore, any catalyst utilized in the hydrocracking a hydrocarbon feedstock to provide the

first hydrocarbon-containing composition preferably contains little or no oxygen. Any catalyst utilized in hydrocracking a hydrocarbon-containing feedstock to provide the first hydrocarbon-containing composition may comprise at most 0.1 wt.%, or at most 0.05 wt.%, or at most 0.01 wt.% oxygen as measured by neutron activation. Oxygen may not be detectable in any catalyst utilized in the catalytic hydrocracking of a hydrocarbon-containing feedstock to provide the first hydrocarbon-containing composition.

The non-acidic, preferably thiometallate, hydrocracking catalyst may be a solid particulate substance having a particle size distribution with a relatively small mean and/or median particle size, where the solid catalyst particles preferably are nanometer size particles. The catalyst may have a particle size distribution with a median particle size and/or mean particle size of at least 50 nm, or at least 75 nm, or up to 1  $\mu\text{m}$ , or up to 750 nm; or up to 500 nm, or from 50 nm up to 1  $\mu\text{m}$ . A solid particulate catalyst having a particle size distribution with a large quantity of small particles, for example having a mean and/or median particle size of up to 1  $\mu\text{m}$ , has a large aggregate surface area since little of the catalytically active components of the catalyst are located within the interior of a particle. A particulate non-acidic, preferably thiometallic, catalyst having a particle size distribution with a large quantity of small particles, therefore, may be desirable for use in the catalytic hydrocracking of a hydrocarbon-containing feedstock to provide a relatively high degree catalytic activity due to the surface area of the catalyst available for catalytic activity. A metal-containing catalyst used in hydrocracking a hydrocarbon-containing feedstock to provide the first hydrocarbon-containing composition may be a solid particulate substance preferably having a particle size distribution with a mean particle size and/or median particle size of up to 1  $\mu\text{m}$ , preferably having a pore size distribution with a mean pore diameter and/or a median pore diameter of from 50 to 1000 angstroms, or from 60 to 350 angstroms, preferably having a pore volume of at least 0.2  $\text{cm}^3/\text{g}$ , or at least 0.25  $\text{cm}^3/\text{g}$  or at least 0.3  $\text{cm}^3/\text{g}$ , or at least 0.35  $\text{cm}^3/\text{g}$ , or at least 0.4  $\text{cm}^3/\text{g}$ , and preferably having a BET surface area of at least 50  $\text{m}^2/\text{g}$ , or at least 100  $\text{m}^2/\text{g}$ , and up to 400  $\text{m}^2/\text{g}$ , or up to 500  $\text{m}^2/\text{g}$ .

A solid particulate non-acidic metal-containing catalyst utilized in hydrocracking the hydrocarbon-containing feedstock may be insoluble in the hydrocarbon-containing feedstock and in the hydrocarbon-depleted feed residuum formed by hydrocracking. A solid particulate catalyst having a particle size distribution with a median and/or mean particle size of at least 50 nm may be insoluble in the hydrocarbon-containing feedstock and the hydrocarbon-depleted residuum due, in part, to the size of the particles, which may

be too large to be solvated by the hydrocarbon-containing feed or the residuum. Use of a solid particulate catalyst which is insoluble in the hydrocarbon-containing feed and the hydrocarbon-depleted feed residuum may be desirable so that the catalyst may be separated from the residuum, and subsequently regenerated for reuse.

5

*Method of Preparing Preferred Non-Acidic Thiometallate Catalysts*

A non-acidic, Lewis basic, thiometallate catalyst material that may be utilized to catalytically hydrocrack a hydrocarbon-containing feedstock to provide the first hydrocarbon-containing composition—wherein the hydrocarbon-containing feedstock, the catalyst, and hydrogen are mixed at a temperature of 375°C to 500°C and a pressure of 6.9 MPa to 27.5 MPa—may be prepared by mixing a first salt and a second salt in an aqueous mixture under anaerobic conditions at a temperature of from 15°C to 150°C, and separating a solid from the aqueous mixture to produce the catalyst material.

The first salt that may be utilized to form a thiometallate hydrocracking catalyst material includes a cationic component comprising a metal in any non-zero oxidation state selected from the group consisting of Cu, Fe, Ni, Co, Bi, Ag, Mn, Zn, Sn, Ru, La, Ce, Pr, Sm, Eu, Yb, Lu, Dy, Pb, and Sb, where the metal of the cationic component is the first metal of the material of the thiometallate catalyst. The cationic component of the first salt may consist essentially of a metal selected from the group consisting of Cu, Fe, Bi, Ni, Co, Ag, Mn, Zn, Sn, Ru, La, Ce, Pr, Su, Eu, Yb, Lu, Dy, Pb, and Sb. The cationic component of the first salt must be capable of bonding with the anionic component of the second salt to form the material of the thiometallate catalyst in the aqueous mixture at a temperature of from 15°C to 150°C under anaerobic conditions.

The first salt also contains an anionic component associated with the cationic component of the first salt to form the first salt. The anionic component of the first salt may be selected from a wide range of counterions to the cationic component of the first salt so long as the combined cationic component and the anionic component of the first salt form a salt that is dispersible, and preferably soluble, in the aqueous mixture in which the first salt and the second salt are mixed, and so long as the anionic component of the first salt does not prevent the combination of the cationic component of the first salt with the anionic component of the second salt in the aqueous mixture to form the material of the thiometallate catalyst. The anionic component of the first salt may be selected from the

group consisting of sulfate, chloride, bromide, iodide, acetate, acetylacetonate, oxalate, citrate, tartrate, and mixtures thereof.

Certain compounds are preferred for use as the first salt to form the thiometallate catalyst material. In particular, the first salt is preferably selected from the group consisting of CuSO<sub>4</sub>, copper acetate, copper acetylacetonate, FeSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, iron acetate, iron acetylacetonate, NiSO<sub>4</sub>, nickel acetate, nickel acetylacetonate, CoSO<sub>4</sub>, cobalt acetate, cobalt acetylacetonate, ZnCl<sub>2</sub>, ZnSO<sub>4</sub>, zinc acetate, zinc acetylacetonate, silver acetate, silver acetylacetonate, SnSO<sub>4</sub>, SnCl<sub>4</sub>, tin acetate, tin acetylacetonate, MnSO<sub>4</sub>, manganese acetate, manganese acetylacetonate, bismuth acetate, bismuth acetylacetonate, and hydrates thereof. These materials are generally commercially available, or may be prepared from commercially available materials according to well-known methods.

The first salt may be contained in an aqueous solution or an aqueous mixture, where the aqueous solution or aqueous mixture containing the first salt (hereinafter the "first aqueous solution") may be mixed with an aqueous solution or an aqueous mixture containing the second salt (hereinafter the "second aqueous solution") to form the material of the preferred catalyst. The first salt may be dispersible, and most preferably soluble, in the first aqueous solution and is dispersible, and preferably soluble, in the aqueous mixture of the first and second salts. The first aqueous solution may contain more than 50 vol.% water, or at least 75 vol.% water, or at least 90 vol.% water, or at least 95 vol.% water, and may contain more than 0 vol.% but less than 50 vol.%, or at most 25 vol.%, or at most 10 vol.%, or at most 5 vol.% of an organic solvent containing from 1 to 5 carbons selected from the group consisting of an alcohol, a diol, an aldehyde, a ketone, an amine, an amide, a furan, an ether, acetonitrile, and mixtures thereof. The organic solvent present in the first aqueous solution, if any, should be selected so that the organic compounds in the organic solvent do not inhibit reaction of the cationic component of the first salt with the anionic component of the second salt upon forming an aqueous mixture containing the first and second salts, e.g., by forming ligands or by reacting with the first or second salts or their respective cationic or anionic components. The first aqueous solution may contain no organic solvent, and may consist essentially of water, preferably deionized water, and the first salt.

The concentration of the first salt in the first aqueous solution may be selected to promote formation of a thiometallate catalyst material having a particle size distribution with a small mean and/or median particle size—where the particles have a relatively large surface area—upon mixing the first salt and the second salt in an aqueous mixture. To

promote the formation of a catalyst material having a relatively large surface area and having a particle size distribution with a relatively small mean and/or median particle size, the first aqueous solution may contain at most 3 moles per liter, or at most 2 moles per liter, or at most 1 mole per liter, or at most 0.6 moles per liter, or at most 0.2 moles per liter of the first salt.

The second salt utilized to form a thiometallate catalyst material may include an anionic component that is a tetrathiometallate of molybdenum, tungsten, tin or antimony. In particular, the second salt may contain an anionic component that is selected from the group consisting of  $\text{MoS}_4^{2-}$ ,  $\text{WS}_4^{2-}$ ,  $\text{SnS}_4^{4-}$ ,  $\text{SbS}_4^{3-}$ , and mixtures thereof.

The second salt also contains a cationic component associated with the anionic component of the second salt to form the second salt. The cationic component of the second salt may be selected from an ammonium counterion, an alkali metal counterion, and/or an alkaline earth metal counterion to the tetrathiometallate anionic component of the second salt so long as the combined cationic component and the anionic component of the second salt form a salt that is dispersable, and preferably soluble, in an aqueous mixture of the first salt and the second salt, and so long as the cationic component of the second salt does not prevent the combination of the cationic component of the first salt with the anionic component of the second salt in the aqueous mixture to form the thiometallate catalyst material. The cationic component of the second salt may comprise one or more sodium ions, or one or more potassium ions, or one or more ammonium ions.

Certain compounds are preferred for use as the second salt used to form a thiometallate catalyst material. In particular, the second salt may be selected from the group consisting of  $\text{Na}_2\text{MoS}_4$ ,  $\text{Na}_2\text{WS}_4$ ,  $\text{K}_2\text{MoS}_4$ ,  $\text{K}_2\text{WS}_4$ ,  $(\text{NH}_4)_2\text{MoS}_4$ ,  $(\text{NH}_4)_2\text{WS}_4$ ,  $\text{Na}_4\text{SnS}_4$ ,  $(\text{NH}_4)_4\text{SnS}_4$ ,  $(\text{NH}_4)_3\text{SbS}_4$ ,  $\text{Na}_3\text{SbS}_4$ , and hydrates thereof.

The second salt may be a commercially available tetrathiomolybdate or tetrathiotungstate salt. For example, the second salt may be ammonium tetrathiomolybdate, which is commercially available from AAA Molybdenum Products, Inc. 7233 W. 116 Pl., Broomfield, Colorado, USA 80020, or ammonium tetrathiotungstate, which is commercially available from Sigma-Aldrich, 3050 Spruce St., St. Louis, Missouri, USA 63103.

Alternatively, the second salt may be produced from a commercially available tetrathiomolybdate or tetrathiotungstate salt. For example, the second salt may be produced from ammonium tetrathiomolybdate or from ammonium tetrathiotungstate. The second salt may be formed from the commercially available ammonium tetrathiometallate

salts by exchanging the cationic ammonium component of the commercially available salt with a desired alkali or alkaline earth cationic component from a separate salt. The exchange of the cationic components to form the desired second salt may be effected by mixing the commercially available salt and the salt containing the desired cationic

5 component in an aqueous solution to form the desired second salt.

A method of forming the second salt is to disperse ammonium tetrathiomolybdate or ammonium tetrathiotungstate in an aqueous solution, preferably water, and to disperse an alkali metal or alkaline earth metal cationic component donor salt, preferably a carbonate, in the aqueous solution, where the cationic component donor salt is provided in  
10 an amount relative to the ammonium tetrathiomolybdate or ammonium tetrathiotungstate salt to provide a stoichiometrically equivalent or greater amount of its cation to ammonium of the ammonium tetrathiomolybdate or ammonium tetrathiotungstate salt. The aqueous solution may be heated to a temperature of at least 50°C, or at least 65°C up to 100°C to evolve ammonia from the ammonium containing salt and carbon dioxide from the  
15 carbonate containing salt as gases, and to form the second salt. For example a  $\text{Na}_2\text{MoS}_4$  salt may be prepared for use as the second salt by mixing commercially available  $(\text{NH}_4)_2\text{MoS}_4$  and  $\text{Na}_2\text{CO}_3$  in water at a temperature of 70°C-80°C for a time period sufficient to permit evolution of a significant amount, preferably substantially all, of ammonia and carbon dioxide gases from the solution, typically from 30 minutes to 4 hours,  
20 and usually about 2 hours.

If the second salt is a sodium tetrathioostannate salt, it may be produced by dissolving  $\text{Na}_2\text{Sn}(\text{OH})_6$  and  $\text{Na}_2\text{S}$  in a 1:4 molar ratio in boiling deionized water (100 g of  $\text{Na}_2\text{Sn}(\text{OH})_6$  per 700 ml of water and 250 g of  $\text{Na}_2\text{S}$  per 700 ml of water), stirring the mixture at 90-100°C for 2-3 hours, adding finely pulverized  $\text{MgO}$  to the mixture at a 2:5  
25 wt. ratio relative to the  $\text{Na}_2\text{Sn}(\text{OH})_6$  and continuing stirring the mixture at 90-100°C for an additional 2-3 hours, cooling and collecting precipitated impurities from the mixture, then concentrating the remaining solution by 50-60 vol.%, allowing the concentrated solution to stand, then collecting the  $\text{Na}_4\text{SnS}_4$  that crystallizes from the concentrated solution. An ammonium tetrathioostannate salt may be produced by mixing  $\text{SnS}_2$  with  $(\text{NH}_4)_2\text{S}$  in a 1:2  
30 mole ratio in liquid ammonia under an inert gas (e.g. nitrogen), filtering, and recovering the solid  $(\text{NH})_4\text{SnS}_4$  as a residue.

The second salt may be contained in an aqueous solution (the second aqueous solution, as noted above), where the second aqueous solution containing the second salt

may be mixed with the first aqueous solution containing the first salt in an aqueous mixture to form the thiometallate catalyst. The second salt is preferably dispersible, and most preferably soluble, in the second aqueous solution and is dispersible, and preferably soluble, in an aqueous mixture containing the first and second salts. The second aqueous solution may contain more than 50 vol.% water, or at least 75 vol.% water, or at least 90 vol.% water, or at least 95 vol.% water, and may contain more than 0 vol.% but less than 50 vol.%, or at most 25 vol.%, or at most 10 vol.%, or at most 5 vol.% of an organic solvent containing from 1 to 5 carbons and selected from the group consisting of an alcohol, a diol, an aldehyde, a ketone, an amine, an amide, a furan, an ether, acetonitrile, and mixtures thereof. The organic solvent present in the second aqueous solution, if any, should be selected so that the organic compounds in the organic solvent do not inhibit reaction of the cationic component of the first salt with the anionic component of the second salt upon forming an aqueous mixture containing the first and second salts, e.g., by forming ligands or by reacting with the first or second salts or their respective cationic or anionic components. The second aqueous solution may contain no organic solvent. The second aqueous solution may consist essentially of water, preferably deionized, and the second salt.

The concentration of the second salt in the second aqueous solution may be selected to promote formation of a thiometallate catalyst having a particle size distribution with a small mean and/or median particle size and having a relatively large surface area per particle upon mixing the first salt and the second salt in an aqueous mixture. To promote the formation of a thiometallate catalyst material having a particle size distribution with a relatively small mean and/or median particle size, the second aqueous solution may contain at most 0.8 moles per liter, or at most 0.6 moles per liter, or at most 0.4 moles per liter, or at most 0.2 moles per liter, or at most 0.1 moles per liter of the second salt.

The first and second solutions containing the first and second salts, respectively, may be mixed in an aqueous mixture to form the thiometallate catalyst. The amount of the first salt relative to the amount of the second salt provided to the aqueous mixture may be selected so that the atomic ratio of the cationic component metal of the first salt to the metal of the anionic component of the second salt is at least 1:2, or at least 2:3, or at least 1:1, and at most 20:1, or at most 15:1, or at most 10:1.

The aqueous mixture containing the first salt and the second salt may be mixed to facilitate interaction and reaction of the cationic component of the first salt with the anionic component of the second salt to form the catalyst material. The aqueous mixture may be

mixed by any conventional means for agitating an aqueous solution or an aqueous dispersion, for example by mechanical stirring.

During mixing of the aqueous mixture of the first and second salts, the temperature of the aqueous mixture may be maintained in the range of from 15°C to 150°C, or from 5 60°C to 125°C, or from 65°C to 100°C. When the cationic component of the second salt is ammonium, the temperature should be maintained in a range from 65°C to 150°C to evolve ammonia as a gas from the second salt. The temperature of the aqueous mixture during mixing may be maintained at less than 100°C so that the mixing may be conducted without the application of positive pressure necessary to inhibit the water in the aqueous mixture 10 from becoming steam. If the second salt is a tetrathioostannate, the temperature of the aqueous mixture may be maintained at 100°C or less to inhibit the degradation of the second salt into tin disulfides.

The first and second salts in the aqueous mixture may be mixed under a pressure of from 0.101 MPa to 10 MPa (1.01 bar to 100 bar). The first and second salts in the aqueous 15 mixture may be mixed at atmospheric pressure, however, if the mixing is effected at a temperature greater than 100°C the mixing may be conducted under positive pressure to inhibit the formation of steam.

During mixing, the aqueous mixture of the first and second salts may be maintained under anaerobic conditions. Maintaining the aqueous mixture under anaerobic conditions 20 during mixing inhibits the oxidation of the thiometallate catalyst material or the anionic component of the second salt so that the thiometallate catalyst material produced by the process contains little, if any oxygen. The aqueous mixture of the first and second salts may be maintained under anaerobic conditions during mixing by conducting the mixing in an atmosphere containing little or no oxygen, preferably an inert atmosphere. The mixing 25 of the first and second salts in the aqueous mixture may be conducted under nitrogen gas, argon gas, and/or steam to maintain anaerobic conditions during the mixing. An inert gas, preferably nitrogen gas or steam, may be continuously injected into the aqueous mixture during mixing to maintain anaerobic conditions and to facilitate mixing of the first and second salts in the aqueous mixture and displacement of ammonia gas if the second salt 30 contains an ammonium cation.

The first and second salts may be mixed in the aqueous mixture at a temperature of from 15°C to 150°C under anaerobic conditions for a period of time sufficient to permit the formation of the thiometallate catalyst material. The first and second salts may be mixed in

the aqueous mixture for a period of at least 1 hour, or at least 2 hours, or at least 3 hours, or at least 4 hours, or from 1 hour to 10 hours, or from 2 hours to 9 hours, or from 3 hours to 8 hours, or from 4 hours to 7 hours to form the thiometallate catalyst material. The first and/or second salt(s) may be added to the aqueous mixture over a period of from 30  
5 minutes to 4 hours while mixing the aqueous mixture, and, after the entirety of the first and second salts have been mixed into the aqueous mixture, the aqueous mixture may be mixed for at least an additional 1 hour, or 2 hours, or 3 hours or 4 hours, or 5 hours to form the thiometallate catalyst material.

After completing mixing of the aqueous mixture of the first and second salts, a  
10 solid may be separated from the aqueous mixture to produce the thiometallate catalyst material. The solid may be separated from the aqueous mixture by any conventional means for separating a solid phase material from a liquid phase material. For example, the solid may be separated by allowing the solid to settle from the resulting mixture, preferably for a period of from 1 hour to 16 hours, and separating the solid from the mixture by  
15 vacuum or gravitational filtration or by centrifugation. To enhance recovery of the solid, water may be added to the aqueous mixture prior to allowing the solid to settle. Water may be added to the aqueous mixture in a volume relative to the volume of the aqueous mixture of from 0.1:1 to 0.75:1. Alternatively, but less preferably, the solid may be separated from the mixture by centrifugation without first allowing the solid to settle and/or without the  
20 addition of water. The solid may also be separated from the mixture by spray drying the mixture to produce the catalyst.

The thiometallate catalyst material may be washed subsequent to separation from the aqueous mixture, if desired. The separated material of the catalyst may be contaminated with minor amounts, typically less than 0.5 wt.%, of the anionic component  
25 from the first salt and/or the cationic component from the second salt. These minor contaminants may be removed from the separated material of the catalyst by washing the separated material with water. Substantial volumes of water may be used to wash the separated catalyst material since the separated catalyst material is insoluble in water, and the yield of catalyst material will not be significantly affected by the wash.

30 The resulting thiometallate catalyst material has little or no acidity as determined by ammonia chemisorption. Typically, the thiometallate catalyst material will have an acidity as measured by ammonia chemisorption of from 0 to 100  $\mu\text{mol}$  ammonia per gram of catalyst.

*Mixing the hydrocarbon-containing feedstock, catalyst, and hydrogen to hydrocrack feedstock*

At least one low acidity or non-acidic transition metal containing catalyst,  
5 preferably a Lewis basic thiometallate catalyst as described above, a hydrocarbon-  
containing feedstock as described above, and hydrogen are mixed, preferably blended, at a  
temperature of from 375°C to 500°C and a pressure of 6.9 MPa to 27.5MPa to hydrocrack  
the hydrocarbon-containing feedstock to provide the first hydrocarbon-containing  
composition. The hydrocarbon-containing feedstock, the non-acidic transition metal  
10 containing catalyst(s), and hydrogen may be mixed by contact with each other in a mixing  
zone maintained at a temperature of from 375°C to 500°C and a pressure of 6.9 MPa to  
27.5 MPa. A vapor that comprises hydrocarbons that are a gas at the temperature and  
pressure within the mixing zone and a hydrocarbon-containing feed residuum comprising  
hydrocarbons that are liquid at the temperature and pressure within the mixing zone are  
15 produced as a result of mixing the non-acidic transition metal-containing catalyst, the  
hydrocarbon-containing feedstock, and hydrogen at a temperature of from 375°C to 500°C  
and a pressure of 6.9 MPa to 27.5MPa. The vapor is comprised of the first hydrocarbon-  
containing composition, where the first hydrocarbon-containing composition comprises  
hydrocarbons that are liquid at STP. The vapor may also comprise hydrogen, hydrogen  
20 sulfide, and hydrocarbons that are gaseous at STP.

As shown in Fig. 1, the mixing zone **1** may be in a reactor **3**, where the conditions  
of the reactor **3** may be controlled to maintain the temperature and pressure in the mixing  
zone **1** at 375°C to 500°C and 6.9 MPa to 27.5 MPa, respectively. The hydrocarbon-  
containing feedstock may be provided continuously or intermittently from a feed supply **2**  
25 to the mixing zone **1** in the reactor **3** through feed inlet **5**. The hydrocarbon-containing  
feedstock may be preheated to a temperature of from 100°C to 350°C by a heating element  
**4**, which may be a heat exchanger, prior to being fed to the mixing zone **1**.

The hydrocarbon-containing feedstock may be provided to the mixing zone **1** of the  
reactor **3** at a rate effective to maintain a mixture volume in the reactor **3** of from 5% to  
30 97% of the volume of the reactor **3**. The mixture volume is defined herein as the combined  
volume of the catalyst(s), the hydrocarbon-depleted feed residuum (as defined herein), and  
the hydrocarbon-containing feedstock in the mixing zone **1**, where the hydrocarbon-  
depleted feed residuum may contribute no volume to the mixture volume (i.e. at the start of  
the process before a hydrocarbon-depleted feed residuum has been produced in the mixing

zone **1**), and where the hydrocarbon-containing feedstock may periodically contribute no volume to the mixture volume (i.e. after initiation of the process during a period between intermittent addition of fresh hydrocarbon-containing feedstock into the mixing zone **1**).

The hydrocarbon-containing feedstock may be provided to the mixing zone **1** of the reactor **3** at a rate of greater than 300, or at least 400, or at least 500, or at least 600, or at least 700, or at least 800, or at least 900, or at least 1000 kg/hr per m<sup>3</sup> of the mixture volume within the mixing zone **1** up to 5000 kg/hr per m<sup>3</sup> of the mixture volume within the mixing zone **1**.

The mixture volume within the mixing zone **1** may be affected by 1) the rate of addition of the hydrocarbon-containing feedstock into the mixing zone **1**; 2) the rate of removal of the vapor from the reactor **3**; and 3) the rate at which a bleed stream **25** of the hydrocarbon-depleted feed residuum, catalyst(s), and hydrocarbon-containing feedstock is separated from and recycled to the reactor **3**, as described in further detail below. The mixture volume of the hydrocarbon-containing feedstock, the hydrocarbon-depleted feed residuum, and the non-acidic transition metal-containing catalyst(s) may be maintained within the mixing zone within a selected range of the reactor volume by selecting 1) the rate at which the hydrocarbon-containing feedstock is provided to the mixing zone **1**; and/or 2) the rate at which a bleed stream is removed from and recycled to the mixing zone **1**; and/or 3) the temperature and pressure within the mixing zone **1** and the reactor **3** to provide a selected rate of vapor removal from the mixing zone **1** and the reactor **3**. The combined volume of the hydrocarbon-containing feedstock and the catalyst(s) initially provided to the mixing zone **1** at the start of the process define an initial mixture volume, and the amount of hydrocarbon-containing feedstock and the amount of the catalyst(s) initially provided to the mixing zone **1** may be selected to provide an initial mixture volume of from 5% to 97% of the reactor volume, preferably from 30% to 75% of the reactor volume. The rate at which the hydrocarbon-containing feedstock is provided to the mixing zone **1** and/or the rate at which a bleed stream is removed from and recycled to the mixing zone **1** and/or the rate at which vapor is removed from the reactor **3** may be selected to maintain the mixture volume of the hydrocarbon-containing feedstock, the hydrocarbon-depleted feed residuum, and the catalyst(s) at a level of at least 10%, or at least 25%, or at least 40%, or at least 50%, or within 70%, or within 50%, or from 10% to 250%, or from 25% to 200%, or from 50% to 150% of the initial mixture volume during the hydrocracking step of the process.

Hydrogen is provided to the mixing zone **1** of the reactor **3** for mixing or blending with the hydrocarbon-containing feedstock and the non-acidic transition metal-containing

catalyst(s). Hydrogen may be provided continuously or intermittently to the mixing zone 1 of the reactor 3 through hydrogen inlet line 7, or, alternatively, may be mixed together with the hydrocarbon-containing feedstock, and optionally the catalyst(s), and provided to the mixing zone 1 through the feed inlet 5. Hydrogen may be provided to the mixing zone 1 of the reactor 3 at a rate sufficient to hydrogenate hydrocarbons cracked in the process. The hydrogen may be provided to the mixing zone 1 in a ratio relative to the hydrocarbon-containing feedstock provided to the mixing zone 1 of from 1 Nm<sup>3</sup>/m<sup>3</sup> to 16,100 Nm<sup>3</sup>/m<sup>3</sup> (5.6 SCFB to 90160 SCFB), or from 2 Nm<sup>3</sup>/m<sup>3</sup> to 8000 Nm<sup>3</sup>/m<sup>3</sup> (11.2 SCFB to 44800 SCFB), or from 3 Nm<sup>3</sup>/m<sup>3</sup> to 4000 Nm<sup>3</sup>/m<sup>3</sup> (16.8 SCFB to 22400 SCFB), or from 5 Nm<sup>3</sup>/m<sup>3</sup> to 320 Nm<sup>3</sup>/m<sup>3</sup> (28 SCFB to 1792 SCFB). The total pressure in the mixing zone 1 may be maintained in a pressure range of from 4 MPa to 27.5 MPa (580-4000 psi) or from 6.9 MPa to 10 MPa (1000-1450 psi), and the hydrogen partial pressure in the mixing zone may be maintained in a pressure range of from 4 MPa to 25 MPa .

One or more of the non-acidic transition metal-containing catalysts, preferably one or more thiometallate catalyst(s) as described above, may be located in the mixing zone 1 in the reactor 3 or may be provided to the mixing zone 1 in the reactor 3 in the hydrocracking step. Any metal-containing catalyst provided for mixing in the mixing zone 1 of the reactor 3 has an acidity as measured by ammonia chemisorption of at most 500  $\mu$ mol ammonia desorbed from the catalyst per gram of catalyst, or at most 200, or at most 100, or at most 50, or at most 10, or at most 5  $\mu$ mol ammonia desorbed from the catalyst per gram of catalyst, and, most preferably 0  $\mu$ mol ammonia desorbed from the catalyst per gram of catalyst.

The non-acidic transition metal-containing catalyst may be located in the mixing zone 1 in a catalyst bed. More preferably, the non-acidic metal-containing catalyst may be provided to the mixing zone 1 during the hydrocracking step, or, if located in the mixing zone initially, may be blended with the hydrocarbon-containing feed and hydrogen, and is not present in a catalyst bed. The non-acidic metal-containing catalyst may be provided to the mixing zone 1 together with the hydrocarbon-containing feedstock through feed inlet 5, where the catalyst may be dispersed in the hydrocarbon-containing feedstock prior to feeding the mixture to the mixing zone 1 through the feed inlet 5. Alternatively, the non-acidic metal-containing catalyst may be provided to the mixing zone 1 through a catalyst inlet 9, where the catalyst may be mixed with sufficient hydrocarbon-containing feedstock or another fluid, for example a hydrocarbon-containing fluid, to enable the catalyst to be delivered to the mixing zone 1 through the catalyst inlet 9.

The non-acidic transition metal-containing catalyst may be provided to be mixed with the hydrocarbon-containing feedstock and hydrogen in the mixing zone **1** in a sufficient amount to catalytically crack the hydrocarbon-containing feedstock and/or to catalyze hydrogenation of the cracked hydrocarbons in the mixing zone. An initial charge of the non-acidic metal-containing catalyst may be provided for mixing with an initial charge of hydrocarbon-containing feedstock in an amount of from 20 grams to 125 grams of catalyst per kilogram of initial hydrocarbon-containing feedstock. Over the course of the process, the non-acidic metal-containing catalyst may be provided for mixing with the hydrocarbon-containing feedstock and hydrogen in an amount of from 0.125 grams to 5 grams of catalyst per kilogram of hydrocarbon-containing feedstock. Alternatively, the non-acidic metal-containing catalyst may be provided for mixing with the hydrocarbon-containing feedstock and hydrogen over the course of the process in an amount of from 0.125 grams to 50 grams of catalyst per kilogram of hydrocarbons in the hydrocarbon-containing feedstock having a boiling point of at least 538°C as determined in accordance with ASTM Method D5307.

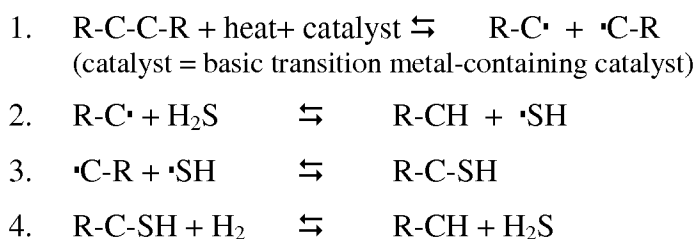
Hydrogen sulfide may also be mixed, and preferably blended, with the hydrocarbon-containing feedstock, hydrogen, any hydrocarbon-depleted feed residuum, and the non-acidic transition metal-containing catalyst in the mixing zone **1** of the reactor **3**. The hydrogen sulfide may be provided continuously or intermittently to the mixing zone **1** of the reactor **3** as a liquid or a gas. The hydrogen sulfide may be mixed with the hydrocarbon-containing feedstock and provided to the mixing zone **1** with the hydrocarbon-containing feedstock through the feed inlet **5**. Alternatively, the hydrogen sulfide may be mixed with hydrogen and provided to the mixing zone **1** through the hydrogen inlet line **7**. Alternatively, the hydrogen sulfide may be provided to the mixing zone **1** through a hydrogen sulfide inlet line **27**.

It is believed that the hydrogen sulfide acts as a further catalyst in cracking hydrocarbons in the hydrocarbon-containing feedstock in the presence of hydrogen and the non-acidic transition metal-containing catalyst and inhibits coke formation and formation of refractory sulfur and nitrogen compounds under cracking conditions. Use of sufficient hydrogen sulfide in the hydrocracking step of the process permits the hydrocracking to be effected at a mixing zone temperature of at least at least 430°C or at least 450°C with little or no increase in coke formation and/or refractory sulfur and/or nitrogen compound formation relative to cracking conducted at lower temperatures since hydrogen sulfide

inhibits coke and refractory sulfur and/or nitrogen compound formation. The rate of the process, in particular the rate that the hydrocarbon-containing feedstock may be provided to the mixing zone **1** for cracking and the vapor containing the first hydrocarbon-containing product may be removed from the reactor **3**, therefore, may be greatly increased with the use of significant quantities of hydrogen sulfide in the hydrocracking mixture since the rate of reaction in the process increases significantly relative to temperature.

Hydrogen sulfide and hydrogen each may act as an atomic hydrogen donor to hydrogenate a cracked hydrocarbon anion radical to produce a stable hydrocarbon having a smaller molecular weight than the hydrocarbon from which the hydrocarbon anion radical was derived. Hydrogen, however, may only act to donate a hydrogen atom to a cracked hydrocarbon anion radical at or near a metal-containing catalyst surface. Hydrogen sulfide, however, may act to provide a hydrogen atom to a cracked hydrocarbon anion radical significantly further from a metal-containing catalyst surface, and, after donation of a hydrogen atom, may accept a hydrogen atom from hydrogen near the surface of the catalyst. The hydrogen sulfide, therefore, may act as an atomic hydrogen shuttle to provide atomic hydrogen to a cracked hydrocarbon anion radical at a distance from the non-acidic catalyst. Hydrogen sulfide also reacts much more rapidly to hydrogenate a cracked hydrocarbon anion radical than hydrogen since the reaction of hydrogen sulfide with a cracked hydrocarbon anion radical to hydrogenate the radical is substantially more energetically favored than hydrogenation of the cracked hydrocarbon anion radical by hydrogen. Hydrogen sulfide may inhibit annealation of cracked hydrocarbon radicals by rapidly reacting with the cracked hydrocarbon radicals before the cracked hydrocarbon radicals react with another hydrocarbon.

Furthermore, the thiol group remaining after hydrogen sulfide has provided a hydrogen atom to a cracked hydrocarbon anion radical may be provided to another hydrocarbon anion radical, thereby forming a meta-stable thiol-containing hydrocarbon. This may be described chemically as follows:



The thiol of the meta-stable thiol-containing hydrocarbon may be replaced by a hydrogen atom from either another hydrogen sulfide molecule or hydrogen, or may react

intramolecularly to form a thiophene compound as a hydrocarbon-containing product. Thus, hydrogen sulfide may open up another reaction pathway for conversion of a cracked hydrocarbon to its hydrogenated counterpart—enhancing the rate of the reaction.

The hydrogen sulfide provided to be mixed with the hydrocarbon-containing feedstock, hydrogen, and the non-acidic transition metal-containing catalyst may be provided in an amount effective to increase the rate of the cracking reaction. In order to increase the rate of the cracking reaction, hydrogen sulfide may be provided in an amount on a mole ratio basis relative to hydrogen provided to be mixed with the hydrocarbon-containing feedstock and catalyst of at least 1 mole of hydrogen sulfide per 10 moles hydrogen. The hydrogen sulfide may be provided in an amount on a mole ratio basis relative to the hydrogen provided of at least 1.5 : 10.0, or at least 1.0 : 5.0, or at least 1.0 : 4.0, or at least 3.0 : 10.0, or at least 2.0 : 5.0.

The non-acidic transition metal-containing catalyst, the hydrocarbon-containing feedstock, hydrogen, and optionally hydrogen sulfide may be mixed by being blended into an intimate admixture in the mixing zone **1**. The catalyst, hydrocarbon-containing feedstock, hydrogen, and optionally hydrogen sulfide may be blended in the mixing zone **1**, for example, by stirring a mixture of the components, for example by a mechanical stirring device located in the mixing zone **1**. The catalyst, hydrocarbon-containing feedstock, hydrogen, and optionally hydrogen sulfide may also be mixed in the mixing zone **1** by blending the components prior to providing the components to the mixing zone **1** and injecting the blended components into the mixing zone **1** through one or more nozzles which may act as the feed inlet **5**. The catalyst, hydrocarbon-containing feedstock, hydrogen, and optionally hydrogen sulfide may also be blended in the mixing zone **1** by blending the hydrocarbon-containing feedstock and catalyst and injecting the mixture into the mixing zone **1** through one or more feed inlet nozzles positioned with respect to the hydrogen inlet line **7** such that the mixture is blended with hydrogen entering the mixing zone **1** through the hydrogen inlet line **7**. Baffles may be included in the reactor **3** in the mixing zone **1** to facilitate blending the hydrocarbon-containing feedstock, catalyst, hydrogen, and optionally hydrogen sulfide. Less preferably, the non-acidic transition metal-containing catalyst is present in the mixing zone **1** in a catalyst bed, and the hydrocarbon-containing feedstock, hydrogen, optionally hydrogen sulfide, and catalyst are mixed by bringing the hydrocarbon-containing feedstock and hydrogen, and optionally hydrogen sulfide, simultaneously into contact with the catalyst in the catalyst bed.

The temperature and pressure conditions in the mixing zone **1** may be maintained so that heavy hydrocarbons in the hydrocarbon-containing feedstock may be cracked. The temperature in the mixing zone **1** may be maintained from 375°C to 500°C. Preferably, the mixing zone **1** is maintained at a temperature of from 425°C to 500°C, or from 430°C to 500°C, or from 440°C to 500°C, or from 450°C to 500°C. The temperature within the mixing zone may be selected and controlled to be at least 430°C, or at least 450°C. Higher temperatures may be preferred in the catalytic hydrocracking step since 1) the rate of conversion of the hydrocarbon-containing feedstock to the vapor containing the first hydrocarbon-containing composition increases with temperature; and 2) the non-acidic catalytic hydrocracking inhibits or prevents the formation of coke, even at temperatures of 450°C or greater, which typically occurs rapidly in conventional cracking processes at temperatures of 430°C or greater.

Mixing the hydrocarbon-containing feedstock, the non-acidic catalyst, hydrogen, and optionally hydrogen sulfide in the mixing zone **1** at a temperature of from 375°C to 500°C and a pressure of from 6.9 MPa to 27.5 MPa produces a vapor that is comprised of hydrocarbons that are vaporizable at the temperature and pressure within the mixing zone **1** which includes the first hydrocarbon-containing composition. The vapor may be comprised of hydrocarbon compounds present initially in the hydrocarbon-containing feedstock that vaporize at the temperature and pressure within the mixing zone **1** and hydrocarbon compounds that are not present initially in the hydrocarbon-containing feedstock but are produced by cracking and hydrogenating hydrocarbon compounds initially in the hydrocarbon-containing feedstock that were not vaporizable at the temperature and pressure within the mixing zone **1**. The vapor may also be comprised of hydrocarbons that are gaseous at STP, hydrogen, and hydrogen sulfide. At least a portion of the vapor comprised of hydrocarbons that are vaporizable at the temperature and pressure within the mixing zone **1** may be continuously or intermittently separated from the mixing zone **1** since the more volatile vapor physically separates from the mixture in the mixing zone **1**.

Separation of the vapor from the mixture in the mixing zone **1** leaves a hydrocarbon-depleted feed residuum from which the hydrocarbons present in the vapor have been removed. The hydrocarbon-depleted feed residuum is comprised of hydrocarbons that are liquid at the temperature and pressure within the mixing zone **1**. The hydrocarbon-depleted feed residuum may also be comprised of solids such as metals freed

from cracked hydrocarbons and minor amounts of coke. The hydrocarbon-depleted feed residuum may contain little coke or proto-coke since the non-acidic catalytic hydrocracking inhibits the generation of substantial quantities of coke. The hydrocarbon-depleted feed residuum may contain, per metric ton of hydrocarbon feedstock provided to the mixing zone **1**, less than 30 kg, or at most 20 kg, or at most 10 kg, or at most 5 kg of hydrocarbons insoluble in toluene as measured by ASTM Method D4072.

At least a portion of the hydrocarbon-depleted feed residuum may be retained in the mixing zone **1** while the vapor is separated from the mixing zone **1**. The portion of the hydrocarbon-depleted feed residuum retained in the mixing zone **1** may be subject to further cracking to produce more vapor that may be separated from the mixing zone **1** and then from the reactor **3**. Hydrocarbon-containing feedstock and hydrogen may be continuously or intermittently provided to the mixing zone **1** at the rates described above and mixed with the non-acidic transition metal-containing catalyst(s) and the hydrocarbon-depleted feed residuum retained in the mixing zone **1** to produce further vapor comprised of hydrocarbons that are vaporizable at the temperature and pressure within the mixing zone **1** for separation from the mixing zone **1** and the reactor **3**.

At least a portion of the vapor separated from the mixing zone **1** may be continuously or intermittently separated from the reactor **3** through a reactor product outlet **11** to provide the first hydrocarbon-containing composition. The reactor **3** is preferably configured and operated so that substantially only vapors and gases may exit the reactor product outlet **11**, where the vapor product exiting the reactor **3** comprises at most 5 wt.%, or at most 3 wt.%, or at most 1 wt.%, or at most 0.5 wt.%, or at most 0.1 wt.%, or at most 0.01 wt.%, or at most 0.001 wt.% solids and liquids at the temperature and pressure at which the vapor product exits the reactor **3**.

A stripping gas may be injected into the reactor **3** over the mixing zone **1** to facilitate separation of the vapor containing the first hydrocarbon-containing composition from the mixing zone **1** and from the reactor **3**. The stripping gas may be heated to a temperature at or above the temperature within the mixing zone **1** to assist in separating the vapor from the mixing zone **1**. The stripping gas may be hydrogen gas and/or hydrogen sulfide gas.

The hydrocarbons in the hydrocarbon-containing feed and hydrocarbon-containing feed residuum may be contacted and mixed with the non-acidic transition metal-containing catalyst, hydrogen, and optionally hydrogen sulfide in the mixing zone **1** of the reactor **3** only as long as necessary to be vaporized and separated from the mixture, and are retained

in the reactor **3** only as long as necessary to be vaporized and exit the reactor product outlet **11**. Low molecular weight hydrocarbons having a low boiling point may be vaporized and separated from the mixing zone **1** almost immediately upon being introduced into the mixing zone **1** when the mixing zone **1** is maintained at a temperature of 375°C to 500°C and a pressure of from 6.9 MPa to 27.5 MPa. These hydrocarbons may be separated rapidly from the reactor **3** in the vapor. High molecular weight hydrocarbons having a high boiling point, for example hydrocarbons having a boiling point greater than 538°C at 0.101 MPa, may remain in the mixing zone **1** until they are cracked into hydrocarbons having a boiling point low enough to be vaporized at the temperature and pressure in the mixing zone **1** and to separate from the mixing zone and exit the reactor **3**. The hydrocarbons of the hydrocarbon-containing feedstock, therefore, may be contacted and mixed with the catalyst and hydrogen, and optionally hydrogen sulfide, in the mixing zone **1** of the reactor **3** for a variable time period, depending on the boiling point of the hydrocarbons under the conditions in the mixing zone **1** and the reactor **3**.

The rate of producing the vapor comprising the first hydrocarbon-containing composition from the hydrocarbon-containing feedstock may be adjusted by selection of the temperature and/or pressure in the reactor **3**, and particularly in the mixing zone **1**, within the temperature range of 375°C-500°C and within the pressure range of 6.9 MPa - 27.5 MPa. Increasing the temperature and/or decreasing the pressure in the mixing zone **1** permits the hydrocarbon-containing feedstock to be provided to the mixing zone **1** of the reactor **3** at an increased rate and permits the vapor to be separated from the mixing zone **1** and the reactor **3** at an increased rate since the hydrocarbons in the hydrocarbon-containing feedstock may experience a decreased residence time in the reactor **3** due to higher cracking activity and/or increased volatility. Conversely, decreasing the temperature and/or increasing the pressure in the mixing zone **1** may reduce the rate at which the hydrocarbon-containing feedstock may be provided to the reactor **3** and the vapor may be separated and removed from mixing zone **1** and the reactor **3** since the hydrocarbons in the hydrocarbon-containing feedstock may experience an increased residence time in the reactor **3** due to lower cracking activity and/or decreased volatility.

As a result of the inhibition and/or prevention of the formation of coke, the hydrocarbons in the hydrocarbon-containing feed may be contacted and mixed with the non-acidic catalyst, hydrogen, and optionally hydrogen sulfide in the mixing zone **1** at a temperature of 375°C to 500°C and a pressure of 6.9 MPa to 27.5 MPa for as long as

necessary to be vaporized, or to be cracked, hydrogenated, and vaporized. It is believed that high boiling, high molecular weight hydrocarbons may remain in the mixing zone **1** in the presence of cracked hydrocarbons since the non-acidic transition metal-containing catalyst promotes the formation of hydrocarbon radical anions upon cracking that react with hydrogen and/or hydrogen sulfide to form stable hydrocarbon products rather than hydrocarbon radical cations that react with other hydrocarbons to form coke or refractory sulfur- and/or nitrogen-containing hydrocarbon compounds. Coke and refractory sulfur- and/or nitrogen-containing hydrocarbon formation is also avoided because the cracked hydrogenated hydrocarbons preferentially exit the mixing zone **1** as a vapor rather than remaining in the mixing zone **1** to combine with hydrocarbon anion radicals in the mixing zone **1** to form coke or proto-coke and refractory heteroatomic hydrocarbons.

Although the hydrocracking step of the process produces little coke, coke and metals may accumulate in the mixing zone **1** over time unless removed. A portion of the hydrocarbon-depleted feed residuum and non-acidic catalyst may be separated from the mixing zone to remove solids including metals and hydrocarbonaceous solids including coke from the hydrocarbon-depleted feed residuum. The reactor **3** may include a bleed stream outlet **25** for removal of a stream of hydrocarbon-depleted feed residuum and catalyst from the mixing zone **1** and the reactor **3**. The bleed stream outlet **25** may be operatively connected to the mixing zone **1** of the reactor **3**.

A portion of the hydrocarbon-depleted feed residuum may be removed from the mixing zone **1** and the reactor **3** as a bleed stream through the bleed stream outlet **25** while the hydrocracking reaction is proceeding. A portion of the non-acidic transition metal-containing catalyst may also be removed from the mixing zone **1** as part of the bleed stream. Solids and the catalyst(s) in the bleed stream may be separated from a liquid portion of the hydrocarbon-depleted feed residuum in the bleed stream in a solid-liquid separator **17**. The solid-liquid separator **17** may be a filter or a centrifuge. After separation from the solids, the liquid portion of the bleed stream may be recycled back into the mixing zone **1** via a recycle inlet **24** for further processing or may be combined with the hydrocarbon-containing feed and recycled into the mixing zone **1** through the feed inlet **5**.

The vapor separated from the mixing zone **1** and the reactor **3** comprises the first hydrocarbon-containing composition and hydrocarbons that are gaseous at STP, where most of the hydrocarbons in the vapor are contained in the first hydrocarbon-containing composition. The first hydrocarbon-containing composition may have a carbon content that is at least 80%, or at least 90%, or at least 95% of the carbon content of the

hydrocarbon-containing feedstock. The hydrocarbons in the vapor that are gaseous at STP may have a carbon content that is at most 10%, or at most 5%, or at most 4%, or at most 3% of the carbon content of the hydrocarbon-containing feedstock.

The first hydrocarbon-containing composition is comprised primarily of non-residue and non-asphaltenic hydrocarbon compounds that have a boiling point of 538°C (1000°F) or less. The first hydrocarbon-containing composition may contain less than 3 wt.%, or at most 2 wt.%, or at most 1 wt.%, or at most 0.5 wt.% of hydrocarbons having a boiling point of greater than 538°C as determined in accordance with ASTM Method D5307. The first hydrocarbon-containing composition may contain VGO hydrocarbons, distillate hydrocarbons, and naphtha hydrocarbons. The first hydrocarbon-containing composition may contain, per gram, at least 0.05 grams, or at least 0.1 grams of hydrocarbons having a boiling point from the initial boiling point of the first hydrocarbon-containing composition up to 204°C (400°F). The first hydrocarbon-containing composition may also contain, per gram, at least 0.1 grams, or at least 0.15 grams of hydrocarbons having a boiling point of from 204°C (400°F) up to 260°C (500°F). The first hydrocarbon-containing composition may also contain, per gram, at least 0.25 grams, or at least 0.3 grams, or at least 0.35 grams of hydrocarbons having a boiling point of from 260°C (500°F) up to 343°C (650°F). The first hydrocarbon-containing composition may also contain, per gram, at least 0.3 grams, or at least 0.35 grams, or at least 0.4, or at least 0.45 grams of hydrocarbons having a boiling point of from 343°C (650°F) up to 538°C (1000°F). The relative amounts of hydrocarbons within each boiling range and the boiling range distribution of the hydrocarbons may be determined in accordance with ASTM Method D5307.

The first hydrocarbon-containing composition may contain significant amounts of sulfur. The first hydrocarbon-containing composition contains, per gram, from 0.001 gram of sulfur to at least 0.05 gram of sulfur. The sulfur content of the first hydrocarbon-containing composition may be determined in accordance with ASTM Method D4294. A significant portion of the sulfur-containing hydrocarbon compounds in the first hydrocarbon-containing composition may be contained in the hydrocarbon fractions having a boiling point up to 343°C (650°F). In the first hydrocarbon-containing composition at least 40%, or at least 45%, or at least 50%, or at least 60%, or at 65%, or at least 70%, or at least 75%, or at least 80% of the sulfur-containing hydrocarbon compounds, by weight of sulfur as determined in accordance with ASTM Method D4294, are contained in the

hydrocarbon fractions having a boiling point from the initial boiling point of the first hydrocarbon-containing product to 343°C (650°F) wherein each boiling range and the boiling range distribution of the hydrocarbons may be determined in accordance with ASTM Method D5307. Less than 50%, or less than 45%, or less than 40%, or less than 35%, or less than 30%, or less than 25%, or less than 20% of the sulfur-containing hydrocarbons in the first hydrocarbon-containing composition, by weight of sulfur in the compounds as determined in accordance with ASTM Method D4294, may be contained in hydrocarbon compounds having a boiling point of greater than 343°C (650°F), where the boiling range and boiling range distribution of hydrocarbons boiling at temperatures from 343°C and above may be determined in accordance with ASTM Method D5307.

At least 40 wt.% of the sulfur of the first hydrocarbon-containing composition may be contained in hydrocarbon compounds having a carbon number of 17 or less as determined by two-dimensional GC-GC sulfur chemiluminescence, where at least 60 wt.% of the sulfur in the sulfur-containing hydrocarbon compounds having a carbon number of 17 or less may be contained in benzothiophenic compounds as determined by GC-GC sulfur chemiluminescence (GCxGC-SCD). In the first hydrocarbon-containing composition, at least 40 wt.%, or at least 45 wt.%, or at least 50 wt.%, or at least 55 wt.%, or at least 60 wt.% of the sulfur may be contained in benzothiophenic compounds. The amount of sulfur in benzothiophenic compounds in the first hydrocarbon-containing composition relative to the amount of sulfur in all sulfur containing compounds in the first hydrocarbon-containing composition may be determined by sulfur chemiluminescence two dimensional gas chromatography (GCxGC-SCD).

Of the benzothiophenic compounds in the first hydrocarbon-containing composition, a substantial portion may have a boiling point in a range below 343°C. At least 65 wt.%, or at least 70 wt.%, or at least 75 wt.%, or at least 80 wt.%, or at least 85 wt.% of the benzothiophenic compounds, on an atomic sulfur basis as determined by sulfur chemiluminescence two dimensional gas chromatography (GCxGC-SCD), may have a boiling point in a range below 343°C as determined in accordance with ASTM Method D5307. Benzothiophenic compounds having a boiling point in a range of 343°C or greater typically are more refractory than benzothiophenic compounds having a lower boiling point.

The first hydrocarbon-containing composition also may contain, per gram, at least 0.0005 gram or at least 0.001 gram of nitrogen as determined in accordance with ASTM Method D5762. The first hydrocarbon-containing composition may have a relatively low

ratio of basic nitrogen compounds to other nitrogen containing compounds therein. The nitrogen-containing hydrocarbon compounds in the first hydrocarbon-containing composition may be primarily contained in the hydrocarbon fractions having a boiling point up to 343°C (650°F). In the first hydrocarbon-containing composition at least 65%,  
5 or at least 70%, or at least 75%, or at least 80% of the nitrogen-containing hydrocarbon compounds, by weight of nitrogen in the compounds as determined in accordance with ASTM Method D5762, may be contained in the hydrocarbon fractions having a boiling point from the initial boiling point of the first hydrocarbon-containing composition to 343°C (650°F) wherein each boiling range and the boiling range distribution of the  
10 hydrocarbons may be determined in accordance with ASTM Method D5307. Less than 35% of the nitrogen-containing hydrocarbons in the first hydrocarbon-containing composition, by weight of nitrogen in the compounds as determined in accordance with ASTM Method D5762, may be contained in hydrocarbon compounds having a boiling point of greater than 343°C (650°F), where the boiling range and boiling range distribution  
15 of hydrocarbons boiling at temperatures from 343°C and above may be determined in accordance with ASTM Method D5307.

The first hydrocarbon-containing composition may contain significant quantities of aromatic hydrocarbon compounds. The first hydrocarbon-containing composition may contain, per gram, at least 0.3 gram, or at least 0.35 gram, or at least 0.4 gram, or at least  
20 0.45 gram, or at least 0.5 gram of aromatic hydrocarbon compounds.

The first hydrocarbon-containing composition may contain relatively few polyaromatic hydrocarbon compounds containing three or more aromatic ring structures (e.g. anthracene, phenanthrene) relative to mono-aromatic hydrocarbon compounds and di-aromatic hydrocarbon compounds. The combined mono-aromatic hydrocarbon  
25 compounds and di-aromatic hydrocarbon compounds in the first hydrocarbon-containing composition may be present in the first hydrocarbon-containing composition in a weight ratio relative to the polyaromatic hydrocarbon compounds (containing three or more aromatic ring structures) of at least 1.5 : 1.0, or at least 2.0 : 1.0, or at least 2.5 : 1.0. The relative amounts of mono-, di-, and polyaromatic compounds in the first hydrocarbon-  
30 containing composition may be determined by flame ionization detection-two dimensional gas chromatography (GCxGC-FID).

The first hydrocarbon-containing composition may contain little metal content. The first hydrocarbon-containing composition may contain less than 1 wppm, or less than 0.5 wppm of vanadium. The first hydrocarbon-containing composition may contain less

than 0.5 wppm, or less than 0.3 wppm of nickel. The first hydrocarbon-containing composition may contain less than 0.3 wppm, or less than 0.2 wppm of iron.

### **Hydrotreating the first hydrocarbon-containing product**

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The first hydrocarbon-containing composition is hydrotreated to reduce the sulfur, nitrogen, and olefin content of the first hydrocarbon-containing composition and to increase the ratio of monoaromatic compounds to polyaromatic compounds containing 2 or more aromatic rings. The first hydrocarbon-containing composition is hydrotreated by contacting the first hydrocarbon-containing composition with a catalyst containing a Column 6 (of the Periodic Table) metal or a compound thereof (hereafter the “Column 6 metal catalyst”) and hydrogen at a temperature of from 260°C to 425°C at a pressure of from 3.4 MPa to 27.5 MPa, and preferably from 3.4 MPa to at most 10.5 MPa or at most 6.9 MPa, to produce a second hydrocarbon-containing composition.

15 The first hydrocarbon-containing composition is contacted with the Column 6 metal catalyst and hydrogen at the hydrotreating temperature and pressure apart from the mixing zone **1** of the reactor **3**, and preferably apart from the reactor **3**. The first hydrocarbon-containing composition may be hydrotreated by contacting the first hydrocarbon-containing composition, the Column 6 metal catalyst, and the hydrogen in a hydrotreating reactor **12**. The hydrotreating reactor **12** may be maintained at a temperature of 260°C to 425°C, preferably from 330°C to 400°C, and at a pressure of from 3.4 MPa to 27.5 MPa, and preferably from 3.4 MPa to at most 10.5 MPa or at most 6.9 MPa to effect the hydrotreatment of the first hydrocarbon-containing composition to produce the second hydrocarbon-containing composition. The first hydrocarbon-containing composition may be effectively hydrotreated at relatively low hydrogen partial pressure since a large proportion of the sulfur and nitrogen containing compounds in the first hydrocarbon-containing composition are non-refractory and may be easily removed. Preferably the first hydrocarbon-containing composition is hydrotreated at relatively low hydrogen partial pressure, *e.g.* a hydrogen partial pressure of from 3.4 MPa to less than 10.5 MPa, and more preferably from 3.4 MPa to at most 6.9 MPa.

The first hydrocarbon-containing composition may be contacted with the Column 6 metal catalyst and hydrogen at the hydrotreating temperature and pressure apart from the mixing zone **1** of the reactor **3** by contacting the vapor separated from the reactor **3** with the Column 6 metal catalyst and the hydrogen at the selected hydrotreating temperature

and pressure, preferably in the hydrotreating reactor **12**. The vapor may be provided from the reactor outlet **11** to the hydrotreating reactor **12**. If necessary, or as desired, the vapor may be cooled to a selected temperature, preferably in the hydrotreating temperature range of from 260°C to 425°C, in a heat exchanger **15** after it exits the reactor **3** prior to being fed to the hydrotreating reactor **12**.

Alternatively, the first hydrocarbon-containing composition may be separated from hydrogen, hydrocarbon compounds that are gaseous at STP, and hydrogen sulfide that are in the vapor along with the first hydrocarbon-containing composition after the vapor is separated from the mixing zone **1** and the reactor **3** and prior to hydrotreating the first hydrocarbon-containing composition. The first hydrocarbon-containing composition may be separated out of the vapor by condensing the first hydrocarbon-containing composition from the vapor. The first hydrocarbon-containing composition may be condensed from the vapor by cooling the vapor to a temperature of from 0°C to 100°C, preferably from 10°C to 50°C, and reducing the pressure of the vapor to a pressure of from 0.05 MPa to 1 MPa.

The condensed first hydrocarbon-containing composition may be collected as a liquid and separated from the gaseous remainder of the vapor. The separated first hydrocarbon-containing composition may then be provided to the hydrotreating reactor **12**, preferably after heating the separated first hydrocarbon-containing composition to the selected hydrotreatment temperature and pressurizing the separated first hydrocarbon-containing composition to the selected hydrotreatment pressure.

Hydrogen may be provided for contact with the first hydrocarbon-containing composition and the Column 6 metal catalyst to effect the hydrotreating. Provided that the first hydrocarbon-containing composition is not separated from the vapor and the vapor is provided for contact with the Column 6 metal catalyst, a portion of the hydrogen that is provided for contact with the first hydrocarbon-containing composition and the Column 6 metal catalyst may be contained in the vapor. Hydrogen provided in addition to hydrogen contained in the vapor is derived from a hydrogen source. The hydrogen source may be hydrogen gas obtained from any conventional sources or methods for producing hydrogen gas.

Hydrogen may be provided, as necessary, in addition to hydrogen present in the vapor separated from the reactor **3**, to the hydrotreating reactor **12** through a hydrotreating hydrogen inlet line **13**. Hydrogen, if necessary, may be provided to the hydrotreating reactor **12** at a ratio relative to the first hydrocarbon-containing composition of from 10 Nm<sup>3</sup>/m<sup>3</sup> to 3570 Nm<sup>3</sup>/m<sup>3</sup> (56 SCFB to 20000 SCFB). The hydrogen may be maintained at

a hydrogen partial pressure of from 3.4 MPa to 27.5 MPa, or from 3.4 MPa to 10.5 MPa or from 3.4 MPa to 6.9 MPa in the hydrotreating reactor **12** in the step of converting the first hydrocarbon-containing composition to the second hydrocarbon-containing composition.

The Column 6 metal catalyst that is contacted with the first hydrocarbon-containing composition and hydrogen to catalyze hydrotreatment of the first hydrocarbon-containing composition may be any conventional hydrotreating catalyst containing a Column 6 metal or a compound thereof. The Column 6 metal utilized in the hydrotreating catalyst is preferably molybdenum, tungsten, or mixtures thereof, and preferred Column 6 metal compounds utilized in the hydrotreating catalyst include molybdenum oxides, molybdenum sulfides, tungsten oxides, tungsten sulfides, and mixtures thereof.

The Column 6 metal catalyst may also include one or more metals selected from Columns 7-10 of the Periodic Table or compounds thereof. Preferred Columns-7-10 metals that may be utilized in the hydrotreating catalyst include cobalt, nickel and iron or compounds thereof. The Column 6 metal catalyst may also include a Column 15 element or a compound thereof as a promoter. A preferred Column 15 element or compound for utilization in the hydrotreating catalyst is phosphorous or a phosphorous containing compound.

The Column 6 metal catalyst may also be comprised of a support material on which the Column 6 metal or a compound thereof is dispersed or within which the Column 6 metal or compound thereof is intercalated. The support material may be a porous refractory oxide or an activated carbon material. The support material may be selected from the group consisting of alumina, silica, silica-alumina, titania, silica-titania, zirconia, silica-zirconia, magnesia, silica-magnesia, carbon, and mixtures thereof. A preferred support material comprises alumina, and preferably contains gamma-alumina.

The supported Column 6 metal catalyst may have a pore structure selected for hydrodesulfurization, hydrodenitrogenation, and/or hydrodearomatization. The supported Column 6 metal catalyst may have a pore size distribution that is unimodal and has a median pore diameter of from 100 angstroms to 350 angstroms, or from 150 angstroms to 250 angstroms, as determined by mercury porosimetry. The supported Column 6 metal catalyst may have a pore size distribution such that at least 90% of the pore volume of the catalyst is contained in pores having a pore diameter of 500 angstroms or less, or 350 angstroms or less, as determined by mercury porosimetry.

The Column 6 metal catalyst may be selected from commercially available hydrotreating catalysts. For example, a suitable commercially available Column 6 metal

catalyst is DN-200, a nickel-molybdenum catalyst available from CRI/Criterion, Inc., Houston, Texas, US.

The Column 6 metal catalyst may be sulfided to activate the catalyst. The Column 6 metal catalyst may be sulfided prior to contact with the first hydrocarbon-containing composition by passing a sulfiding gas, *e.g.* hydrogen sulfide, or a sulfur-containing liquid hydrocarbon over the catalyst, preferably at a temperature of from 50°C to 250°C. The Column 6 metal catalyst may also be sulfided *in situ* in the hydrotreating reactor **12** by contacting the Column 6 metal catalyst with the vapor separated from the reactor **3**, where the first hydrocarbon-containing composition is not separated from hydrogen sulfide contained in the vapour after separating the vapor from the reactor **3**.

The hydrotreating reactor **12** may be a fixed-bed catalyst reactor and the Column 6 metal catalyst may be located in a fixed bed in the hydrotreating reactor **12**. The first hydrocarbon-containing composition and hydrogen may be passed through the fixed Column 6 metal catalyst bed to contact the first hydrocarbon-containing composition, the Column 6 metal catalyst, and hydrogen to produce the second hydrocarbon-containing composition. The first hydrocarbon-containing composition may be passed through the hydrotreating reactor **12** along with the hydrogen over or through the fixed Column 6 catalyst bed at a liquid hourly space velocity (LHSV) of from 0.5 h<sup>-1</sup> to 10 h<sup>-1</sup>, and preferably at an LHSV of from 1 h<sup>-1</sup> to 5 h<sup>-1</sup>. Alternatively, the hydrotreating reactor **12** may be a slurry-type reactor, an ebullating-bed reactor, or a plug-flow reactor in which the Column 6 metal catalyst, the first hydrocarbon-containing composition and hydrogen flow together through the reactor. The mixture of the first hydrocarbon-containing composition and Column 6 metal catalyst may be passed through a slurry-type reactor at a LHSV of from 0.5 h<sup>-1</sup> to 10 h<sup>-1</sup>, or from 1 h<sup>-1</sup> to 5 h<sup>-1</sup>.

The second hydrocarbon-containing composition is produced by the hydrotreatment of the first hydrocarbon-containing composition. The second hydrocarbon-containing composition is comprised primarily of non-residue and non-asphaltenic hydrocarbon compounds that have a boiling point of 538°C (1000°F) or less. The second hydrocarbon-containing composition may contain less than 1.5 wt.%, or at most 1 wt.%, or at most 0.5 wt.%, or at most 0.1 wt.% of hydrocarbons having a boiling point of greater than 538°C as determined in accordance with ASTM Method D5307. The second hydrocarbon-containing composition may contain VGO hydrocarbons, distillate hydrocarbons, and naphtha hydrocarbons. The second hydrocarbon-containing composition may contain, per gram, at

least 0.05 grams, or at least 0.1 grams of hydrocarbons having a boiling point from the initial boiling point of the second hydrocarbon-containing composition up to 204°C (400°F). The second hydrocarbon-containing composition may also contain, per gram, at least 0.1 grams, or at least 0.15 grams of hydrocarbons having a boiling point of from 204°C (400°F) up to 260°C (500°F). The second hydrocarbon-containing composition may also contain, per gram, at least 0.25 grams, or at least 0.3 grams, or at least 0.35 grams of hydrocarbons having a boiling point of from 260°C (500°F) up to 343°C (650°F). The second hydrocarbon-containing composition may also contain, per gram, at least 0.3 grams, or at least 0.35 grams, or at least 0.4, or at least 0.45 grams of hydrocarbons having a boiling point of from 343°C (650°F) up to 538°C (1000°F). The relative amounts of hydrocarbons within each boiling range and the boiling range distribution of the hydrocarbons may be determined in accordance with ASTM Method D5307.

The second hydrocarbon-containing composition contains little sulfur relative to the hydrocarbon-containing feedstock and the first hydrocarbon-containing composition. The second hydrocarbon-containing composition may contain at most 5%, or at most 2.5%, or at most 1% of the sulfur content, by weight of sulfur, of the hydrocarbon-containing feedstock as determined by ASTM Method D4294. The second hydrocarbon-containing composition may contain at most 10%, or at most 5%, or at most 2.5% of the sulfur content of the first hydrocarbon-containing composition, by weight of sulfur, as determined by ASTM Method D4294. The second hydrocarbon-containing composition may contain at most 2000, or at most 1500, or at most 1000 wppm of sulfur.

The second hydrocarbon-containing composition may contain little nitrogen relative to the hydrocarbon-containing feedstock and the first hydrocarbon-containing composition. The second hydrocarbon-containing composition may contain at most 40%, or at most 35%, or at most 30% of the nitrogen content, by weight of nitrogen, of the hydrocarbon-containing feedstock as determined by ASTM Method D5762. The second hydrocarbon-containing composition may contain at most 50%, or at most 40%, or at most 30% of the nitrogen content of the first hydrocarbon-containing composition, by weight of nitrogen, as determined by ASTM Method D5762. The second hydrocarbon-containing composition may contain at most 1500, or at most 1000, or at most 500 wppm of nitrogen.

Basic nitrogen-containing hydrocarbons may be significantly reduced in the second hydrocarbon-containing composition relative to the first hydrocarbon-containing composition. Basic nitrogen-containing hydrocarbons may be reduced by at least 70%, or at least 75%, as determined by measuring basicity in accordance with ASTM D2896, in the

second hydrocarbon-containing composition relative to the first hydrocarbon-containing composition.

The second hydrocarbon-containing composition may contain relatively few polyaromatic hydrocarbon compounds containing three or more aromatic ring structures (e.g. anthracene, phenanthrene, di-benzothiophene) relative to mono-aromatic hydrocarbon compounds (e.g. benzene, toluene, pyridine) and di-aromatic hydrocarbon compounds (e.g. naphthalene, benzothiophene, bi-phenyl, quinoline). The combined mono-aromatic hydrocarbon compounds and di-aromatic hydrocarbon compounds in the second hydrocarbon-containing composition may be present in the second hydrocarbon-containing composition in a weight ratio relative to the polyaromatic hydrocarbon compounds (containing three or more aromatic ring structures) of at least 4 : 1, or at least 5 : 1, or at least 6 : 1. The relative amounts of mono-, di-, and polyaromatic compounds in the second hydrocarbon-containing composition may be determined by flame ionization detection-two dimensional gas chromatography (GCxGC-FID).

The second hydrocarbon-containing composition may contain little metal content. The second hydrocarbon-containing composition may contain less than 0.5 wppm, or less than 0.3 wppm of vanadium. The second hydrocarbon-containing composition may contain less than 0.3 wppm, or less than 0.2 wppm of nickel. The second hydrocarbon-containing composition may contain less than 0.2 wppm of iron.

The second hydrocarbon-containing composition is separated into fractions, where the separated fractions are separated based on the boiling point range of each fraction. At least one of the separated fractions is a heavy hydrocarbon fraction comprised of hydrocarbons having a boiling point of from 343°C (650°F) to 538°C (1000°F) as determined in accordance with ASTM Method D5307. The heavy hydrocarbon fraction may also contain at most 5 wt.%, or at most 1 wt.%, of hydrocarbons having a boiling point of less than 343°C. Other hydrocarbon fractions separated from the second hydrocarbon-containing composition may include a fraction comprised of hydrocarbons having a boiling point in the range of from the initial boiling point of the second hydrocarbon-containing composition up to 204°C (light and heavy naphtha), a fraction comprised of hydrocarbons having a boiling point in the range from 204°C up to 260°C (kerosene), a fraction comprised of hydrocarbons having a boiling point in the range from 260°C up to 343°C (diesel), and a fraction comprising gases that are gaseous at STP including hydrocarbon gases, hydrogen, and hydrogen sulfide.

### Cracking the Heavy Hydrocarbon Fraction of the Second Hydrocarbon-Containing Composition by FCC

The second hydrocarbon-containing composition may be fed from the hydrotreating reactor **12** to a heavy hydrocarbon fraction separator **19** via line **21**. The second

5 hydrocarbon-containing composition may be cooled to a temperature effective to separate the heavy hydrocarbon fraction from the second hydrocarbon-containing composition in a heat exchanger **23** prior to being fed to the heavy hydrocarbon fraction separator **19**. The heavy hydrocarbon fraction may be separated from the second hydrocarbon-containing composition in the heavy hydrocarbon fraction separator **19** by selecting the temperature

10 and the pressure in the separator **19** to condense and separate the heavy hydrocarbon fraction **20** from a non-condensed vapor containing hydrocarbons having a boiling point of less than 343°C at 0.101 MPa. The non-condensed vapor may be fed to a light hydrocarbon fraction separator **25** operated at a lower temperature and/or lower pressure than the heavy hydrocarbon fraction separator **19** via line **27**. One or more light

15 hydrocarbon fractions such as a naphtha fraction **29** and/or a kerosene fraction **31** and/or a diesel fraction **33** may be separated from non-condensable gases **35** in the light hydrocarbon fraction separator **25**. The non-condensable gases **35** may be scrubbed in an amine scrubber **37** to remove hydrogen sulfide and to produce a non-condensable gas stream comprising hydrocarbons having a carbon number of from 1 to 4 and hydrogen.

20 Alternatively, referring to Fig. 2, the second hydrocarbon-containing composition may be fed from the hydrotreating reactor **12** to a condenser **39** via line **21**. The second hydrocarbon-containing composition may be cooled in heat exchanger **41** to a temperature effective to separate hydrocarbons that are liquid at STP from non-condensable gases that are gaseous at STP. The hydrocarbons that are liquid at STP may be condensed in

25 condenser **39** and separated from the non-condensable gases. The non-condensable gases may be scrubbed in an amine scrubber **43** to remove hydrogen sulfide from the non-condensable gases and to produce a non-condensable gas comprising hydrocarbons having a carbon number of from 1 to 4 and hydrogen. The liquid hydrocarbons condensed in

30 condenser **39** may be fed via line **44** to distillation column **45** which may be operated at atmospheric pressure and at a temperature effective to separate the heavy hydrocarbon fraction **20** from lighter hydrocarbon fractions, which may include a naphtha fraction **47**, a kerosene fraction **49**, and/or a diesel fraction **51**. The temperature at which the distillation column may be operated may be from 335 to 350°C at atmospheric pressure, or from 160°C to 165°C at a pressure of 0.00027 MPa (2 mm Hg).

Referring now to Figs. 1 and 2, the heavy hydrocarbon fraction **20** may be fed to a fluidized catalytic cracking riser **53** and separator **55** to further crack the heavy hydrocarbon fraction **20**. If necessary, the heavy hydrocarbon fraction **20** may be heated in heat exchanger **57** to a temperature of from 315°C to 430°C prior to being fed into the riser **53**.

The heavy hydrocarbon fraction **20** is mixed with a hot powdered fluidizable cracking catalyst **59** upon entering the riser **53** or immediately preceding entry into the riser **53**. The mass ratio of catalyst **59** and heavy hydrocarbon fraction **20** mixture may be from 1 to 15 kg of catalyst per 1 kg of the heavy hydrocarbon fraction, and preferably is from 3 to 10 kg of catalyst per 1 kg of the heavy hydrocarbon fraction.

The fluidizable catalyst is comprised of a strongly acidic components that catalyze the cracking reaction. The fluidizable catalyst may be comprised of a Type Y zeolite, a matrix component comprised of amorphous alumina, a binder component comprised of silica sol, and a filler comprised of kaolin. The fluidizable catalyst is a fine powder that may be fluidized to flow upwards through the riser **53** with vaporized heavy hydrocarbon fraction **20**, typically having a bulk density of from 0.7 to 1.1 gram/cm<sup>3</sup>, and preferably from 0.80 to 0.96 gram/cm<sup>3</sup>, a particle size distribution of from 10 to 150 μm, and an average particle size of from 60 to 100μm. Suitable fluidizable cracking catalysts are available commercially, e.g. from W.R. Grace Company, BASF Catalysts, and Albemarle Corporation.

The fluidizable cracking catalyst **59** has a temperature of at least 550°C, and may have a temperature of from 700°C to 850°C, upon mixing with the heavy hydrocarbon fraction **20**. The cracking catalyst **59** is heated by combusting coke from the surface of the catalyst, as discussed in further detail below. The heavy hydrocarbon fraction **20** may be vaporized upon mixing with the cracking catalyst or may be in vapor form prior to and during mixing with the cracking catalyst. The mixture of the catalyst and the vaporized heavy hydrocarbon fraction has a temperature of at least 500°C, preferably from 525°C to 600°C, most preferably from 530°C to 550°C. The pressure of the catalyst/vaporized heavy hydrocarbon mixture in the fluidized catalytic cracking riser **53** and separator **55** may be from 0.1 MPa to 0.3 MPa.

The mixture of vaporized heavy hydrocarbon fraction and fluidized catalyst may flow upwards through the riser **53**. The heavy hydrocarbons in the mixture of vaporized heavy hydrocarbon fraction and fluidized catalyst are cracked as the mixture flows upwards through the riser **53** to produce smaller molecule hydrocarbons. The cracked

hydrocarbon stream **61** is then separated from the fluidized catalyst. The cracked hydrocarbon stream **61** may be separated from the fluidized catalyst in the separator **55** upon exiting the riser **53**, for example by flowing the mixture through a set of two-stage cyclones. The cracked hydrocarbon stream **61** may be fed to a distillation column **63**, wherein the cracked hydrocarbon stream **61** may be separated into hydrocarbon fractions having a selected boiling point range, for example a non-condensable gas fraction **62**, a hydrocarbon fraction **65** comprising hydrocarbons boiling from 35°C to 204°C (light and heavy naphtha), a hydrocarbon fraction **67** comprising hydrocarbons boiling from 204°C up to 343°C (fuel oil, including kerosene and diesel), and a hydrocarbon fraction **69** comprising hydrocarbons boiling at 343°C or above (gas oil), where the boiling ranges are as determined in accordance with ASTM D5307. Alternatively, the cracked hydrocarbon stream **61** may be separated into a gasoline fraction comprised of hydrocarbons having a carbon number of at least 6 that have a boiling point of up to 232°C, a light cycle oil fraction comprised of hydrocarbons having a boiling point of from 232°C to 343°C, and a heavy cycle oil fraction comprised of hydrocarbons having a boiling point of at least 343°C. The gasoline fraction may have a sulfur content of at most 500 wppm, or at most 300 wppm, or at most 20 wppm sulfur; and the light cycle oil fraction may have a sulfur content of at most 0.75 wt.%, or at most 0.5 wt.% sulfur. The hydrocarbon fraction **69** or heavy cycle oil comprising hydrocarbons boiling at 343°C or above may be recycled to be mixed with the fluidizable cracking catalyst at the bottom of the riser **53**.

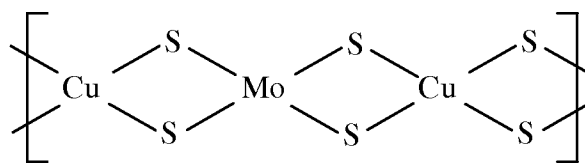
Coke deposits on the fluidized cracking catalyst particles **59** as the mixture of catalyst and vaporized heavy hydrocarbon fraction flows upwards through the riser **53** as a result of cracking the heavy hydrocarbon fraction **20** with the strongly acidic fluidized cracking catalyst. Upon separation of the catalyst **59** from the cracked hydrocarbon stream **61** in the separator **55**, the coked catalyst particles may be fed to a catalyst regenerator **73** wherein the coke on the catalyst particles is combusted with oxygen to heat the catalyst and to burn the coke off of the catalyst particles. Compressed air **75** may be injected into the catalyst regenerator to provide the oxygen for combustion with the coked catalyst. The combustion heats the catalyst, preferably to a temperature of from 700°C to 850°C and regenerates the catalyst particles by removing coke from the catalyst particles. The hot regenerated catalyst **59** is mixed with the heavy hydrocarbon fraction **20** as discussed above to heat, and preferably vaporize, the heavy hydrocarbon fraction, and the mixture of fluidized regenerated catalyst and vaporized heavy hydrocarbon fraction is passed through the riser **53** to crack the heavy hydrocarbon fraction.

Boiling point fractions produced by cracking the heavy hydrocarbon fraction **20** may be combined with comparable boiling point fractions separated from the second hydrocarbon-containing product, if desired. For example, the naphtha fraction **65** having a boiling point of up to 204 °C produced by cracking the heavy hydrocarbon fraction **20** may be combined with the naphtha fraction **29** or **47** separated from the second hydrocarbon-containing product; and fuel oil fraction **67** may be combined with kerosene fraction **31** or **49** and diesel fraction **33** or **51** separated from the second hydrocarbon-containing product.

To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the scope of the invention. The scope of the invention is to be defined by the claims appended hereto.

#### EXAMPLE 1

A non-acidic thiometallate catalyst for use in a process of the present invention containing copper, molybdenum, and sulfur was produced, where at least a portion of the catalyst had a structure according to Formula (XI).



(XI)

1199 grams of  $\text{CuSO}_4$  was mixed with sufficient deionized water to make a 2 liter solution. Separately, 520.6 grams of  $(\text{NH}_4)_2\text{MoS}_4$  was mixed in 3.5 liters of deionized water to form an aqueous solution. The  $\text{CuSO}_4$  solution was heated to 85°C, then the  $(\text{NH}_4)_2\text{MoS}_4$  solution was transferred into the heated  $\text{CuSO}_4$  solution through an injection nozzle over a period of 4 hours while stirring the heated solution. After the addition of the  $(\text{NH}_4)_2\text{MoS}_4$  solution to the heated  $\text{CuSO}_4$  solution was complete, the mixture was stirred for an additional 4 hours at a temperature of from 85-93°C. Addition of the  $(\text{NH}_4)_2\text{MoS}_4$  solution to the heated  $\text{CuSO}_4$  solution and subsequent stirring was conducted under a nitrogen atmosphere. The resulting dark red slurry was then allowed to settle under nitrogen at room temperature overnight. The slurry was then centrifuged at 12000G to separate the solid thiometallate catalyst as a red sludge from the solution. The solid thiometallate catalyst was washed with deionized water until the conductivity measurements of the wash were under 100  $\mu\text{S}$  at 33°C. The resulting solid thiometallate catalyst material was heated

to 55°C for 5 days under 29 Hg vacuum to dry the catalyst. Just over 409 g of the solid thiometallate catalyst was recovered. Semi-quantitative XRF indicated that the thiometallate catalyst contained, on an element mass % basis, 16.4% Cu, 35.6% Mo, 47.7% S, and <0.1 wt.% Fe and Co. On an atomic basis the thiometallate catalyst composition may be described as Cu<sub>2</sub>Mo<sub>3</sub>S<sub>12</sub>. Thiometallate catalysts prepared in a similar manner having substantially the same composition were determined to have an acidity of from 0 to 80 μmol of ammonia desorbed per gram of catalyst as determined by ammonia chemisorption. The thiometallate catalyst was particulate having a bimodal particle size distribution with a mean particle size of the first mode of 3 microns and a mean particle size of the second mode of 110 microns as determined by laser diffractometry using a Mastersizer S made by Malvern Instruments. The BET surface area of the thiometallate catalyst was measured and found to be 113 m<sup>2</sup>/g. The pore volume of the thiometallate catalyst was found to be 0.157 cm<sup>3</sup>/g and the median pore diameter of a pore size distribution of the catalyst was found to be 56 angstroms. Determination of the surface area, pore volume, and pore size distribution was effected using techniques consistent with ASTM Method D3663 and ASTM Method D4641. X-ray diffraction and Raman IR spectroscopy confirmed that at least a portion of the thiometallate catalyst had a structure in which copper, sulfur, and molybdenum were arranged as shown in Formula (XI) above.

## EXAMPLE 2

Bitumen from Peace River, Canada was selected as a hydrocarbon-containing feedstock to be processed according to the process of the present invention. The Peace River bitumen was analyzed to determine its composition. The properties of the Peace River bitumen feedstock are set forth in Table 1:

TABLE 1

| Property                                                                                                    | Value |
|-------------------------------------------------------------------------------------------------------------|-------|
| Hydrogen (wt.%)                                                                                             | 10.1  |
| Carbon (wt.%)                                                                                               | 82    |
| Oxygen (wt.%)                                                                                               | 0.62  |
| Nitrogen (wt.%)                                                                                             | 0.37  |
| Sulfur (wt.%)                                                                                               | 6.69  |
| Sulfur content in compounds having a boiling point of 482°C or greater relative to total sulfur content (%) | 65    |
| Nickel (wppm)                                                                                               | 70    |
| Vanadium (wppm)                                                                                             | 205   |
| microcarbon residue (wt.%)                                                                                  | 12.5  |

|                                                        |      |
|--------------------------------------------------------|------|
| C5 asphaltenes (wt.%)                                  | 16.2 |
| C7 asphaltenes (wt.%)                                  | 10.9 |
| density (g/ml) (15.6°C)                                | 1.01 |
| viscosity at 38°C (cSt)                                | 8357 |
| API Gravity (15.6°C)                                   | 8.5  |
| TAN-E (ASTM D664) (mg KOH/g)                           | 3.91 |
| Boiling Range Distribution                             |      |
| Initial boiling point - 204°C (400°F) (wt.%) [Naphtha] | 0    |
| 204°C (400°F) - 260°C (500°F) (wt.%) [Kerosene]        | 1    |
| 260°C (500°F) - 343°C (650°F) (wt.%) [Diesel]          | 14   |
| 343°C (650°F) - 538°C (1000°F) (wt.%) [VGO]            | 38   |
| >538°C (1000°F) (wt.%) [Residue]                       | 47   |

Two samples of Peace River bitumen feedstock were catalytically hydrocracked utilizing the copper tetrathiomolybdate catalyst prepared in Example 1. In each catalytic hydrocracking treatment, the Peace River bitumen feed sample was preheated to approximately 125°C-150°C in a 10 gallon feed drum from which the bitumen was fed into a semi-continuous stirred tank reactor with vapor effluent capability, where the reactor had an internal volume capacity of 1000 cm<sup>3</sup>. The reactor was operated in a continuous mode with respect to the bitumen feedstream and the vapor effluent product, however, the reactor did not include a bleed stream to remove accumulating metals and/or carbonaceous solids. Each feed sample was fed to the reactor as needed to maintain a working volume of feed in the reactor of approximately 500 ml, where the working volume in the reactor was maintained utilizing a <sup>137</sup>Cs gamma Ray level detector coupled to hot oil feed pump variable speed controller. 50 grams of the copper tetrathiomolybdate catalyst prepared in Example 1 was mixed with each respective feed sample in the reactor. Hydrogen was fed to the reactor at a flow rate of 642 to 742 standard liters per hour, and the hydrogen partial pressure in the reactor was maintained at 9.4 MPa (1369 psig) for the first feed sample and at 9.0 MPa (1304 psig) for the second feed sample. Hydrogen sulfide was fed to the reactor at a flow rate of 210-310 standard liters per hour, and the hydrogen sulfide partial pressure in the reactor was maintained at 3.7 MPa (531 psig) for the first feed sample and at 4.1 MPa (597 psig) for the second feed sample. The total pressure in the reactor was maintained at 13.1 MPa while hydrocracking each sample, and the total gas flow rate was maintained at 950 standard liters per hour. The individual bitumen feed sample, hydrogen, hydrogen sulfide and the catalyst were mixed together in the reactor by stirring with a Autoclave Engineers MAGNADRIVE<sup>®</sup> impeller, where the impeller was driven at 1200

rpm or higher. The temperature in the reactor was maintained at 428°C when hydrocracking the first feed sample and at 426°C when hydrocracking the second feed sample. Vaporized product exited the reactor, where a liquid product was separated from the vaporized product by passing the vaporized product through a high pressure separator and then through a low pressure separator to condense and separate the liquid “first hydrocarbon-containing product” from non-condensable gases, where the condensation and separation was effected at 80-85°C to avoid condensation of hydrogen sulfide with the first hydrocarbon-containing product. The reaction was halted when the magnetic coupling of the internal mixer magnet with the external driven magnet was broken due to accumulated solids in the reactor.

The first hydrocarbon-containing product samples were then mixed together and homogenized. The homogenized liquid was split into two aliquots. The first aliquot was tested analytically to determine properties of the homogenized “first hydrocarbon-containing product” samples. Properties of the homogenized “first hydrocarbon-containing product” collected from the hydrocracking of each feed sample are provided in Table 2.

TABLE 2

|                                                                                                                            | <b>1<sup>st</sup> Hydrocarbon-Containing Product</b> |
|----------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|
| <b>Liquid In, kg</b>                                                                                                       | 57.07                                                |
| <b>Liquid Out, kg</b>                                                                                                      | 47.46                                                |
| <b>Liquid Recovery, wt. %</b>                                                                                              | 83.1                                                 |
| <b>Density, g/cm<sup>3</sup> (15.6°C)</b>                                                                                  | 0.9331                                               |
| <b>API Gravity (15.6°C)</b>                                                                                                | 20.1                                                 |
| <b>Kinematic viscosity, cSt (20°C)</b>                                                                                     | 27.48                                                |
| <b>H/C atomic ratio</b>                                                                                                    | 1.58                                                 |
| <b>Carbon content, wt. %</b>                                                                                               | 84.72                                                |
| <b>Hydrogen content, wt. %</b>                                                                                             | 11.26                                                |
| <b>Nitrogen content, wt. %</b>                                                                                             | 0.31                                                 |
| <b>Sulfur content, wt. %</b>                                                                                               | 3.45                                                 |
| <b>Sulfur content in hydrocarbon compounds having a boiling point less than 343°C relative to total sulfur content (%)</b> | 86                                                   |
| <b>Nickel content, ppmw</b>                                                                                                | 0.2                                                  |
| <b>Vanadium content, ppmw</b>                                                                                              | 0.4                                                  |
| <b>Iron content, ppmw</b>                                                                                                  | <0.2                                                 |
| <b>BOILING RANGE DISTRIBUTION, Simulated distillation as per ASTM D5307</b>                                                |                                                      |
| <b>Initial BP-204°C</b>                                                                                                    | 8.5                                                  |

|                    |      |
|--------------------|------|
| <b>204°C-260°C</b> | 10.5 |
| <b>260°C-343°C</b> | 31.0 |
| <b>343°C-538°C</b> | 48.5 |
| <b>538°C+</b>      | 1.5  |

As shown by comparing the properties of the feedstock from Table 1 with the properties of the first hydrocarbon-containing product from Table 2, the hydrocarbon boiling range of the first hydrocarbon-containing product is shifted significantly lower than hydrocarbon boiling range of the feedstock, the viscosity and density of the first hydrocarbon-containing product are significantly lower than that of the feedstock, and the API gravity of the first hydrocarbon-containing product is significantly higher than that of the feedstock. Further, a significant portion of the sulfur in the first hydrocarbon-containing product is contained in compounds that have a boiling point less than 343°C, which are likely easier to hydrodesulfurize than sulfur-containing heteroatoms having a higher boiling point, at least in part due to the generally smaller size of the lower boiling compounds.

The second aliquot of the homogenized first hydrocarbon-containing product was hydrotreated in a fixed bed reactor separate from the hydrocracking reactor in which the first hydrocarbon-containing product was produced. DN-200, a catalyst formed of nickel and molybdenum supported on an alumina support available from Criterion Inc., was loaded in the catalyst bed of the reactor. Hydrogen and the second aliquot of the homogenized first hydrocarbon-containing product were fed through the fixed bed reactor and contacted with the DN-200 catalyst at a weighted average bed temperature of 371°C (700°F). The first hydrocarbon-containing product was fed through the fixed bed reactor at a liquid hourly space velocity of 1 h<sup>-1</sup>. Hydrogen was fed through the fixed bed reactor at a hydrogen/oil ratio of 3000 SCFB. The total pressure in the fixed bed reactor was maintained at 6.9 MPa (1000 psig). The hydrotreated “second hydrocarbon-containing product” was then collected at the outlet of the fixed bed reactor.

The average liquid mass yield of second hydrocarbon-containing product relative to the first hydrocarbon-containing product feed in the hydrotreating step was 96.7 wt.%, and the hydrogen consumption was 700 to 750 SCF per barrel of the first hydrocarbon-containing product feed input into the fixed bed reactor. The properties of the second hydrocarbon-containing product were analyzed, and are shown in Table 3.

TABLE 3

|                                                                                                                            | <b>2nd Hydrocarbon-Containing Product</b> |
|----------------------------------------------------------------------------------------------------------------------------|-------------------------------------------|
| <b>Liquid Recovery, wt. %</b>                                                                                              | 96.7                                      |
| <b>Density, g/cm<sup>3</sup> (15.6°C)</b>                                                                                  | 0.8879                                    |
| <b>API Gravity (15.6°C)</b>                                                                                                | 27.9                                      |
| <b>Kinematic viscosity, cSt (20°C)</b>                                                                                     | 13.53                                     |
| <b>H/C atomic ratio</b>                                                                                                    | 1.70                                      |
| <b>Carbon content, wt. %</b>                                                                                               | 87.23                                     |
| <b>Hydrogen content, wt. %</b>                                                                                             | 12.44                                     |
| <b>Nitrogen content, wt. %</b>                                                                                             | 0.11                                      |
| <b>Sulfur content, wt. %</b>                                                                                               | 0.17                                      |
| <b>Sulfur content in hydrocarbon compounds having a boiling point less than 343°C relative to total sulfur content (%)</b> | 48                                        |
| <b>Nickel content, ppmw</b>                                                                                                | <0.2                                      |
| <b>Vanadium content, ppmw</b>                                                                                              | 0.3                                       |
| <b>Iron content, ppmw</b>                                                                                                  | <0.2                                      |
| <b>BOILING RANGE DISTRIBUTION, Simulated distillation as per ASTM D5307</b>                                                |                                           |
| <b>Initial BP-204°C</b>                                                                                                    | 10.5                                      |
| <b>204°C-260°C</b>                                                                                                         | 14.2                                      |
| <b>260°C-343°C</b>                                                                                                         | 29.6                                      |
| <b>343°C-538°C</b>                                                                                                         | 45.5                                      |
| <b>538°C+</b>                                                                                                              | 0.2                                       |

The second hydrocarbon-containing product produced by hydrotreating the first  
 5 hydrocarbon-containing product contains substantially less sulfur and nitrogen than the  
 bitumen feedstock and the first hydrocarbon-containing product. As shown by comparing  
 the sulfur content of the second hydrocarbon-containing product in Table 3 relative to the  
 sulfur content of the bitumen feedstock and the first hydrocarbon-containing product in  
 Tables 1 and 2, respectively, the second hydrocarbon-containing product contains 2.5% of  
 10 the sulfur of the bitumen feedstock and 4.9% of the sulfur of the first hydrocarbon-  
 containing product, on a weight basis. As shown by comparing the nitrogen content of the  
 second hydrocarbon-containing product in Table 3 relative to the nitrogen content of the  
 bitumen feedstock and the first hydrocarbon-containing product in Tables 1 and 2,  
 respectively, the second hydrocarbon-containing product contains 30% of the nitrogen of  
 15 the bitumen feedstock and 35.5% of the nitrogen of the first hydrocarbon-containing  
 product, on a weight basis.

The second hydrocarbon-containing product also contains substantially less vanadium and nickel than the bitumen feedstock. Comparing the metals content of the second hydrocarbon-containing product with the metals content of the bitumen feedstock in Tables 3 and 1, respectively, the second hydrocarbon-containing feedstock contains 0.15  
5 % of the vanadium content of the bitumen feedstock, by weight; and contains less than 0.28% of the nickel content of the bitumen feedstock, by weight.

The second hydrocarbon-containing product contains a large proportion of the carbon, 80.3%, contained in the bitumen feedstock. The carbon recovery yield is expected to be even greater when the first hydrocarbon-containing product is separated from non-  
10 condensable gases at temperatures from 25°C-50°C, rather than from 80°C-85°C, or if the first hydrocarbon-containing product is not separated from the vapor prior to hydrotreatment. Much of the carbon in the second hydrocarbon-containing product is contained in hydrocarbons in lower boiling fractions relative to the bitumen feedstock; and has substantially less sulfur, nitrogen, and metals content than the bitumen feedstock.

15 The second hydrocarbon-containing product was then fractionated by distillation to produce a heavy hydrocarbon fraction comprised of hydrocarbons having a boiling point of at least 343°C and a light hydrocarbon fraction comprised of hydrocarbons having a boiling point of less than 343°C, where the boiling points of the hydrocarbons in the hydrocarbon fractions is as determined in accordance with ASTM Method D5307. The second  
20 hydrocarbon-containing product was distilled in accordance with ASTM Method D2892 to separate the light hydrocarbon fraction from the heavy hydrocarbon fraction, where the distillation was effected at a temperature of 161°C and a pressure of 0.00027 MPa (2 mm Hg) to separate the light hydrocarbon fraction as overheads from the heavy hydrocarbon fraction as bottoms.

25 The heavy hydrocarbon fraction was sub-divided into multiple samples for fluidized catalytic cracking. Each sample was heated to 315°C and cracked by mixing the sample in a mixing zone with aged Naphthamax-SPS1 FCC catalyst to produce a fluidized mixture, and then passing the fluidized mixture through an adiabatic riser having a 10.9 mm inner diameter.. Naphthamax SPS1 is an FCC catalyst available from BASF that was  
30 aged in a conventional FCC catalytic cracking unit prior to its use to crack the heavy hydrocarbon fraction.

The catalyst to heavy hydrocarbon oil fraction sample weight ratio in the fluidized mixture was selected to be 4:1 for the first sample, 6:1 for the second sample, 8:1 for the third sample, and 10:1 for the fourth sample. The temperature of the catalyst mixed with

each heavy hydrocarbon oil sample to produce the fluidized mixture was selected so each fluidized mixture was reacted at a temperature of 538°C (1000°F) in the riser. The catalyst utilized in the fluidized mixture was heated by burning off the coke deposited on the catalyst in a catalyst regeneration unit. The reaction conditions utilized for each sample are set forth in Table 4.

TABLE 4

| Sample #                     | 1    | 2    | 3    | 4    |
|------------------------------|------|------|------|------|
| Catalyst Temperature (°C)    | 754  | 737  | 694  | 652  |
| Riser Temperature (°C)       | 538  | 538  | 538  | 538  |
| Residence Time (seconds)     | 1.97 | 1.90 | 1.88 | 1.84 |
| Catalyst/Sample Weight ratio | 4    | 6    | 8    | 10   |
| Feed Rate (gram/min)         | 13   | 13   | 13   | 13   |

Cracked product was recovered and separated into boiling point fractions for each sample. The product yield is shown in Table 5.

TABLE 5

| Sample #                   | 1    | 2    | 3    | 4    |
|----------------------------|------|------|------|------|
| Cut 1, C6-154°C (wt. %)    | 26.6 | 26.1 | 27.2 | 26.8 |
| Cut 2, 154°C-232°C (wt. %) | 14.6 | 13.6 | 13.9 | 13.0 |
| Cut 3, 232°C-343°C (wt. %) | 15.8 | 14.6 | 13.6 | 13.0 |
| Cut 4, 343°C-398°C (wt. %) | 10.3 | 7.5  | 6.2  | 5.5  |
| Cut 5, 398°C+ (wt. %)      | 8.9  | 7.2  | 6.2  | 5.5  |
| Coke (wt. %)               | 2.9  | 4.3  | 5.2  | 6.2  |
| Conversion (wt. %)         | 64.9 | 70.7 | 73.9 | 76.0 |

The total sulfur content of the gasoline fractions (cut 1 and cut 2) and the light cycle oil fraction (cut 3) of the cracked product of each sample was measured, since low sulfur content is an important for commercial use of these cuts. The total sulfur content was determined by GC-GC sulfur chemiluminescence. The results are shown in Table 6.

TABLE 6

| Sample #                          | 1    | 2    | 3    | 4    |
|-----------------------------------|------|------|------|------|
| Gasoline--S content (wppm)        | 94   | 122  | 180  | 294  |
| Light Cycle Oil—S content (wt. %) | 0.37 | 0.44 | 0.46 | 0.68 |

The product slate produced by the FCC cracking of the samples is comparable to that produced by FCC cracking of conventional FCC cracking of vacuum gas oils comprised of hydrocarbons having a boiling point in a range of greater than 343°C, including low sulfur content. Thus, the process of the present invention is effective to  
5 provide a commercially attractive product slate from a heavy crude oil or bitumen feedstock at a high yield, with little loss of carbon from the feedstock in a non-condensable gas and/or as carbonaceous solids such as coke.

The present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are  
10 illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. While compositions and methods are described in terms of “comprising,” “containing,” or “including” various  
15 components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, “from a to b,” or, equivalently, “from a-b”) disclosed herein is to be understood to set forth every  
20 number and range encompassed within the broader range of values. Whenever a numerical range having a specific lower limit only, a specific upper limit only, or a specific upper limit and a specific lower limit is disclosed, the range also includes any numerical value “about” the specified lower limit and/or the specified upper limit. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined  
25 by the patentee. Moreover, the indefinite articles “a” or “an”, as used in the claims, are defined herein to mean one or more than one of the element that it introduces.

## CLAIMS

1. A process, comprising:  
providing a first hydrocarbon-containing composition comprising, per gram of the  
5 first hydrocarbon-containing composition, at least 0.05 grams of hydrocarbons  
having a boiling point in the range from 25°C up to 204°C, at least 0.1 gram of  
hydrocarbons having a boiling point in the range from 204°C up to 260°C, at least  
0.25 gram of hydrocarbons having a boiling point in the range from 260°C up to  
343°C, at least 0.3 gram of hydrocarbons having a boiling point in the range from  
10 343°C to 538°C, at most 0.03 gram of hydrocarbons having a boiling point of  
greater than 538°C, where the boiling point ranges of the first hydrocarbon-  
containing composition are as determined by ASTM Method D5307, and from  
0.001 to 0.05 gram of sulfur on an atomic basis as determined by ASTM Method  
D4294, wherein at least 40 wt.% of the sulfur, on an atomic sulfur basis as  
15 determined by ASTM Method D4294, is contained in hydrocarbon compounds  
having a boiling point of less than 343°C as determined by ASTM Method D5307,  
and at least 40 wt. % of the sulfur contained in hydrocarbon compounds having a  
boiling point of less than 343°C in the first hydrocarbon-containing composition is  
contained in benzothiophenic compounds as determined by GC-GC sulfur  
20 chemiluminescence;  
apart from the mixing zone, contacting the first hydrocarbon-containing  
composition with hydrogen and a catalyst comprising a Column 6 metal of the  
Periodic Table or a compound thereof at a temperature of from 260°C to 425°C and  
a pressure of from 3.4 MPa to 27.5 MPa to produce a product stream comprising a  
25 second hydrocarbon-containing composition;  
separating the second hydrocarbon-containing composition into fractions wherein  
one fraction is comprised of hydrocarbons having a boiling point of from 343°C to  
538°C as determined in accordance with ASTM Method D5307; and  
contacting the fraction comprised of hydrocarbons having a boiling point of from  
30 343°C to 538°C with a fluidizable cracking catalyst at a temperature of at least  
500°C.

2. The process of claim 1 wherein the first hydrocarbon-containing composition contains at most 0.5 wppm of vanadium, at most 0.5 wppm of nickel, and at most 0.3 wppm of iron.
- 5 3. The process of claim 1 or claim 2 wherein the catalyst comprising a Column 6 metal further comprises a support material selected from alumina, silica, titania, zirconia, or mixtures thereof.
- 10 4. The process of claim 1 wherein the catalyst comprising a Column 6 metal further comprises a Column 7-10 metal or a compound thereof.
- 15 5. The process of claim 1 or any of claims 2-3 wherein the first hydrocarbon-containing composition is contacted with hydrogen and the catalyst comprising a Column 6 metal of the Periodic Table or a compound thereof at a temperature of from 260°C to 425°C and a pressure of from 3.4 MPa to less than 10.3 MPa to produce a product stream comprising the second hydrocarbon-containing composition.
- 20 6. The process of claim 1 or any of claims 2-5 wherein the fluidizable cracking catalyst comprises a zeolite, and has a bulk density of from 0.7 g/cm<sup>3</sup> to 1.1 g/cm<sup>3</sup>, a particle size distribution of from 10 μm to 150 μm, and an average particle size of from 60 μm to 100 μm.
- 25 7. The process of claim 1 or any of claims 2-6 wherein the fluidizable cracking catalyst is provided for contact with the fraction comprised of hydrocarbons having a boiling point of at least 343°C at a temperature of from 700°C to 850°C.
- 30 8. The process of claim 1 of any of claims 2-7 wherein the fraction comprised of hydrocarbons having a boiling point of at least 343°C is provided for contact with the fluidizable cracking catalyst at a temperature of from 315°C to 430°C.
9. The process of claim 1 or any of claims 2-8 wherein the fluidizable cracking catalyst is regenerated and heated by combusting coke deposited on the fluidizable cracking catalyst, then providing the regenerated fluidizable cracking catalyst for

contact with the fraction comprised of hydrocarbons having a boiling point of at least 343°C.

- 5 10. The process of claim 1 or any of claims 2-9 wherein the fluidizable cracking catalyst and the fraction comprised of hydrocarbons having a boiling point of at least 343°C are contacted at a weight ratio of from 1 to 15 kg catalyst to 1 kg of the fraction comprised of hydrocarbons having a boiling point of at least 343°C.
- 10 11. The process of claim 1 or any of claims 2-10 wherein contacting the fraction comprised of hydrocarbons having a boiling point of at least 343°C with a fluidizable cracking catalyst at a temperature of at least 500°C produces a hydrocarbon mixture comprised of a gasoline fraction comprising at most 500 wppm sulfur and a light cycle oil fraction comprising at most 0.75 wt.% sulfur.