

CATALYST SYSTEMS AND METHODS FOR CONVERTING A CRUDE FEED WITH  
SUCH CATALYST SYSTEMS

This patent application claims the benefit of U.S.  
Provisional Application 61/043941, filed April 10, 2008,  
which is incorporated herein by reference

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Field of the Invention

The present invention relates to catalyst systems and  
methods for converting a crude feed with such catalyst  
systems.

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Background of the invention

Crudes that have one or more unsuitable properties that  
do not allow the crudes to be economically transported, or  
processed using conventional facilities, are commonly referred  
to as "disadvantaged crudes". Disadvantaged crudes may have a  
15 high viscosity that renders the disadvantaged crude  
undesirable for conventional transportation and/or treatment  
facilities. The high viscosity of the disadvantaged crude can  
be reduced by contacting the disadvantaged crude at elevated  
temperatures and pressure with hydrogen in the presence of a  
20 catalyst, also sometimes referred to as hydrotreating of the  
disadvantaged crude.

U.S. Published Patent Application Nos. 20050133414  
through 20050133418 to Bhan et al.; 20050139518 through  
20050139522 to Bhan et al., 20050145543 to Bhan et al.,  
25 20050150818 to Bhan et al., 20050155908 to Bhan et al.,  
20050167320 to Bhan et al., 20050167324 through 20050167332 to  
Bhan et al., 20050173301 through 20050173303 to Bhan et al.,  
20060060510 to Bhan; 20060231465 to Bhan; 20060231456 to Bhan;  
20060234876 to Bhan; 20060231457 to Bhan and 20060234877 to  
30 Bhan; 20070000810 to Bhan et al.; 20070000808 to Bhan;

20070000811 to Bhan et al.; International Publication Nos. WO 2008/016969 and WO 2008/106979 to Bhan; and U.S. Patent Application Nos. 11/866,909; 11/866,916; 11/866,921 through 11/866,923; 11/866,926; 11/866,929 and 11/855,932 to Bhan et  
5 al., filed October 3, 2007 describe various processes, systems, and catalysts for processing crudes and/or disadvantaged crudes.

U.S. Patent Nos. 6,554,994 to Reynolds et al., 6,436,280 to Harle et al., 5,928,501 to Sudhakar et al., 4,937,222 to  
10 Angevine et al., 4,886,594 to Miller, 4,746,419 to Peck et al., 4,548,710 to Simpson, 4,525,472 to Morales et al., 4,499,203 to Toulhoat et al., 4,389,301 to Dahlberg et al., and 4,191,636 to Fukui et al. also describe various processes, systems, and catalysts for processing crudes and/or  
15 disadvantaged crudes.

U.S. Patent Application No. 11/866,926 describes in example 24 a catalyst that comprises a support containing silica and alumina and that contains both nickel and molybdenum. In example 25 of U.S. Patent Application No.  
20 11/866,926 the catalyst of example 24 is contacted with a crude. During the total contact time of 2952 hours the temperature was raised from 385°C to 410°C, i.e. the temperature increase per 1000 hours was about 8.3° C.

When using conventional hydrotreating methods, the  
25 catalyst may deactivate due to deposits that are formed and that accumulate in the pores of the catalyst.

Deactivation of the catalyst can, to a certain extent be compensated by increasing the temperatures at which the hydrotreating is carried out. Such temperature increments,  
30 however, increase the costs of the hydrotreatment. In addition, higher temperatures may lead to more deposits and further deactivation of the catalyst

It would therefore be desirable to have a method and/or a catalyst system that allows for a prolonged runtime, wherein the catalyst remains sufficiently active without the necessity of extensively increasing the operating temperature during the runtime. In addition, it would be advantageous to have a method wherein the P-value, reflecting the stability of the reaction mixture during the runtime, remains above 1.

#### Summary of the invention

The above can be achieved by using the catalyst systems and methods according to the invention. Accordingly the present invention provides a catalyst system comprising:

a first catalyst with a bimodal pore size distribution, which first catalyst comprises a hydrogenation metal, mineral oxide particles and a support, wherein the hydrogenation metal consists of a column 6 metal and wherein the mineral oxide particles have an average particle size of at most 150 micrometers;

a second catalyst comprising a hydrogenation metal and a support wherein the hydrogenation metal consists of a column 6 metal and the support comprises silica-alumina.

In addition the present invention provides a method for treatment of a crude feed comprising contacting a crude feed in the presence of a hydrogen source with a catalyst system as described herein.

It was found that the catalyst system and the use thereof in a method for hydrotreating a crude feed allows for a prolonged runtime wherein the catalyst remains active whilst the weighted average bed temperature is increased by less than 5°C per 1000 hours.

One of the catalysts that may be used in the invention is novel. The present invention therefore also provides a

catalyst comprising a first hydrogenation metal, a second hydrogenation metal and a support, wherein the first hydrogenation metal is a column 6 metal, the second hydrogenation metal is a column 9 metal or a column 10 metal and the support comprises silica and alumina, which catalyst was obtained by calcining a co-mulled mixture of the support, a column 6 metal oxide and a column 9 or column 10 metal solution at a temperature of at least 650°C.

Brief description of the drawings

The invention is illustrated by the following figure:

FIG. 1 schematically shows an embodiment of the process of the invention

Detailed description of the invention

Terms used herein are defined as follows.

"ASTM" refers to American Standard Testing and Materials.

"API gravity" refers to API gravity at 15.5 °C (60 °F). API gravity is as determined by ASTM Method D6822.

"Atomic hydrogen percentage" and "atomic carbon percentage" of the crude feed and the crude product are as determined by ASTM Method D5291.

"Mono-modal catalyst" refers to a catalyst in which at least the majority of the pore volume is distributed in one statistical distributions of pore diameters, which statistical distribution has a significant peak when displayed on a pore volume versus pore diameter plot.

"Bimodal catalyst" refers to a catalyst in which at least the majority of the pore volume is distributed in two statistical distributions of pore diameters, each statistical distribution having a significant peak when displayed on a pore volume versus pore diameter plot.

Boiling range distributions for the crude feed and crude product are as determined by ASTM Method D5307 unless otherwise mentioned.

"C<sub>5</sub> asphaltenes" refers to asphaltenes that are insoluble in n-pentane. C<sub>5</sub> asphaltenes content is as determined by ASTM Method D2007.

5 "C<sub>7</sub> asphaltenes" refers to asphaltenes that are insoluble in n-heptane. C<sub>7</sub> asphaltenes content is as determined by ASTM Method D3279.

"Column X metal(s)" refers to one or more metals of Column X of the Periodic Table and/or one or more compounds of one or more metals of Column X of the Periodic Table, in which  
10 X corresponds to a column number (for example, 1-12) of the Periodic Table.

"Column X element(s)" refers to one or more elements of Column X of the Periodic Table, and/or one or more compounds of one or more elements of Column X of the Periodic Table, in  
15 which X corresponds to a column number (for example, 13-18) of the Periodic Table.

In the scope of this application, weight of a metal from the Periodic Table, weight of a compound of a metal from the Periodic Table, weight of an element from the Periodic Table,  
20 or weight of a compound of an element from the Periodic Table is calculated as the weight of metal or the weight of element.

"Comulling" refers to contacting, combining, or pulverizing of at least two substances together such that at least two substances are mixed through mechanical and physical  
25 forces. Comulling can often form a substantially uniform or homogeneous mixture. Comulling includes the contacting of substances to yield a paste that can be extruded. Comulling does not include impregnation methods in which a formed solid is immersed in a liquid or gas to absorb/adsorb components  
30 from the liquid or gas.

"Content" refers to the weight of a component in a substrate (for example, a crude feed, a total product, or a

crude product) expressed as weight fraction or weight percentage based on the total weight of the substrate.

"Wtppm" refers to parts per million by weight.

"Distillate" refers to hydrocarbons with a boiling range distribution between 182 °C (360°F) and 343 °C (650 °F) at 0.101 MPa. Distillate content is as determined by ASTM Method D5307.

"Total basic nitrogen" refers to nitrogen compounds that have a pKa of less than 40. Basic nitrogen ("bN") is as determined by ASTM Method D2896.

"Hydrogen source" refers to hydrogen, and/or a compound and/or compounds, that when in the presence of a crude feed and the catalyst, react to provide hydrogen to compound(s) in the crude feed. A hydrogen source may include, but is not limited to, hydrocarbons (for example, C<sub>1</sub> to C<sub>4</sub> hydrocarbons such as methane, ethane, propane, and butane), water, or mixtures thereof.

"LHSV" refers to a volumetric liquid feed rate per total volume of catalyst and is expressed in hours (h<sup>-1</sup>). Total volume of catalyst is calculated by summation of all catalyst volumes in the contacting zones, as described herein.

"Micro-Carbon Residue" ("MCR") content refers to a quantity of carbon residue remaining after evaporation and pyrolysis of a substrate. MCR content is as determined by ASTM Method D4530.

"Naphtha" refers to hydrocarbon components with a boiling range distribution between 38 °C (100 °F) and 182 °C (360 °F) at 0.101 MPa. Naphtha content is as determined by ASTM Method D5307.

"Ni/V/Fe content" refers to the content of nickel, vanadium, iron, or combinations thereof. The Ni/V/Fe content includes inorganic nickel, vanadium and iron compounds and/or

organonickel, organovanadium, and organoiron compounds. The Ni/V/Fe content is as determined by ASTM Method D5708.

"Nm<sup>3</sup>/m<sup>3</sup>" refers to normal cubic meters of gas per cubic meter of crude feed.

5 "Non-condensable gas" refers to components and/or mixtures of components that are gases at STP.

"Periodic Table" refers to the Periodic Table as specified by the International Union of Pure and Applied Chemistry (IUPAC), November 2003.

10 "P (peptization) value" or "P-value" refers to a numeral value, which represents the flocculation tendency of asphaltenes in the crude feed. P-Value is as determined by ASTM Method D7060.

"Pore diameter", "median pore diameter", and "pore  
15 volume" refer to pore diameter, median pore diameter, and pore volume, as determined by ASTM Method D4284 (mercury porosimetry at a contact angle equal to 140°). A micromeritics® A9220 instrument (Micromeritics Inc., Norcross, Georgia, U.S.A.) may be used to determine these values.

20 "Residue" refers to components that have a boiling range distribution above 538 °C (1000 °F), as determined by ASTM Method D5307.

"Sediment" refers to impurities and/or coke that are insoluble in the crude feed/total product mixture. Sediment  
25 is as determined by ASTM Method D4807. Sediment may also be determined by the Shell Hot Filtration Test ("SHFST") as described by Van Kernoort et al. in the Jour. Inst. Pet., 1951, pages 596-604.

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

"Surface area" of a catalyst is as determined by ASTM Method D3663.

"VGO" refers to hydrocarbons with a boiling range distribution between 343 °C (650 °F) and 538 °C (1000 °F) at 0.101 MPa. VGO content is as determined by ASTM Method D5307.

"Viscosity" refers to kinematic viscosity at 37.8 °C (100 °F). Viscosity is as determined using ASTM Method D445.

The catalyst system according to the invention comprises at least a first catalyst and a second catalyst. In addition to the first and second catalyst, the catalyst system may contain one or more additional catalysts. Preferably the catalyst system comprises a first, second, and a third catalyst. Most preferably the catalyst system consists of 2 or 3 catalysts.

The second catalyst is preferably located downstream of the first catalyst. Further, if the catalyst system contains a third catalyst, such third catalyst is preferably located downstream of the second catalyst.

The volumetric ratio of the first catalyst to the second catalyst preferably lies in the range from 1:20 to 10:1, more preferably in the range of 1:9 to 3:2 and still more preferably in the range from 1:4 to 1:1. If the catalyst system contains a third catalyst, such third catalyst is preferably present in a volumetric amount that is equal or less than the volumetric amount of second catalyst. A third catalyst, if present is preferably present in a volumetric ratio of the third catalyst to the second catalyst of 2:1 or less, more preferably 1:1 or less.

The first catalyst has a bimodal pore size distribution, and comprises a hydrogenation metal, mineral oxide particles and a support, wherein the hydrogenation metal consists of a column 6 metal and wherein the mineral oxide particles have an average particle size of at most 150 micrometers;

Mineral oxide particles, as used herein, are to be understood to be particles of metal oxides that have been ground to a specific particle size.

Examples of metal oxides include alumina, silica, silica-  
5 alumina, titanium oxide, zirconium oxide, magnesium oxide, or mixtures thereof.

The mineral oxides particles may for example be obtained by extruding a composition comprising a mineral oxide to obtain a mineral oxide extrudate and subsequently grinding of  
10 the mineral oxide extrudate. Preferably the mineral oxide may be calcined after extrusion, for example at a temperature about 500°C for 1 or more hours.

Preferably the mineral oxide particles have an average particle size of at most 100 micrometers, more preferably at  
15 most 75 micrometers, and still more preferably at most 40 micrometers. The mineral oxide particles preferably have an average particle size of at least 0.1 micrometers, more preferably at least 0.5 micrometers and most preferably at least 1 micrometer.

20 The support for the first catalyst may for example include refractory oxides, porous carbon based materials, zeolites, or combinations thereof. Refractory oxides may include alumina, silica, silica-alumina, titanium oxide, zirconium oxide, magnesium oxide, or mixtures thereof. The  
25 support may for example include gamma alumina, delta alumina, alpha alumina, or combinations thereof.

Preferably the first catalyst has a pore size distribution with a median pore diameter in a range from 80-200 Å, more preferably in the range from 90-180 Å and most  
30 preferably in the range from 100 to 150 Å. Further the pore size distribution of the first catalyst is preferably such that at least 10% of the total number of pores in the pore size distribution has a pore diameter greater than 5000 Å,

more preferably at least 15% of the total number of pores in the pore size distribution has a pore diameter greater than 1000 Å, and still more preferably at least 20% of the total number of pores in the pore size distribution has a pore  
5 diameter greater than 350 Å.

Preferably the first catalyst has a surface area of at least 200 m<sup>2</sup>/g, more preferably at least 240 m<sup>2</sup>/g.

The second catalyst comprises a hydrogenation metal and a support wherein the hydrogenation metal consists of a column 6  
10 metal and the support comprises silica-alumina.

The silica-alumina is preferably amorphous or essentially amorphous. The support can include gamma alumina, theta alumina or delta alumina, or combinations thereof. Preferably the alumina comprises at least 90 wt%, more preferably at  
15 least 95 wt% gamma alumina. Preferably the support includes from 0.0001 grams to 0.20 grams, 0.001 grams to 0.11 grams, or 0.01 grams to 0.05 grams of silica; and 0.80 grams to 0.9999 grams, 0.90 grams to 0.999 grams, or 0.95 to 0.99 grams of alumina. Most preferably the support comprises from 0.01 grams  
20 to 0.2 gram of silica and from 0.80 grams to 0.99 grams of alumina per gram of support. The ratio of silica to alumina preferably lies in the range from 1:1000 to 1:3, more preferably in the range from 1:200 to 1:4.

In some embodiments, the support of the second catalyst  
25 includes silica and alumina in combination with limited amounts of other refractory oxides, porous carbon based materials, zeolites, or combinations thereof. Refractory oxides may include, but are not limited to, alumina, silica, silica-alumina, titanium oxide, zirconium oxide, magnesium  
30 oxide, or mixtures thereof.

Preferably the second catalyst has a surface area of at least 300, more preferably at least 340 m<sup>2</sup>/g.

The second catalyst is preferably obtained by co-mulling one or more metals from Column 6 of the Periodic Table and/or one or more compounds of one or more metals from Column 6 of the Periodic Table with a support to provide a metal/support composition, wherein the support comprises from 0.01 grams to 0.2 gram of silica and from 0.8 grams to 0.99 grams of alumina per gram of support; and calcining the metal/support composition at a temperature from 315 °C to 760 °C to provide a calcined catalyst.

Preferably the second catalyst has a pore size distribution with a median pore diameter of at most 150 Å, more preferably at most 100 Å. Preferably the median pore diameter is at least 50 Å, more preferably at least 70 Å. Preferably the second catalyst has at least 50%, more preferably at least 70 %, most preferably at least 75 % of its pore volume in pores having a pore diameter of at most 100 Å.

Preferably the second catalyst is mono-modal.

The first catalyst and the second catalyst each comprise at least one hydrogenation metal consisting of a column 6 metal. The column 6 metal may be in elemental form or in the form of a compound of the metal.

The first catalyst and/or the second catalyst can comprise one column 6 catalyst or a combination of two or more column 6 metals. Examples of column 6 metals include chromium, molybdenum and tungsten. Preferably the first catalyst and/or the second catalyst comprise only one column 6 metal. Preferably the column 6 metal is molybdenum.

The first catalyst comprises preferably at least 0.01 wt% , more preferably at least 0.1 wt%, still more preferably at least 0.5 wt% and most preferably at least 1 wt% of column 6 metal, based on the total weight of the catalyst. Preferably the first catalyst comprises at most 15 wt%, more preferably at most 10 wt% and still more preferably at most 6 wt%, and

most preferably at most 4 wt% of column 6 metal based on the total weight of the catalyst.

The second catalyst comprises preferably at least 0.1 wt% , more preferably at least 1 wt%, still more preferably at least 2 wt% and most preferably at least 5 wt% of column 6 metal, based on the total weight of the catalyst. Preferably the second catalyst comprises at most at most 15 wt% and more preferably at most 10 wt% of column 6 metal based on the total weight of the catalyst.

In addition to the column 6 metal the first catalyst and/or the second catalyst can contain one or more additional metals, such as for example metals from Column 5 and/or Columns 7-10 of the Periodic Table. The metals may be in elemental form or in the form of a compound of the metal. Examples of such additional metals include nickel and cobalt. It is, however, preferred that the first catalyst and/or the second catalyst contains essentially no hydrogenation metals other than the column 6 metal. Without wishing to be bound to any kind of theory, it is thought that the absence of any hydrogenation metals other than the column 6 metal allows for a further improvement of the run time without the necessity to substantially increase the weighted average bed temperature. It is therefore preferred that the first catalyst and/or the second catalyst contains no or essentially no metals from column 9 or column 10 of the Periodic Table. Examples of such column 9 or column 10 metals include nickel or cobalt.

The first catalyst and/or the second catalyst can also include a Column 15 element in addition to the Column 6 metal. Preferably, however, the first catalyst and/or the second catalyst does not contain any column 15 element.

If present, the third catalyst preferably comprises a first hydrogenation metal, a second hydrogenation metal and a support, wherein the first hydrogenation metal is a column 6

metal, the second hydrogenation metal is a column 9 metal or a column 10 metal.

The support of the third catalyst can include for example refractory oxides, porous carbon based materials, zeolites, or combinations thereof. Refractory oxides may include, but are not limited to, alumina, silica, silica-alumina, titanium oxide, zirconium oxide, magnesium oxide, or mixtures thereof.

The support of the third catalyst preferably comprises silica and alumina. The silica-alumina in the third catalyst is preferably amorphous or essentially amorphous. The support can include gamma alumina, theta alumina or delta alumina, or combinations thereof. Preferably the alumina comprises at least 90 wt%, more preferably at least 95 wt% gamma alumina. Preferably the support includes from 0.0001 grams to 0.20 grams, 0.001 grams to 0.11 grams, or 0.01 grams to 0.05 grams of silica; and 0.80 grams to 0.9999 grams, 0.90 grams to 0.999 grams, or 0.95 to 0.99 grams of alumina. Most preferably the support comprises from 0.01 grams to 0.2 gram of silica and from 0.80 grams to 0.99 grams of alumina per gram of support. The ratio of silica to alumina preferably lies in the range from 1:1000 to 1:3, more preferably in the range from 1:200 to 1:4.

The column 6 metal in the third catalyst can for example be molybdenum, tungsten or chromium. The third catalyst comprises preferably at least 0.1 wt%, more preferably at least 1 wt%, still more preferably at least 2 wt% and most preferably at least 5 wt% of column 6 metal, based on the total weight of the catalyst. Preferably the third catalyst comprises at most 30wt%, more preferably at most 15wt% and still more preferably at most 10 wt% of column 6 metal based on the total weight of the catalyst.

The column 9 metal or column 10 metal is preferably cobalt or nickel. The third catalyst comprises preferably at

least 0.01 wt%, more preferably at least 0.1 wt%, still more preferably at least 0.5 wt% and most preferably at least 1 wt% of column 9 or column 10 metal, based on the total weight of the catalyst.

5        Preferably the third catalyst comprises at most 15 wt%, more preferably at most 10 wt% and still more preferably at most 6 wt%, and most preferably at most 4 wt% of column 9 or column 10 metal, based on the total weight of the catalyst.

10        Preferably the third catalyst has a pore size distribution with a median pore diameter of at most 150 Å, more preferably at most 110 Å. Preferably the median pore diameter is at least 50 Å, more preferably at least 80 Å.

15        As illustrated in the examples the presence of the third catalyst has an advantageous effect on the P-value of the reaction mixture that contains both crude feed as well as crude product.

20        Preferably the first catalyst, the second catalyst and/or the third catalyst are prepared by comulling the required ingredients to a mulled mixture. The mulled mixture can be extruded to extrudate particles, which may subsequently be dried and/or calcined.

25        The third catalyst is preferably a catalyst comprising a first hydrogenation metal, a second hydrogenation metal and a support, wherein the first hydrogenation metal is a column 6 metal, the second hydrogenation metal is a column 9 metal or a column 10 metal and the support comprises silica and alumina, which catalyst was obtained by calcining a co-mulled mixture of the support, a column 6 metal oxide and a column 9 or column 10 metal solution at a temperature of at least 650°C.

30        In the catalyst system according to the invention, the content of hydrogenation metal in the catalysts preferably increases from upstream catalyst(s) to downstream catalyst(s).

By a crude feed, also referred to herein as crude, is understood a feed of hydrocarbons which has been produced and/or retorted from hydrocarbon containing formations and which has not yet been distilled and/or fractionated (for  
5 example in an atmospheric distillation unit or a vacuum distillation unit) in a treatment facility to produce multiple components with specific boiling range distributions. That is, the multiple components have not been fractionated from the crude by methods such as atmospheric distillation methods  
10 and/or vacuum distillation methods.

The crude feed used in the method according to the invention may be any crude feed known in the art. The crude feed may be solid, semi-solid, and/or liquid. Examples of crude feeds include coal, bitumen, tar sands and crude oil.  
15 The crude feed can be pretreated before being used in the method of the invention. For example the crude feed may be pretreated to remove non-condensable gases, water, salts, or combinations thereof. The crude feed may also be topped, that is, it may be pretreated such that at least some of the  
20 components that have a boiling point below 35 °C at 0.101 MPa (95 °F at 1 atm) have been removed.

If the crude feed is diluted with a diluent directly after production from the hydrocarbon containing formation in order to facilitate transportation, such diluent may be  
25 removed before use of the crude feed in the method according to the invention.

Examples of crude feeds include whole crude oils, topped crude oils, desalted crude oils or combinations thereof. Examples of crude feed that can be treated using the method of  
30 the invention include crude feeds from the following regions of the world: U.S. Gulf Coast and southern California, Canada Tar sands, Brazilian Santos and Campos basins, Egyptian Gulf of Suez, Chad, United Kingdom North Sea, Angola Offshore,

Chinese Bohai Bay, Venezuelan Zulia, Malaysia, and Indonesia Sumatra.

The crude feed preferably has a viscosity at 37.8 °C of at least 100 cSt, more preferably at least 1000 cSt, still  
5 more preferably at least 2000 cSt and most preferably at least 6000 cSt. Preferably its viscosity at 37.8 °C is at most 1,000,000.

The crude feed preferably has an API gravity of at most 19, more preferably at most 15. Preferably its API gravity is  
10 at least 5.

The crude feed preferably has a total Ni/V/Fe content of at least 0.002 grams, more preferably at least 0.01 wt% Ni/V/Fe based on the total crude feed;

The crude feed preferably has a residue content of at  
15 least 1wt%, more preferably at least 20 wt%, still more preferably at least 30wt % based on the total crude feed.

The crude feed preferably has a sulfur content of at least 0.5 wt%, more preferably at least 1 wt% and still more preferably at least 2 wt% based on the total crude feed.

20 The crude feed preferably has a nitrogen content of at least 0.05 wt%, more preferably at least 0.1 wt% and still more preferably at least 0.2 wt% based on the total crude feed.

The crude feed preferably has a C<sub>5</sub> asphaltenes content of  
25 at least 4 wt%, more preferably at least 8 wt% based on the total crude feed and a C<sub>7</sub> asphaltenes content of at least 2 wt%, more preferably at least 4 wt% based on the total crude feed.

The crude feed preferably has a Micro-Carbon Residue  
30 (MCR) content of at least 0.2 wt% based on the total crude feed.

FIG. 1 schematically illustrated an embodiment of the method of the invention. System 100 includes a series of

contacting zones 102. The crude feed enters upstream the series of contacting zones 102 via crude feed conduit 104. Each contacting zone may be a reactor, a portion of a reactor, multiple portions of a reactor, or combinations thereof.

5 Examples of a contacting zone include a stacked bed reactor, a fixed bed reactor, an ebullating bed reactor, a continuously stirred tank reactor ("CSTR"), a fluidized bed reactor, a spray reactor, and a liquid/liquid contactor. Preferably the catalysts of the catalyst system are situated in a fixed bed.

10 The hydrogen source may enter contacting zone 102 cocurrently with the crude feed via crude feed conduit 104 or separately via gas conduit 106. In contacting zone 102, contact of the crude feed with a catalyst produces a total product that includes a crude product, and, in some  
15 embodiments, gas. In some embodiments, a carrier gas is combined with the crude feed and/or the hydrogen source in conduit 106. The total product, including the crude product, may exit contacting zone 102 and be transported to other processing zones, storage vessels, or combinations thereof via  
20 conduit 108.

The method according to the invention may be carried out as a continuous process or a batch process.

In the method according to the invention a crude feed is contacted in the presence of a hydrogen source with a catalyst  
25 system as described above. The method according to the invention can for example produce a crude product as exemplified in the examples.

The hydrogen source may be any source that provides hydrogen during contact of the crude feed and the catalyst.  
30 Preferably the hydrogen source is hydrogen gas.

Preferably the contacting is carried out at a temperature of at least 200°C, more preferably at a temperature in the range from 350 °C and 450 °C.

Preferably the contacting is carried out at a partial hydrogen pressure of at least 3 MPa, more preferably at least 5 MPa and still more preferably at least 6 MPa. Preferably the contacting is carried out at a partial hydrogen pressure below  
5 20 MPa, more preferably below 15 MPa.

Preferably the contacting is carried out at a LHSV of the crude feed in the range from  $0.01 \text{ h}^{-1}$  to  $30 \text{ h}^{-1}$ , more preferably in the range from  $0.1 \text{ h}^{-1}$  to  $25 \text{ h}^{-1}$ , still more preferably in the range from  $0.2 \text{ h}^{-1}$  to  $20 \text{ h}^{-1}$  and most preferably in the  
10 range from  $0.4 \text{ h}^{-1}$  to  $5 \text{ h}^{-1}$ .

Preferably the weighted average bed temperature is increased by less than  $5^{\circ}\text{C}$ , preferably less than  $4^{\circ}\text{C}$  per 1000 hours during the runtime of the method.

Preferably the P-value of mixture of crude feed and crude  
15 product (which is produced) remains above 1 during contacting.

#### Examples

Example 1. Catalyst A The comparative catalyst was prepared in the following manner.  $\text{MoO}_3$  (94.44 grams) was combined with wide pore alumina (2742.95 grams) and crushed and sieved  
20 calcined alumina fines having a particle size between 5 and 10 micrometers (1050.91 grams) in a Lancaster muller. With the muller running, nitric acid (43.04 grams, 69.7 M) and deionized water (4207.62 grams) were added to the mixture and the resulting mixture was mulled for 5 minutes. Superfloc® 16  
25 (30 grams, Cytec Industries, West Paterson, New Jersey, USA) was added to the mixture in the muller, and the mixture was mulled for a total of 25 minutes. The resulting mixture had a pH of 6.0 and a loss on ignition (as measured at 1 hour at  $700^{\circ}\text{C}$ ) of 0.6232 grams per gram of mixture. The mulled mixture  
30 was extruded using 1.3 mm trilobe dies to form 1.3 trilobe extrudate particles. The extrudate particles were dried at  $125^{\circ}\text{C}$  for several hours and then calcined at  $676^{\circ}\text{C}$  ( $1250^{\circ}\text{F}$ ) for two hours to produce the catalyst. The catalyst

contained, per gram of catalyst, 0.02 grams of molybdenum, with the balance being alumina fines and support. The catalyst is a bimodal catalyst having a pore size distribution with a median pore diameter of 117 Å with 60% of the total number of pores in the pore size distribution having a pore diameter within 33 Å of the median pore diameter, a total pore volume of 0.924 cc/g, and a surface area of 249 m<sup>2</sup>/g.

The pore size distribution measured using mercury porosimetry at a contact angle of 140 is shown in TABLE 1.

TABLE 1

| Pore Diameter<br>in Å | % Pore<br>Volume |
|-----------------------|------------------|
| <70                   | 0.91             |
| 70-100                | 20.49            |
| 100-130               | 37.09            |
| 130-150               | 4.51             |
| 150-180               | 2.9              |
| 180-200               | 1.06             |
| 200-1000              | 0.85             |
| 1000-5000             | 5.79             |
| >5000                 | 22.04            |

#### Example 2. Preparation of a catalyst B1.

A support (4103.4 grams) that contained 0.02 grams of silica and 0.98 grams alumina per gram of support was combined with molybdenum trioxide (409 grams) to form a Mo/support mixture in a Lancaster muller. With the muller running, deionized water (2906.33 grams) to the Mo/support mixture and the mixture was muller until a loss on ignition of 58% was obtained. During comulling, the compactness of the powder was monitored every 20 to 30 minutes and 1 wt% (based on loss of ignition as measured at 1 hour at 700°C) of deionized water was

added to the mixture until the loss on ignition value was obtained. The pH of the compact Mo/support powder was 4.63.

The compact Mo/support powder was extruded using 1.3 mm trilobe dies to form 1.3 trilobe extrudate particles. The  
5 extruded particles were dried at 125 °C and then calcined at 537 °C (1000 °F) for two hours to form the catalyst. The bulk density of the catalyst was 0.547 g/mL. The resulting catalyst contained, per gram of catalyst, 0.08 grams of molybdenum, with the balance being support. The molybdenum  
10 catalyst is a monomodal catalyst having a median pore diameter of 81 Å, with at least 60% of the total number of pores in the pore size distribution having a pore diameter within 33 Å of the median pore diameter, a pore volume of 0.633 mL/g, and a surface area of 355 m<sup>2</sup>/g. The pore distribution as measured by  
15 mercury porosimetry at contact angle of 140 is shown in TABLE 2.

**TABLE 2**

| <b>Pore Diameter<br/>in Å</b> | <b>% Pore<br/>Volume</b> |
|-------------------------------|--------------------------|
| <70                           | 25.61                    |
| 70-100                        | 57.76                    |
| 100-130                       | 8.96                     |
| 130-150                       | 1.50                     |
| 150-300                       | 4.38                     |
| 300-5000                      | 2.44                     |
| >5000                         | 0.47                     |

20 Example 3 Preparation of a catalyst B2. A support (3000 grams) that contained 0.02 grams of silica and 0.98 grams alumina per gram of support was combined with molybdenum trioxide (797.84 grams) to form a Mo/support mixture in a Lancaster muller. With the muller running, deionized water (4092.76 grams) was

added to the Mo/support mixture, and the mixture was mulled until a loss of ignition of 0.5787 grams per gram of mixture was obtained (for about 45 minutes). The pH of the Mo/support mixture was 3.83.

5        The Mo/support mixture was extruded using 1.3 mm trilobe dies to form 1.3 trilobe extrudate particles. The particles were dried at 125 °C and then calcined at 537 °C (1000 °F) for two hours. The compacted bulk density of the extrudates was 0.545 g/mL. The resulting catalyst contained, per gram of  
 10 catalyst, 0.133 grams of molybdenum, with the balance being support. The molybdenum catalyst is a monomodal catalyst having a median pore diameter of 88 Å, with at least 60% of the total number of pores in the pore size distribution having a pore diameter within 47 Å of the median pore diameter, a  
 15 pore volume of 0.651 mL/g, and a surface area of 365 m<sup>2</sup>/g. The pore distribution as measured by mercury porosimetry at a contact angle of 140 is shown in TABLE 3.

TABLE 3

| Pore Diameter<br>in Å | % Pore<br>Volume |
|-----------------------|------------------|
| <70                   | 23.58            |
| 70-100                | 40.09            |
| 100-130               | 12.77            |
| 130-150               | 3.02             |
| 150-180               | 2.56             |
| 180-300               | 4.04             |
| 300-1000              | 4.53             |
| 1000-3000             | 5.16             |
| 3000-5000             | 3.19             |
| >5000                 | 1.04             |

Example 4. Preparation of a catalyst C

The catalyst was prepared in the following manner. A nickel solution was made by combining 377.7 grams of  $\text{Ni}(\text{NO}_3)_2$ , and  
5 137.7 grams of deionized water to form a slurry. The slurry was heated until clear and sufficient deionized water was added to bring the combined nickel solution weight up the 3807 grams. A support (3208.56 grams) that contained 2 wt% of silica and 98 wt% of alumina (weight percentage based on the  
10 support) was combined with the nickel solution and  $\text{MoO}_3$  (417.57 grams) in a muller. During mulling, 4191.71 deionized water was added to the mixture and the mixture was mulled for 45 minutes. The resulting mixture had a pH of 4.75 and a LOI of 59.4 wt% per mixture.

15 The mulled mixture was extruded using 1.3 mm trilobe dies to form 1.3 trilobe extrudate particles. The extrudates were dried at 100 °C for several hours and then calcined at 676 °C (1250 °F) for two hours. The resulting catalyst contained, per gram of catalyst, 0.079 grams of Mo, and 0.022 grams Ni,  
20 with the balance being support. The molybdenum/nickel catalyst had a median pore diameter of 98 Å, a pore volume of 0.695 mL/g. The pore distribution as measured by mercury porosimetry at a contact angle of 140 is shown in TABLE 4.

**TABLE 4**

| <b>Pore Diameter<br/>in Å</b> | <b>% Pore<br/>Volume</b> |
|-------------------------------|--------------------------|
| <70                           | 5.5                      |
| 70-100                        | 53.6                     |
| 100-130                       | 33.6                     |
| 130-150                       | 2.1                      |
| 150-180                       | 1.4                      |
| 180-300                       | 2.2                      |

| Pore Diameter<br>in Å | % Pore<br>Volume |
|-----------------------|------------------|
| 300-1000              | 1.5              |
| 1000-3000             | 0.1              |
| 3000-5000             | 0.0              |
| >5000                 | 0.0              |

5 Example 5. Contact of a Crude feed with Catalysts A and B1 in  
a volumetric ratio of catalyst A to catalyst B1 of 2:8.

A tubular reactor with a centrally positioned thermowell  
was equipped with thermocouples to measure temperatures  
throughout a catalyst bed. The catalyst bed was formed by  
10 filling the space between the thermowell and an inner wall of  
the reactor with catalysts and silicon carbide (20-grid,  
Stanford Materials; Aliso Viejo, CA). Such silicon carbide is  
believed to have low, if any, catalytic properties under the  
process conditions described herein. All catalysts were  
15 blended with an equal volume amount of silicon carbide before  
placing the mixture into the contacting zone portions of the  
reactor.

A volume of catalyst B1 (24 cm<sup>3</sup>) as described in Example 2  
was mixed with silicone carbide (24 cm<sup>3</sup>) and the mixture was  
20 positioned in a bottom contacting zone.

A volume of catalyst A (6 cm<sup>3</sup>) as described in Example 1  
was mixed with silicone carbide (6 cm<sup>3</sup>) and the mixture was  
positioned on top of the contacting zone to form a top  
contacting zone. The volume ratio of catalyst A to catalyst  
25 B1 was thus 2:8.

The crude feed flow to the reactor was from the top of  
the reactor to the bottom of the reactor. Silicon carbide was

positioned at the bottom of the reactor to serve as a bottom support.

The catalysts were sulfided by introducing a gaseous mixture of 5 vol% hydrogen sulfide and 95 vol% hydrogen gas into the contacting zones at a rate of 1.5 liters/hour of gaseous mixture per volume (mL) of total catalyst (silicon carbide was not counted as part of the volume of catalyst). Temperatures of the contacting zones were increased to 204 °C (400 °F) over 1 hour and held at 204 °C for 2 hours. After holding at 204 °C, the temperature of the contacting zones was increased incrementally to 316 °C (600 °F) at a rate of 10 °C (50 °F) per hour. The contacting zones were maintained at 316 °C for an hour, then the temperature was raised to 370 °C (700 °F) over 1 hour and held at 370 °C for two hours. The contacting zones were allowed to cool to ambient temperature.

After sulfidation of the catalysts, the temperature of the contacting zones was raised to a temperature of 410 °C. A crude feed (Peace River), having the properties listed in Table 4 was flowed through the top contacting zone and bottom contacting zone of the reactor. The crude feed was contacted with each of the catalysts in the presence of hydrogen gas. Contacting conditions were as follows: ratio of hydrogen gas to feed was 318 Nm<sup>3</sup>/m<sup>3</sup> (2000 SCFB) and LHSV was about 0.5 h<sup>-1</sup> and at a system pressure of 6.55 MPa (950 psig) as the crude feed flowed through the reactor.

The runtime, viscosity, API, P-value, weighted average bed temperature (WABT) and WABT increase during the runtime are illustrated in table 5.

Example 6. Contact of a Crude feed with Catalysts A, B1 and C in a volumetric ratio of catalyst A to catalyst B1 to catalyst C of 2:6:2.

Example 5 was repeated and the apparatus, sulfiding procedure, crude feed and operating conditions were the same

as for Example 5, with the exception of the catalysts used. Instead of the catalysts used in example 5, a combination of catalysts A, B1 and C was used in a volumetric ratio of catalyst A to catalyst B1 to catalyst C of 2:6:2

5       A volume of catalyst C ( $6\text{ cm}^3$ ) as described in Example 4 was mixed with silicone carbide ( $6\text{ cm}^3$ ) and the mixture was positioned in a bottom contacting zone.

          A volume of catalyst B1 ( $18\text{ cm}^3$ ) as described in Example 2 was mixed with silicone carbide ( $18\text{ cm}^3$ ) and the mixture was  
10       positioned in a middle contacting zone.

          A volume of catalyst A ( $6\text{ cm}^3$ ) as described in Example 1 was mixed with silicone carbide ( $6\text{ cm}^3$ ) and the mixture was positioned in a top contacting zone.

          The runtime, viscosity, API, P-value, weighted average  
15       bed temperature (WABT) and WABT increase during the runtime are illustrated in table 5.

Example 7. Contact of a Crude feed with Catalysts A, B1 and C in a volumetric ratio of catalyst A to catalyst B1 to catalyst C of 4:4:2.

20       Example 5 was repeated and the apparatus, sulfiding procedure, crude feed and operating conditions were the same as for Example 5, with the exception of the catalysts used. Instead of the catalysts used in example 5, a combination of catalysts A, B1 and C was used in a volumetric ratio of  
25       catalyst A to catalyst B1 to catalyst C of 4:4:2

          A volume of catalyst C ( $6\text{ cm}^3$ ) as described in Example 4 was mixed with silicone carbide ( $6\text{ cm}^3$ ) and the mixture was positioned in a bottom contacting zone.

          A volume of catalyst B1 ( $12\text{ cm}^3$ ) as described in Example 2  
30       was mixed with silicone carbide ( $12\text{ cm}^3$ ) and the mixture was positioned in a middle contacting zone.

A volume of catalyst A (12 cm<sup>3</sup>) as described in Example 1 was mixed with silicone carbide (12 cm<sup>3</sup>) and the mixture was positioned in a top contacting zone.

The runtime, viscosity, API, P-value, weighted average  
5 bed temperature (WABT) and WABT increase during the runtime are illustrated in table 5.

In conventional processes it is expected that the P-value decreases during a hydrotreatment. Surprisingly it was found that the P-value during the runs of examples 5, 6 and 7  
10 remained stable. A comparison of example 5, which does not contain any catalyst C, with example 6 and 7, which do contain catalyst C, further illustrates that the presence of catalyst C has a further positive effect on the P-value and the stability of the reaction mixture.

TABLE 5

| Property                                | Crude feed | Crude Product |      |      |                                                                     |
|-----------------------------------------|------------|---------------|------|------|---------------------------------------------------------------------|
| Example                                 |            | 5             | 6    | 7    | <b>Examples 24 and 25 of U.S. Patent Application No. 11/866,926</b> |
| Run Time, hours                         | n.a.       | 5800          | 5300 | 4700 | 2952                                                                |
| Pressure, MPa                           | n.a.       | 6.55          | 6.55 | 6.55 | 3.8                                                                 |
| API Gravity                             | 7.9        | 17            | 19   | 18.5 | 14.44                                                               |
| Viscosity at 37.8 °C (100 °F), cSt      | 8357       | 40            | 35.3 | 33.5 | 74.4                                                                |
| P-Value                                 | 2.6        | 1.25          | 1.4  | 1.3  | 1.2                                                                 |
| Start temperature, °C                   | n.a.       | 399           | 394  | 391  | 385                                                                 |
| End temperature, °C                     | n.a.       | 408           | 403  | 408  | 410                                                                 |
| Temperature increase per 1000 hours, °C | n.a.       | 1.6           | 1.7  | 3.6  | 8.5                                                                 |

CLAIMS

1. A catalyst system comprising:

a first catalyst with a bimodal pore size distribution,  
5 which first catalyst comprises a hydrogenation metal, mineral  
oxide particles and a support, wherein the hydrogenation metal  
consists of a column 6 metal and wherein the mineral oxide  
particles have an average particle size of at most 150  
micrometers;

10 a second catalyst comprising a hydrogenation metal and a  
support wherein the hydrogenation metal consists of a column 6  
metal and the support comprises silica-alumina.

2. The catalyst system of claim 1, wherein the second catalyst  
is located downstream of the first catalyst.

15 3. The catalyst system of claim 1, wherein the volumetric ratio  
of first catalyst to second catalyst lies in the range from 1:9  
to 6:4.

4. The catalyst system of claim 1, wherein the first catalyst  
contains essentially no hydrogenation metals other than the  
20 column 6 metal and wherein further the second catalyst contains  
essentially no hydrogenation metals other than the column 6  
metal.

5. The catalyst system of claim 1, wherein the catalyst system  
further comprises a subsequent third catalyst, which third  
25 catalyst comprises a first hydrogenation metal, a second  
hydrogenation metal and a support, wherein the first  
hydrogenation metal is a column 6 metal, the second hydrogenation  
metal is a column 9 metal or a column 10 metal.

6. The catalyst system of claim 5, wherein the third catalyst  
30 is present in a volumetric amount that is equal or less than the  
volumetric amount of the second catalyst.

7. The catalyst system of claim 1, wherein the first and/or  
second catalyst contains a column 15 element.

8. The catalyst system of claim 1, wherein the amount of  
35 hydrogenation metal in the catalysts increases from the catalyst  
located most upstream to the catalyst located most downstream.

hydrogenation metal in the catalysts increases from the catalyst located most upstream to the catalyst located most downstream.

10. A method for treatment of a crude feed comprising contacting  
5 a crude feed in the presence of a hydrogen source with a catalyst system as claimed in any one of claims 1 to 8.

11. The method as claimed in claim 10 where the contacting is carried out at a temperature in the range from 350 °C and 450 °C.

12. The method as claimed in claim 10 where the contacting is  
10 carried out at a pressure of at least 3 MPa.

13. The method as claimed in claim 10, wherein the catalysts of the catalyst system are situated in a fixed bed.

14. The method as claimed in claim 13, wherein the weighted average bed temperature is increased by less than 5°C per 1000  
15 hours.

15. A catalyst comprising comprises a first hydrogenation metal, a second hydrogenation metal and a support, wherein the first hydrogenation metal is a column 6 metal, the second hydrogenation metal is a column 9 metal or a column 10 metal and the support  
20 comprises silica and alumina, which catalyst was obtained by calcining a co-mulled mixture of the support, a column 6 metal oxide and a column 9 or column 10 metal solution at a temperature of at least 650°C.