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(54) Title: POST DEWAXING HYDROTREATMENT OF LOW CLOUD POINT DIESEL

(57) Abstract: Methods are provided for reducing the sulfur content of dewaxed distillate fractions, such as dewaxed diesel fuel fractions. A bed or partial bed of hydrotreating catalyst can be placed in a position to serve as a post-dewaxing hydrotreatment catalyst. Such a post-hydrotreatment catalyst can assist in removing organic sulfur that is generated during catalytic dewaxing.

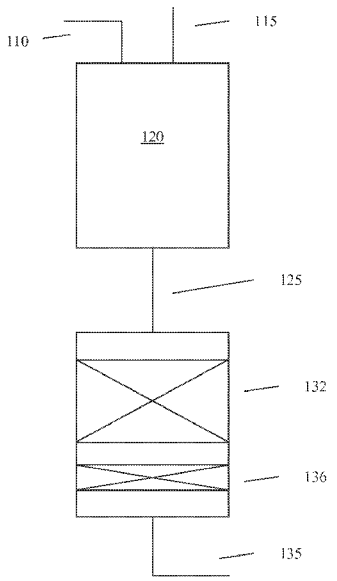

FIGURE 1

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POST DEWAXING HYDROTREATMENT OF LOW CLOUD POINT DIESEL

FIELD OF THE INVENTION

[0001] This invention relates to hydroprocessing of distillate boiling range feeds.

BACKGROUND OF THE INVENTION

[0002] Diesel fuel products are among the commonly desired products formed during hydroprocessing of distillate feeds. The type of hydroprocessing required to form a diesel fuel product can vary depending on the type of distillate feedstock. For some types of feeds, forming a suitable diesel product may only require hydrotreating or hydrocracking the feed to reduce the sulfur and nitrogen content in the diesel product. However some feeds will not have acceptable cold flow properties and therefore will also require some type of dewaxing to meet a desired diesel product specification.

[0003] U.S. Patent 3,338,819 describes a method for hydrocracking a distillate boiling range feed to produce naphtha boiling range products. A final portion of the catalyst bed in a hydrocracking reactor includes a hydrotreating catalyst. According to the method, when a hydrocracking catalyst has a high cracking activity relative to hydrogenation activity, mercaptans are formed in the resulting naphtha. The hydrotreating catalyst is described as allowing for reduction of the amount of mercaptans in the final naphtha product.

[0004] U.S. Patent 5,885,440 describes a method for hydrocracking a distillate boiling range feed to produce naphtha. The method also generates a jet fuel and/or diesel fuel product. A final portion of a catalyst bed in the

hydrocracking reactor includes a hydrotreating catalyst. The hydrotreating catalyst is described as allowing for reduction of the amount of mercaptans in the final naphtha product, as well as hydrogenation of aromatics and olefins.

SUMMARY OF THE INVENTION

[0005] In an embodiment, a method for producing a distillate boiling range product is provided. The method includes hydrotreating a feedstock having T5 boiling point of at least about 250°F (121°C) and a T95 boiling point of about 700°F (371°C) or less and a sulfur conlent of at least about 1000 wppm in the presence of a first hydrotreating catalyst under first effective hydrotreating conditions to produce a liquid hydrotreated effluent having a sulfur content of about 50 wppm or less and a gas phase effluent containing H_2S, the effective hydrotreating conditions resulting in conversion of 10 wt% or less of the feedstock into molecules boiling below 250°F (121°C) contacting the liquid hydrotreating effluent and at least a portion of the gas phase effluent containing H_2S with a dewaxing catalyst under effective dewaxing conditions to produce a dewaxed effluent having a cloud point at least about 10°C lower than a cloud point of the feedstock, the effective dewaxing conditions resulting in conversion of about 25 wt% or less of the liquid hydrotreating effluent into molecules boiling below 250°F (121°C); and_contacting the dewaxed effluent with a second hydrotreating catalyst under second effective hydrotreating conditions to produce distillate boiling range product having a sulfur content of about 25 wppm or less, the second effective hydrotreating conditions including a LHSV of at least about 10.0 hr^{-1}.

[0006] In another embodiment, a method for producing a diesei boiling range product is provided. The method mcludesjiydrotreating a feedstock having T5 boiling point of at least about 250°F (121°C) and a T95 boiling point of about 700°F (371°C) or less and a sulfur content of at least about 1000 wppm

in the presence of a first hydrotreating catalyst under first effective hydrotreating conditions to produce a liquid hydrotreated effluent having a sulfur content of about 50 wppm or less and a gas phase effluent containing H_2S, the effective hydrotreating conditions resulting in conversion of 10 wt% or less of the feedstock into molecules boiling below 350°F (177°C); contacting the liquid hydrotreating effluent and at least a portion of the gas phase effluent containing H_2S with a dewaxing catalyst under effective dewaxing conditions to produce a dewaxed effluent having a cloud point at least about 10°C lower than a cloud point of the feedstock, the effective dewaxing conditions resulting in conversion of about 25 wt% or less of the liquid hydrotreating effluent into molecules boiling below 350°F (177°C); and_contactmg the dewaxed effluent with a second hydrotreating catalyst under second effective hydrotreating conditions to produce diesel boiling range product having a sulfur content of about 50 wppm or less, the second effective hydrotreating conditions including a LHSV of at least about 10.0 hr^{-1}.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007J FIGURE 1 depicts a reaction system suitable for performing a process according to the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0008J In various embodiments, methods are provided for reducing the sulfur content of dewaxed distillate fractions, such as dewaxed diesel fuel fractions. A bed or partial bed of hydrotreating catalyst can be placed in a position to serve as a post-dewaxing hydrotreatment catalyst. Such a post-hydrotreatment catalyst can assist in removing organic sulfur that is generated during catalytic dewaxing.

[0009] Some feedstocks for producing distillate fractions contain sulfur at levels above the acceptable or desirable amount for meeting various regulatory standards. Such distillate feedstocks are typically hydrotreated to reduce the amount of sulfur. It may also be desirable to dewaxing the hydrotreated effluent in order to improve the cold flow properties of the feedstock. One option is to perform a gas / liquid separation on the hydrotreated effluent prior to passing the effluent into the dewaxing stage. Such a separation will allow gas phase sulfur species generated during hydrotreatment, such as H_2S, to be removed before dewaxing.

[0010] In some reaction systems, however an intermediate gas / liquid separation may not be desired. Instead, the entire effluent can be passed into the dewaxing stage, or at least a portion of the gas phase effluent can be passed into the dewaxing stage along with the liquid effluent. In such embodiments, gas phase H_2S formed during hydrotreatment of the feed will also be passed into the dewaxing stage. Alternatively, only a partial gas / liquid separation may be performed, so that at least a portion of the gas phase H_2S is passed into the dewaxing stage.

[0011] A typical dewaxing catalyst will often include a Group VIII metal, such as Pt, Pd, or Ni. Typically, the goal of the dewaxing stage is to improve the cold flow properties of the hydrotreated distillate. Because the goal is to form a hydrotreated distillate (such as a hydrotreated diesel) with improved cold flow properties, cracking and/or other conversion of the hydrotreated distillate to lower boiling point molecules is not desired. Conversion of the distillate feedstock to lower boiling point molecules results in increased production of naphtha at the expense of the desired diesel or other distillate. As a result, a dewaxing catalyst that operates primarily by isomerization is preferable.

[0012] Conventionally it was believed that a catalyst with a high cracking activity relative to hydrogenation activity would lead to mercaptan formation for naphtha boiling range products. Isomerization dewaxing has little in common with this conventional situation. A dewaxing catalyst that operates primarily by isomerization has a low cracking activity and therefore will not satisfy the condition of having a high cracking activity relative to hydrogenation activity. Additionally, isomerization dewaxing leads to reduced or minimized formation of naphtha boiling range products. Additionally, even if naphtha boiling range products are formed, any mercaptans in such products can be removed by fractionation, and thus do not directly impact the sulfur content of a distillate fraction.

[0013] Although conversion to naphtha boiling range molecules is reduced or minimized in an isomerization dewaxing process, some mercaptans may still be formed. Exposing the hydrotreated effluent to a dewaxing (isomerization) catalyst under dewaxing conditions may lead to creation of distillate boiling range mercaptans. Without being bound by any particular theory, isomerization type dewaxing of a distillate boiling range feedstock may result in generation of olefins as an intermediate product during isomerization. If sufficient gas phase sulfur is present, these intermediate product olefins may be converted to mercaptans. Thus, even though olefin creation due to cracking or other conversion is minimized, distillate boiling range mercaptans may still be formed. When the desired product is, for example, a diesel fuel with less than about 10 wppm of sulfur, even a few wppm of distillate boiling range mercaptans can pose difficulties.

[0014] In various embodiments, mercaptans formed during isomerization dewaxing of a hydrotreated distillate effluent can be removed by performing a post-dewaxing hydrotreatnient. This can be accomplished by including a portion of hydrotreating catalyst at the end of the dewaxing stage. The conditions for

the post-dewaxing hydrotreatment can be similar to the dewaxing conditions. The amount of catalyst used for the post-dewaxing hydrotreatment can also be small relative to the amount of dewaxing catalyst. As a result, the liquid hourly space velocity (LHSV) for the feedstock relative to the post-dewaxing hydrotreating catalyst is typically high relative to the space velocity for the dewaxing catalyst.

Feedstocks

[0015] In an embodiment, a feedstock can have an initial boiling point of at least about 200°F (93°C), or at least about 250°F (I21°C), or at least about 300°F (I49°C), or at least about 350°F (177°C), or at least about 400°F (204°C), or at least about 450°F (232°C). The initial boiling can vary widely, depending on how much kerosene or other lighter distillate components are included in a feedstock. In another embodiment, the feedstock can have a final boiling point of about 800°F (427°C) or less, or about 750°F (399°C) or less, or about 700°F (371°C) or less. Another way of characterizing a feedstock is based on the boiling point required to boil a specified percentage of the feed. For example, the temperature required to boil at least 5 wt% of a feed is referred to as a "T5" boilmg point. When characterizing a feed based on a T5 boilmg point, the feedstock can have a T5 boiling point at least about 200°F (93°C), or at least about 250°F (121°C), or at least about 300°F (149°C), or at least about 350°F (177°C), or at least about 400°F (204°C), or at least about 450°F (232°C). In another embodiment, the feed can have a T95 boilmg point of about 800°F (427°C) or less, or about 750° F (399°C) or less, or about 700°F (371 °C) or less. Examples of suitable feeds include various atmospheric and/or vacuum gas oil feeds, diesel boilmg range feeds, and feeds corresponding to mixtures thereof.

[0016] In some embodiments, the feedstock generally comprises a mineral oil. By "mineral oil" is meant a fossil/mineral fuel source, such as crude oil, and

not the commercial organic product, such as sold under the CAS number 8020-83-5, *e.g.*, by Aldrich. Examples of mineral oils can include, but are not limited to, straight run (atmospheric) gas oils, vacuum gas oils, demetallized oils, coker distillates, cat cracker distillates, heavy naphthas, diesel boiling range distillate fraction, jet fuel boiling range distillate fraction, kerosene boiling range distillate fraction, and coal liquids. The mineral oil portion of the feedstock can comprise any one of these example streams or any combination thereof. Preferably, the feedstock does not contain any appreciable asphaltenes.

[0017] Mineral feedstreams suitable for use in various embodiments can have a nitrogen content from about 10 wppm to about 6000 wppm nitrogen, such as at least about 50 wppm, and preferably at least about 500 wppm, such as at least about 750 wppm or at least about 1000 wppm or at least about 1500 wppm. In an embodiment, feedstreams suitable for use herein have a sulfur content from about 500 wppm to about 15,000 wppm sulfur, preferably about 1,000 wppm to about 15,000 wppm, such as from about 2000 wppm to about 10,000 wppm. It is noted that feedstocks with lower sulfur contents could be processed in accordance with the invention. However, a feedstock with a low starting amount of sulfur is unlikely to generate sufficient gas phase H_2S during hydrotreatnient to cause distillate mercaptan formation.

[0018] In the discussion below, a biocomponent feedstock refers to a hydrocarbon feedstock derived from a biological raw material component, such as vegetable fats/oils or animal fats/oils (including fish and algae fats/oils). Note that for the purposes of this document, vegetable fats/oils refer generally to any plant based material, and include fat/oils derived from a source such as plants from the genus Jatropha. The vegetable fats/oils, animal fats/oils, and algae fats/oils that can be used in the present invention include any of those which comprise primarily triglycerides and free fatty acids (FFA). The triglycerides and FFAs contain aliphatic hydrocarbon chains in their structure having 12 - 24

carbons. Other types of feed that are derived from biological raw material components include fatty acid esters, such as fatty acid methyl esters. Examples of biocomponent feedstocks include but are not limited to rapeseed (canola) oil, com oil, soy oils, castor oil, and palm oil.

[0019] In an embodiment, the feedstock can include at least about 5% by weight of glycerides, fatty acid alkyl esters, or a combination thereof. The gylcerides can include monoglycerides, digiycerides, or triglycerides. Preferably, the feedstock can include at least about 5 wt%, or at least about 10 wt%, or at least 20 wt% of glycerides, fatty acid alkyl esters, or a combination thereof. Alternatively, the feedstock can include about 55 wt% or less, or about 35 wt.% or less, or about 25 wt% or less, or about 20 wt.% or less of glycerides, fatty acid alkyl esters, or a combination thereof. Preferably, the feedstock can include triglycerides, fatty acid methyl esters, or a combination thereof.

[0020] In an embodiment, the biocomponent portion of the feedstock (such as the triglycerides and/or fatty acid methyl esters) can be a non-hydrotreated portion. A non-hydrotreated feed can typically have an olefin content and an oxygen content similar to the content of the corresponding raw biocomponent material. Examples of suitable biocomponent feeds can include food grade vegetable oils, and biocomponent feeds that are refined, bleached, and/or deodorized.

[0021] Biocomponent based diesel boiling range feedstreams typically have low nitrogen and sulfur content. Instead of nitrogen and/or sulfur, the primary heteroatom component in biocomponent based feeds is oxygen. Suitable biocomponent diesel boiling range feedstreams can include up to about 10 wt% oxygen, or up to about 12 wt% oxygen, or up to about 14 wt% oxygen. Suitable biocomponent diesel boiling range feedstreams can include at least about 5 wt% oxygen, or at least about 8 wt% oxygen. A biocomponent feedstream can

include an olefin content of at least about 3 wt%, or at least about 5 wt%, or at least about 10 wt%.

[0022] The content of sulfur, nitrogen, oxj'gen, and olefins in a feedstock created by blending two or more feedstocks can typically be determined using a weighted average based on the blended feeds. For example, a mineral feed and a biocomponent feed can be blended in a ratio of 80 wt% mineral feed and 20 wt% biocomponent feed. If the mineral feed has a sulfur content of about 1000 wppm, and the biocomponent feed has a sulfur content of about 10 wppm, the resulting blended feed could be expected to have a sulfur content of about 802 wppm.

Hydroprocessing – Initial Hydrotreatment

[0023] As an initial step, the distillate (or diesei) boiling range feedstock is hydrotreated to reduce the sulfur content of the feedstock. A hydrotreatment process can remove sulfur and nitrogen from a feedstock, as well as other potential contaminant heteroatoms such as oxygen. A hydrotreatment process can also saturate olefins.

[0024] A typical hydrotreatment catalyst can include at least one of a Group VIA and a Group VIII metal on a support such as alumina or silica. Examples include Ni/Mo, Co/Mo and Ni/W catalysts. Hydrotreating conditions can include a temperature of about 315°C to about 425°C, a pressure of about 300 psig (2.1 MPa) to about 3000 psig (20.6 MPa), an LHSV of about 0.2 hr^{-1} to about 10 hr^{-1}, and a hydrogen treat gas rate of about 500 scf/bbl (84 m^3/m^3) to about 10000 sef/bbi (1685 m^3/m^3).

[0025] During hydrotreatment, the sulfur and nitrogen contents of a feedstock are reduced. In an embodiment, one or more hydrotreating stages can

preferably reduce the sulfur content to a suitable level, such as less than about 100 wppm, or less than about 50 wppm, or less than about 25 wppm, preferably less than about 15 wppm or about 10 wppm. In another preferred embodiment, the hydrotreating stage(s) can reduce the sulfur content of the feed to less than about 5 wppm, preferably less than about 3 wppm. With regard to nitrogen, the hydrotreating stage(s) can preferably reduce the nitrogen content of the feed to about 20 wppm or less, or about 10 wppm or less, or about 5 wppm or less, or about 3 wppm or less. In alternative embodiments, amounts of organic sulfur greater than 100 wppm can be retained in the feedstock after hydrotreatment. Although such a hydrotreated effluent is not likely to be suitable for use as an ultra-low sulfur diesel (ULSD), other types of distillate products may tolerate a higher sulfur content.

[0026J Hydrotreatment processes for removing sulfur and"or nitrogen are also capable of converting molecules within a feedstock from higher to lower boiling ranges. In various embodiments, it is desirable to reduce or minimize the amount of conversion occurring during hydrotreatment, so that a distillate or diesel boiling range feed is used to produce a distillate or diesel boiling range product with improved cold flow properties. In other words, conversion of distillate or diesel boiling range molecules to lower boiling molecules (such as naphtha or light ends) is not desired. For example, the amount of conversion can be about 15 wt% or less, such as about 10 wt% or less, and preferably about 5 wt% or less. Note that the hydrotreating conversions described herein exclude any molecules that were naphtha or light ends prior to hydrotreatment. Another way to characterize the amount of conversion is based on the amount of naphtha produced after hydrotreatment. In various embodiments, the amount of naphtha generated is about 15 wt% or less of the feed, such as about 10 wt% or less, and preferably about 5 wt% or less. The amount of naphtha can be defined in any convenient manner. In some embodiments, it is desirable to retain kerosene boiling range molecules in the diesel or distillate boiling range product. In such

embodiments, about 15 wt% or less of the feedstock is converted from molecules boiling above 250°F (121°C) to molecules boiling below 250°F (121°C), such as about 10 wt% or less, and preferably about 5 wt% or less. In other embodiments, a heavy naphtha fraction may be desirable that is separated out from a diesel boiling range product. In such embodiments, about 15 wt% or less of the feedstock is converted from molecules boiling above 350°F (177°C) to molecules boiling below 350°F (177°C), such as about 10 wt% or less, and preferably about 5 wt% or less.

[0027] After hydrotreatnient, a complete gas / liquid separation is not performed. A full gas / liquid separation would remove the gas phase H_2S from the effluent. Without sufficient gas phase H_2S, diesel or distillate boiling range mercaptans will not be formed. While performing a full gas phase separation would remove H_2S, this is not always feasible and/or desirable. In various embodiments, one option is to cascade the entire effluent from hydrotreatnient to a dewaxing stage. Alternatively, a partial gas / liquid separation may be performed that results in some gas phase sulfur (typically H_2S) being passed into the dewaxing stage.

Hydroprocessing — Dewaxing

[0028] Catalytic dewaxing relates to the removal and/or isomerization of long chain, paraffinie molecules from feeds. Catalytic dewaxing can be accomplished by selective hydrocracking or by hydroisomerizing these long chain molecules. In various embodiments, catalytic dewaxmg methods will be used that operate primarily by isomerization. As a result, the feedstock being dewaxed will undergo a reduced or minimal amount of conversion during dewaxing while improving the cloud point of the feedstock. In other words, conversion of distillate or diesel boiling range molecules to lower boiling molecules (such as naphtha or light ends) is not desired. For example, the

amount of conversion can be about 20 wt% or less, such as about 15 wt% or less, and preferably about 10 wt% or less or 5 wt% or less. Note that the dewaxing conversions described herein exclude any molecules that were naphtha or light ends prior to dewaxing. As noted above, another way to characterize the amount of conversion is based on the amount of naphtha produced, such as the amount of naphtha produced after dewaxing. In various embodiments, the amount of naphtha generated is about 20 wt% or less of the hydrotreated feed, such as about 15 wt% or less, and preferably about 10 wt% or less or about 5 wt% or less. The amount of naphtha can be defined in any convenient manner. In some embodiments, it is desirable to retain kerosene boiling range molecules in the diesel or distillate boiling range product. In such embodiments, about 20 wt% or less of the feedstock is converted from molecules boiling above 250°F (121°C) to molecules boiling below 250°F (121°C), such as about 15 wt% or less, and preferably about 10 wt% or less or about 5 wt% or less. In other embodiments, a heavy naphtha fraction may be desirable that is separated out from a diesel boiling range product. In such embodiments, about 20 wt% or less of the feedstock is converted from molecules boilmg above 350°F (177°C) to molecules boilmg below 350°F (177°C), such as about 15 wt% or less, and preferably about 10 wt% or less or about 5 wt% or less. Still another option is to characterize the amount of naphtha generated after the combined hydrotreating and dewaxing of the feedstock. The amount of naphtha generated after the combination of hydrotreating and dewaxing can be about 30 wt% or less of the feedstock, such as 20 wt% or less, and preferably 10 wt% or less or 5 wt% or less. The combined hydrotreating and dewaxing conversion can be characterized at any of the conversion temperatures noted above, such as 25Q°F (121°C) or 350°F (177°C).

[0029] Although the amount of conversion is reduced or minimized, the cloud point of the feedstock after dewaxing is substantially reduced. Typical mineral distillate feeds suitable for conversion into a diesel fuel product have

initial cloud points ranging from about -20°C to about 5°C. The initial cloud point of biocomponent feeds can be higher still, including feeds with an initial cloud point of up to about 20°C. In various embodiments, the cloud point of the feedstock is reduced by at least about 10°C, such as at least about 15°C, preferably at least about 20°C or at least about 25°C, and possibly at least about 30°C.

[0030] Hydrodewaxing catalysts can be selected from molecular sieves such as crystalline aluminosilicates (zeolites) or silico-aluminophosphates (SAPOs). In an embodiment, the molecular sieve can be a 1-D or 3-D molecular sieve. In an embodiment, the molecular sieve can be a 10-member ring 1-D molecular sieve. Examples of molecular sieves that operate primarily by isomerization include ZSM-48, ZSM-23, ZSM-35, SSZ-32, and combinations thereof. In an embodiment, the molecular sieve can be ZSM-48, ZSM-23, or a combination thereof. Optionally, the dewaxing catalyst can include a binder for the molecular sieve, such as alumina, titania, silica, silica-alumina, zirconia, or a combination thereof. In an embodiment, the binder can be alumina, titania, or a combination thereof. In another embodiment, the binder can be titania, silica, zirconia, or a combination thereof.

[0031] One feature of molecular sieves that can impact the activity of the molecular sieve is the ratio of silica to alumina in the molecular sieve. In an embodiment, the molecular sieve can have a silica to alumina ratio of about 200 to 1 or less, or about 120 to 1 or less, or about 100 to 1 or less, or about 90 to 1 or less, or about 75 to 1 or less. In an embodiment, the molecular sieve can have a silica to alumina ratio of at least about 30 to 1, or at least about 50 to 1, or at least about 65 to 1.

[0032] The dewaxing catalyst can also include a metal hydrogenation component, such as a Group VIII metal. Suitable Group VIII metals can include

Pt, Pd, or Ni. The dewaxing catalyst can include at least about 0.1 wt% of a Group VIII metal, or at least about 0.3 wt%, or at least about 0.5 wt%, or at least about 1.0 wt%, or at least about 2.5 wt%, or at least about 5.0 wt%. Alternatively, the dewaxing catalyst can include about 10.0 wt% or less of a Group VIII metal, or about 5.0 wt% or less, or about 2.5 wt% or less, or about 1.5 wt% or less.

[0033] In some embodiments, the dewaxing catalyst can also include a Group VIB metal, such as W or Mo. An example of such an embodiment could be a dewaxing catalyst that includes Ni and W, Mo, or a combination of W and Mo. In such an embodiment, the dewaxing catalyst can include at least about 0.5 wt% of a Group VIB metal, or at least about 1.0 wt%, or at least about 2.5 wt%, or at least about 5.0 wt%. Alternatively, the dewaxing catalyst can include about 20.0 wt% or less of a Group VIB metal, or about 15.0 wt% or less, or about 10.0 wt% or less, or about 5.0 wt% or less, or about 1.0 wt% or less. In an embodiment, the dewaxing catalyst can include Pt, Pd, or a combination thereof. In another embodiment, the dewaxing catalyst can include Ni and W, Ni and Mo, or Ni, W, and Mo.

[0034] Catalytic dewaxing can be performed by exposing a feedstock to a dewaxing catalyst under effective (catalytic) dewaxing conditions. Effective dewaxing conditions can include a temperature of at least about 500°F (260°C), or at least about 550°F (288°C), or at least about 600°F (316°C), or at least about 650°F (343°C). Alternatively, the temperature can be about 750°F (399°C) or less, or about 700°F (371 °C) or less, or about 650°F (343°C) or less. The pressure can be at least about 400 psig (2.8 MPa), or at least about 500 psig (3.4 MPa), or at least about 750 psig (5.2 MPa), or at least about 1000 psig (6.9 MPa). Alternatively, the pressure can be about 1500 psig (10.3 MPa) or less, or about 1200 psig (8.2 MPa) or less, or about 1000 psig (6.9 MPa) or less, or about 800 psig (5.5 MPa) or less. The Liquid Hourly Space Velocity can be at least

about 0.5 hr^{-1}, or at least about 1.0 hr^{-1}, or at least about 1.5 hr^{-1}. Alternatively, the LHSV can be about 5.0 hr^{-1} or less, or about 3.0 hr^{-1} or less, or about 2.0 hr^{-1} or less. The treat gas rate can be at least about 500 scf/bbl (84 m^3/m^3), at least about 750 scf/bbl (126 m^3/m^3), or at least about 1000 scf/bbl (169 m^3/m^3). Alternatively, the treat gas rate can be about 2000 scf/bbl (337 m^3/m^3) or less, or about 1500 scf/bbl (253 m^3/m^3) or less, or about 1250 scf/bbl (211 m^3/m^3) or less.

Post-Dewaxing Hydrotreatment

[0035] After dewaxing, the dewaxing effluent can be hydrotreated again using a small portion of hydrotreating catalyst at the end of the dewaxing stage. The dewaxed feed has already been hydrotreated, so the conditions can be more gentle. Typically, conditions similar to the conditions for dewaxing will be used so that the hydrotreatment catalyst can be located in the same reactor as the dewaxing stage. Alternatively, hydrotreating conditions similar to those described for the initial hydrotreatment stage can be used. Suitable hydrotreating catalysts are described above. The post-dewaxing hydrotreatment catalyst can be located as part of a bed that also contains dewaxing catalyst, or the post-dewaxing hydrotreating catalyst can be located in a separate bed and/or stage.

[0036] One difference in the hydrotreating conditions is the liquid hourly space velocity (LHSV). Due to the initial hydrotreatment, most of the organically-bound sulfur remaining in the feed will be in the form of mercaptans. Such mercaptans can be removed under mild conditions. As a result, a relatively small amount of hydrotreatment catalyst can be used to remove the mercaptans. For example, the amount of hydrotreatment catalyst located in the dewaxing stage can correspond to about 1 wt% to about 10 wt% of

the catalyst in the stage. This can lead to an LHSV relative to the amount of post-dewaxmg hydrotreatment catalyst of about 10.0 hr^{-1} to about 40.0 hr^{-1}.

[0037] After dewaxing, the dewaxed feedstock can optionally also be hydrofinished. A hydrofinishing stage can be similar to a hydrotreating stage. For example, hydrofinishing can be a mild hydrotreating directed to saturating any remaining olefins and/or residual aromatics. A post dewaxing hydrofinishing can be carried out in cascade with the dewaxing step. A hydrofinishing stage can operate at temperatures from about 150°C to about 350°C, preferably about 180°C to about 250°C. Total pressures can be from about 2859 kPa (400 psig) to about 20786 kPa (3000 psig). Liquid hourly space velocity can be from about 0.1 hr^{-1} to about 5 hr^{-1}, preferably about 0.5 hr^{-1} to about 3 hr^{-1}. Hydrogen treat gas rates can be from about 42 m^3/m^3 (250 scf/bbl) to about 1685 m^3/m^3 (10,000 scf/bbl).

[0038] In some embodiments, the goal of the post-de waxing hydrotreatment is to return a distillate or diesel boiling range feed to a desired level of organic sulfur. For example, an initial hydrotreatment process can produce a hydrotreated liquid effluent with a sulfur content of less than 10 wppm or less. However, due to mercaptans formed during dewaxing, the sulfur content can increase to greater than 10 wppm. The post-dewaxing hydrotreatment can return the sulfur content of the feed to below 10 wppm.

[0039] In other embodiments, the post-dewaxing hydrotreatment can be used to remove some additional sulfur from a feedstock. For example, the initial hydrotreatment may reduce the sulfur content of a feedstock to less than about 100 wppm, or less than about 50 wppm, or less than about 15 wppm. The post-dewaxing hydrotreatment can then be used to reduce the sulfur content further. Thus, a hydrotreated liquid effluent with 100 wppm of sulfur can be reduced to 50 wppm or less after the post-dewaxing hydrotreatment. A hydrotreated liquid

effluent with 50 wppm of sulfur can be reduced to 25 wppm or less after the post-dewaxing hydrotreatment. A hydrotreated liquid effluent with 15 wppm of sulfur can be reduced to 10 wppm or less after the post-dewaxing hydrotreatment.

[0040] More generally, the diesel or distillate boiling range product resulting from the post-dewaxing hydrotreatment can have a sulfur content of less than about 100 wppm, or less than about 50 wppm, or less than about 25 wppm, preferably less than about 15 wppm or about 10 wppm. In another preferred embodiment, the hydrotreating stage(s) can reduce the sulfur content of the feed to less than about 5 wppm, preferably less than about 3 wppm.

[0041] Suitable catalysts for hydrofmishing can include hydrotreating catalysts. Alternatively, a hydrofmishing or aromatic saturation catalyst can be used, such as a Group VIII and/or Group VI metal supported on a bound support from the M41S family, such as bound MCM-41. Suitable binders for a support from the M41S family, such as MCM-41, can include Al, Si, or any other binder or combination of binders that provides a high productivity and/or low density catalyst. One example of a suitable aromatic saturation catalyst is Pt and/or another metal on alumina bound mesoporous MCM-41. Such a catalyst can be impregnated with a hydrogenation metal such as Pt, Pd, another Group VIII metal, a Group VI metal, or a mixture of metals thereof. In an embodiment, the amount of Group VIII metal is at least 0.1 wt. % per weight of catalyst. Preferably, the amount of Group VIII metal is at least 0.5 wt. %, or at least 0.6 wt. %. In such embodiments, the amount of metals can be 1.0 wt % or less, or 0.9 wt % or less, or 0.75 wt % or less, or 0.6 wt % or less. In still other embodiments, the amount of metals, either individually or in mixtures, is at least 0.1 wt %, or at least 0.25 wt %, or at least 0.5 wt %, or at least 0.6 wt %, or at least 0.75 wt %, or at least 1 wt %. In yet other embodiments, the amount of

metals, either individually or in mixtures, is 35 wt % or less, or 20 wt % or less, or 15 wt % or less, or 10 wt % or less, or 5 wt % or less.

[0042] In an embodiment, the hydrofinishing stage can be performed in the same reactor as the hydrodewaxing, with the same treat gas and at the same temperature. In another embodiment, stripping does not occur between the hydrofinishing and catalytic dewaxing stages. The hydrofinishing stage can be located prior to or after the post-dewaxing hydrotreatment stage.

Example of a Reaction System

[0043] A reaction system suitable for carrying out the above processes is shown schematically in Figure 1. In Figure 1, a feedstock 110 is introduced into a first hydrotreatment reactor 120. The feedstock can be a mineral feedstock or a mixture of mineral and biocomponent feedstocks. A hydrogen treat gas stream 115 is also introduced into hydrotreatment reactor 120. The feedstock 110 is exposed to hydrotreating conditions in first hydrotreatment reactor 120 in the presence of one or more catalyst beds that contain hydrotreating catalyst. Alternatively, more than one reactor can be used to contain various hydrotreatment catalyst beds. Preferably, the hydrotreatment reduces the sulfur content of the treated feedstock to about 50 ppm by weight or less, or about 10 wppm or less, or about 5 wppm or less, or about 3 wppm or less. Preferably, the hydrotreatment reduces the nitrogen content of the treated feedstock to about 10 wppm or less, or about 5 wppm or less, or about 3 wppm or less. In FIG. 1, the hydrotreated effluent 125 is cascaded into a second reactor that includes a dewaxing stage 132 and a post-dewaxing hydrotreatment stage 136. Alternatively, a partial gas / liquid separation can be performed on hydrotreated effluent 125 prior to passing the effluent into the second reactor.

[0044] The hydrotreated effluent is then dewaxed in dewaxing stage 132. In FIG. 1, the reactor containing dewaxing stage 132 is also shown as containing a post-dewaxing hydrotreatment stage 136. Dewaxing stage can include one or more beds of dewaxing catalyst. In FIG. 1, the effluent from dewaxing stage 132 is passed without separation into post-dewaxing hydrotreatment stage 136. The resulting effluent 135 is a distillate or diesel boiling range product with a reduced mercaptan content. Alternatively, post-dewaxing hydrotreatment stage 136 could be located in a separate reactor. In such an alternative embodiment, a gas / liquid separation could also be performed prior to post-dewaxing hydrotreatment stage 136.

Example 1 – Mercaptan formation in commercial scale reactor

[0045] In a commercial-scale single-stage reactor, a feedstock was exposed to a hydrotreatment catalyst and a dewaxing catalyst. The feedstock was a distillate boiling range feedstock with an initial boiling point of 209°C, a T5 boiling point of 344°C, a T95 boiling point of 663°C, and a final boiling point of 697°C. The sulfur content of the feedstock was 222 vvppm and the nitrogen content was 34.9 wppm. The pour point of the initial feedstock was 2.7°C and the cloud point was 2°C. The specific gravity of the feedstock was 0.8188. Under these conditions, little or no conversion of the feed took place, so the entire effluent was considered as a distillate product.

[0046] The hydrotreatment catalyst was a commercially available hydrotreating catalyst including a Group VI and a Group VIII metal on an alumina support. The dewaxmg catalyst was an alumina-bound ZSM-48 catalyst with 0.6 wt% of Pt. The reaction conditions for were selected so that the dewaxing catalyst reduced the cloud point of the product by 50°C relative to the initial cloud point of the feedstock. The reaction conditions also resulted in some desulfurization, although the feed was relatively clean prior to any

hydroprocessing. The reaction conditions included a reaction pressure of 900 psig (6.2 MPag) and a treat gas rate of 1500 scf/B (253 Nm^3/m^3) of 85% hydrogen. The reactor inlet temperature was 775°F (413°C) while the outlet temperature was 823°F (439°C). The liquid hourly space velocity (LHSV) relative to the hydrotreating catalyst was 8.3 hr^{-1} and the LHSV relative to the dewaxing catalyst was 2.6 hr^{-1}.

[0047] The reaction conditions resulted in a hydrotreated, dewaxed effluent with 46 wppm of sulfur. Based on a gas chromatography analysis, between 3 – 11 wppm of the sulfur corresponded to mercaptans. Due to the relative ease of removal of mercaptans by a hydrotreating catalyst, it is believed that the mercaptans were formed during contact of the hydrotreated feedstock with the dewaxing catalyst. The mercaptans are believed to be formed due to the presence of H_2S formed during the liydrotreatment. Because ail of the catalyst is in a single reactor, the H_2S was not removed prior to the feedstock contacting the dewaxing catalyst.

Example 2 – Pilot scale study of mercaptan formation

[0048] In this example, a pilot scale reactor was used with a clean feed to study the potential for mercaptan formation. The initial feedstock had a sulfur content of 3.6 wppm. Prior to introducing the feed into the pilot reactor, the feed was spike with dimethyl disulfide (DMDS) and tertial-normal-butyl amine. This resulted in spiked feed concentrations for sulfur and nitrogen of 0.49 wt% and 83 wppm, respectively. The boiling range of the spiked feed was from 289°F to 761°F. The spiking compounds decompose to form H_2S and NH_3 under dewaxing conditions. As a result, even though only dewaxing catalyst was present in the pilot reactor, processing of the spiked feed is believed to simulate a hydrotreated feed that is passed into a dewaxing stage without intermediate separation.

[0049] The spiked feed was then exposed to the dewaxing catalyst in the pilot reactor under effective dewaxing conditions. The dewaxing catalyst was an alumina-bound ZSM-48 catalyst with 0.6 wt% of Pt. The conditions were again selected to reduce the cloud point of the feedstock by 50°F. The pressure in the reactor was 600 psig (4.1 MPag). The treat gas rate was 2000 scf/B (337 Nm^3/m^3) of 100% hydrogen. The reactor temperature was 780°F (416°C). The LHSV relative to the dewaxing catalyst was 3.0 hr^{-1}.

[0050] After dewaxing the organic sulfur content of the dewaxed feed was determined to be 38 wppm. Based on the initial sulfur content of the feedstock before spiking, any organic sulfur content in the final product greater than 4 wppm represented additional organic sulfur generated during dewaxing. Based on analysis of the species, 13 wppm of the sulfur corresponded to mercaptans with 5 or more carbons. The remaining mercaptans were incorporated into a naphtha or light end boiling range molecules. The mercaptans with more than 5 carbons have a sufficiently high boiling point to potentially be included as part of a distillate fraction. Using a post-dewaxing hydrotreatment catalyst allows for removal of these distillate boiling range mercaptans from a diesel or distillate product. When a similar pilot reactor study was performed with a catalyst system that included a post-dewaxing hydrotreatment catalyst, the amount of mercaptans in the effluent was reduced to 2 - 3 wppm total, with all of the mercaptans being molecules boiling in the naphtha or light ends boiling range.

Additional embodiments

[0051] Embodiment 1. A method for producing a distillate boiling range product, comprising: hydrotreating a feedstock having T5 boiling point of at least about 250°F (121°C) and a T95 boiling point of about 700°F (371°C) or less and a sulfur content of at least about 1000 wppm in the presence of a first

hydrotreating catalyst under first effective hydrotreating conditions to produce a liquid hydrotreated effluent having a sulfur content of about 50 wppm or less and a gas phase effluent containing H_2S, the effective hydrotreating conditions resulting in conversion of about 10 wt% or less of the feedstock into molecules boiling below 250°F (121°C); contacting the liquid hydrotreating effluent and at least a portion of the gas phase effluent containing H_2S with a dewaxing catalyst under effective dewaxing conditions to produce a dewaxed effluent having a cloud point at least about 10°C lower than a cloud point of the feedstock, the effective dewaxing conditions resulting in conversion of about 25 wt% or less of the liquid hydrotreating effluent into molecules boiling below 250°F (121°C); and contacting the devvaxed effluent with a second hydrotreating catalyst under second effective hydrotreating conditions to produce distillate boiling range product having a sulfur content of about 25 wppm or less, the second effective hydrotreating conditions including a LHSV of at least about 10.0 hr^{-1}.

[0052] Embodiment 2. A method for producing a diesel boiling range product, comprising: hydrotreating a feedstock having T5 boiling point of at least about 250°F (121°C) and a T95 boiling point of about 700°F (371°C) or less and a sulfur content of at least about 1000 wppm in the presence of a first hydrotreating catalyst under first effective hydrotreating conditions to produce a liquid hydrotreated effluent having a sulfur content of about 50 wppm or less and a gas phase effluent containing H_2S, the effective hydrotreating conditions resulting in conversion of about 10 wt% or less of the feedstock into molecules boiling below 350°F (177°C); contacting the liquid hydrotreating effluent and at least a portion of the gas phase effluent containing H_2S with a dewaxing catalyst under effective dewaxing conditions to produce a dewaxed effluent having a cloud point at least about 10°C lower than a cloud point of the feedstock, the effective dewaxing conditions resulting in conversion of about 25 wt% or less of the liquid hydrotreating effluent into molecules boiling below 350°F (177°C); and contacting the dewaxed effluent with a second hydrotreating catalyst under

second effective hydrotreating conditions to produce diesel boiling range product having a sulfur content of about 50 wppm or less, the second effective hydrotreating conditions including a LHSV of at least about 10.0 hr^{-1}.

[0053] Embodiment 3. A method according to any of the above embodiments, wherein the effective dewaxing conditions produce a dewaxed effluent having a cloud point at least about 20°C lower than the cloud point of the feedstock, preferably at least about 25°C lower.

[0054] Embodiment 4. A method according to any of the above embodiments, wherein the effective hydrotreating conditions result in conversion of about 5 wt.% or less of the feedstock, or wherein the effective dewaxing conditions result in conversion of about 5 wt% or less of the liquid hydrotreating effluent, or wherein the combined effective hydrotreating conditions and effective dewaxing conditions result in conversion of about 30 wt.% or less of the feedstock, or about 20 wt% or less, or about 10 wt% or less, or about 5 wt% or less.

[0055] Embodiment 5. A method according to any of the above embodiments, wherein the effective dewaxing conditions result in conversion of about 15 wt% or less of the feedstock, preferably about 10 wt% or less, and more preferably about 5 wt.% or less, or wherein the effective dewaxing conditions result in conversion of about 15 wt% or less of the liquid hydrotreating effluent, preferably about 10 wt.%, and more preferably about 5 wt.% or less.

[0056] Embodiment 6. A method according to any of the above embodiments, wherein the first effective hydrotreating conditions produce a liquid hydrotreating effluent having a sulfur content of about 15 wppm or less, preferably 10 wppm or less, and wherein the second effective hydrotreating conditions produce a distil Sate boiling range product or diesel boiling range

product having a sulfur content of about 15 wppm or less, preferably about 10 wppm or less.

[0057] Embodiment 7. A method according to any of the above embodiments, wherein the second effective hydrotreating conditions include a temperature, pressure, and treat gas rate that correspond to the first effective hydrotreating conditions or to the effective dewaxing conditions.

[0058] Embodiment 8. A method according to any of the above embodiments, wherein the first effective hydrotreating conditions comprise a temperature of about 315°C to about 425°C, a pressure of about 300 psig (2.1 MPa) to about 3000 psig (20.6 MPa), an LHSV of about 0.2 hr^{-1} to about 10 hr^{-1}, and a hydrogen treat gas rate of about 500 scf/bbl (84 m^3/m^3) to about 10000 scf/bbl (1685 m^3/m^3).

[0059] Embodiment 9. A method according to any of the above embodiments, wherein the effective dewaxing conditions comprise a temperature of about 500°F (260°C) to about 750°F (399°C), a pressure of about 400 psig (2.8 MPa) to about 1500 psig, an LHSV of about 0.5 hr^{-1} to about 5.0 hr^{-1}, and a hydrogen treat gas rate of about 500 scf/bbl (84 m^3/m^3) to about 2000 scf/bbl (337 m^3/m^3).

[0060] Embodiment 10. A method according to any of the above embodiments, wherein the feedstock contains from about 1000 wppm to about 15000 wppm of sulfur, preferably from about 2000 wppm to about 10000 wppm.

CLAIMS:

1. A method for producing a distillate boiling range product, comprising:

hydrotreating a feedstock having T5 boiling point of at least about 250°F (121°C) and a T95 boiling point of about 700°F (371°C) or less and a sulfur content of at least about 1000 wppm in the presence of a first hydrotreating catalyst under first effective hydrotreating conditions to produce a liquid hydrotreated effluent having a sulfur content of about 50 wppm or less and a gas phase effluent containing H_2S, the effective hydrotreating conditions resulting in conversion of about 10 wt% or less of the feedstock into molecules boiling below 250°F (121°C);

contacting the liquid hydrotreating effluent and at least a portion of the gas phase effluent containing H_2S with a dewaxing catalyst under effective dewaxing conditions to produce a dewaxed effluent having a cloud point at least about 10°C lower than a cloud point of the feedstock, the effective dewaxing conditions resulting in conversion of about 25 wt% or less of the liquid hydrotreating effluent into molecules boiling below 250°F (121°C); and

contacting the dewaxed effluent with a second hydrotreating catalyst under second effective hydrotreating conditions to produce distillate boiling range product having a sulfur content of about 25 wppm or less, the second effective hydrotreating conditions including a LHSV of at least about 10.0 hr^{-1}.

2. A method for producing a diesel boiling range product, comprising:

hydrotreating a feedstock having T5 boiling point of at least about 250°F (121°C) and a T95 boiling point of about 700°F (371°C) or less and a

sulfur content of at least about 1000 wppm in the presence of a first hydrotreating catalyst under first effective hydrotreating conditions to produce a liquid hydrotreated effluent having a sulfur content of about 50 wppm or less and a gas phase effluent containing H_2S, the effective hydrotreating conditions resulting in conversion of about 10 wt% or less of the feedstock into molecules boiling below 350°F (177°C);

contacting the liquid hydrotreating effluent and at least a portion of the gas phase effluent containing H_2S with a dewaxing catalyst under effective dewaxing conditions to produce a dewaxed effluent having a cloud point at least about 10°C lower than a cloud point of the feedstock, the effective dewaxing conditions resulting in conversion of about 25 wt% or less of the liquid hydrotreating effluent into molecules boiling below 350°F (177°C); and

contacting the dewaxed effluent with a second hydrotreating catalyst under second effective hydrotreating conditions to produce diesei boiling range product having a sulfur content of about 50 wppm or less, the second effective hydrotreating conditions including a LHSV of at least about 10.0 hr^{-1}.

3. The method of any of the above claims, wherein the effective dewaxing conditions produce a dewaxed effluent having a cloud point at least about 20°C lower than the cloud point of the feedstock, preferably at least about 25°C lower.

4. The method of any of the above claims, wherein the effective hydrotreating conditions result in conversion of about 5 wt% or less of the feedstock, or wherein the effective dewaxing conditions result in conversion of about 5 wt% or less of the liquid hydrotreating effluent, or wherein the combined effective hydrotreating conditions and effective dewaxing conditions result in conversion of about 30 wt% or less of the feedstock, or about 20 wt% or less, or about 10 wt% or less, or about 5 wt% or less.

5. The method of any of the above claims, wherein the effective dewaxing conditions result in conversion of about 15 wt% or less of the feedstock, preferably about 10 wt% or less, and more preferably about 5 wt% or less, or wherein the effective dewaxing conditions result in conversion of about 15 wt% or less of the liquid hydrotreating effluent, preferably about 10 wt%, and more preferably about 5 wt% or less.

6. The method of any of the above claims, wherein the first effective hydrotreating conditions produce a liquid hydrotreating effluent having a sulfur content of about 15 wppm or less, preferably 10 wppm or less, and wherein the second effective hydrotreating conditions produce a distillate boiling range product or diesel boiling range product having a sulfur content of about 15 wppm or less, preferably about 10 wppm or less.

7. The method of any of the above claims, wherein the second effective hydrotreating conditions include a temperature, pressure, and treat gas rate that correspond to the first effective hydrotreating conditions or to the effective dewaxing conditions.

8. The method of any of the above claims, wherein the first effective hydrotreating conditions comprise a temperature of about 315°C to about 425°C, a pressure of about 300 psig (2.1 MPa.) to about 3000 psig (20.6 MPa), an LHSV of about 0.2 hr^{-1} to about 10 hr^{-1}, and a hydrogen treat gas rate of about 500 scf/bbl (84 m^3/m^3) to about 10000 scf/bbl (1685 $\mathbf{m^3/m^3}$).

9. The method of any of the above claims, wherein the effective dewaxing conditions comprise a temperature of about 500° F (26Q°C) to about 750°F (399°C), a pressure of about 400 psig (2.8 MPa) to about 1500 psig, an LHSV of about 0.5 hr^{-1} to about 5.0 hr^{-1}, and a hydrogen treat gas rate of about 500 scf/bbl (84 m^3/m^3) to about 2000 scf/bbl (337 m^3/m^3).

10. The method of any of the above claims, wherem the feedstock contains from about 1000 wppm to about 15000 wppm of sulfur, preferably from about 2000 wppm to about 10000 wppm.

AMENDED CLAIMS
received by the International Bureau on 30 August 2012 (30.08.2012)

1. A method for producing a distillate boiling range product, comprising:

hydrotreating a feedstock having T5 boiling point of at least about 250°F (121°C) and a T95 boiling point of about 700°F (371°C) or less and a sulfur content of at least about 1000 wppm in the presence of a first hydrotreating catalyst under first effective hydrotreating conditions to produce a liquid hydrotreated effluent having a sulfur content of about 50 wppm or less and a gas phase effluent containing ¾ S, the effective hydrotreating conditions resulting in conversion of about 10 wt% or less of the feedstock into molecules boiling below 250°F (121°C);

contacting the liquid hydrotreating effluent and at least a portion of the gas phase effluent containing H_2S with a dewaxmg catalyst under effective dewaxing conditions to produce a dewaxed effluent having a cloud point at least about 10°C lower than a cloud point of the feedstock, the effective dewaxing conditions resulting in conversion of about 25 wt% or less of the liquid hydrotreating effluent into molecules boiling below 250°F (121°C); and

contacting the dewaxed effluent with a second hydrotreating catalyst under second effective hydrotreating conditions to produce distillate boiling range product having a sulfur content of about 25 wppm or less, the second effective hydrotreating conditions including a LHSV of at least about 10.0 hr^{-1}.

2. A method for producing a diesel boiling range product, comprising:

hydrofreating a feedstock having T5 boiling point of at least about 250°F (121°C) and a T95 boiling point of about 700°F (371°C) or less and a sulfur content of at least about 1000 wppm in the presence of a first hydrotreating catalyst under first effective hydrotreating conditions to produce a liquid hydrotreated effluent having a sulfur content of about 50 wppm or less and a gas phase effluent containing H_2S, the

effective hydrotreating conditions resulting in conversion of about 10 wt% or less of the feedstock into molecules boiling below 350°F (177°C);

contacting the liquid hydrotreating effluent and at least a portion of the gas phase effluent containing H_2S with a dewaxing catalyst under effective dewaxing conditions to produce a dewaxed effluent having a cloud point at least about 10°C lower than a cloud point of the feedstock, the effective dewaxing conditions resulting in conversion of about 25 wt% or less of the liquid hydrotreating effluent into molecules boiling below 350°F (177°C); and

contacting the dewaxed effluent with a second hydrotreating catalyst under second effective hydrotreating conditions to produce diesel boiling range product having a sulfur content of about 50 wppm or less, the second effective hydrotreating conditions including a LHSV of at least about 10.0 hr^{-1}.

3. The method of any of the above claims, wherein the effective dewaxing conditions produce a dewaxed effluent having a cloud point at least about 20°C lower than the cloud point of the feedstock, preferably at least about 25°C lower.

4. The method of any of the above claims, wherein the effective hydrotreating conditions result in conversion of about 5 wt% or less of the feedstock, or wherein the effective dewaxing conditions result in conversion of about 5 wt% or less of the liquid hydrotreating effluent, or wherein the combined effective hydrotreating conditions and effective dewaxing conditions result in conversion of about 30 wt% or less of the feedstock, or about 20 wt% or less, or about 10 wt% or less, or about 5 wt% or less.

5. The method of any of the above claims, wherein the effective dewaxing conditions result in conversion of about 15 wt% or less of the feedstock, preferably about 10 wt% or less, and more preferably about 5 wt% or less, or wherein the effective dewaxing conditions result in conversion of about 15 wt% or less of the

liquid hydrotreating effluent, preferably about 10 wt%, and more preferably about 5 wt% or less.

6. The method of any of the above claims, wherein the first effective hydrotreating conditions produce a liquid hydrotreating effluent having a sulfur content of about 15 wppm or less, preferably 10 wppm or less, and wherem the second effective hydrotreating conditions produce a distillate boiling range product or diesel boiling range product having a sulfur content of about 15 wppm or less, preferably about 10 wppm or less.

7. The method of any of the above claims, wherein the second effective hydrotreating conditions include a temperature, pressure, and treat gas rate that correspond to the first effective hydrotreating conditions or to the effective dewaxing conditions.

8. The method of any of the above claims, wherem the first effective hydrotreating conditions comprise a temperature of about 315°C to about 425"C. a pressure of about 300 psig (2.1 MPa) to about 3000 psig (20.6 MPa), an LHSV of about 0.2 hr^{-1} to about 10 hr^{-1}, and a hydrogen treat gas rate of about 500 scfTbbl (84 m^3/m^3) to about 10000 scfTbbl (1685 m^3/m^3).

9. The method of any of the above claims, wherein the effective dewaxing conditions comprise a temperature of about 500°F (260°C) to about 750°F (399°C), a pressure of about 400 psig (2.8 MPa) to about 1500 psig, an LHSV of about 0.5 hr^{-1} to about 5.0 hr^{-1}, and a hydrogen treat gas rate of about 500 scfTbbl (84 m^3/m^3) to about 2000 scf/bbl (337 m^3/m^3).

10. The method of any of the above claims, wherem the feedstock contains from about 1000 wppm to about 15000 wppm of sulfur, preferably from about 2000 wppm to about 10000 wppm.

11. The method of any of the above claims, wherein a partial gas / liquid separation is performed on the combined liquid hydrotreated effluent and gas phase effluent prior to the contacting of the liquid hydrotreating effluent and the portion of the gas phase effluent with the dewaxing catalyst.

12. The method of any of the claims 1-10, wherein all of the gas phase effluent containing H_2S is contacted with the dewaxing catalyst.

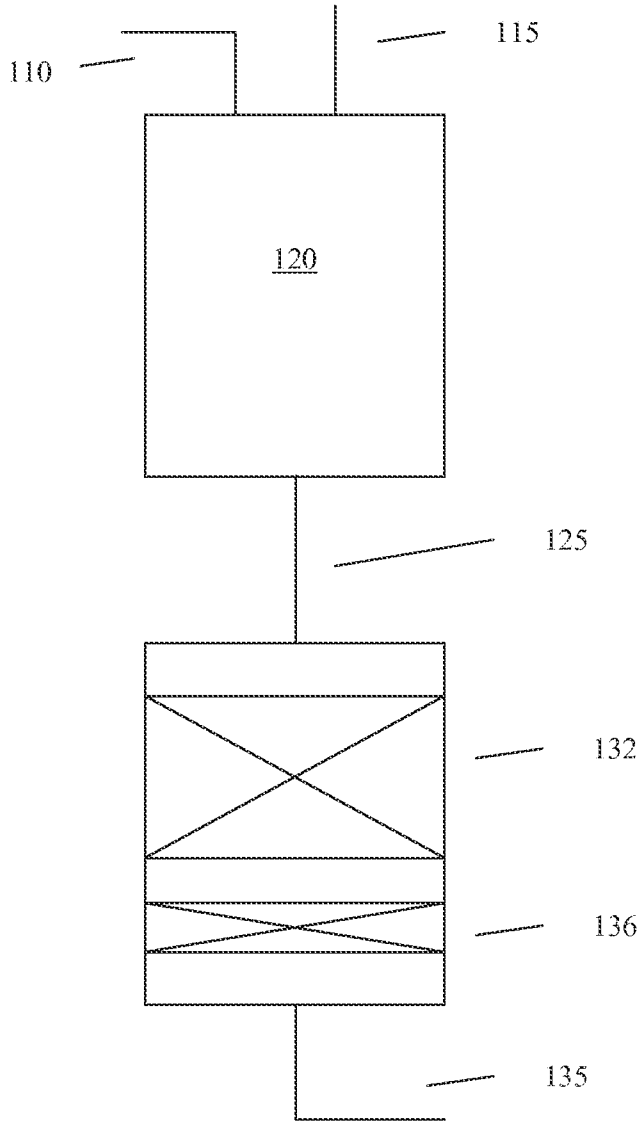

FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/064O8O

A. CLASSIFICATION OF SUBJECT MATTER
INV. C1QG65/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
CIOG

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/259793 Al (UMANSKY BENJAMIN S [US] ET AL) 27 October 2011 (2011-10-27) claim 1; figure 1 page 5, paragraphs 38,40-42 page 6, paragraphs 45,46,47 page 7, paragraph 51	1-10
A	US 4 913 797 A (ALBINS0N KENNETH R [US] ET AL) 3 April 1990 (1990-04-03) claim 1; figure 1 column 3, line 67 - column 4, line 9	1-10
A	US 5 273 645 A (CLARK FREDERICK T [US] ET AL) 28 December 1993 (1993-12-28) claim 1; examples 2,4	1-10

-/ -

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
28 June 2012	05/07/2012

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
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