

HYDROPROCESSING FOR DISTILLATE PRODUCTION

FIELD

[0001] Systems and methods are provided for processing distillate boiling range feeds for production of distillate boiling range products.

BACKGROUND

[0002] As methods for recovering natural gas from shale formations and other non-conventional sources have improved, the cost of using natural gas has decreased. This reduction in natural gas cost means that processes dependent on natural gas as a substantial feed are also more economically favorable. One process that can directly benefit from a reduced natural gas cost is steam reforming of methane to form hydrogen and/or syngas.

[0003] One of the challenges in processing of liquid petroleum feeds is that the hydrogen to carbon ratio of the petroleum feed is often lower than the hydrogen to carbon ratio of the desired products from a feed. Some refinery processes can generate small volumes of excess hydrogen, but in general hydrogen is a limited resource.

[0004] U.S. Patents 8,722,563 and 8,722,564 describe multimetallic hydroprocessing catalysts prepared by forming a catalyst precursor and then heating the catalyst precursor to form the catalyst. The multimetallic catalysts are described as having improved activity for hydrodenitrogenation of various types of feeds.

[0005] U.S. Patent 6,582,590 and U.S. Patent 6,929,738 describe various types of processing sequences that include hydroprocessing in the presence of a bulk multimetallic catalyst. The processes are described as being suitable for production of various product fractions, including distillate fuels.

SUMMARY

[0006] In an aspect, a hydroprocessing process is provided, comprising: reacting a feedstream having a sulfur content of at least about 3000 wppm, or at least about 4000

wppm, or at least about 5000 wppm (such as up to about 50000 wppm), and a T90 boiling point of about 900°F (482°C) or less, in a first hydrotreating stage in the presence of a hydrogen-containing treat gas and in the presence of at least one first stage hydrotreating catalyst, the first hydrotreating stage being operated at first stage hydrotreating conditions, to produce a first liquid effluent having a sulfur content of about 5000 wppm or less, or about 4000 wppm or less, or about 3000 wppm or less, the sulfur content of the first liquid effluent being less than the sulfur content of the feedstream; separating the first liquid effluent to produce a first vapor phase stream and a first liquid product stream, the first liquid product stream optionally having a T10 boiling point and a T90 boiling point; reacting at least a portion of the first liquid product stream in a second hydrotreating stage in the presence of a hydrogen-containing treat gas and a second hydrotreating catalyst, the second hydrotreating stage being operated at second stage hydrotreating conditions to produce a second liquid effluent; and separating the second liquid effluent to produce a second vapor phase stream and a second liquid product stream having a sulfur content of about 500 wppm or less, or about 250 wppm or less, or about 100 wppm or less, wherein about 15 wt% or less of the feedstream is converted relative to a conversion temperature of 350°F (177°C) during the reacting in the first hydrotreating stage and the second hydrotreating stage. Optionally, the first liquid effluent can have a sulfur content of at least about 1000 wppm, or at least about 1500 wppm, or at least about 2000 wppm.

[0007] In another aspect, a hydroprocessing process is provided, comprising: reacting a feedstream having a T90 boiling point of about 900°F (482°C) or less in a first hydrotreating stage in the presence of a hydrogen-containing treat gas and in the presence of at least one first stage hydrotreating catalyst, the first hydrotreating stage being operated at first stage hydrotreating conditions, to produce a first liquid effluent; separating at least a portion of the first liquid effluent to produce a first vapor phase stream and a first liquid product stream, the first liquid product stream having a sulfur content of about 1000 wppm to about 20,000 wppm, the first liquid product stream having a) a T10 boiling point of at least about 350°F (177°C), b) a T90 boiling point of about 850°F (454°C) or less, or c) a combination thereof; reacting at least a portion of the first liquid product stream in a second hydrotreating stage in the presence of a hydrogen-containing treat gas and a mixed metal catalyst, the second hydrotreating stage

being operated at second stage hydrotreating conditions to produce a second liquid effluent, the second stage hydrotreating conditions being effective for conversion of about 10 wt% or less of the at least a portion of the first liquid product stream relative to a conversion temperature of about 350°F (177°C); and separating at least a portion of the second liquid effluent to produce a second vapor phase stream and a second liquid product stream, the second liquid product stream having a sulfur content of about 250 wppm or less, or about 100 wppm or less.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 schematically shows an example of a configuration suitable for processing a feed to produce distillate boiling range products.

[0009] FIG. 2 schematically shows an example of a configuration suitable for processing a feed to produce distillate boiling range products.

DETAILED DESCRIPTION

[0010] All numerical values within the detailed description and the claims herein are modified by “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

Overview

[0011] In various aspects, methods are provided for hydrotreating a feed to generate a product with a reduced or minimized aromatics content. For example, a distillate boiling range feed having an elevated content of sulfur and/or nitrogen can be hydrotreated using at least two hydrotreating stages with intermediate separation to produce a hydrotreated distillate boiling range product with a reduced or minimized aromatics content. Additionally or alternately, a mixed metal catalyst formed from a suitable precursor can be used during the hydrotreating. A mixed metal catalyst formed from a suitable precursor can provide an unexpectedly superior activity for aromatic saturation. A still further unexpected benefit can be achieved by combining a

multi-stage hydrotreating process with intermediate separation with hydrotreating in the presence of a mixed metal catalyst formed from a suitable precursor.

[0012] Some feeds that have an appropriate boiling range for use as a distillate fuel correspond to feeds with both a substantial content of heteroatoms, such as sulfur and nitrogen, and a substantial content of aromatic compounds. The aromatic compounds can optionally include multi-ring aromatic compounds. Such aromatic compounds have a high density relative to aliphatic compounds. By increasing the amount of hydrogenation of aromatics in a distillate boiling range feed, the overall density of the resulting liquid product can be reduced at a given level of feed conversion while also maintaining a (relatively) constant absolute number of carbon atoms within the feed. Using hydrogenation to decrease the density of a petroleum feed can be referred to as a “volume swell” for the feed. This type of volume swell can be economically valuable for distillate fuel products, due to the fact that many types of distillate fuel are sold on a volume basis. By increasing the volume of distillate fuel corresponding to a given number of carbon atoms, the overall yield of distillate fuel from a feedstock can be increased. It is noted that the benefit from volume swell can be dependent on the ability to increase hydrogenation of the feed without increasing conversion of the distillate boiling range feed to naphtha boiling range products.

[0013] The amount of aromatic saturation that occurs during hydrotreatment can be suppressed for feeds that have elevated contents of sulfur and/or nitrogen. For example, cycle oils and other cracked distillate feeds can have sulfur contents of at least about 3000 wppm or greater, such as about 5000 wppm or greater, or even about 10000 wppm or greater. A conventional hydrotreating process can be suitable for reducing the sulfur content of such a feed to a desired level, such as about 500 wppm or less, or about 250 wppm or less, or about 100 wppm or less. However, the H_2S generated during hydrotreatment can tend to suppress the aromatic saturation activity of a hydrotreating catalyst. This can result in an increased level of aromatics in the hydrotreated product.

[0014] As an example, during a typical hydrotreatment process, the early (upstream) portions of a hydrotreatment process typically cause removal of sulfur from compounds that have a faster reaction rate. The removal of this more easily removed sulfur is not believed to be strongly impacted by the absence or presence of H_2S in the hydrogen treat

gas. Thus, a treat gas containing H_2S can be suitable for the initial catalyst beds and/or stages of a distillate hydrotreater when removing sulfur from a feed having an elevated sulfur content. However, this easily removed sulfur can still generate H_2S . As a result, in a conventional distillate hydrotreater that does not have interstage separation, the downstream stage(s) / catalyst bed(s) / portions of a catalyst bed are exposed to the feed in the presence of a treat gas that can contain at least about 1 vol% H_2S , or at least about 2 vol% H_2S , depending on the amount of sulfur initially present in the feed. Thus, even though a conventional hydrotreater may start with a contaminant free hydrogen treat gas, after removal of a portion of the sulfur in the feed, the downstream portions of the distillate hydrotreating system effectively receive a treat gas having an H_2S content of at least about 1 vol% or more. This H_2S content in the downstream portions of a conventional distillate hydrotreater can suppress the activity of the downstream portions of the hydrotreating catalyst for both desulfurization and aromatic saturation activity.

[0015] In addition to difficulties in performing aromatic saturation in an environment containing substantial amounts of H_2S , traditionally increasing the amount of hydrogenation that occurs when forming a distillate fuel product from a distillate boiling range feed has not been desirable. Because hydrogen is a limited resource in a refinery setting, the cost of hydrogen consumed by saturation of aromatic rings in a distillate fuel was difficult to justify based on the resulting increase in value in the distillate fuel products. As a result, the amount of aromatic saturation performed on a distillate feed was usually limited to be sufficient for meeting regulatory requirements, such as specifications for the maximum allowable amounts of polyaromatic compounds.

[0016] In contrast to conventional processes, a catalyst and/or hydroprocessing conditions have been identified that allow for increased or improved aromatic saturation during hydrotreatment of a distillate feed that contains elevated levels of sulfur. Use of a catalyst and/or process conditions that allow for improved aromatic saturation can allow for production of increased volumes of distillate fuels while reducing or minimizing the amount of “overcracking” or other excess conversion of a feed. In some aspects, this can allow processing conditions to be selected based on a desired level of heteroatom removal while also providing the volume swell benefit that comes from increased aromatic saturation.

[0017] Volume swelling in a product can be characterized in any convenient manner, such as by directly measuring the volume, measuring the specific gravity of a product, or by measuring the API gravity of a product. Volume swelling due to processing a feed as described herein can generally lead to an increase in volume of about 0.25 vol% to about 2.5 vol% (or possibly more). Although an increase in volume of less than 1 vol% may appear to be small, due to the size of typical commercial processing units, and based on the typical continuous (or near-continuous) operation schedule of such commercial processing units, an increase in volume of a few tenths of a percent for a distillate product can correspond to a substantial and significant increase in total product generated and/or in commercial value generated over time.

[0018] In some aspects, the methods for distillate hydrotreating can include use of a catalyst formed from a catalyst precursor composition comprising at least one metal from Group 6 of the Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, and a reaction product formed from (i) a first organic compound containing at least one amine group and at least 10 carbons or (ii) a second organic compound containing at least one carboxylic acid group and at least 10 carbons, but not both (i) and (ii).

[0019] In other aspects, the process can use a catalyst formed from a catalyst precursor composition comprising at least one metal from Group 6 of the Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, and a reaction product formed from (i) a first organic compound containing at least one amine group, and (ii) a second organic compound separate from said first organic compound and containing at least one carboxylic acid group. More broadly, this aspect of the present invention relates to use of a catalyst formed from a catalyst precursor composition comprising at least one metal from Group 6 of the Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, and a condensation reaction product formed from (i) a first organic compound containing at least one first functional group, and (ii) a second organic compound separate from said first organic compound and containing at least one second functional group, wherein said first functional group and said second functional group are capable

of undergoing a condensation reaction and/or a (decomposition) reaction causing an additional unsaturation to form an associated product.

[0020] In still other aspects, the process can use a catalyst formed from a catalyst precursor composition comprising at least one metal from Group 6 of the Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, and a reaction product comprising an amide group. In this type of aspect, the reaction product is formed prior to incorporation into the catalyst precursor. The reaction product is an amide-containing reaction product formed from an ex-situ reaction of (i) a first organic compound containing at least one amine group, and (ii) a second organic compound separate from said first organic compound and containing at least one carboxylic acid group.

[0021] In yet other aspects, a reaction system including a plurality of reaction stages with intermediate separation for removal of gases can be used to produce a hydrotreated distillate product with reduced aromatic content by processing a distillate feed in the presence of a conventional hydrotreating catalyst and/or a mixed metal catalyst. One or more initial stages can be used to reduce the sulfur from an elevated amount to an amount less than about 5000 wppm, such as less than about 3000 wppm. Gases can be separated from the effluent of the initial stages to reduce or minimize the H₂S and/or NH₃ content prior to one or more additional hydrotreating stages. Reducing or minimizing the H₂S content can allow for increased aromatic saturation activity in the additional hydrotreating stages.

Feedstock

[0022] In various aspects, methods are provided for improving the yield of distillate products from hydrotreatment of distillate feedstocks and/or heavier feedstocks that have elevated sulfur content. Examples of suitable feedstocks can include, but are not limited to, atmospheric gas oils, vacuum gas oil feeds, cycle oils, and/or other feeds (such as cracked feeds) having a similar type of boiling range, during the production of distillate fuels. In addition to using a mixed metal catalyst formed from a suitable precursor, the methods can involve stripping of gases to separate out contaminant gases (such as H₂S and/or NH₃) during hydrotreatment of a feed. This can allow for an improved yield of

distillate products at a desired level of heteroatom removal. The improved yield of distillate can be achieved while reducing or minimizing production of lower boiling compounds, such as light ends or naphtha boiling range products. In some aspects, the improved yield can be based in part on increased volume swell of the distillate products due to having a reduced or minimized amount of aromatics in the resulting distillate products. Particular examples of suitable feeds can include raw virgin distillate feeds, such as straight run light vacuum gas oils, and catalytically cracked feeds, such as distillate boiling range cycle oils produced during fluid catalytic cracking or coker distillate feeds.

[0023] More generally, a wide range of petroleum and chemical feedstocks can be hydroprocessed in accordance with the present invention. Suitable feedstocks include whole and reduced petroleum crudes, atmospheric and vacuum residua, propane deasphalted residua, e.g., brightstock, cycle oils, FCC tower bottoms, gas oils, including atmospheric and vacuum gas oils and coker gas oils, light to heavy distillates including raw virgin distillates, hydrocrackates, hydrotreated oils, dewaxed oils, slack waxes, Fischer-Tropsch waxes, raffinates, and mixtures thereof.

[0024] In this discussion, the distillate boiling range is defined as 350°F (177°C) to 700°F (371°C). Distillate boiling range products can include products suitable for use as kerosene products (including jet fuel products) and diesel products, such as premium diesel or winter diesel products. Such distillate boiling range products can be suitable for use directly, or optionally after further processing. With regard to other boiling ranges, the lubricant boiling range is defined as 700°F (371°C) to 950°F (482°C) and the naphtha boiling range is defined as 100°F (37°C) to 350°F (177°C).

[0025] One way of defining a feedstock is based on the boiling range of the feed. One option for defining a boiling range is to use an initial boiling point for a feed and/or a final boiling point for a feed. Another option, which in some instances may provide a more representative description of a feed, is to characterize a feed based on the amount of the feed that boils at one or more temperatures. The amount of a feed that boils at a given temperature can be referred to as a fractional weight boiling point. For example, a "T5" boiling point for a feed is defined as the temperature at which 5 wt% of the feed will boil off. Similarly, a "T95" boiling point is a temperature at which 95 wt% of the

feed will boil, while a “T99.5” boiling point is a temperature at which 99.5 wt% of the feed will boil.

[0026] In some aspects, a distillate boiling range feedstock can correspond to a feed where at least a substantial portion of the feed has a boiling point in the distillate boiling range. In various aspects, a distillate boiling range feedstock can have a T20 boiling point, or a T10 boiling point, or a T5 boiling point of at least about 350°F (177°C), or at least about 400°F (204°C), or at least about 450°F (232°C). Additionally or alternately, a distillate boiling range feedstock can have a T95 boiling point, or a T90 boiling point, or a T75 boiling point of about 900°F (482°C) or less, or about 850°F (454°C) or less, or about 800°F (427°C) or less, or about 750°F (399°C) or less, or about 700°F (371°C) or less. In still further additional or alternate aspects, a distillate boiling range feedstock can have two or more of the above fractional weight boiling points, or three or more of the above fractional weight boiling points, or any other convenient combination. Examples of distillate boiling range feedstocks having two or more of the above fractional weight boiling points include feeds with a T5 boiling point of at least about 350°F (177°C) and a T20 boiling point of at least about 450°F (232°C), or a T5 boiling point of at least about 400°F (204°C) and a T95 boiling point of 850°F (454°C) or less, or another convenient combination. It is noted that all combinations of explicitly recited fractional weight boiling points are also explicitly contemplated in conjunction with each other to provide distillate boiling range feedstocks having two or more of the above fractional weight boiling points, or three or more of the above fractional weight boiling points.

[0027] In various aspects, a distillate boiling range feedstock containing high levels of sulfur and/or nitrogen can be passed into one or more hydrodesulfurization reaction stages to remove sulfur and nitrogen. Suitable distillate boiling range feedstocks can be feeds containing at least about 3000 wppm sulfur, or at least about 4000 wppm sulfur, or at least about 5000 wppm sulfur, or at least about 7500 wppm sulfur, or at least about 10,000 wppm sulfur, or at least about 15,000 wppm sulfur, or at least about 20,000 wppm sulfur, such as up to about 50,000 wppm sulfur.

[0028] In some alternative aspects, a feed with a higher boiling range can be used, such as a feed with an initial boiling point of at least about 650°F (343°C), or at least

about 700°F (371°C), or at least about 750°F (399°C). Alternatively, a feed may be characterized using a T5 boiling point, such as a feed with a T5 boiling point of at least about 650°F (343°C), or at least about 700°F (371°C), or at least about 750°F (399°C). Such a feed can have a final boiling point of about 1150°F (621°C), or about 1100°F (593°C) or less, or about 1050°F (566°C) or less. Alternatively, such a feed may be characterized using a T95 boiling point, such as a feed with a T95 boiling point of about 1150°F (621°C), or about 1100°F (593°C) or less, or about 1050°F (566°C) or less.

[0029] In some aspects, the aromatics content of the feed prior to hydroprocessing can be at least about 30 wt% aromatics, or at least about 40 wt%, or at least about 50 wt%, or at least about 60 wt%, or at least about 70 wt%, such as up to about 80 wt% or more or up to about 90 wt% or more. After hydroprocessing, the aromatics content of the distillate boiling range liquid product from the final hydrotreating stage can be about 60 wt% or less, or about 50 wt% or less, or about 40 wt% or less, or about 30 wt% or less. Each of the above upper bounds for the aromatics content is explicitly contemplated herein in combination with each of the above lower bounds for the aromatics content.

[0030] In some aspects, the content of multi-ring aromatics in the feed prior to hydroprocessing can be at least about 20 wt% multi-ring aromatics, or at least about 25 wt%, or at least about 30 wt%, or at least about 35 wt%, or at least about 40 wt%, or at least about 45 wt%, or at least about 50 wt%, such as up to about 60 wt% or more. After hydroprocessing, the multi-ring aromatics content of the distillate boiling range liquid product from the final hydrotreating stage can be about 10 wt% or less, or about 7.5 wt% or less, or about 5 wt% or less, or about 3 wt% or less. Each of the above upper bounds for the multi-ring aromatics content is explicitly contemplated herein in combination with each of the above lower bounds for the multi-ring aromatics content.

[0031] In some aspects, at least a portion of the feed can correspond to a feed derived from a biocomponent source. In this discussion, a biocomponent feedstock refers to a hydrocarbon feedstock derived from a biological raw material component, from biocomponent sources such as vegetable, animal, fish, and/or algae. Note that, for the purposes of this document, vegetable fats/oils refer generally to any plant based material, and can include fats/oils derived from a source such as plants of the genus *Jatropha*.

Generally, the biocomponent sources can include vegetable fats/oils, animal fats/oils, fish oils, pyrolysis oils, and algae lipids/oils, as well as components of such materials, and in some embodiments can specifically include one or more type of lipid compounds. Lipid compounds are typically biological compounds that are insoluble in water, but soluble in nonpolar (or fat) solvents. Non-limiting examples of such solvents include alcohols, ethers, chloroform, alkyl acetates, benzene, and combinations thereof.

Process Configuration

[0032] In various aspects, methods are provided for improving the yield of distillate products from hydrotreatment of distillate feedstocks and/or heavier feedstocks that have elevated sulfur content. Examples of suitable feedstocks can include, but are not limited to, atmospheric gas oils, vacuum gas oil feeds, cycle oils, and/or other feeds (such as cracked feeds) having a similar type of boiling range, during the production of distillate fuels. In addition to using a mixed metal catalyst formed from a suitable precursor, the methods can involve stripping of gases to separate out contaminant gases (such as H₂S and/or NH₃) during hydrotreatment of a feed. This can allow for an improved yield of distillate products at a desired level of heteroatom removal. The improved yield of distillate can be achieved while reducing or minimizing production of lower boiling compounds, such as light ends or naphtha boiling range products. In some aspects, the improved yield can be based in part on increased volume swell of the distillate products due to having a reduced or minimized amount of aromatics in the resulting distillate products.

[0033] In some aspects, a feed can be hydrodesulfurized in a first stage, which contains one or more reaction zones, in the presence of hydrogen and a first hydrotreating catalyst under hydrodesulfurizing conditions. The product stream can then be passed to a separation zone wherein a vapor phase stream and a liquid phase (product) stream are produced. The liquid phase product stream is passed to a second hydrodesulfurization stage, which contains at least one reaction zone, where it is further hydrodesulfurized in the presence of hydrogen and a second hydrodesulfurization catalyst. The liquid product stream from the second hydrodesulfurization stage is passed to a second separation zone wherein a vapor product stream is collected for further processing or blending. Optionally, the liquid product stream from the second

hydrodesulfurization zone can be passed to a third reaction stage which is operated in the presence of a dewaxing catalyst, a hydrogenation catalyst, or another hydrotreating catalyst. Optionally, the liquid product stream from the first hydrodesulfurization zone can be passed to an additional intermediate hydrodesulfurization stage between the first and second stage. It is within the scope of this invention that at least a portion of the vapor product stream from either or both of the first and second reaction stages can be recycled to the first reaction stage. Optionally but preferably, the vapor product stream from the first reaction stage and/or the second reaction stage is not recycled to the second reaction stage. The vapor product stream from a hydrotreating reaction stage can typically contain H_2S and/or NH_3 . Recycling such a stream to the second reaction stage could reduce or minimize the desired additional aromatic saturation that can provide volume swell of the hydrotreated distillate product.

[0034] A variety of process schemes can be used for hydroprocessing a feed as described above. In some aspects, a reaction system can include at least two hydrotreatment stages. Each hydrotreatment stage can include a hydrotreating catalyst, such as a conventional hydrotreating catalyst, a mixed metal catalyst formed from a suitable precursor, or a combination thereof. A gas-liquid separation can be performed between the hydrotreatment stages to reduce or minimize the content of contaminant gases in the second hydrotreatment stage.

[0035] As another example, at least three separate reaction stages can be used, each containing one or more reaction zones, with each zone containing at least one bed of catalyst. The first two reaction stages can contain hydrodesulfurization catalysts and the third reaction stage (and any further downstream stages) can contain a hydrogenation catalyst, a dewaxing catalyst, a hydrocracking catalyst, and/or a hydrotreating catalyst. Each reaction stage can optionally further include a mixed metal catalyst. Depending on the aspect, the mixed metal catalyst can serve as the hydrodesulfurization catalyst in a stage, or the mixed metal catalyst can be present in addition to a hydrodesulfurization catalyst (or hydrogenation catalyst or dewaxing catalyst or hydrocracking catalyst). In some aspects, when this process scheme is practiced the feedstock introduced into the first reaction stage can be a distillate boiling range feedstock. One suitable type of feedstock can be a distillate boiling range feedstock from an atmospheric distillation

tower, such as a raw virgin petroleum distillate. Another example of a suitable feedstock can be a cracked feedstock, such as a light cycle oil from a fluid catalytic cracking process. Such feedstocks can contain (for example) at least about 3000 wppm sulfur, or at least about 4000 wppm sulfur, or at least about 5000 wppm sulfur, or at least about 10,000 wppm sulfur, or at least about 15,000 wppm sulfur, and optionally can further contain a relatively high nitrogen content. In other aspects, such as some aspects where the third reaction stage (and/or a later reaction stage) includes a dewaxing catalyst and/or a hydrocracking catalyst, a feed having a boiling range suitable for production of lubricant base oils can be used in addition to or in place of a distillate boiling range feed.

[0036] After being hydrodesulfurized in a first hydrodesulfurization stage the feed product stream can contain from about 500 to about 20000 wppm sulfur, or about 500 to about 5000 wppm, or about 500 to about 3000 wppm, or about 750 to about 20000 wppm, or about 750 to about 5000 wppm, or about 750 to about 3000 wppm, or about 1000 to about 20000 wppm, or about 1000 to about 5000 wppm, or about 1000 to about 3000 wppm, or about 1500 to about 20000 wppm, or about 1500 to about 5000 wppm, or about 1500 to about 3000 wppm. This amount of sulfur removal can correspond to removal of about 40% to about 80% of the sulfur initially present in the feedstock, and optionally can correspond to removal of about 40% to about 70% of the sulfur, or about 40% to about 60%. It is preferred that at least one of the reaction zones can contain a bed of the mixed metal catalyst. For example, the reactor of the first and/or second hydrodesulfurization stage can contain a stacked bed arrangement wherein a conventional hydrodesulfurization catalyst comprises one or more reaction zones and a mixed metal catalyst comprises the other one or more reaction zones. It is preferred that if a conventional hydrodesulfurization catalyst and a mixed metal catalyst are used, the conventional catalyst can be in the upstream reaction zone or zones. It is preferred that the mixed metal catalyst is present in at least the second hydrodesulfurization stage. In some aspects, the plurality of reaction stages can correspond to two reaction stages, with the second reaction stage preferably containing the mixed metal catalyst.

[0037] The reaction product is passed to a separation zone where a vapor phase product stream and a liquid phase product stream is produced. The liquid phase product stream (having a reduced sulfur content) can then be introduced into the second

hydrodesulfurization stage, which also contains one or more reaction zones. This second hydrodesulfurization stage, like the first, can contain, in one or more of its reaction zones the mixed metal catalyst. If present, the other catalyst can be a conventional hydrodesulfurization catalyst. The product stream is passed to a second separation zone wherein a vapor phase and liquid phase product streams are produced. The resulting liquid phase product stream can then contain less than about 150 wppm sulfur, or less than about 100 wppm, or less than about 50 wppm sulfur, or less than about 25 wppm sulfur, or less than about 10 wppm sulfur. This twice hydrodesulfurized product stream can optionally be passed to a third reaction stage. In some aspects, the twice hydrodesulfurized liquid product stream can be reacted in the presence of hydrogen and a catalyst capable of further reducing the sulfur and nitrogen levels and hydrogenating aromatics. In such aspects, the sulfur level of the final product stream can be less than about 10 wppm, preferably less than about 5 wppm, and more preferably less than about 1 wppm sulfur. In such aspects, the third reaction stage can contain, in at least one reaction zone, a hydrogenation catalyst and optionally the mixed metal catalyst. In other aspects, the third reaction stage can include a dewaxing catalyst.

[0038] FIGS. 1 and 2 provide a comparison between a conventional hydrotreating configuration and a hydrotreating configuration suitable for increasing the amount of volume swell during processing of a distillate boiling range feed to form a distillate boiling range product. As noted above, examples of suitable feedstocks can include (but are not limited to) distillate boiling range feedstocks, gas oil (atmospheric and/or vacuum) boiling range feedstocks, or another type of feedstock having a T10 boiling point of at least about 350°F (177°C) and at least about 3000 wppm of sulfur prior to hydrotreatment.

[0039] In the conventional configuration shown in FIG. 1, a feed 105 is hydrotreated in multiple stages for removal of sulfur and/or nitrogen. For example, the feed 105 can be hydrotreated in two stages (and/or reactors) using hydrotreatment stage (and/or reactor) 110 and hydrotreatment stage (and/or reactor) 120. The effluent 115 from hydrotreatment stage 110 is cascaded into second hydrotreatment stage 120 without stripping or other intermediate separation. The second hydrotreatment stage generates a

hydrotreated effluent 122 that can include a distillate boiling range product with reduced heteroatom content.

[0040] FIG. 2 shows configuration where the effluent 115 can pass through a separation stage 225 after hydrotreatment stage 110 and prior to second hydrotreatment stage 120. One option is to use a gas-liquid separator or stripper as separation stage 225. In this option, contaminant gases 228 formed during hydrotreatment in first hydrotreatment stage 110, such as H_2S and NH_3 , as well as other light ends, can be removed from the effluent prior to second hydrotreatment stage 120.

[0041] The types of configurations exemplified by FIG. 2 can provide at least two types of benefits relative to a configuration similar to FIG. 1. For configurations where contaminant gases are removed prior to passing the hydrotreated effluent into the second hydrotreatment stage, the removal of contaminant gases allows for use of milder reaction conditions in the second hydrotreatment stage while achieving a similar level of contaminant removal and/or feed conversion. This can be due, for example, to the catalysts in the second hydrotreatment stage having a higher effective catalytic activity for desulfurization when catalyst suppressants or poisons (such as contaminant gases) are removed. Additionally, for a given level of reaction condition severity for desulfurization, the amount of aromatic saturation performed can be increased due to removal of contaminants that suppress aromatic saturation activity.

[0042] In various alternative aspects, a mixed metal catalyst formed from a suitable precursor can be used in one or more reactors of a convenient reaction system, such as the reaction system schematically represented in FIG. 1. A mixed metal catalyst formed from a suitable precursor can be suitable for hydroprocessing under sour conditions, such as for hydrotreating in reactor 110, hydrotreating in reactor 120, or in a combination thereof.

[0043] In this discussion, the severity of hydroprocessing performed on a feed can be characterized based on an amount of conversion of the feedstock. In various aspects, the reaction conditions in the reaction system can be selected to generate a desired level of conversion of a feed. Conversion of a feed is defined in terms of conversion of molecules that boil above a temperature threshold to molecules below that threshold.

The conversion temperature can be any convenient temperature. Unless otherwise specified, the conversion temperature in this discussion is a conversion temperature of 350°F (177°C).

[0044] The amount of conversion can correspond to the total conversion of molecules within any stage of the reaction system that is used to hydroprocess the lower boiling portion of the feed from the vacuum distillation unit. The amount of conversion desired for a suitable feedstock can depend on a variety of factors, such as the boiling range of the feedstock, the amount of heteroatom contaminants (such as sulfur and/or nitrogen) in the feedstock, and/or the nature of the desired lubricant products. Suitable amounts of conversion across all hydroprocessing stages can correspond to about 15 wt% or less conversion of 350°F+ (177°C+) portions of the feedstock to portions boiling below 350°F, such as about 10 wt% or less, or about 5 wt% or less, or about 3 wt% or less. It is noted that a conversion temperature of 350°F (177°C) is an indicator of preserving the distillate boiling range nature of compounds in a feed. Portions of a feed that are converted relative to a conversion temperature of 350°F (177°C) can tend to correspond to compounds that are more suitable for inclusion in a naphtha product as opposed to a distillate product. It is also noted that sulfur and/or nitrogen in a distillate boiling range feed can tend to be present primarily in heavier and/or higher boiling compounds within a feed. During hydrodesulfurization, these sulfur and/or nitrogen containing compounds may be altered when sulfur and/or nitrogen is removed, and this alteration may lower the boiling point. However, if the boiling point of the desulfurized (or denitrogenated) product compound is still greater than the conversion temperature, this is not considered “conversion” of the feed relative to the conversion temperature.

[0045] In this discussion, a stage can correspond to a single reactor or a plurality of reactors. Optionally, multiple parallel reactors can be used to perform one or more of the processes, or multiple parallel reactors can be used for all processes in a stage. Each stage and/or reactor can include one or more catalyst beds containing hydroprocessing catalyst. Note that a “bed” of catalyst in the discussion below can refer to a partial physical catalyst bed. For example, a catalyst bed within a reactor could be filled partially with a hydrocracking catalyst and partially with a dewaxing catalyst. For convenience in description, even though the two catalysts may be stacked together in a

single catalyst bed, the hydrocracking catalyst and dewaxing catalyst can each be referred to conceptually as separate catalyst beds.

Process Conditions – Hydrotreatment

[0046] In various aspects, hydrotreating of a feed can be performed by exposing the feed to a hydrotreating catalyst and/or a mixed metal catalyst formed from a suitable precursor in the presence of hydrogen. A hydrogen stream is, therefore, fed or injected into a vessel or reaction zone or hydroprocessing zone in which the hydroprocessing catalyst is located. Hydrogen, which is contained in a hydrogen-containing “treat gas,” is provided to the reaction zone. Treat gas, as referred to in this invention, can be either pure hydrogen or a hydrogen-containing gas, which is a gas stream containing hydrogen in an amount that is sufficient for the intended reaction(s), optionally including one or more other gasses (e.g., nitrogen and light hydrocarbons such as methane), and which will not adversely interfere with or affect either the reactions or the products. Impurities, such as H₂S and NH₃ are undesirable and would typically be removed from the treat gas before it is conducted to the reactor. The treat gas stream introduced into a reaction stage will preferably contain at least about 50 vol. % and more preferably at least about 75 vol. % hydrogen.

[0047] Hydrotreating conditions can include temperatures of about 200°C to about 450°C, or about 315°C to about 425°C; pressures of about 250 psig (1.8 MPag) to about 5000 psig (34.6 MPag) or about 300 psig (2.1 MPag) to about 3000 psig (20.8 MPag); liquid hourly space velocities (LHSV) of about 0.1 hr⁻¹ to about 10 hr⁻¹; and hydrogen treat rates of about 200 scf/B (35.6 m³/m³) to about 10,000 scf/B (1781 m³/m³), or about 500 (89 m³/m³) to about 10,000 scf/B (1781 m³/m³).

[0048] The catalysts used for hydrotreatment can include conventional hydroprocessing catalysts, such as those that comprise at least one Group VIII non-noble metal (Columns 8 – 10 of IUPAC periodic table), preferably Fe, Co, and/or Ni, such as Co and/or Ni; and at least one Group VIB metal (Column 6 of IUPAC periodic table), preferably Mo and/or W. Such hydroprocessing catalysts can optionally include transition metal sulfides. These metals or mixtures of metals are typically present as oxides or sulfides on refractory metal oxide supports. Suitable metal oxide supports

include low acidic oxides such as silica, alumina, titania, silica-titania, and titania-alumina. Suitable aluminas are porous aluminas such as gamma or eta having average pore sizes from 50 to 200 Å, or 75 to 150 Å; a surface area from 100 to 300 m²/g, or 150 to 250 m²/g; and a pore volume of from 0.25 to 1.0 cm³/g, or 0.35 to 0.8 cm³/g. The supports are preferably not promoted with a halogen such as fluorine as this generally increases the acidity of the support.

[0049] The at least one Group VIII non-noble metal, in oxide form, can typically be present in an amount ranging from about 1 wt% to about 40 wt%, preferably from about 4 wt% to about 15 wt%. The at least one Group VIB metal, in oxide form, can typically be present in an amount ranging from about 2 wt% to about 70 wt%, preferably for supported catalysts from about 6 wt% to about 40 wt% or from about 10 wt% to about 30 wt%. These weight percents are based on the total weight of the catalyst. Suitable metal catalysts include cobalt/molybdenum (1-10% Co as oxide, 10-40% Mo as oxide), nickel/molybdenum (1-10% Ni as oxide, 10-40% Co as oxide), or nickel/tungsten (1-10% Ni as oxide, 10-40% W as oxide) on alumina, silica, silica-alumina, or titania.

[0050] Alternatively, the hydrotreating catalyst can be a bulk metal catalyst, or a combination of stacked beds of supported and bulk metal catalyst. By bulk metal, it is meant that the catalysts are unsupported wherein the bulk catalyst particles comprise 30-100 wt. % of at least one Group VIII non-noble metal and at least one Group VIB metal, based on the total weight of the bulk catalyst particles, calculated as metal oxides and wherein the bulk catalyst particles have a surface area of at least 10 m²/g. It is furthermore preferred that the bulk metal hydrotreating catalysts used herein comprise about 50 to about 100 wt%, and even more preferably about 70 to about 100 wt%, of at least one Group VIII non-noble metal and at least one Group VIB metal, based on the total weight of the particles, calculated as metal oxides. The amount of Group VIB and Group VIII non-noble metals can easily be determined VIB TEM-EDX.

[0051] Bulk catalyst compositions comprising one Group VIII non-noble metal and two Group VIB metals are preferred. It has been found that in this case, the bulk catalyst particles are sintering-resistant. Thus the active surface area of the bulk catalyst particles is maintained during use. The molar ratio of Group VIB to Group VIII non-noble metals ranges generally from 10:1-1:10 and preferably from 3:1-1:3. In the case of a core-shell

structured particle, these ratios of course apply to the metals contained in the shell. If more than one Group VIB metal is contained in the bulk catalyst particles, the ratio of the different Group VIB metals is generally not critical. The same holds when more than one Group VIII non-noble metal is applied. In the case where molybdenum and tungsten are present as Group VIB metals, the molybdenum:tungsten ratio preferably lies in the range of 9:1-1:9. Preferably the Group VIII non-noble metal comprises nickel and/or cobalt. It is further preferred that the Group VIB metal comprises a combination of molybdenum and tungsten. Preferably, combinations of nickel/molybdenum/tungsten and cobalt/molybdenum/tungsten and nickel/cobalt/molybdenum/tungsten are used. These types of precipitates appear to be sinter-resistant. Thus, the active surface area of the precipitate is maintained during use. The metals are preferably present as oxidic compounds of the corresponding metals, or if the catalyst composition has been sulfided, sulfidic compounds of the corresponding metals.

[0052] It is also preferred that the bulk metal hydrotreating catalysts used herein have a surface area of at least 50 m²/g and more preferably of at least 100 m²/g. It is also desired that the pore size distribution of the bulk metal hydrotreating catalysts be approximately the same as the one of conventional hydrotreating catalysts. Bulk metal hydrotreating catalysts have a pore volume of 0.05-5 ml/g, or of 0.1-4 ml/g, or of 0.1-3 ml/g, or of 0.1-2 ml/g determined by nitrogen adsorption. Preferably, pores smaller than 1 nm are not present. The bulk metal hydrotreating catalysts can have a median diameter of at least 50 nm, or at least 100 nm. The bulk metal hydrotreating catalysts can have a median diameter of not more than 5000 µm, or not more than 3000 µm. In an embodiment, the median particle diameter lies in the range of 0.1-50 µm and most preferably in the range of 0.5-50 µm.

Process Conditions - Dewaxing

[0053] In some aspects, a dewaxing catalyst may also be included in a reaction system for dewaxing a hydrotreated effluent or liquid product. Typically, the dewaxing catalyst is located in a bed downstream from any hydrotreating catalyst stages and/or any hydrotreating catalyst present in a stage. This can allow the dewaxing to occur on molecules that have already been hydrotreated to remove a significant fraction of organic sulfur- and nitrogen-containing species. In some configurations, the effluent from a

reactor containing hydrotreating catalyst, optionally after a gas-liquid separation, can be fed into a separate stage or reactor containing the dewaxing catalyst.

[0054] Suitable dewaxing catalysts can include molecular sieves such as crystalline aluminosilicates (zeolites). In an embodiment, the molecular sieve can comprise, consist essentially of, or be ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-48, zeolite Beta, ZSM-57, or a combination thereof, for example ZSM-23 and/or ZSM-48, or ZSM-48 and/or zeolite Beta. Optionally but preferably, molecular sieves that are selective for dewaxing by isomerization as opposed to cracking can be used, such as ZSM-48, zeolite Beta, ZSM-23, or a combination thereof. Additionally or alternately, the molecular sieve can comprise, consist essentially of, or be a 10-member ring 1-D molecular sieve. Examples include EU-1, ZSM-35 (or ferrierite), ZSM-11, ZSM-57, NU-87, SAPO-11, ZSM-48, ZSM-23, and ZSM-22. Preferred materials are EU-2, EU-11, ZBM-30, ZSM-48, or ZSM-23. ZSM-48 is most preferred. Note that a zeolite having the ZSM-23 structure with a silica to alumina ratio of from about 20:1 to about 40:1 can sometimes be referred to as SSZ-32. Other molecular sieves that are isostructural with the above materials include Theta-1, NU-10, EU-13, KZ-1, and NU-23. Optionally but preferably, the dewaxing catalyst can include a binder for the molecular sieve, such as alumina, titania, silica, silica-alumina, zirconia, or a combination thereof, for example alumina and/or titania or silica and/or zirconia and/or titania.

[0055] Preferably, the dewaxing catalysts used in processes according to the invention are catalysts with a low ratio of silica to alumina. For example, for ZSM-48, the ratio of silica to alumina in the zeolite can be less than 200:1, or less than 110:1, or less than 100:1, or less than 90:1, or less than 80:1. In various embodiments, the ratio of silica to alumina can be from 30:1 to 200:1, 60:1 to 110:1, or 70:1 to 100:1.

[0056] In various embodiments, the catalysts according to the invention further include a metal hydrogenation component. The metal hydrogenation component is typically a Group VI and/or a Group VIII metal. Preferably, the metal hydrogenation component is a Group VIII noble metal. Preferably, the metal hydrogenation component is Pt, Pd, or a mixture thereof. In an alternative preferred embodiment, the metal hydrogenation component can be a combination of a non-noble Group VIII metal with a

Group VI metal. Suitable combinations can include Ni, Co, or Fe with Mo or W, preferably Ni with Mo or W.

[0057] The metal hydrogenation component may be added to the catalyst in any convenient manner. One technique for adding the metal hydrogenation component is by incipient wetness. For example, after combining a zeolite and a binder, the combined zeolite and binder can be extruded into catalyst particles. These catalyst particles can then be exposed to a solution containing a suitable metal precursor. Alternatively, metal can be added to the catalyst by ion exchange, where a metal precursor is added to a mixture of zeolite (or zeolite and binder) prior to extrusion.

[0058] The amount of metal in the catalyst can be at least 0.1 wt% based on catalyst, or at least 0.15 wt%, or at least 0.2 wt%, or at least 0.25 wt%, or at least 0.3 wt%, or at least 0.5 wt% based on catalyst. The amount of metal in the catalyst can be 20 wt% or less based on catalyst, or 10 wt% or less, or 5 wt% or less, or 2.5 wt% or less, or 1 wt% or less. For embodiments where the metal is Pt, Pd, another Group VIII noble metal, or a combination thereof, the amount of metal can be from 0.1 to 5 wt%, preferably from 0.1 to 2 wt%, or 0.25 to 1.8 wt%, or 0.4 to 1.5 wt%. For embodiments where the metal is a combination of a non-noble Group VIII metal with a Group VI metal, the combined amount of metal can be from 0.5 wt% to 20 wt%, or 1 wt% to 15 wt%, or 2.5 wt% to 10 wt%.

[0059] Dewaxing catalysts can also include a binder. In some embodiments, the dewaxing catalysts used in process according to the invention are formulated using a low surface area binder, a low surface area binder represents a binder with a surface area of 100 m²/g or less, or 80 m²/g or less, or 70 m²/g or less.

[0060] A zeolite can be combined with binder in any convenient manner. For example, a bound catalyst can be produced by starting with powders of both the zeolite and binder, combining and mulling the powders with added water to form a mixture, and then extruding the mixture to produce a bound catalyst of a desired size. Extrusion aids can also be used to modify the extrusion flow properties of the zeolite and binder mixture. The amount of framework alumina in the catalyst may range from 0.1 to 3.33 wt%, or 0.1 to 2.7 wt%, or 0.2 to 2 wt%, or 0.3 to 1 wt%.

[0061] In yet another embodiment, a binder composed of two or more metal oxides can also be used. In such an embodiment, the weight percentage of the low surface area binder is preferably greater than the weight percentage of the higher surface area binder. Alternatively, if both metal oxides used for forming a mixed metal oxide binder have a sufficiently low surface area, the proportions of each metal oxide in the binder are less important. When two or more metal oxides are used to form a binder, the two metal oxides can be incorporated into the catalyst by any convenient method. For example, one binder can be mixed with the zeolite during formation of the zeolite powder, such as during spray drying. The spray dried zeolite/binder powder can then be mixed with the second metal oxide binder prior to extrusion. In yet another embodiment, the dewaxing catalyst is self-bound and does not contain a binder.

[0062] A bound dewaxing catalyst can also be characterized by comparing the micropore (or zeolite) surface area of the catalyst with the total surface area of the catalyst. These surface areas can be calculated based on analysis of nitrogen porosimetry data using the BET method for surface area measurement. Previous work has shown that the amount of zeolite content versus binder content in catalyst can be determined from BET measurements (*see, e.g., Johnson, M.F.L., Jour. Catal., (1978) 52, 425*). The micropore surface area of a catalyst refers to the amount of catalyst surface area provided due to the molecular sieve and/or the pores in the catalyst in the BET measurements. The total surface area represents the micropore surface plus the external surface area of the bound catalyst. In one embodiment, the percentage of micropore surface area relative to the total surface area of a bound catalyst can be at least about 35%, for example at least about 38%, at least about 40%, or at least about 45%. Additionally or alternately, the percentage of micropore surface area relative to total surface area can be about 65% or less, for example about 60% or less, about 55% or less, or about 50% or less.

[0063] Additionally or alternately, the dewaxing catalyst can comprise, consist essentially of, or be a catalyst that has not been dealuminated. Further additionally or alternately, the binder for the catalyst can include a mixture of binder materials containing alumina.

[0064] Process conditions in a catalytic dewaxing zone can include a temperature of about 200°C to about 450°C, preferably about 270°C to about 400°C, a hydrogen partial pressure of about 1.8 MPag to about 34.6 MPag (250 psig to 5000 psig), preferably about 4.8 MPag to about 20.8 MPag, and a hydrogen treat gas rate of about 35.6 m³/m³ (200 SCF/B) to about 1781 m³/m³ (10,000 scf/B), preferably about 178 m³/m³ (1000 SCF/B) to about 890.6 m³/m³ (5000 SCF/B). In still other embodiments, the conditions can include temperatures in the range of about 600°F (343°C) to about 815°F (435°C), hydrogen partial pressures of from about 500 psig to about 3000 psig (3.5 MPag-20.9 MPag), and hydrogen treat gas rates of from about 213 m³/m³ to about 1068 m³/m³ (1200 SCF). The LHSV can be from about 0.1 h⁻¹ to about 10 h⁻¹, such as from about 0.5 h⁻¹ to about 5 h⁻¹ and/or from about 1 h⁻¹ to about 4 h⁻¹.

Process Conditions - Hydrofinishing and/or Aromatic Saturation Processes

[0065] In various aspects, a hydrofinishing stage, an aromatic saturation stage, or a hydrofinishing and an aromatic saturation stage may also be provided. The hydrofinishing and/or aromatic saturation stage(s) or reaction zones can occur after the last hydrotreating stage, and before and/or after any hydrocracking or dewaxing stages. The hydrofinishing and/or aromatic saturation can occur either before or after fractionation. If hydrofinishing and/or aromatic saturation occurs after fractionation, the hydrofinishing can be performed on one or more portions of the fractionated product, such as being performed on one or more lubricant base oil portions. Alternatively, the entire effluent from the last hydrocracking or dewaxing process can be hydrofinished and/or undergo aromatic saturation.

[0066] In some situations, a hydrofinishing process and an aromatic saturation process can refer to a single process performed using the same catalyst. Alternatively, one type of catalyst or catalyst system can be provided to perform aromatic saturation, while a second catalyst or catalyst system can be used for hydrofinishing. As still another alternative, aromatic saturation sometimes refers to a higher temperature range of processing than a hydrofinishing process. In such an alternative, a hydrofinishing process may be suitable for removing (for example) color bodies from a product, but otherwise result in a lower amount of aromatic saturation than an aromatic saturation process. Typically a hydrofinishing and/or aromatic saturation process will be performed

in a separate reactor from dewaxing or hydrocracking processes for practical reasons, such as facilitating use of a lower temperature for the hydrofinishing or aromatic saturation process.

[0067] Hydrofinishing and/or aromatic saturation catalysts can include catalysts containing Group VI metals, Group VIII metals, and mixtures thereof. In an embodiment, preferred metals include at least one metal sulfide having a strong hydrogenation function. In another embodiment, the hydrofinishing catalyst can include a Group VIII noble metal, such as Pt, Pd, or a combination thereof. The mixture of metals may also be present as bulk metal catalysts wherein the amount of metal is about 30 wt. % or greater based on catalyst. Suitable metal oxide supports include low acidic oxides such as silica, alumina, silica-aluminas or titania, preferably alumina. The preferred hydrofinishing catalysts for aromatic saturation can comprise at least one metal having relatively strong hydrogenation function on a porous support. The support materials may also be modified, such as by halogenation, or in particular fluorination. The metal content of the catalyst is often as high as about 20 weight percent for non-noble metals. In some optional aspects, hydrotreating catalysts as described above can be used as hydrofinishing catalysts. In other optional aspects, a preferred hydrofinishing catalyst can include a crystalline material belonging to the M41S class or family of catalysts. The M41S family of catalysts are mesoporous materials having high silica content. Examples include MCM-41, MCM-48 and MCM-50. A preferred member of this class is MCM-41. If separate catalysts are used for aromatic saturation and hydrofinishing, an aromatic saturation catalyst can be selected based on activity and/or selectivity for aromatic saturation, while a hydrofinishing catalyst can be selected based on activity for improving product specifications, such as product color and polynuclear aromatic reduction.

[0068] Hydrofinishing conditions can include temperatures from about 125°C to about 425°C, preferably about 180°C to about 280°C, total pressures from about 500 psig (3.4 MPa) to about 3000 psig (20.7 MPa), preferably about 1500 psig (10.3 MPa) to about 2500 psig (17.2 MPa), and liquid hourly space velocity from about 0.1 hr⁻¹ to about 5 hr⁻¹ LHSV, preferably about 0.5 hr⁻¹ to about 1.5 hr⁻¹.

[0069] In aspects where aromatic saturation is contemplated as a distinct process from hydrofinishing, aromatic saturation conditions can include temperatures from about 175°C to about 425°C, or about 200°C to about 425°C, preferably about 225°C to about 325°C, or about 225°C to about 280°C, total pressures from about 500 psig (3.4 MPa) to about 3000 psig (20.7 MPa), preferably about 1500 psig (10.3 MPa) to about 2500 psig (17.2 MPa), and liquid hourly space velocity from about 0.1 hr⁻¹ to about 5 hr⁻¹ LHSV, preferably about 0.5 hr⁻¹ to about 1.5 hr⁻¹.

Alternative Configurations - Hydrocracking Conditions

[0070] In some alternative configurations, the plurality of hydrotreating stages described above, including separation between the stages, can be used to prepare a feed for subsequent hydrocracking for further conversion of the feed. Hydrocracking catalysts typically contain sulfided base metals on acidic supports, such as amorphous silica alumina, cracking zeolites or other cracking molecular sieves such as USY, or acidified alumina. In some preferred aspects, a hydrocracking catalyst can include at least one molecular sieve, such as a zeolite. Often these acidic supports are mixed or bound with other metal oxides such as alumina, titania or silica. Non-limiting examples of supported catalytic metals for hydrocracking catalysts include nickel, nickel-cobalt-molybdenum, cobalt-molybdenum, nickel-tungsten, nickel-molybdenum, and/or nickel-molybdenum-tungsten. Additionally or alternately, hydrocracking catalysts with noble metals can also be used. Non-limiting examples of noble metal catalysts include those based on platinum and/or palladium. Support materials which may be used for both the noble and non-noble metal catalysts can comprise a refractory oxide material such as alumina, silica, alumina-silica, kieselguhr, diatomaceous earth, magnesia, zirconia, or combinations thereof, with alumina, silica, alumina-silica being the most common (and preferred, in one embodiment).

[0071] In some aspects, a hydrocracking catalyst can include a large pore molecular sieve that is selective for cracking of branched hydrocarbons and/or cyclic hydrocarbons. Zeolite Y, such as ultrastable zeolite Y (USY) is an example of a zeolite molecular sieve that is selective for cracking of branched hydrocarbons and cyclic hydrocarbons. Depending on the aspect, the silica to alumina ratio in a USY zeolite can be at least about 10, such as at least about 15, or at least about 25, or at least about 50, or at least about 100.

Depending on the aspect, the unit cell size for a USY zeolite can be about 24.50 Angstroms or less, such as about 24.45 Angstroms or less, or about 24.40 Angstroms or less, or about 24.35 Angstroms or less, such as about 24.30 Angstroms.

[0072] In various embodiments, the conditions selected for hydrocracking can depend on the desired level of conversion, the level of contaminants in the input feed to the hydrocracking stage, and potentially other factors. A hydrocracking process performed under sour conditions, such as conditions where the sulfur content of the input feed to the hydrocracking stage is at least 500 wppm, can be carried out at temperatures of about 550°F (288°C) to about 840°F (449°C), hydrogen partial pressures of from about 250 psig to about 5000 psig (1.8 MPag to 34.6 MPag), liquid hourly space velocities of from 0.05 h⁻¹ to 10 h⁻¹, and hydrogen treat gas rates of from 35.6 m³/m³ to 1781 m³/m³ (200 SCF/B to 10,000 SCF/B). In other embodiments, the conditions can include temperatures in the range of about 600°F (343°C) to about 815°F (435°C), hydrogen partial pressures of from about 500 psig to about 3000 psig (3.5 MPag-20.9 MPag), liquid hourly space velocities of from about 0.2 h⁻¹ to about 2 h⁻¹ and hydrogen treat gas rates of from about 213 m³/m³ to about 1068 m³/m³ (1200 SCF/B to 6000 SCF/B).

[0073] A hydrocracking process performed under non-sour conditions can be performed under conditions similar to those used for sour conditions, or the conditions can be different. Alternatively, a non-sour hydrocracking stage can have less severe conditions than a similar hydrocracking stage operating under sour conditions. Suitable hydrocracking conditions can include temperatures of about 550°F (288°C) to about 840°F (449°C), hydrogen partial pressures of from about 250 psig to about 5000 psig (1.8 MPag to 34.6 MPag), liquid hourly space velocities of from 0.05 h⁻¹ to 10 h⁻¹, and hydrogen treat gas rates of from 35.6 m³/m³ to 1781 m³/m³ (200 SCF/B to 10,000 SCF/B). In other embodiments, the conditions can include temperatures in the range of about 600°F (343°C) to about 815°F (435°C), hydrogen partial pressures of from about 500 psig to about 3000 psig (3.5 MPag-20.9 MPag), liquid hourly space velocities of from about 0.2 h⁻¹ to about 2 h⁻¹ and hydrogen treat gas rates of from about 213 m³/m³ to about 1068 m³/m³ (1200 SCF/B to 6000 SCF/B).

[0074] After such a hydrocracking process, a suitable feed can undergo further additional processing, such as dewaxing and/or hydrofinishing and/or aromatic saturation. This type of process can be suitable for formation of both distillate fuel and lubricant base oil products with increased yield.

Multimetallic Catalyst and Forming Multimetallic Catalyst from a Precursor

[0075] As used herein, the term "bulk", when describing a mixed metal oxide catalyst composition, indicates that the catalyst composition is self-supporting in that it does not require a carrier or support. It is well understood that bulk catalysts may have some minor amount of carrier or support material in their compositions (e.g., about 20 wt % or less, about 15 wt % or less, about 10 wt % or less, about 5 wt % or less, or substantially no carrier or support, based on the total weight of the catalyst composition); for instance, bulk hydroprocessing catalysts may contain a minor amount of a binder, e.g., to improve the physical and/or thermal properties of the catalyst. In contrast, heterogeneous or supported catalyst systems typically comprise a carrier or support onto which one or more catalytically active materials are deposited, often using an impregnation or coating technique. Nevertheless, heterogeneous catalyst systems without a carrier or support (or with a minor amount of carrier or support) are generally referred to as bulk catalysts and are frequently formed by co-precipitation or solid-solid reactions in slurries.

[0076] In some aspects, the methods described herein can include use of a catalyst formed from a catalyst precursor composition comprising at least one metal from Group 6 of the Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, and a reaction product formed from (i) a first organic compound containing at least one amine group and at least 10 carbons or (ii) a second organic compound containing at least one carboxylic acid group and at least 10 carbons, but not both (i) and (ii), wherein the reaction product contains additional unsaturated carbon atoms, relative to (i) the first organic compound or (ii) the second organic compound, wherein the metals of the catalyst precursor composition are arranged in a crystal lattice, and wherein the reaction product is not located within the crystal lattice. This catalyst precursor composition can be a bulk metal catalyst precursor composition or a supported metal catalyst precursor composition. When it is a bulk mixed metal

catalyst precursor composition, the reaction product can be obtained by heating the composition (though specifically the amine-containing compound or the carboxylic acid-containing compound) to a temperature from about 195°C to about 260°C for a time sufficient for the first or second organic compounds to react to form additional in situ unsaturated carbon atoms and/or become more oxidized than the first or second organic compounds, but not for so long that more than 50% by weight of the first or second organic compound is volatilized, thereby forming a catalyst precursor composition that contains in situ formed unsaturated carbon atoms and/or that is further oxidized.

[0077] Other aspects can relate to using a catalyst formed from a catalyst precursor composition containing in situ formed unsaturated carbon atoms. The catalyst can be formed from the precursor by a process comprising: (a) treating a catalyst precursor composition comprising at least one metal from Group 6 of the Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, with a first organic compound containing at least one amine group and at least 10 carbon atoms or a second organic compound containing at least one carboxylic acid group and at least 10 carbon atoms, to form an organically treated precursor catalyst composition; and (b) heating said organically treated precursor catalyst composition at a temperature from about 195°C to about 260°C for a time sufficient for the first or second organic compounds to react to form additional in situ unsaturated carbon atoms and/or become more oxidized, but not for so long that more than 50% by weight of the first or second organic compound is volatilized, thereby forming a catalyst precursor composition that contains in situ formed unsaturated carbon atoms and/or that is further oxidized. This process can be used to make a bulk metal catalyst precursor composition or a supported metal catalyst precursor composition. When used to make a bulk mixed metal catalyst precursor composition, the catalyst precursor composition containing in situ formed unsaturated carbon atoms can, in one embodiment, consist essentially of the reaction product, an oxide form of the at least one metal from Group 6, an oxide form of the at least one metal from Groups 8-10, and optionally about 20 wt % or less of a binder.

[0078] As an example, when the catalyst precursor is a bulk mixed metal catalyst precursor composition, the reaction product can be obtained by heating the composition (though specifically the first or second organic compounds, or the amine-containing or

carboxylic acid-containing compound) to a temperature from about 195°C to about 260°C for a time sufficient to effectuate a dehydrogenation, and/or an at least partial decomposition, of the first or second organic compound to form an additional unsaturation and/or additional oxidation in the reaction product in situ. Accordingly, a bulk mixed metal hydroprocessing catalyst composition can be produced from this bulk mixed metal catalyst precursor composition by sulfiding it under sufficient sulfiding conditions, which sulfiding should begin in the presence of the in situ additionally unsaturated reaction product (which may result from at least partial decomposition, e.g., via oxidative dehydrogenation in the presence of oxygen and/or via non-oxidative dehydrogenation in the absence of an appropriate concentration of oxygen, of typically-unfunctionalized organic portions of the first or second organic compounds, e.g., of an aliphatic portion of an organic compound and/or through conjugation/aromatization of unsaturations expanding upon an unsaturated portion of an organic compound).

[0079] In still other aspects, a feed can be processed in a reaction system that includes a catalyst formed from a catalyst precursor composition comprising at least one metal from Group 6 of the Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, and a reaction product formed from (i) a first organic compound containing at least one amine group, and (ii) a second organic compound separate from said first organic compound and containing at least one carboxylic acid group. When this reaction product is an amide, the presence of the reaction product in any intermediate or final composition can be determined by methods well known in the art, e.g., by infrared spectroscopy (FTIR) techniques. When this reaction product contains additional unsaturation(s) not present in the first and second organic compounds, e.g., from at least partial decomposition/dehydrogenation at conditions including elevated temperatures, the presence of the additional unsaturation(s) in any intermediate or final composition can be determined by methods well known in the art, e.g., by FTIR and/or nuclear magnetic resonance (^{13}C NMR) techniques. This catalyst precursor composition can be a bulk metal catalyst precursor composition or a heterogeneous (supported) metal catalyst precursor composition.

[0080] More broadly, this type of aspect relates to use of a catalyst formed from a catalyst precursor composition comprising at least one metal from Group 6 of the

Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, and a condensation reaction product formed from (i) a first organic compound containing at least one first functional group, and (ii) a second organic compound separate from said first organic compound and containing at least one second functional group, wherein said first functional group and said second functional group are capable of undergoing a condensation reaction and/or a (decomposition) reaction causing an additional unsaturation to form an associated product. Though the description above and herein often refers specifically to the condensation reaction product being an amide, it should be understood that any in situ condensation reaction product formed can be substituted for the amide described herein. For example, if the first functional group is a hydroxyl group and the second functional group is a carboxylic acid or an acid chloride or an organic ester capable of undergoing transesterification with the hydroxyl group, then the in situ condensation reaction product formed would be an ester.

[0081] As an example, when the catalyst precursor is a bulk mixed metal catalyst precursor composition, the reaction product can be obtained by heating the composition (such as the condensation reactants, or the amine-containing compound and/or the carboxylic acid-containing compound) to a temperature from about 195°C to about 260°C for a time sufficient for the first and second organic compounds to form a condensation product, such as an amide, and/or an additional (decomposition) unsaturation in situ. Accordingly, a bulk mixed metal hydroprocessing catalyst composition can be produced from this bulk mixed metal catalyst precursor composition by sulfiding it under sufficient sulfiding conditions, which sulfiding should begin in the presence of the in situ product, e.g., the amide (i.e., when present, the condensation product moiety, or amide, can be substantially present and/or can preferably not be significantly decomposed by the beginning of the sulfiding step), and/or containing additional unsaturations (which may result from at least partial decomposition, e.g., via oxidative dehydrogenation in the presence of oxygen and/or via non-oxidative dehydrogenation in the absence of an appropriate concentration of oxygen, of typically-unfunctionalized organic portions of the first and/or second organic compounds, e.g., of an aliphatic portion of an organic compound and/or through conjugation/aromatization of unsaturations expanding upon an unsaturated portion of an organic compound or

stemming from an interaction of the first and second organic compounds at a site other than their respective functional groups).

[0082] In yet other aspects, a feed can be processed using a catalyst formed from a catalyst precursor composition containing an ex-situ formed reaction product. The catalyst can be formed from the precursor by a process comprising: (a) treating a catalyst precursor composition comprising at least one metal from Group 6 of the Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, with an amide-containing reaction product formed from a first organic compound containing at least one amine group and at least 10 carbon atoms or a second organic compound containing at least one carboxylic acid group and at least 10 carbon atoms, to form an organically treated precursor catalyst composition; and (b) heating said organically treated precursor catalyst composition at a temperature from about 195°C to about 260°C for a time sufficient for the amide-containing reaction product to form additional in situ unsaturated carbon atoms and/or become more oxidized, but not for so long that more than 50% by weight of the first or second organic compound is volatilized, thereby forming a catalyst precursor composition that contains in situ formed unsaturated carbon atoms and/or that is further oxidized. This process can be used to make a bulk metal catalyst precursor composition or a supported metal catalyst precursor composition. When used to make a bulk mixed metal catalyst precursor composition, the catalyst precursor composition can, in one embodiment, consist essentially of the reaction product containing further unsaturated carbon atoms and/or further oxidation, an oxide form of the at least one metal from Group 6, an oxide form of the at least one metal from Groups 8-10, and optionally about 20 wt % or less of a binder.

[0083] When the catalyst precursor is a bulk mixed metal catalyst precursor composition, the thermal treatment of the amide-impregnated metal oxide component is carried out by heating the impregnated composition to a temperature and for a time which does not result in gross decomposition of the amide, although additional unsaturation may arise from partial *in situ* decomposition; the temperature is typically from about 195°C to about 250°C (or optionally about 195°C to about 260°C), but higher temperatures, e.g. in the range of 250 to 280°C, can be used in order to abbreviate the duration of the heating although due care is required to avoid the gross decomposition of

the pre-formed amide, as discussed further below. The bulk mixed metal hydroprocessing catalyst can be produced from this precursor by sulfiding it with the sulfiding taking place with the amide present on the metal oxide component (*i.e.*, when the thermally treated amide, is substantially present and/or preferably not significantly decomposed by the beginning of the sulfiding step). Additional unsaturation may be present in the organic component of the catalyst precursor resulting from a variety of mechanisms including partial decomposition, (*e.g.*, via oxidative dehydrogenation in the presence of oxygen and/or via non-oxidative dehydrogenation in the absence of an appropriate concentration of oxygen), of typically-unfunctionalized organic portions of the amide and/or through conjugation/aromatization of unsaturations expanding upon an unsaturated portion the amide. The treated organic component may also contain additional oxygen in addition to the unsaturation when the treatment is carried out in an oxidizing atmosphere.

[0084] Catalyst precursor compositions and hydroprocessing catalyst compositions useful in various aspects of the present invention can advantageously comprise (or can have metal components that consist essentially of) at least one metal from Group 6 of the Periodic Table of Elements and at least one metal from Groups 8-10 of the Periodic Table of Elements, and optionally at least one metal from Group 5 of the Periodic Table of Elements. Generally, these metals are present in their substantially fully oxidized form, which can typically take the form of simple metal oxides, but which may be present in a variety of other oxide forms, *e.g.*, such as hydroxides, oxyhydroxides, oxycarbonates, carbonates, oxynitrates, oxysulfates, or the like, or some combination thereof. In one preferred embodiment, the Group 6 metal(s) can be Mo and/or W, and the Group 8-10 metal(s) can be Co and/or Ni. Generally, the atomic ratio of the Group 6 metal(s) to the metal(s) of Groups 8-10 can be from about 2:1 to about 1:3, for example from about 5:4 to about 1:2, from about 5:4 to about 2:3, from about 5:4 to about 3:4, from about 10:9 to about 1:2, from about 10:9 to about 2:3, from about 10:9 to about 3:4, from about 20:19 to about 2:3, or from about 20:19 to about 3:4. When the composition further comprises at least one metal from Group 5, that at least one metal can be V and/or Nb. When present, the amount of Group 5 metal(s) can be such that the atomic ratio of the Group 6 metal(s) to the Group 5 metal(s) can be from about 99:1 to about 1:1, for example from about 99:1 to about 5:1, from about 99:1 to about 10:1, or from

about 99:1 to about 20:1. Additionally or alternately, when Group 5 metal(s) is(are) present, the atomic ratio of the sum of the Group 5 metal(s) plus the Group (6) metal(s) compared to the metal(s) of Groups 8-10 can be from about 2:1 to about 1:3, for example from about 5:4 to about 1:2, from about 5:4 to about 2:3, from about 5:4 to about 3:4, from about 10:9 to about 1:2, from about 10:9 to about 2:3, from about 10:9 to about 3:4, from about 20:19 to about 2:3, or from about 20:19 to about 3:4.

[0085] The metals in the catalyst precursor compositions and in the hydroprocessing catalyst compositions according to the invention can be present in any suitable form prior to sulfiding, but can often be provided as metal oxides. When provided as bulk mixed metal oxides, such bulk oxide components of the catalyst precursor compositions and of the hydroprocessing catalyst compositions according to the invention can be prepared by any suitable method known in the art, but can generally be produced by forming a slurry, typically an aqueous slurry, comprising (1) (a) an oxyanion of the Group 6 metal(s), such as a tungstate and/or a molybdate, or (b) an insoluble (oxide, acid) form of the Group 6 metal(s), such as tungstic acid and/or molybdenum trioxide, (2) a salt of the Group 8-10 metal(s), such as nickel carbonate, and optionally, when present, (3) (a) a salt or oxyanion of a Group 5 metal, such as a vanadate and/or a niobate, or (b) insoluble (oxide, acid) form of a Group 5 metal, such as niobic acid and/or diniobium pentoxide. The slurry can be heated to a suitable temperature, such as from about 60°C to about 150°C, at a suitable pressure, e.g., at atmospheric or autogenous pressure, for an appropriate time, e.g., about 4 hours to about 24 hours.

[0086] Non-limiting examples of suitable mixed metal oxide compositions can include, but are not limited to, nickel-tungsten oxides, cobalt-tungsten oxides, nickel-molybdenum oxides, cobalt-molybdenum oxides, nickel-molybdenum-tungsten oxides, cobalt-molybdenum-tungsten oxides, cobalt-nickel-tungsten oxides, cobalt-nickel-molybdenum oxides, cobalt-nickel-tungsten-molybdenum oxides, nickel-tungsten-niobium oxides, nickel-tungsten-vanadium oxides, cobalt-tungsten-vanadium oxides, cobalt-tungsten-niobium oxides, nickel-molybdenum-niobium oxides, nickel-molybdenum-vanadium oxides, nickel-molybdenum-tungsten-niobium oxides, nickel-molybdenum-tungsten-vanadium oxides, and the like, and combinations thereof.

[0087] Suitable mixed metal oxide compositions can advantageously exhibit a specific surface area (as measured via the nitrogen BET method using a Quantachrome Autosorb.TM. apparatus) of at least about 20 m²/g, for example at least about 30 m²/g, at least about 40 m²/g, at least about 50 m²/g, at least about 60 m²/g, at least about 70 m²/g, or at least about 80 m²/g. Additionally or alternately, the mixed metal oxide compositions can exhibit a specific surface area of not more than about 500 m²/g, for example not more than about 400 m²/g, not more than about 300 m²/g, not more than about 250 m²/g, not more than about 200 m²/g, not more than about 175 m²/g, not more than about 150 m²/g, not more than about 125 m²/g, or not more than about 100 m²/g.

[0088] In some aspects, after separating and drying the mixed metal oxide (slurry) composition, it can be treated, generally by impregnation, with (i) an effective amount of a first organic compound containing at least one amine group or (ii) an effective amount of a second organic compound separate from the first organic compound and containing at least one carboxylic acid group, but not both (i) and (ii).

[0089] In other aspects, after separating and drying the mixed metal oxide (slurry) composition, it can be treated, generally by impregnation, with (i) an effective amount of a first organic compound containing at least one amine group, and (ii) an effective amount of a second organic compound separate from the first organic compound and containing at least one carboxylic acid group.

[0090] In still other aspects, after separating and drying the mixed metal oxide (slurry) composition, it can be treated, generally by impregnation, with the pre-formed amide derived from (i) an effective amount of a first organic compound containing at least one amine group, and (ii) an effective amount of a second organic compound separate from the first organic compound and containing at least one carboxylic acid group. The amide is formed by a condensation reaction between the amine reactant and the carboxylic acid reactant; this reaction, carried out ex situ, is usually accomplished at mildly elevated temperatures.

[0091] In aspects where either a first or second organic compound is used, the first organic compound can comprise at least 10 carbon atoms, for example can comprise from 10 to 20 carbon atoms or can comprise a primary monoamine having from 10 to 30

carbon atoms. Additionally or alternately, the second organic compound can comprise at least 10 carbon atoms, for example can comprise from 10 to 20 carbon atoms or can comprise only one carboxylic acid group and can have from 10 to 30 carbon atoms.

[0092] In other aspects where both a first and second organic compound are used (including aspects where a first and second organic compound are reacted ex situ to form an amide), the first organic compound can comprise at least 10 carbon atoms, for example can comprise from 10 to 20 carbon atoms or can comprise a primary monoamine having from 10 to 30 carbon atoms. Additionally or alternately, the second organic compound can comprise at least 10 carbon atoms, for example can comprise from 10 to 20 carbon atoms or can comprise only one carboxylic acid group and can have from 10 to 30 carbon atoms. Further additionally or alternately, the total number of carbon atoms comprised among both the first and second organic compounds can be at least 15 carbon atoms, for example at least 20 carbon atoms, at least 25 carbon atoms, at least 30 carbon atoms, or at least 35 carbon atoms. Although in such embodiments there may be no practical upper limit on total carbon atoms from both organic compounds, in some embodiments, the total number of carbon atoms comprised among both the first and second organic compounds can be 100 carbon atoms or less, for example 80 carbon atoms or less, 70 carbon atoms or less, 60 carbon atoms or less, or 50 carbon atoms or less.

[0093] Representative examples of organic compounds containing amine groups can include, but are not limited to, primary and/or secondary, linear, branched, and/or cyclic amines, such as triacontaniline, octacosaniline, hexacosaniline, tetracosaniline, docosaniline, erucylamine, eicosaniline, octadecylamine, oleylamine, linoleylamine, hexadecylamine, sapienylamine, palmitoleylamine, tetradecylamine, myristoleylamine, dodecylamine, decylamine, nonylamine, cyclooctylamine, octylamine, cycloheptylamine, heptylamine, cyclohexylamine, n-hexylamine, isopentylamine, n-pentylamine, t-butylamine, n-butylamine, isopropylamine, n-propylamine, adamantanamine, adamantanemethylamine, pyrrolidine, piperidine, piperazine, imidazole, pyrazole, pyrrole, pyrrolidine, pyrroline, indazole, indole, carbazole, norbornylamine, aniline, pyridylamine, benzylamine, aminotoluene, alanine, arginine, aspartic acid, glutamic acid, glutamine, glycine, histidine, isoleucine,

leucine, lysine, phenylalanine, serine, threonine, valine, 1-amino-2-propanol, 2-amino-1-propanol, diaminoeicosane, diaminooctadecane, diaminohexadecane, diaminotetradecane, diaminododecane, diaminodecane, 1,2-diaminocyclohexane, 1,3-diaminocyclohexane, 1,4-diaminocyclohexane, ethylenediamine, ethanolamine, p-phenylenediamine, o-phenylenediamine, m-phenylenediamine, 1,2-propylenediamine, 1,3-propylenediamine, 1,4-diaminobutane, 1,3diamino-2-propanol, and the like, and combinations thereof. In an embodiment, the molar ratio of the Group 6 metal(s) in the composition to the first organic compound during treatment can be from about 1:1 to about 20:1.

[0094] Additionally or alternately, in some aspects the amine portion of the first organic compound can be a part of a larger functional group in that compound, so long as the amine portion (notably the amine nitrogen and the constituents attached thereto) retains its operability as a Lewis base. For instance, the first organic compound can comprise a urea, which functional group comprises an amine portion attached to the carbonyl portion of an amide group. In such an instance, the urea can be considered functionally as an "amine-containing" functional group for the purposes of the present invention herein, except in situations where such inclusion is specifically contradicted. Aside from ureas, other examples of such amine-containing functional groups that may be suitable for satisfying the at least one amine group in the first organic compound can generally include, but are not limited to, hydrazides, sulfonamides, and the like, and combinations thereof.

[0095] The amine functional group from the first organic compound can include primary or secondary amines, as mentioned above, but generally does not include quaternary amines, and in some instances does not include tertiary amines either. Furthermore, the first organic compound can optionally contain other functional groups besides amines. For instance, the first organic compound can comprise an aminoacid, which possesses an amine functional group and a carboxylic acid functional group simultaneously. Aside from carboxylic acids, other examples of such secondary functional groups in amine-containing organic compounds can generally include, but are not limited to, hydroxyls, aldehydes, anhydrides, ethers, esters, imines, imides, ketones, thiols (mercaptans), thioesters, and the like, and combinations thereof.

[0096] Additionally or alternately, in other aspects involving formation of a condensation product (including aspects involving ex situ formation of an amide), the amine functional group from the first organic compound can include primary or secondary amines, as mentioned above, but generally does not include tertiary or quaternary amines, as tertiary and quaternary amines tend not to be able to form amides. Furthermore, the first organic compound can contain other functional groups besides amines, whether or not they are capable of participating in forming an amide or other condensation reaction product with one or more of the functional groups from second organic compound. For instance, the first organic compound can comprise an aminoacid, which possesses an amine functional group and a carboxylic acid functional group simultaneously. In such an instance, the aminoacid would qualify as only one of the organic compounds, and not both; thus, in such an instance, either an additional amine-containing (first) organic compound would need to be present (in the circumstance where the aminoacid would be considered the second organic compound) or an additional carboxylic acid-containing (second) organic compound would need to be present (in the circumstance where the aminoacid would be considered the first organic compound). Aside from carboxylic acids, other examples of such secondary functional groups in amine-containing organic compounds can generally include, but are not limited to, hydroxyls, aldehydes, anhydrides, ethers, esters, imines, imides, ketones, thiols (mercaptans), thioesters, and the like, and combinations thereof.

[0097] Additionally or alternately, the amine portion of the first organic compound can be a part of a larger functional group in that compound, so long as the amine portion (notably the amine nitrogen and the constituents attached thereto) retains the capability of participating in forming an amide or other condensation reaction product with one or more of the functional groups from second organic compound. For instance, the first organic compound can comprise a urea, which functional group comprises an amine portion attached to the carbonyl portion of an amide group. In such an instance, provided the amine portion of the urea functional group of the first organic compound would still be able to undergo a condensation reaction with the carboxylic acid functional group of the second organic compound, then the urea can be considered functionally as an "amine-containing" functional group for the purposes of the present invention herein, except in situations where such inclusion is specifically contradicted. Aside from ureas,

other examples of such amine-containing functional groups that may be suitable for satisfying the at least one amine group in the first organic compound can generally include, but are not limited to, hydrazides, sulfonamides, and the like, and combinations thereof.

[0098] Representative examples of organic compounds containing carboxylic acids can include, but are not limited to, primary and/or secondary, linear, branched, and/or cyclic amines, such as triacontanoic acid, octacosanoic acid, hexacosanoic acid, tetracosanoic acid, docosanoic acid, erucic acid, docosahexanoic acid, eicosanoic acid, eicosapentanoic acid, arachidonic acid, octadecanoic acid, oleic acid, elaidic acid, stearidonic acid, linoleic acid, alpha-linolenic acid, hexadecanoic acid, sapienic acid, palmitoleic acid, tetradecanoic acid, myristoleic acid, dodecanoic acid, decanoic acid, nonanoic acid, cyclooctanoic acid, octanoic acid, cycloheptanoic acid, heptanoic acid, cyclohexanoic acid, hexanoic acid, adamantanecarboxylic acid, norbornaneacetic acid, benzoic acid, salicylic acid, acetylsalicylic acid, citric acid, maleic acid, malonic acid, glutaric acid, lactic acid, oxalic acid, tartaric acid, cinnamic acid, vanillic acid, succinic acid, adipic acid, phthalic acid, isophthalic acid, terephthalic acid, ethylenediaminetetracarboxylic acids (such as EDTA), fumaric acid, alanine, arginine, aspartic acid, glutamic acid, glutamine, glycine, histidine, isoleucine, leucine, lysine, phenylalanine, serine, threonine, valine, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, and the like, and combinations thereof. In an embodiment, the molar ratio of the Group 6 metal(s) in the composition to the second organic compound during treatment can be from about 3:1 to about 20:1.

[0099] In some aspects, the second organic compound can optionally contain other functional groups besides carboxylic acids. For instance, the second organic compound can comprise an aminoacid, which possesses a carboxylic acid functional group and an amine functional group simultaneously. Aside from amines, other examples of such secondary functional groups in carboxylic acid-containing organic compounds can generally include, but are not limited to, hydroxyls, aldehydes, anhydrides, ethers, esters, imines, imides, ketones, thiols (mercaptans), thioesters, and the like, and combinations

thereof. In some embodiments, the second organic compound can contain no additional amine or alcohol functional groups in addition to the carboxylic acid functional group(s).

[00100] Additionally or alternately, the reactive portion of the second organic compound can be a part of a larger functional group in that compound and/or can be a derivative of a carboxylic acid that behaves similarly enough to a carboxylic acid, such that the reactive portion and/or derivative retains its operability as a Lewis acid. One example of a carboxylic acid derivative can include an alkyl carboxylate ester, where the alkyl group does not substantially hinder (over a reasonable time scale) the Lewis acid functionality of the carboxylate portion of the functional group.

[00101] In other aspects involving formation of a condensation product (including aspects involving *ex situ* formation of an amide), the second organic compound can contain other functional groups besides carboxylic acids, whether or not they are capable of participating in forming an amide or other condensation reaction product with one or more of the functional groups from first organic compound. For instance, the second organic compound can comprise an aminoacid, which possesses a carboxylic acid functional group and an amine functional group simultaneously. In such an instance, the aminoacid would qualify as only one of the organic compounds, and not both; thus, in such an instance, either an additional amine-containing (first) organic compound would need to be present (in the circumstance where the aminoacid would be considered the second organic compound) or an additional carboxylic acid-containing (second) organic compound would need to be present (in the circumstance where the aminoacid would be considered the first organic compound). Aside from amines, other examples of such secondary functional groups in carboxylic acid-containing organic compounds can generally include, but are not limited to, hydroxyls, aldehydes, anhydrides, ethers, esters, imines, imides, ketones, thiols (mercaptans), thioesters, and the like, and combinations thereof.

[00102] Additionally or alternately, the reactive portion of the second organic compound can be a part of a larger functional group in that compound and/or can be a derivative of a carboxylic acid that behaves similarly enough to a carboxylic acid in the presence of the amine functional group of the first organic compound, such that the reactive portion and/or derivative retains the capability of participating in forming an

amide or other desired condensation reaction product with one or more of the functional groups from first organic compound. One example of a carboxylic acid derivative can include an alkyl carboxylate ester, where the alkyl group does not substantially hinder (over a reasonable time scale) the condensation reaction between the amine and the carboxylate portion of the ester to form an amide.

[00103] For aspects involving formation of a condensation product (including aspects involving ex situ formation of an amide), while there is not a strict limit on the ratio between the first organic compound and the second organic compound, because the goal of the addition of the first and second organic compounds is to attain a condensation reaction product, it may be desirable to have a ratio of the reactive functional groups within the first and second organic compounds, respectively, from about 1:4 to about 4:1, for example from about 1:3 to about 3:1 or from about 1:2 to about 2:1.

[00104] In certain aspects, the organic compound(s)/additive(s) and/or the reaction product(s) are not located/incorporated within the crystal lattice of the mixed metal oxide precursor composition, e.g., instead being located on the surface and/or within the pore volume of the precursor composition and/or being associated with (bound to) one or more metals or oxides of metals in a manner that does not significantly affect the crystalline lattice of the mixed metal oxide precursor composition, as observed through XRD and/or other crystallographic spectra. It is noted that, in these certain embodiments, a sulfided version of the mixed metal oxide precursor composition can still have its sulfided form affected by the organic compound(s)/additive(s) and/or the reaction product(s), even though the oxide lattice is not significantly affected.

[00105] In some aspects, one way to attain a catalyst precursor composition containing a decomposition/dehydrogenation reaction product, such as one containing additional unsaturations, includes: (a) treating a catalyst precursor composition, which comprises at least one metal from Group 6 of the Periodic Table of the Elements and at least one metal from Groups 8-10 of the Periodic Table of the Elements, with a first organic compound containing at least one amine group or a second organic compound separate from said first organic compound and containing at least one carboxylic acid group, but not both, to form an organically treated precursor catalyst composition; and (b) heating the organically treated precursor catalyst composition at a temperature

sufficient and for a time sufficient for the first or second organic compounds to react to form an in situ product containing additional unsaturation (for example, depending upon the nature of the first or second organic compound, the temperature can be from about 195°C to about 260°C, such as from about 200°C to about 250°C), thereby forming the additionally-unsaturated and/or additionally oxidized catalyst precursor composition.

[00106] In certain advantageous embodiments, the heating step (b) above can be conducted for a sufficiently long time so as to form additional unsaturation(s), which may result from at least partial decomposition (e.g., oxidative and/or non-oxidative dehydrogenation and/or aromatization) of some (typically-unfunctionalized organic) portions of the first or second organic compounds, but generally not for so long that the at least partial decomposition volatilizes more than 50% by weight of the first or second organic compounds. Without being bound by theory, it is believed that additional unsaturation(s) formed in situ and present at the point of sulfiding the catalyst precursor composition to form a sulfided (hydroprocessing) catalyst composition can somehow assist in controlling one or more of the following: the size of sulfided crystallites; the coordination of one or more of the metals during sulfidation, such that a higher proportion of the one or more types of metals are in appropriate sites for promoting desired hydroprocessing reactions (such as hydrotreating, hydrodenitrogenation, hydrodesulfurization, hydrodeoxygenation, hydrodemetallation, hydrocracking including selective hydrocracking, hydroisomerization, hydrodewaxing, and the like, and combinations thereof, and/or for reducing/minimizing undesired hydroprocessing reactions, such as aromatic saturation, hydrogenation of double bonds, and the like, and combinations thereof) than for sulfided catalysts made in the absence of the in situ formed reaction product having additional unsaturation(s); and coordination/catalysis involving one or more of the metals after sulfidation, such that a higher proportion (or each) of the one or more types of metals are more efficient at promoting desired hydroprocessing reactions (e.g., because the higher proportion of metal sites can catalyze more hydrodesulfurization reactions of the same type in a given timescale and/or because the higher proportion of the metal sites can catalyze more difficult hydrodesulfurization reactions in a similar timescale) than for sulfided catalysts made in the absence of the in situ formed reaction product having additional unsaturation(s).

[00107] In other aspects, one way to attain a catalyst precursor composition containing a condensation reaction product, such as an amide, and/or a reaction product containing additional unsaturations includes: (a) treating a catalyst precursor composition, which comprises at least one metal from Group 6 of the Periodic Table of the Elements and at least one metal from Groups 8-10 of the Periodic Table of the Elements, with a first organic compound containing at least one amine group and a second organic compound separate from said first organic compound and containing at least one carboxylic acid group to form an organically treated precursor catalyst composition; and (b) heating the organically treated precursor catalyst composition at a temperature sufficient and for a time sufficient for the first and second organic compounds to react to form an in situ condensation product and/or an in situ product containing additional unsaturation (for amides made from amines and carboxylic acids, for example, the temperature can be from about 195°C to about 260°C, such as from about 200°C to about 250°C), thereby forming the amide-containing and/or additionally-unsaturated and/or additionally oxidized catalyst precursor composition.

[00108] Practically, the treating step (a) above can comprise one (or more) of three methods: (1) first treating the catalyst precursor composition with the first organic compound and second with the second organic compound; (2) first treating the catalyst precursor composition with the second organic compound and second with the first organic compound; and/or (3) treating the catalyst precursor composition simultaneously with the first organic compound and with the second organic compound.

[00109] In certain advantageous embodiments, the heating step (b) above can be conducted for a sufficiently long time so as to form the amide, but not for so long that the amide so formed substantially decomposes. Additionally or alternately in such advantageous embodiments, the heating step (b) above can be conducted for a sufficiently long time so as to form additional unsaturation(s), which may result from at least partial decomposition (e.g., oxidative and/or non-oxidative dehydrogenation and/or aromatization) of some (typically-unfunctionalized organic) portions of the organic compounds, but generally not for so long that the at least partial decomposition (i) substantially decomposes any condensation product, such as amide, and/or (ii) volatilizes more than 50% by weight of the combined first and second organic compounds. Without

being bound by theory, it is believed that in situ formed amide and/or additional unsaturation(s) present at the point of sulfiding the catalyst precursor composition to form a sulfided (hydroprocessing) catalyst composition can somehow assist in controlling one or more of the following: the size of sulfided crystallites; the coordination of one or more of the metals during sulfidation, such that a higher proportion of the one or more types of metals are in appropriate sites for promoting desired hydroprocessing reactions (such as hydrotreating, hydrodenitrogenation, hydrodesulfurization, hydrodeoxygenation, hydrodemetallation, hydrocracking including selective hydrocracking, hydroisomerization, hydrodewaxing, and the like, and combinations thereof, and/or for reducing/minimizing undesired hydroprocessing reactions, such as aromatic saturation, hydrogenation of double bonds, and the like, and combinations thereof) than for sulfided catalysts made in the absence of the in situ formed reaction product having an amide (condensation reaction product of functional groups) and/or additional unsaturation(s); and coordination/catalysis involving one or more of the metals after sulfidation, such that a higher proportion (or each) of the one or more types of metals are more efficient at promoting desired hydroprocessing reactions (e.g., because the higher proportion of metal sites can catalyze more hydrodesulfurization reactions of the same type in a given timescale and/or because the higher proportion of the metal sites can catalyze more difficult hydrodesulfurization reactions in a similar timescale) than for sulfided catalysts made in the absence of the in situ formed reaction product having an amide (condensation reaction product of functional groups) and/or additional unsaturation(s).

[00110] When used to make a bulk mixed metal catalyst precursor composition, the in situ reacted catalyst precursor composition can, in one embodiment, consist essentially of the reaction product, an oxide form of the at least one metal from Group 6, an oxide form of the at least one metal from Groups 8-10, and optionally about 20 wt % or less of a binder (e.g., about 10 wt % or less).

[00111] After treatment of the catalyst precursor containing the at least one Group 6 metal and the at least one Group 8-10 metal with the first and/or second organic compounds, the organically treated catalyst precursor composition can be heated to a temperature high enough to form the reaction product and optionally but preferably high

enough to enable any dehydrogenation/decomposition/condensation byproduct to be easily removed (e.g., in order to drive the reaction equilibrium to the at least partially dehydrogenated/decomposed product and/or condensation product). Additionally or alternately, the organically treated catalyst precursor composition can be heated to a temperature low enough so as to substantially retain the reaction product containing the additional unsaturations and/or the condensation product, so as not to significantly decompose the reaction product, and/or so as not to significantly volatilize (more than 50% by weight of) the first and/or second organic compounds (whether reacted or not).

[00112] It is contemplated that the specific lower and upper temperature limits based on the above considerations can be highly dependent upon a variety of factors that can include, but are not limited to, the atmosphere under which the heating is conducted, the chemical and/or physical properties of the first organic compound, the second organic compound, the reaction product, and/or any reaction byproduct, or a combination thereof. In one embodiment, the heating temperature can be at least about 120°C, for example at least about 150°C, at least about 165°C, at least about 175°C, at least about 185°C, at least about 195°C, at least about 200°C, at least about 210°C, at least about 220°C, at least about 230°C, at least about 240°C, or at least about 250°C. Additionally or alternately, the heating temperature can be not greater than about 400°C, for example not greater than about 375°C, not greater than about 350°C, not greater than about 325°C, not greater than about 300°C, not greater than about 275°C, not greater than about 250°C, not greater than about 240°C, not greater than about 230°C, not greater than about 220°C, not greater than about 210°C, or not greater than about 200°C.

[00113] In one embodiment, the heating can be conducted in a low- or non-oxidizing atmosphere (and conveniently in an inert atmosphere, such as nitrogen). In an alternate embodiment, the heating can be conducted in a moderately- or highly-oxidizing environment. In another alternate embodiment, the heating can include a multi-step process in which one or more heating steps can be conducted in the low- or non-oxidizing atmosphere, in which one or more heating steps can be conducted in the moderately- or highly-oxidizing environment, or both. Of course, the period of time for the heating in the environment can be tailored to the first or second organic compound, but can typically extend from about 5 minutes to about 168 hours, for example from

about 10 minutes to about 96 hours, from about 10 minutes to about 48 hours, from about 10 minutes to about 24 hours, from about 10 minutes to about 18 hours, from about 10 minutes to about 12 hours, from about 10 minutes to about 8 hours, from about 10 minutes to about 6 hours, from about 10 minutes to about 4 hours, from about 20 minutes to about 96 hours, from about 20 minutes to about 48 hours, from about 20 minutes to about 24 hours, from about 20 minutes to about 18 hours, from about 20 minutes to about 12 hours, from about 20 minutes to about 8 hours, from about 20 minutes to about 6 hours, from about 20 minutes to about 4 hours, from about 30 minutes to about 96 hours, from about 30 minutes to about 48 hours, from about 30 minutes to about 24 hours, from about 30 minutes to about 18 hours, from about 30 minutes to about 12 hours, from about 30 minutes to about 8 hours, from about 30 minutes to about 6 hours, from about 30 minutes to about 4 hours, from about 45 minutes to about 96 hours, from about 45 minutes to about 48 hours, from about 45 minutes to about 24 hours, from about 45 minutes to about 18 hours, from about 45 minutes to about 12 hours, from about 45 minutes to about 8 hours, from about 45 minutes to about 6 hours, from about 45 minutes to about 4 hours, from about 1 hour to about 96 hours, from about 1 hour to about 48 hours, from about 1 hour to about 24 hours, from about 1 hour to about 18 hours, from about 1 hour to about 12 hours, from about 1 hour to about 8 hours, from 1 hour minutes to about 6 hours, or from about 1 hour to about 4 hours.

[00114] Additionally or alternately, in aspects where an ex situ formed amide is used, the amide can be formed prior to impregnation into the metal oxide component of the catalyst precursor by reaction of the amine component and the carboxylic acid component. Reaction typically takes place readily at mildly elevated temperatures up to about 200°C with liberation of water as a by-product of the reaction at temperatures above 100°C and usually above 150°C. The reactants can usually be heated together to form a melt in which the reaction takes place and the melt impregnated directly into the metal oxide component which is preferably pre-heated to the same temperature as the melt in order to assist penetration into the structure of the metal oxide component. The reaction can also be carried out in the presence of a solvent if desired and the resulting solution used for the impregnation step. In certain embodiments, the amide and its heat treated derivative may not be located/incorporated within the crystal lattice of the mixed metal oxide precursor, *e.g.*, may instead be located on the surface and/or within the pore

volume of the precursor and/or be associated with (bound to) one or more metals or oxides of metals in a manner that does not significantly affect the crystalline lattice of the mixed metal oxide precursor composition, as observed through XRD and/or other crystallographic spectra. A sulfided version of the mixed metal oxide precursor composition can still have its sulfided form affected by the organic compound(s)/additive(s) and/or the reaction product(s), even though the oxide lattice is not significantly affected.

[00115] There is not a strict limit on the ratio between the amine reactant and the carboxylic reactant, and accordingly, the ratio of the reactive amine and carboxylic acid groups in the two reactants may vary, respectively, from about 1:4 to about 4:1, for example from about 1:3 to about 3:1 or from about 1:2 to about 2:1. It has been observed that catalysts made with amides from equimolar quantities of the amine and carboxylic acid reactants compounds show performance improvements in hydroprocessing certain feeds and for this reason, amides made with an equimolar ratio are preferred.

[00116] The pre-formed amide is suitably impregnated into the metal oxide precursor by incipient wetness impregnation with the amount determined according to the pore volume of the metal oxide component. Following impregnation, a heat treatment is carried out which first removes any residual water and/or solvent but also creates a reaction product containing additional unsaturation sites and possibly additional oxygen. The amide-impregnated metal oxide component is then heated at a temperature sufficient and for a time sufficient to form a product containing the additional unsaturation which is characteristic of the desired organic component; this treatment with the pre-formed amide is typically from about 195°C to about 280°C, for example from about 200°C to about 250°C).

[00117] The heating step should not be conducted for so long that the amide becomes substantially decomposed but is continued for a sufficiently long time to form additional unsaturation(s), which may result from at least partial decomposition (e.g., oxidative and/or non-oxidative dehydrogenation and/or aromatization) of some (typically-unfunctionalized organic) portions of the organic compounds. On the other hand, the heating should not be conducted for so long that the decomposition substantially results in gross decomposition of the amide or any condensation product. The impregnated

catalyst precursor composition can be heated to a temperature high enough to form the unsaturated reaction product and typically high enough to enable any byproducts such as water to be removed. The temperature to which the impregnated precursor composition is heated should, however, maintained low enough so as to substantially retain the amide reaction product with the additional unsaturations and any oxygen, and so as not to significantly decompose the functionalized reaction product, and/or so as not to significantly volatilize (more than 50% by weight of) the amide.

[00118] The specific lower and upper temperature limits based on the above considerations can be dependent upon a variety of factors that can include, but are not limited to, the atmosphere under which the heating is conducted, the chemical and/or physical properties of the amide, the amide reaction product, and/or any functionalized reaction byproduct as well as the desired duration of the heating with higher temperatures, e.g. over the optimal temperature range up to 250°C, enabling shorter heating durations to be utilized.. The minimum heating temperature can, for example, suitably be at least about 120°C, for example at least about 150°C, at least about 165°C, at least about 175°C, at least about 185°C, at least about 195°C, at least about 200°C, at least about 210°C, at least about 220°C, at least about 230°C, at least about 240°C, or at least about 250°C. The maximum heating temperature should not be greater than about 400°C, for example, not greater than about 375°C, not greater than about 350°C, not greater than about 325°C, not greater than about 300°C, not greater than about 275°C, not greater than about 250°C, not greater than about 240°C, not greater than about 230°C, not greater than about 220°C, not greater than about 210°C, or not greater than about 200°C. Resort to temperatures above the preferred maximum of 250°C should be made with due care to avoid the gross decomposition of the amide as noted above but a slightly higher range, for example, 250-280°C, e.g. 260 or 275°C may permit usefully shorter heating steps in commercial scale operation. The temperature to be used should therefore be selected on an empirical basis depending on the nature of the amide used in the impregnation. The progress of the heating can be monitored according to the properties of the treated product, including analysis by GC-MS and by its infrared spectrum as described below.

[00119] In an embodiment, the organically treated catalyst precursor composition and/or the catalyst precursor composition containing the reaction product can contain from about 4 wt % to about 20 wt %, for example from about 5 wt % to about 15 wt %, carbon resulting from the first and second organic compounds and/or from the condensation product, as applicable, based on the total weight of the relevant composition.

[00120] Additionally or alternately, as a result of the heating step, the reaction product from the organically treated catalyst precursor can exhibit a content of unsaturated carbon atoms (which includes aromatic carbon atoms), as measured according to peak area comparisons using ^{13}C NMR techniques, of at least 29%, for example at least about 30%, at least about 31%, at least about 32%, or at least about 33%. Further additionally or alternately, the reaction product from the organically treated catalyst precursor can optionally exhibit a content of unsaturated carbon atoms (which includes aromatic carbon atoms), as measured according to peak area comparisons using ^{13}C NMR techniques, of up to about 70%, for example up to about 65%, up to about 60%, up to about 55%, up to about 50%, up to about 45%, up to about 40%, or up to about 35%. Still further additionally or alternately, as a result of the heating step, the reaction product from the organically treated catalyst precursor can exhibit an increase in content of unsaturated carbon atoms (which includes aromatic carbon atoms), as measured according to peak area comparisons using ^{13}C NMR techniques, of at least about 17%, for example at least about 18%, at least about 19%, at least about 20%, or at least about 21% (e.g., in an embodiment where the first organic compound is oleylamine and the second organic compound is oleic acid, such that the combined unsaturation level of the unreacted compounds is about 11.1% of carbon atoms, a .about.17% increase in unsaturated carbons upon heating corresponds to about 28.1% content of unsaturated carbon atoms in the reaction product). Yet further additionally or alternately, the reaction product from the organically treated catalyst precursor can optionally exhibit an increase in content of unsaturated carbon atoms (which includes aromatic carbon atoms), as measured according to peak area comparisons using ^{13}C NMR techniques, of up to about 60%, for example up to about 55%, up to about 50%, up to about 45%, up to about 40%, up to about 35%, up to about 30%, or up to about 25%.

[00121] Again further additionally or alternately, as a result of the heating step, the reaction product from the organically treated catalyst precursor can exhibit a ratio of unsaturated carbon atoms to aromatic carbon atoms, as measured according to peak area ratios using infrared spectroscopic techniques of a deconvoluted peak centered from about 1700 cm^{-1} to about 1730 cm^{-1} (e.g., at about 1715 cm^{-1}), compared to a deconvoluted peak centered from about 1380 cm^{-1} to about 1450 cm^{-1} (e.g., from about 1395 cm^{-1} to about 1415 cm^{-1}), of at least 0.9, for example at least 1.0, at least 1.1, at least 1.2, at least 1.3, at least 1.4, at least 1.5, at least 1.7, at least 2.0, at least 2.2, at least 2.5, at least 2.7, or at least 3.0. Again still further additionally or alternately, the reaction product from the organically treated catalyst precursor can exhibit a ratio of unsaturated carbon atoms to aromatic carbon atoms, as measured according to peak area ratios using infrared spectroscopic techniques of a deconvoluted peak centered from about 1700 cm^{-1} to about 1730 cm^{-1} (e.g., at about 1715 cm^{-1}), compared to a deconvoluted peak centered from about 1380 cm^{-1} to about 1450 cm^{-1} (e.g., from about 1395 cm^{-1} to about 1415 cm^{-1}), of up to 15, for example up to 10, up to 8.0, up to 7.0, up to 6.0, up to 5.0, up to 4.5, up to 4.0, up to 3.5, or up to 3.0.

[00122] A (sulfided) hydroprocessing catalyst composition can then be produced by sulfiding the catalyst precursor composition containing the reaction product. Sulfiding is generally carried out by contacting the catalyst precursor composition containing the reaction product with a sulfur-containing compound (e.g., elemental sulfur, hydrogen sulfide, polysulfides, or the like, or a combination thereof, which may originate from a fossil/mineral oil stream, from a biocomponent-based oil stream, from a combination thereof, or from a sulfur-containing stream separate from the aforementioned oil stream(s)) at a temperature and for a time sufficient to substantially sulfide the composition and/or sufficient to render the sulfided composition active as a hydroprocessing catalyst. For instance, the sulfidation can be carried out at a temperature from about 300°C to about 400°C , e.g., from about 310°C to about 350°C , for a period of time from about 30 minutes to about 96 hours, e.g., from about 1 hour to about 48 hours or from about 4 hours to about 24 hours. The sulfiding can generally be conducted before or after combining the metal (oxide) containing composition with a binder, if desired, and before or after forming the composition into a shaped catalyst. The sulfiding can additionally or alternately be conducted in situ in a hydroprocessing

reactor. Obviously, to the extent that a reaction product of the first or second organic compounds contains additional unsaturations formed in situ, it would generally be desirable for the sulfidation (and/or any catalyst treatment after the organic treatment) to significantly maintain the in situ formed additional unsaturations of said reaction product.

[00123] The sulfided catalyst composition can exhibit a layered structure comprising a plurality of stacked YS_2 layers, where Y is the Group 6 metal(s), such that the average number of stacks (typically for bulk organically treated catalysts) can be from about 1.5 to about 3.5, for example from about 1.5 to about 3.0, from about 2.0 to about 3.3, from about 2.0 to about 3.0, or from about 2.1 to about 2.8. For instance, the treatment of the metal (oxide) containing precursor composition according to the invention can afford a decrease in the average number of stacks of the treated precursor of at least about 0.8, for example at least about 1.0, at least about 1.2, at least about 1.3, at least about 1.4, or at least about 1.5, as compared to an untreated metal (oxide) containing precursor composition. As such, the number of stacks can be considerably less than that obtained with an equivalent sulfided mixed metal (oxide) containing precursor composition produced without the first or second organic compound treatment. The reduction in the average number of stacks can be evidenced, e.g., via X-ray diffraction spectra of relevant sulfided compositions, in which the (002) peak appears significantly broader (as determined by the same width at the half-height of the peak) than the corresponding peak in the spectrum of the sulfided mixed metal (oxide) containing precursor composition produced without the organic treatment (and/or, in certain cases, with only a single organic compound treatment using an organic compound having less than 10 carbon atoms) according to the present invention. Additionally or alternately to X-ray diffraction, transmission electron microscopy (TEM) can be used to obtain micrographs of relevant sulfided compositions, including multiple microcrystals, within which micrograph images the multiple microcrystals can be visually analyzed for the number of stacks in each, which can then be averaged over the micrograph visual field to obtain an average number of stacks that can evidence a reduction in average number of stacks compared to a sulfided mixed metal (oxide) containing precursor composition produced without the organic treatment (and/or, in certain cases, with only a single organic compound treatment) according to the present invention.

[00124] The sulfided catalyst composition described above can be used as a hydroprocessing catalyst, either alone or in combination with a binder. If the sulfided catalyst composition is a bulk catalyst, then only a relatively small amount of binder may be added. However, if the sulfided catalyst composition is a heterogeneous/supported catalyst, then usually the binder is a significant portion of the catalyst composition, e.g., at least about 40 wt %, at least about 50 wt %, at least about 60 wt %, or at least about 70 wt %; additionally or alternately for heterogeneous/supported catalysts, the binder can comprise up to about 95 wt % of the catalyst composition, e.g., up to about 90 wt %, up to about 85 wt %, up to about 80 wt %, up to about 75 wt %, or up to about 70 wt %. Non-limiting examples of suitable binder materials can include, but are not limited to, silica, silica-alumina (e.g., conventional silica-alumina, silica-coated alumina, alumina-coated silica, or the like, or a combination thereof), alumina (e.g., boehmite, pseudo-boehmite, gibbsite, or the like, or a combination thereof), titania, zirconia, cationic clays or anionic clays (e.g., saponite, bentonite, kaoline, sepiolite, hydrotalcite, or the like, or a combination thereof), and mixtures thereof. In some preferred embodiments, the binder can include silica, silica-alumina, alumina, titania, zirconia, and mixtures thereof. These binders may be applied as such or after peptization. It may also be possible to apply precursors of these binders that, during precursor synthesis, can be converted into any of the above-described binders. Suitable precursors can include, e.g., alkali metal aluminates (alumina binder), water glass (silica binder), a mixture of alkali metal aluminates and water glass (silica-alumina binder), a mixture of sources of a di-, tri-, and/or tetravalent metal, such as a mixture of water-soluble salts of magnesium, aluminum, and/or silicon (cationic clay and/or anionic clay), chlorohydrol, aluminum sulfate, or mixtures thereof.

[00125] Generally, the binder material to be used can have lower catalytic activity than the remainder of the catalyst composition, or can have substantially no catalytic activity at all (less than about 5%, based on the catalytic activity of the bulk catalyst composition being about 100%). Consequently, by using a binder material, the activity of the catalyst composition may be reduced. Therefore, the amount of binder material to be used, at least in bulk catalysts, can generally depend on the desired activity of the final catalyst composition. Binder amounts up to about 25 wt % of the total composition can be suitable (when present, from above 0 wt % to about 25 wt %), depending on the

envisaged catalytic application. However, to take advantage of the resulting unusual high activity of bulk catalyst compositions according to the invention, binder amounts, when added, can generally be from about 0.5 wt % to about 20 wt % of the total catalyst composition.

[00126] If desired in bulk catalyst cases, the binder material can be composited with a source of a Group 6 metal and/or a source of a non-noble Group 8-10 metal, prior to being composited with the bulk catalyst composition and/or prior to being added during the preparation thereof. Compositing the binder material with any of these metals may be carried out by any known means, e.g., impregnation of the (solid) binder material with these metal(s) sources.

[00127] A cracking component may also be added during catalyst preparation. When used, the cracking component can represent from about 0.5 wt % to about 30 wt %, based on the total weight of the catalyst composition. The cracking component may serve, for example, as an isomerization enhancer. Conventional cracking components can be used, e.g., a cationic clay, an anionic clay, a zeolite (such as ZSM-5, zeolite Y, ultra-stable zeolite Y, zeolite X, an AIPO, a SAPO, or the like, or a combination thereof), amorphous cracking components (such as silica-alumina or the like), or a combination thereof. It is to be understood that some materials may act as a binder and a cracking component at the same time. For instance, silica-alumina may simultaneously have both a cracking and a binding function.

[00128] If desired, the cracking component may be composited with a Group 6 metal and/or a Group 8-10 non-noble metal, prior to being composited with the catalyst composition and/or prior to being added during the preparation thereof. Compositing the cracking component with any of these metals may be carried out by any known means, e.g., impregnation of the cracking component with these metal(s) sources. When both a cracking component and a binder material are used and when compositing of additional metal components is desired on both, the compositing may be done on each component separately or may be accomplished by combining the components and doing a single compositing step.

[00129] The selection of particular cracking components, if any, can depend on the intended catalytic application of the final catalyst composition. For instance, a zeolite can be added if the resulting composition is to be applied in hydrocracking or fluid catalytic cracking. Other cracking components, such as silica-alumina or cationic clays, can be added if the final catalyst composition is to be used in hydrotreating applications. The amount of added cracking material can depend on the desired activity of the final composition and the intended application, and thus, when present, may vary from above 0 wt % to about 80 wt %, based on the total weight of the catalyst composition. In a preferred embodiment, the combination of cracking component and binder material can comprise less than 50 wt % of the catalyst composition, for example, less than about 40 wt %, less than about 30 wt %, less than about 20 wt %, less than about 15 wt %, or less than about 10 wt %.

[00130] If desired, further materials can be added, in addition to the metal components already added, such as any material that would be added during conventional hydroprocessing catalyst preparation. Suitable examples of such further materials can include, but are not limited to, phosphorus compounds, boron compounds, fluorine-containing compounds, sources of additional transition metals, sources of rare earth metals, fillers, or mixtures thereof.

Additional Embodiments

[00131] Embodiment 1. A hydrotreating process comprising: reacting a feedstream having a sulfur content of at least about 3000 wppm, or at least about 4000 wppm, or at least about 5000 wppm (such as up to about 50000 wppm), and a T90 boiling point of about 900°F (482°C) or less, in a first hydrotreating stage in the presence of a hydrogen-containing treat gas and in the presence of at least one first stage hydrotreating catalyst, the first hydrotreating stage being operated at first stage hydrotreating conditions, to produce a first liquid effluent having a sulfur content of about 5000 wppm or less, or about 4000 wppm or less, or about 3000 wppm or less, the sulfur content of the first liquid effluent being less than the sulfur content of the feedstream; separating the first liquid effluent to produce a first vapor phase stream and a first liquid product stream, the first liquid product stream optionally having a T10 boiling point and a T90 boiling point; reacting at least a portion of the first liquid product stream in a second hydrotreating

stage in the presence of a hydrogen-containing treat gas and a second hydrotreating catalyst, the second hydrotreating stage being operated at second stage hydrotreating conditions to produce a second liquid effluent; and separating the second liquid effluent to produce a second vapor phase stream and a second liquid product stream having a sulfur content of about 500 wppm or less, or about 250 wppm or less, or about 100 wppm or less, wherein about 15 wt% or less of the feedstream is converted relative to a conversion temperature of 350°F (177°C) during the reacting in the first hydrotreating stage and the second hydrotreating stage.

[00132] Embodiment 2. The process of Embodiment 1, wherein the first liquid effluent has a sulfur content of at least about 1000 wppm, or at least about 1500 wppm, or at least about 2000 wppm.

[00133] Embodiment 3. A hydrotreating process comprising: reacting a feedstream having a T90 boiling point of about 900°F (482°C) or less in a first hydrotreating stage in the presence of a hydrogen-containing treat gas and in the presence of at least one first stage hydrotreating catalyst, the first hydrotreating stage being operated at first stage hydrotreating conditions, to produce a first liquid effluent; separating at least a portion of the first liquid effluent to produce a first vapor phase stream and a first liquid product stream, the first liquid product stream having a sulfur content of about 1000 wppm to about 20,000 wppm, the first liquid product stream having a) a T10 boiling point of at least about 350°F (177°C), b) a T90 boiling point of about 850°F (454°C) or less, or c) a combination thereof; reacting at least a portion of the first liquid product stream in a second hydrotreating stage in the presence of a hydrogen-containing treat gas and a second hydrotreating catalyst, the second hydrotreating stage being operated at second stage hydrotreating conditions to produce a second liquid effluent, the second stage hydrotreating conditions being effective for conversion of about 10 wt% or less of the at least a portion of the first liquid product stream relative to a conversion temperature of about 350°F (177°C); and separating at least a portion of the second liquid effluent to produce a second vapor phase stream and a second liquid product stream, the second liquid product stream having a sulfur content of about 250 wppm or less, or about 100 wppm or less.

[00134] Embodiment 4. The process of any of the above embodiments, wherein the T90 boiling point of the first liquid product stream is about 800°F (427°C) or less, or about 750°F (399°C) or less, or about 700°F (371°C) or less.

[00135] Embodiment 5. The process of any of the above embodiments, wherein the T10 boiling point of the feedstream is at least about 400°F (204°C), or at least about 450°F (232°C).

[00136] Embodiment 6. The process of any of the above embodiments, wherein the T90 boiling point of the feedstream is about 850°F (454°C) or less, or about 800°F (427°C) or less, or about 750°F (399°C) or less, or about 700°F (371°C) or less.

[00137] Embodiment 7. The process of any of the above embodiments, wherein the first stage hydrotreating conditions are effective for conversion of about 10 wt% or less of the feedstream relative to a conversion temperature of about 350°F (177°C), or about 5 wt% or less; or wherein the second stage hydrotreating conditions are effective for conversion of about 10 wt% or less of the feedstream relative to a conversion temperature of about 350°F (177°C), or about 5 wt% or less; or wherein about 10 wt% or less of the feedstream is converted relative to a conversion temperature of 350°F (177°C) during the reacting in the first hydrotreating stage and the second hydrotreating stage, or about 5 wt% or less, or about 3 wt% or less; or a combination thereof.

[00138] Embodiment 8. The process of any of the above embodiments, further comprising hydroprocessing at least a portion of the first liquid product stream in an intermediate hydrotreating stage.

[00139] Embodiment 9. The process of any of the above embodiments, wherein the hydrotreating catalyst comprises Mo, W, or a combination thereof, and wherein the hydrotreating catalyst comprises Ni, Co, Fe, or a combination thereof, the hydrotreating catalyst optionally being a supported catalyst or optionally being a bulk catalyst.

[00140] Embodiment 10. The process of Embodiment 9, wherein the hydrotreating catalyst comprises i) about 1 wt% to about 40 wt% of the Mo, W, or a combination thereof, ii) wherein the hydrotreating catalyst comprises about 2 wt% to about 70 wt% of the Ni, Co, Fe, or a combination thereof, or both i) and ii).

[00141] Embodiment 11. The process of any of the above embodiments, wherein the first stage hydrotreating conditions, the second stage hydrotreating conditions, or a combination thereof comprise temperatures of about 200°C to about 450°C; pressures of about 250 psig (1.8 MPa) to about 5000 psig (34.6 MPa); liquid hourly space velocities (LHSV) of about 0.1 hr⁻¹ to about 10 hr⁻¹; and hydrogen treat rates of about 200 scf/B (35.6 m³/m³) to about 10,000 scf/B (1781 m³/m³).

[00142] Embodiment 12. The process of any of the above embodiments, further comprising performing catalytic dewaxing, hydrofinishing, aromatic saturation, or a combination thereof on at least a portion of the second liquid product stream.

[00143] Embodiment 13. The process of Embodiment 12, wherein the catalytic dewaxing is performed at effective catalytic dewaxing conditions comprising temperatures of about 200°C to about 450°C, hydrogen partial pressures of about 1.8 MPa to about 34.6 MPa (250 psig to 5000 psig), liquid hourly space velocities of from 0.05 hr⁻¹ to 10 hr⁻¹, and hydrogen treat gas rates of about 35.6 m³/m³ (200 SCF/B) to about 1781 m³/m³ (10,000 scf/B).

[00144] Embodiment 14. The process of Embodiment 12 or 13, wherein the hydrofinishing is performed at effective hydrofinishing conditions comprising temperatures from about 125°C to about 425°C, total pressures from about 500 psig (3.4 MPa) to about 3000 psig (20.7 MPa), liquid hourly space velocities from about 0.1 hr⁻¹ to about 5 hr⁻¹ LHSV, and hydrogen treat gas rates of from 500 to 5000 scf/B (89 to 890 m³/m³).

[00145] Embodiment 15. The process of Embodiment 12 or 13 or 14, wherein the aromatic saturation is performed at effective aromatic saturation conditions comprising temperatures from about 200°C to about 425°C, total pressures from about 500 psig (3.4 MPa) to about 3000 psig (20.7 MPa), liquid hourly space velocities from about 0.1 hr⁻¹ to about 5 hr⁻¹ LHSV, and hydrogen treat gas rates of from 500 to 5000 scf/B (89 to 890 m³/m³).

[00146] Embodiment 16. The process of any of the above embodiments, wherein the feedstream has an aromatics content of at least about 60 wt%, or at least about 70 wt%.

[00147] Embodiment 17. The process of any of the above embodiments, wherein the feedstream has a multi-ring aromatics content of at least about 40 wt%, or at least about 45 wt%, or at least about 50 wt%.

[00148] Embodiment 18. The process of any of the above embodiments, wherein the first hydrotreating catalyst and the second hydrotreating catalyst are different, or wherein the first hydrotreating catalyst and the second hydrotreating catalyst are the same.

[00149] Embodiment 19. The process of any of the above embodiments, wherein the second hydrotreating catalyst comprises a mixed metal catalyst, the mixed metal catalyst comprising a sulfided mixed metal catalyst formed by sulfiding a mixed metal catalyst precursor composition, the mixed metal catalyst precursor composition being produced by a) heating a composition comprising at least one metal from Group 6 of the Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, and a reaction product formed from (i) a first organic compound containing at least one amine group, and (ii) a second organic compound separate from said first organic compound and containing at least one carboxylic acid group to a temperature from about 195°C to about 260°C for a time sufficient for the first and second organic compounds to form a reaction product in situ that contains an amide moiety, unsaturated carbon atoms not present in the first or second organic compounds, oxygen atoms not present in the first or second organic compounds, or a combination thereof; b) heating a composition comprising one metal from Group 6 of the Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, and a reaction product formed from (iii) a first organic compound containing at least one amine group and at least 10 carbon atoms or (iv) a second organic compound containing at least one carboxylic acid group and at least 10 carbon atoms, but not both (iii) and (iv), wherein the reaction product contains additional unsaturated carbon atoms, relative to (iii) the first organic compound or (iv) the second organic compound, wherein the metals of the catalyst precursor composition are arranged in a crystal lattice, and wherein the reaction product is not located within the crystal lattice, to a temperature from about 195°C to about 260°C for a time sufficient for the first or second organic compounds to form a reaction product in situ that contains unsaturated carbon atoms not present in the first or second organic compounds, oxygen atoms not present in the first or second organic

compounds, or a combination thereof; or c) heating a composition comprising at least one metal from Group 6 of the Periodic Table of the Elements, at least one metal from Groups 8-10 of the Periodic Table of the Elements, and a pre-formed amide formed from (v) a first organic compound containing at least one amine group, and (vi) a second organic compound separate from said first organic compound and containing at least one carboxylic acid group, to form at least one of additional in situ unsaturated carbon atoms or in situ added oxygen atoms not present in the first organic compound, the second organic compound, or both, but not for so long that the pre-formed amide substantially decomposes, thereby forming a catalyst precursor containing at least one of in situ formed unsaturated carbon atoms or in situ added oxygen atoms.

Examples

[00150] The following examples illustrate various methods for increasing distillate yield based in part on additional aromatic saturation of an appropriate feed. In some examples, distillate yield can be improved based on use of a catalyst with improved activity for aromatic saturation at a desired level of severity for removal of heteroatoms. In other examples, distillate yield can be improved based on using interstage separation prior to a second (or subsequent) hydrotreating stage.

Example 1 – Distillate Hydrotreating with Interstage Separation

[00151] To demonstrate the benefits of using interstage separation for distillate hydrotreating, a light cycle oil was hydrotreated under a series of conditions. Various properties of the light cycle oil feed prior to the initial hydrotreatment stage are shown in Table 1. In addition to the properties in Table 1, the light cycle oil had a T5 boiling point of about 412°F (211°C), a T95 boiling point of about 724°F (384°C), and a final boiling point of about 788°F (420°C).

[00152] In an initial stage, the light cycle oil was hydrotreated to reduce the sulfur content, nitrogen content, and specific gravity of the liquid product. The effluent from the initial stage was either cascaded into second hydrotreatment stage without stripping or other intermediate separation as shown in process configuration FIG. 1, or was separated to separate the liquid product from the gas phase portion of the effluent and the liquid phase product was then hydrotreated in a second reaction stage as shown in

process configuration FIG. 2. The hydrotreating catalyst in both stages was a commercially available supported NiMo distillate hydrotreating catalyst.

[00153] The liquid phase effluent from the first stage was hydrotreated using a treat gas containing substantially no H₂S to simulate the two stage hydroprocessing with intermediate separation, such as the configuration shown in FIG. 2, and a treat gas containing about 2 vol% H₂S to simulate the two stage hydroprocessing without intermediate separation, such as the configuration shown in FIG. 1. As shown in Table 1, the liquid product from the second hydrotreating stage has a substantially lower aromatics content than the feed to the initial hydrotreating stage. Additionally, the aromatics present in the liquid product from the second hydrotreating stage are primarily 1-ring aromatics. This is in contrast to the initial feed, where the majority of the aromatics are multi-ring aromatics.

[00154] The reduction in multi-ring aromatics in the final product as H₂S is removed from the treat gas (as shown in Table 1) is believed to contribute to the reduced specific gravity (or increased API gravity) of the liquid products formed during hydrotreatment with lower concentrations of H₂S and/or no H₂S in the treat gas. The change in specific gravity shown in Table 1 corresponds to about a 0.44 vol% increase for the volume of liquid product generated with no H₂S in the second stage treat gas relative to the volume of liquid product generated with 2 vol% H₂S in the second stage treat gas. The reduction in multi-ring aromatics also causes a corresponding increase in the amount of H₂ consumed during the second stage hydrotreatment. It is noted that the net conversion of the distillate feed relative to a conversion temperature of 350°F (177°C) appears to be relatively unaffected by the amount of H₂S present in the second hydrotreating stage, at least for H₂S amounts of about 2 vol% or less. Thus, the increase in distillate yield appears to be achieved at a substantially constant level of process severity.

Table 1 – Light Cycle Oil Feed and Hydrotreated Product Properties

	Feed	Product 1	Product 2
Process Conditions			
Treat Gas H ₂ S Content, vol%		0	2
Temperature, F		655	656
Pressure, psig		1637	1632
LHSV, hr ⁻¹		0.76	0.77
Treat Gas Rate, SCF/B		4431	4405
Treat Gas Purity, % H ₂		80	78
Product Properties			
S, ppm	20100	9.5	19
N, wppm	708	0.4	0.4
API	16.5	28.4	27.7
SpGr, g/ml	0.9561	0.8849	0.8888
Aromatics, wt%			
1 Ring	18.7	48.3	52.1
2 Ring	40.9	3.8	4.5
3+ Ring	13.1	0.5	0.4
Total	72.7	52.6	57
Hydrogen Consumption, scf/bbl		1708	1589
350+% conversion, wt%		2.22%	2.28%

[00155] As an example of the commercial benefit, an example of a suitable feed for commercial distillate hydrotreater can be a feed containing about 30 vol% light cycle oil, such as the light cycle oil used for the processes shown in Table 1, with the remaining portion of the feed corresponding to a virgin gas oil having a roughly comparable boiling range. For this type of feed, a 0.44 vol% increase in the product resulting from the light cycle oil portion (30 vol%) of the feed can correspond to about 23,100 barrels of additional distillate product per year generated by a 50,000 barrel per day distillate hydrotreater under typical operating conditions.

Example 2 – Hydrotreating of Light Vacuum Gas Oil with Mixed Metal Catalyst

[00156] A mixed metal catalyst formed from a suitable precursor can also be used to improve aromatic saturation during distillate hydrotreating. In Examples 2 and 3, various feeds were hydrotreated in a single processing stage (i.e., no separation to remove H₂S) using various catalysts or catalyst systems.

[00157] In a first distillate hydrotreating process, a straight run light vacuum gas oil feed was hydrotreated in a single stage distillate hydrotreating system. The catalyst in the reaction system was a stacked bed of a commercial NiMo supported hydrotreating catalyst, a mixed metal catalyst formed from a suitable precursor, and the commercial NiMo supported hydrotreating catalyst. About one third of the catalyst volume corresponded to the mixed metal catalyst, with the mixed metal catalyst being approximately in the middle of the catalyst bed. For comparison, the straight run light vacuum gas oil was hydrotreated in a similar reaction system with a catalyst bed composed only of the commercial NiMo supported hydrotreating catalyst.

[00158] As shown in Table 2, the light vacuum gas oil had an initial sulfur content of about 0.86 wt% and a specific gravity of about 0.876 g/ml. The light vacuum gas oil was exposed to the catalyst or catalyst system at 340°C and at 840 psig (5800 kPa) of pressure. The treat gas rate was about 560 scf/B (950 Nm³/m³) of a gas containing about 80 vol% hydrogen. The LHSV was about 0.85 hr⁻¹.

[00159] Under the hydrotreating conditions, the stacked bed catalyst including the mixed metal catalyst resulted in a liquid product yield with a volume increase of about 0.29 vol% relative to the product yield from hydrotreating over just the commercial supported NiMo catalyst. This increase in volume was achieved with similar levels of conversion relative to a 300°F (149°C) conversion temperature. This demonstrates the ability of the mixed metal catalyst to improve yield (volume swell) for a feed having a sulfur content of less than about 10000 wppm at a roughly constant level of process severity.

Table 2: Process Conditions for Distillate Hydrotreating of Straight Run Feed

Straight Run Feed		Stacked Bed Including Mixed Metal Catalyst	Commercial HDT catalyst
Feed Properties			
S, wt%	0.856		
N, wppm	242		
SpGr	0.8756		
Processing Conditions			
Temp, °C		340	340
Pressure, psig		840	840
TGR, SCF/B		560	560
TGR purity, vol%		80	80
LHSV, hr ⁻¹		0.85	0.85
300+F Conversion, %		2.2	2.3
Product Properties			
Liquid yield, vol%		Base + 0.29%	Base

Example 3 – Hydrotreating of High Sulfur Content Feeds with a Mixed Metal Catalyst

[00160] In this example, the impact of sulfur content on yield when using a mixed metal catalyst is further investigated. Two different feeds were hydrotreated over hydrotreating catalysts to demonstrate the yield improvement of the mixed metal catalyst. One hydrotreating catalyst was a mixed metal catalyst formed from a suitable precursor, as described herein. A second catalyst was a bulk NiMoW hydrotreating catalyst made according to the methods described in U.S. Patent 6,156,695, U.S. Patent 6,582,590 and/or U.S. Patent 6,929,738.

[00161] Table 3 below shows the processing conditions used for single stage hydrotreatment of a feed corresponding to about 20 wt% of a light cycle oil similar to the feed in Example 1, with the remainder of the feed corresponding to a straight run light vacuum gas oil similar to the feed described in Example 2. As a result, the feed had an initial sulfur content of about 11,000 wppm. The process conditions for hydrotreatment are also shown in Table 3.

Table 3 – Process Conditions for Distillate Hydrotreating of Partially Cracked Feed

20% Cracked Feed (LCO)	Mixed Metal Catalyst	Comparative Bulk Catalyst
Processing Conditions		
Temp (°C)	~300	~300
Pressure (kPa)	~5800	~5800
Treat Gas Rate (Nm ³ /m ³)	~250	~250
Treat Gas Purity (vol %)	~100	~100
LHSV (hr ⁻¹)	~1.2	~1.2
Product – Liquid Yield (vol %)	Base + ~0.37%	Base

[00162] As shown in Table 3, the mixed metal catalyst provided a liquid product yield increase of about 0.37 vol% relative to the yield from the comparative bulk catalyst. The amount of conversion of the feed was similar for both catalysts. Thus, based on the results in Table 2 and Table 3, for a given level of process severity, the mixed metal catalyst formed from a suitable precursor appears to provide a yield advantage over various conventional catalysts.

[00163] The process conditions and results from processing a feed composed of only the light cycle oil are shown in Table 4. As shown in Table 4, the increase in yield using the mixed metal catalyst is 0.93 vol%. As indicated by the process conditions, this yield increase was again achieved at roughly constant process severity.

Table 4 - Process Conditions for Distillate Hydrotreating of Cracked Feed

100% Cracked Feed (LCO)	Mixed Metal Catalyst	Comparative Bulk Catalyst
Processing Conditions		
Temp (°C)	~295	~295
Pressure (kPa)	~8300	~8300
Treat Gas Rate (Nm ³ /m ³)	~780	~780
Treat Gas Purity (vol %)	~100	~100
LHSV (hr ⁻¹)	~2.1	~2.1
Product – Liquid Yield (vol %)	Base + ~0.93%	Base

Example 4 – Distillate Hydrotreating with Interstage Separation with Mixed Metal Catalyst

[00164] A mixed metal catalyst formed from a suitable precursor can also be used in conjunction with interstage separation to achieve still larger increases in distillate yield. In this example, a process configuration similar to Example 1 was used, so that a light cycle oil feed could be processed with interstage separation. In this Example, the initial hydrotreatment stage included a conventional supported NiMo catalyst to produce a first stage hydrotreated liquid product having the properties shown in Table 4. The first stage hydrotreated liquid product was then hydrotreated using either the mixed metal catalyst formed from a suitable precursor or the comparative bulk NiMoW catalyst made according to the methods described in U.S. Patent 6,156,695, U.S. Patent 6,582,590 and/or U.S. Patent 6,929,738. The process conditions and resulting product properties are shown in Table 5.

Table 5 – Second Stage Distillate Hydrotreating of Cracked Feed after Separation

	Total Liquid Product after first stage	Comparative Bulk Catalyst	Mixed Metal Catalyst
Conditions			
LHSV (hr ⁻¹)		~1	~1
Temp (°C)		~300	~300
Treat Gas Rate (Nm ³ /m ³)		~820	~820
H ₂ Pressure (kPa)		~8300	~8300
Product Sulfur (wppm)	~3940	~140	~25
Product Nitrogen (wppm)	~275	~0.3	<0.2
API Gravity	~22.12	~27.20	~29.10

[00165] As shown in Table 5, at a similar level of conversion relative to a conversion temperature of 350°F (177°C), the mixed metal catalyst produced a liquid product with a yield about 1.9 vol% greater than the liquid product from hydrotreating with the comparative bulk catalyst. This is almost a doubling of the volume swell benefit relative to the processing of the cracked feed as shown in Table 4 of Example 3. Such a volume

swell benefit is unexpectedly larger than the benefit that would be expected based on mere addition of the volume swell provided by the mixed metal catalyst and the volume swell provided by two stage hydrotreatment with interstage separation. This shows that the benefits of interstage separation can be synergistically combined with use of a mixed metal catalyst to provide an unexpectedly larger yield increase during distillate hydrotreating of a high sulfur distillate boiling range feed. This also demonstrates that the benefits of interstage separation can be realized for a variety of types of hydrotreating catalysts.

[00166] Although the present invention has been described in terms of specific embodiments, it is not so limited. Suitable alterations/modifications for operation under specific conditions should be apparent to those skilled in the art. It is therefore intended that the following claims be interpreted as covering all such alterations/modifications as fall within the true spirit/scope of the invention.

CLAIMS:

1. A hydrotreating process comprising:

reacting a feedstream having a sulfur content of at least about 3000 wppm and a T90 boiling point of about 900°F (482°C) or less in a first hydrotreating stage in the presence of a hydrogen-containing treat gas and in the presence of at least one first stage hydrotreating catalyst, the first hydrotreating stage being operated at first stage hydrotreating conditions, to produce a first liquid effluent having a sulfur content of about 5000 wppm or less, the sulfur content of the first liquid effluent being less than the sulfur content of the feedstream;

separating the first liquid effluent to produce a first vapor phase stream and a first liquid product stream;

reacting at least a portion of the first liquid product stream in a second hydrotreating stage in the presence of a hydrogen-containing treat gas and a second hydrotreating catalyst, the second hydrotreating stage being operated at second stage hydrotreating conditions to produce a second liquid effluent; and

separating the second liquid effluent to produce a second vapor phase stream and a second liquid product stream having a sulfur content of about 500 wppm or less,

wherein about 15 wt% or less of the feedstream is converted relative to a conversion temperature of 350°F (177°C) during the reacting in the first hydrotreating stage and the second hydrotreating stage.

2. The process of claim 1, wherein the first liquid effluent has a sulfur content of at least about 1000 wppm.

3. The process of claim 1, wherein a T90 boiling point of the first liquid product stream is about 800°F (427°C) or less.

4. The process of claim 1, wherein a T10 boiling point of the feedstream is at least about 350°F (177°C), or wherein the T90 boiling point of the feedstream is about 850°F (454°C) or less, or a combination thereof.

5. The process of claim 1,

wherein the first stage hydrotreating conditions are effective for conversion of about 10 wt% or less of the feedstream relative to a conversion temperature of about 350°F (177°C), or

wherein the second stage hydrotreating conditions are effective for conversion of about 10 wt% or less of the feedstream relative to a conversion temperature of about 350°F (177°C), or

wherein about 10 wt% or less of the feedstream is converted relative to a conversion temperature of 350°F (177°C) during the reacting in the first hydrotreating stage and the second hydrotreating stage, or

a combination thereof.

6. The process of claim 1, further comprising hydroprocessing at least a portion of the first liquid product stream in an intermediate hydrotreating stage.

7. The process of claim 1, wherein the hydrotreating catalyst comprises Mo, W, or a combination thereof, and wherein the hydrotreating catalyst comprises Ni, Co, Fe, or a combination thereof, the hydrotreating catalyst optionally being a supported catalyst or optionally being a bulk catalyst.

8. The process of claim 7, wherein the hydrotreating catalyst comprises i) about 1 wt% to about 40 wt% of the Mo, W, or a combination thereof, ii) wherein the hydrotreating catalyst comprises about 2 wt% to about 70 wt% of the Ni, Co, Fe, or a combination thereof, or both i) and ii).

9. The process of claim 1, wherein the first stage hydrotreating conditions, the second stage hydrotreating conditions, or a combination thereof comprise temperatures of about 200°C to about 450°C; pressures of about 250 psig (1.8 MPa) to about 5000 psig (34.6 MPa); liquid hourly space velocities (LHSV) of about 0.1 hr⁻¹ to about 10 hr⁻¹; and hydrogen treat rates of about 200 scf/B (35.6 m³/m³) to about 10,000 scf/B (1781 m³/m³).

10. The process of any of the above claims, further comprising performing catalytic dewaxing, hydrofinishing, aromatic saturation, or a combination thereof on at least a portion of the second liquid product stream.
11. The process of claim 10, wherein the catalytic dewaxing is performed at effective catalytic dewaxing conditions comprising temperatures of about 200°C to about 450°C, hydrogen partial pressures of about 1.8 MPag to about 34.6 MPag (250 psig to 5000 psig), liquid hourly space velocities of from 0.05 h⁻¹ to 10 h⁻¹, and hydrogen treat gas rates of about 35.6 m³/m³ (200 SCF/B) to about 1781 m³/m³ (10,000 scf/B).
12. The process of claim 10, wherein the hydrofinishing is performed at effective hydrofinishing conditions comprising temperatures from about 125°C to about 425°C, total pressures from about 500 psig (3.4 MPa) to about 3000 psig (20.7 MPa), liquid hourly space velocities from about 0.1 hr⁻¹ to about 5 hr⁻¹ LHSV, and hydrogen treat gas rates of from 500 to 5000 scf/B (89 to 890 m³ / m³).
13. The process of claim 10, wherein the aromatic saturation is performed at effective aromatic saturation conditions comprising temperatures from about 200°C to about 425°C, total pressures from about 500 psig (3.4 MPa) to about 3000 psig (20.7 MPa), liquid hourly space velocities from about 0.1 hr⁻¹ to about 5 hr⁻¹ LHSV, and hydrogen treat gas rates of from 500 to 5000 scf/B (89 to 890 m³ / m³).
14. A hydrotreating process comprising:
- reacting a feedstream having a T90 boiling point of about 900°F (482°C) or less in a first hydrotreating stage in the presence of a hydrogen-containing treat gas and in the presence of at least one first stage hydrotreating catalyst, the first hydrotreating stage being operated at first stage hydrotreating conditions, to produce a first liquid effluent;
- separating at least a portion of the first liquid effluent to produce a first vapor phase stream and a first liquid product stream, the first liquid product stream having a sulfur content of about 1000 wppm to about 20,000 wppm, the first liquid product stream having a) a T10 boiling point of at least about 350°F (177°C), b) a T90 boiling point of about 850°F (454°C) or less, or c) a combination thereof;

reacting at least a portion of the first liquid product stream in a second hydrotreating stage in the presence of a hydrogen-containing treat gas and a second hydrotreating catalyst, the second hydrotreating stage being operated at second stage hydrotreating conditions to produce a second liquid effluent, the second stage hydrotreating conditions being effective for conversion of about 10 wt% or less of the at least a portion of the first liquid product stream relative to a conversion temperature of about 350°F (177°C); and

separating at least a portion of the second liquid effluent to produce a second vapor phase stream and a second liquid product stream, the second liquid product stream having a sulfur content of about 100 wppm or less.

15. The process of claim 14, wherein the first stage hydrotreating conditions, the second stage hydrotreating conditions, or a combination thereof comprise temperatures of about 200°C to about 450°C; pressures of about 250 psig (1.8 MPa) to about 5000 psig (34.6 MPa); liquid hourly space velocities (LHSV) of about 0.1 hr⁻¹ to about 10 hr⁻¹; and hydrogen treat rates of about 200 scf/B (35.6 m³/m³) to about 10,000 scf/B (1781 m³/m³).

16. The process of claim 14, wherein a T90 boiling point of the first liquid product stream is about 800°F (427°C) or less.

17. The process of claim 14, wherein a T10 boiling point of the feedstream is at least about 350°F (177°C), or wherein the T90 boiling point of the feedstream is about 850°F (454°C) or less, or a combination thereof.

18. The process of claim 14,

wherein the first stage hydrotreating conditions are effective for conversion of about 10 wt% or less of the feedstream relative to a conversion temperature of about 350°F (177°C), or

wherein the second stage hydrotreating conditions are effective for conversion of about 10 wt% or less of the feedstream relative to a conversion temperature of about 350°F (177°C), or

wherein about 10 wt% or less of the feedstream is converted relative to a conversion temperature of 350°F (177°C) during the reacting in the first hydrotreating stage and the second hydrotreating stage, or

a combination thereof.

19. The process of claim 14, further comprising hydroprocessing at least a portion of the first liquid product stream in an intermediate hydrotreating stage.

20. The process of claim 14, further comprising performing catalytic dewaxing, hydrofinishing, aromatic saturation, or a combination thereof on at least a portion of the second liquid product stream.