HYDROPROCESSING FEEDSTOCK CONTAINING LIPID MATERIAL TO PRODUCE TRANSPORTATION FUEL

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ABSTRACT

This invention provides processes for producing fuel, particularly transportation fuel, from biological material, e.g., lipid material. One aspect of the invention involves hydroprocessing a feedstock in a hydroprocessing zone that is maintained at conditions that promote the efficiency of converting the lipid-containing feedstock into transportation fuel. Such conditions include one or more of maintaining CO content of the hydroprocessing zone at a predetermined amount and recycling or providing a hydrogen-containing gas to the hydroprocessing zone that has been treated to remove CO.
HYDROPROCESSING FEEDSTOCK CONTAINING LIPID MATERIAL TO PRODUCE TRANSPORTATION FUEL


FIELD OF THE INVENTION

[0002] This invention relates to the production of a fuel composition from a feedstock that comprises lipid material and mineral oil. More particularly, this invention relates to the production of at least one transportation fuel composition from a feedstock that comprises lipid material selected from the group consisting of triglycerides, fatty acid alkyl ester and a combination thereof, and mineral oil, wherein the transportation fuel is produced by hydroprocessing the feedstock.

BACKGROUND OF THE INVENTION

[0003] An increased demand for fuel has generated interest in finding feedstock other than crude oil or mineral oil. Various biological oils have been under study for their potential use as feedstock to produce fuel, particularly transportation fuel. For example, plant oils such as corn, rapeseed, canola and soybean oils and greases, such as inedible tallow, yellow, and brown greases, have been under study. A common feature of these types of oils is that they are composed of triglycerides and free fatty acids that generally have hydrocarbon chains from 8-20 carbons, which is also a common characteristic of crude oil.

[0004] U.S. Pat. No. 7,511,818 discloses a process for producing a hydrocarbon component useful as diesel fuel from biorenewable feedstocks such as plant oils and greases. The process involves hydrogenating and deoxygenating, i.e., decarboxylating and/or deoxygenating, the feedstock to provide a hydrocarbon fraction useful as a diesel fuel. An optional pretreatment step to remove contaminants such as alkali metals from the feedstock can also be carried out. The hydrocarbon fraction can be isomerized to improve cold flow properties.

[0005] U.S. Pat. No. 7,232,935 discloses a process for producing a hydrocarbon component of biological origin. The process comprises at least two steps, the first of which is a deoxygenation step, and the second of which is an isomerization step operated using a counter-current flow principle. A biological raw material containing fatty acids and/or fatty acid esters serves as the feed stock.

[0006] In spite of the ongoing efforts to produce fuels using biological materials as the feedstock, significant improvements still need to be sought as there are many problems that must be addressed. For example, transportation fuels such as diesel and various jet fuels must meet tight specifications. Biological materials alone cannot meet such specifications, without hydroprocessing. However, hydroprocessing biological materials is problematic to the extent that processing the biological materials using current processes quite often result in excess heats of reaction, a reduction in catalyst activity, and significant shifts in co-product formation. Accordingly, there is a need for additional improvement in producing fuels, particularly transportation fuels, from feedstock containing biologically derived material.

SUMMARY OF THE INVENTION

[0007] This invention provides processes for producing fuel, particularly transportation fuel, from biological material, e.g., lipid material. The product can advantageously include one or more high quality transportation fuels, such as gasoline, kerosene, jet fuel, and diesel.

[0008] According to one aspect of the invention, there is provided a method of producing transportation fuel, including providing a feedstock containing lipid material and mineral oil. Preferably, the lipid material can be selected from the group consisting of triglycerides, fatty acid alkyl esters and combinations thereof.

[0009] The feedstock can be hydroprocessed in a hydroprocessing zone to produce the transportation fuel. Preferably, the hydroprocessing zone can be maintained at not greater than 1000 vppm CO, based on total vapor content of the hydroprocessing zone.

[0010] In one embodiment of the invention, a hydrogen-containing stream that contains not greater than 200 vppm CO, based on total volume of the hydrogen-containing stream, is added to the hydroprocessing zone during hydroprocessing. Preferably, the hydrogen-containing stream that is added to the hydroprocessing zone during hydroprocessing contains greater than 60 vol % H₂, based on total volume of the hydrogen-containing stream.

[0011] In another embodiment, the hydroprocessing zone contains a CoMo or a NiMo hydroprocessing catalyst.

[0012] In yet another embodiment, the hydroprocessing can produce a hydroprocessed product comprised of a liquid fraction and a gas fraction, and the gas fraction can advantageously be separated from the liquid fraction, with at least a portion of the liquid fraction forming the transportation fuel. Preferably, the separated gas fraction can be treated or contacted with a membrane or an adsorbent to remove at least a majority of the CO from the gas stream to form a treated gas stream.

[0013] In one embodiment, the treated gas stream can contain greater than 60 vol % H₂, and not greater than 200 vppm CO, based on total volume of the treated gas stream. In another embodiment, the separated gas fraction can be treated or contacted with an adsorbent contained in a pressure swing adsorption system or a rapid cycle pressure swing adsorption system to form the treated gas stream. Preferably, at least a portion of the treated gas stream can be added to the hydroprocessing zone during hydroprocessing. Additionally or alternately, at least a portion of the separated gas fraction can be acid gas treated.

[0014] In general, the feedstock can include at least 0.05 wt % lipid material, based on total weight of the feedstock. Additionally or alternately, the lipid material portion of the feedstock can be comprised of at least 20 wt % fatty acid alkyl ester, based on total weight of the lipid material in the feedstock.

[0015] According to another aspect of the invention, there is provided a process for producing a transportation fuel that includes hydroprocessing feedstock containing lipid material and mineral oil in a hydroprocessing zone to produce a hydroprocessed product comprised of a liquid fraction and a gas fraction. At least a portion of the gas fraction can be separated from the hydroprocessed product, and at least a portion of the liquid fraction can be recovered as the transportation fuel.
In one embodiment, at least a majority of CO contained in the separated gas fraction can be removed from the separated gas fraction to form a treated gas stream, which can be provided or recycled to the hydroprocessing zone. In another embodiment, at least a portion of the gas fraction separated from the hydrotreated product can be acid gas treated prior to removing the CO.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE demonstrates two Cases (A and B) according to the invention in which differing levels of hydrogen are added with a combined mineral and biocomponent feed to hydrotreat the combined feed.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention can increase, or maximize, the amount of lipid or bio-material that can be converted to transportation fuel. One aspect of this increase maximization involves hydrotreating a feedstock that comprises the lipid material, while controlling the process to limit undesirable side reactions that can cause substantial increases in heats of reaction and that can produce compounds that negatively impact catalyst efficiency.

Feedstock

The feedstock that is used in the invention is preferably a combination feed containing both lipid material and 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. In one embodiment, the lipid material and mineral oil are mixed together prior to processing. In another embodiment, the lipid material and mineral oil are provided as separate streams into appropriate processing unit(s) or vessel(s).

The term “lipid material” as used according to the invention is a composition comprised of biological materials. Generally, these biological materials include vegetable fats/oils, animal fats/oils, fish oils, pyrolysis oils, and algae lipids/oils, as well as components of such materials. More specifically, the lipid material includes 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.

Major classes of lipids include, but are not necessarily limited to, fatty acids, glycerol-derivied lipids (including fats, oils and phospholipids), sphingosine-derived lipids (including ceramides, cererobides, gangliosides, and sphingomyelins), steroids and their derivatives, terpenes and their derivatives, fat-soluble vitamins, aromatic compounds, and long-chain alcohols and waxes.

In living organisms, lipids generally serve as the basis for cell membranes and as a form of fuel storage. Lipids can also be found conjugated with proteins or carbohydrates, such as in the form of lipoproteins and lipopolysaccharides.

Examples of vegetable oils that can be used in accordance with this invention include, but are not limited to: rape-seed (canola) oil, soybean oil, coconut oil, sunflower oil, palm oil, palm kernel oil, peanut oil, linseed oil, tall oil, corn oil, castor oil, jatropho oil, jojoba oil, olive oil, flaxseed oil, canola oil, safflower oil, babassu oil, tallow oil, and rice bran oil.

Vegetable oils as referred to herein can also include processed vegetable oil material. Non-limiting examples of processed vegetable oil material include fatty acids and fatty acid alkyl esters. Alkyl esters typically include C1-C2 alkyl esters. One or more of methyl, ethyl, and propyl esters are preferred.

Examples of animal fats that can be used in accordance with the invention include, but are not limited to, beef fat (tallow), hog fat (lard), turkey fat, fish fat/oil, and chicken fat. The animal fats can be obtained from any suitable source including restaurants and meat production facilities.

Animal fats as referred to herein also include processed animal fat material. Non-limiting examples of processed animal fat material include fatty acids and fatty acid alkyl esters. Alkyl esters typically include C1-C2 alkyl esters. One or more of methyl, ethyl, and propyl esters are preferred.

Algae oils or lipids are typically contained in algae in the form of membrane components, storage products, and metabolites. Certain algal strains, particularly microalgae such as diatoms and cyanobacteria, contain proportionally high levels of lipids. Algal sources for the algae oils can contain varying amounts, e.g., from 2 wt% to 40 wt% of lipids, based on total weight of the biomass itself.

Algal sources for algae oils include, but are not limited to, unicellular and multicellular algae. Examples of such algae include a rhodophyte, chlorophyte, heterokontophyte, trichophyte, glaucophyte, chlororachiophyte, Euglena, haptophyte, cryptomonad, dinoflagellum, phytoplankton, and the like, and combinations thereof. In one embodiment, algae can be of the classes Chlorophyceae and/or Haptophyta. Specific species can include, but are not limited to, Neochloris oleoabundans, Scenedesmus dimorphus, Euglena gracilis, Phaeodactylum tricornutum, Pleurochrysis carterae, Prymnesium parvum, Tetraselmis chui, and Chlamydomonas reinhardtii.

The lipid material portion of the feedstock is preferably comprised of triglycerides, fatty acid alkyl esters, or preferably combinations thereof. In one embodiment, the feedstock includes at least 0.05 wt%, for example at least 0.1 wt%, at least 0.5 wt%, or at least 1 wt% lipid material, based on total weight of the feedstock provided for processing into fuel.

In a particular embodiment of the invention, the feedstock includes not more than 40 wt%, preferably not more than 30 wt%, for example not more than 20 wt%, not more than 10 wt%, or not more than 5 wt% lipid material, based on total weight of the feedstock.

In one embodiment, the lipid material contains one or more triglycerides. Types of triglycerides can be determined according to their fatty acid constituents. The fatty acid constituents can be readily determined using Gas Chromatography (GC) analysis. This analysis involves extracting the fat or oil, saponifying (hydrolyzing) the fat or oil, preparing an alkyl (e.g., methyl) ester of the saponified fat or oil, and determining the type of (methyl) ester using GC analysis. In one embodiment, a majority (i.e., greater than 50%) of the triglyceride present in the lipid material can be comprised of C10 to C22 fatty acid constituents, based on total triglyceride present in the lipid material. For clarity, when a fatty acid or fatty acid ester molecule is specified as a “Cnn,” fatty acid, fatty acid constituent, or fatty acid ester, what is meant is that “nn” is the number of carbons on the carbon side of the carboxylate linkage, i.e., including the carboxylate carbon, whereas, in fatty acid esters, the ester carbons are not included in the
“C,” and are the carbons on the oxygen side of the carboxylate linkage, i.e., stopping at the carboxylate oxygen. Further, a triglyceride is a molecule having a structure identical to the reaction product of glycerol and three fatty acids. Thus, although a triglyceride is described herein as being comprised of fatty acids, it should be understood that the fatty acid component does not necessarily contain a carboxylic acid hydrogen. In the processes of the present invention, a majority of the triglyceride present in the lipid material can preferably be comprised of C<sub>10</sub> to C<sub>18</sub>, for example C<sub>12</sub> to C<sub>18</sub>, fatty acid constituents, based on total triglyceride present in the lipid material.

[0032] In a particular embodiment, the lipid material includes triglyceride, with at least 20 wt %, preferably at least 30 wt %, for example at least 40 wt %, of the triglyceride being comprised of lauric acid (C<sub>12</sub>0) constituents. Using the notation “C<sub>xx:yy</sub>" indicates a compound having “xx" carbons on the main chain, i.e., on the carbon side of the carboxylate group including the carboxylate carbon, and having “yy" double bonds on that main chain. Additionally or alternately, the lipid material includes triglyceride, with 40 wt % to 60 wt %, for example from 42 wt % to 58 wt % or from 44 wt % to 55 wt %, of the triglyceride being comprised of lauric acid constituents. Unless otherwise unambiguously specified, percentages expressed herein are percentages based on a number total of elements or constituents.

[0033] Additionally or alternately, the lipid material includes triglyceride, with at least 2 wt %, preferably at least 5 wt %, for example at least 10 wt %, of the triglyceride being comprised of myristic acid (C<sub>14</sub>0) constituents. Additionally or alternately, the lipid material includes triglyceride, with 10 wt % to 28 wt %, for example from 12 wt % to 26 wt % or 14 wt % to 24 wt %, of the triglyceride being comprised of myristic acid constituents.

[0034] Additionally or alternately, the lipid material includes triglyceride, with at least 2 wt %, preferably at least 3 wt %, for example at least 5 wt %, of the triglyceride being comprised of palmitic acid (C<sub>16</sub>0) constituents. Additionally or alternately, the lipid material includes triglyceride, with 2 wt % to 12 wt %, for example 3 wt % to 10 wt % or 5 wt % to 8 wt %, of the triglyceride being comprised of palmitic acid constituents.

[0035] Additionally or alternately, the lipid material includes triglyceride, with at least 0.5 wt %, preferably at least 1 wt %, for example at least 2 wt %, of the triglyceride being comprised of stearic acid (C<sub>18</sub>0) constituents. Additionally or alternately, the lipid material includes triglyceride, with 0.5 wt % to 60 wt %, for example 1 wt % to 55 wt % or 2 wt % to 50 wt %, of the triglyceride being comprised of stearic acid constituents.

[0036] Additionally or alternately, the lipid material includes triglyceride, with at least 5 wt %, preferably at least 6 wt %, for example at least 7 wt %, of the triglyceride being comprised of oleyic acid (C<sub>18</sub>1) constituents. Additionally or alternately, the lipid material includes triglyceride, with 5 wt % to 30 wt %, for example 6 wt % to 25 wt % or 7 wt % to 20 wt %, of the triglyceride being comprised of oleyic acid constituents.

[0037] Additionally or alternately, the lipid material includes triglyceride, with at least 2 wt %, preferably at least 3 wt %, for example at least 4 wt %, of the triglyceride being comprised of erucic acid (C<sub>22</sub>1) constituents. Additionally or alternately, the lipid material includes triglyceride, with 2 wt % to 70 wt %, for example 3 wt % to 65 wt % or 4 wt % to 60 wt % of the triglyceride being comprised of erucic acid constituents.

[0038] In one embodiment, the lipid material comprises fatty acid alkyl ester. Preferably, the fatty acid alkyl ester comprises fatty acid methyl esters (FAME), fatty acid ethyl esters (FAEE), and/or fatty acid propyl esters. Additionally or alternately, the lipid material includes triglyceride, with at least 5 wt %, preferably at least 10 wt %, for example at least 20 wt %, of the triglyceride being comprised of erucic acid constituents. Additionally or alternately, the lipid material includes triglyceride, with at least 5 wt %, preferably at least 10 wt %, for example at least 20 wt %, of the triglyceride being comprised of erucic acid constituents.

[0039] In a particular embodiment of the invention, the lipid material portion of the feedstock comprises fatty acid alkyl ester, and a majority of the fatty acid alkyl ester present in the lipid material is preferably FAME.

[0040] In another embodiment of the invention, the lipid material portion of the feedstock can comprise at least 20 wt %, preferably at least 30 wt %, for example at least 40 wt % of the triglyceride being comprised of erucic acid alkyl ester, preferably FAME, based on total weight of the lipid material. Preferably, a majority of the fatty acid constituents of the fatty acid alkyl ester, preferably FAME, can be selected from the group consisting of caprylic acid (C<sub>8</sub>0), capric acid (C<sub>10</sub>0), lauric acid (C<sub>12</sub>0), myristic acid (C<sub>14</sub>0), palmitic acid (C<sub>16</sub>0), palmitoleic acid (C<sub>16</sub>1), stearic acid (C<sub>18</sub>0), oleic acid (C<sub>18</sub>1), linoleic acid (C<sub>18</sub>2), linolenic acid (C<sub>18</sub>3), erucic acid (C<sub>22</sub>1), and combinations thereof. In a particular embodiment, a majority of the fatty acid constituents of the FAME present in the lipid material portion of the feedstock can comprise at least 20 wt %, preferably at least 30 wt %, of the triglyceride being comprised of erucic acid constituents. Additionally or alternately, the lipid material includes triglyceride, with at least 5 wt %, preferably at least 10 wt %, of the triglyceride being comprised of erucic acid constituents.

[0041] The feedstock provided according to this invention comprises a mineral oil. 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 (optionally but preferably at least partially denitrogenated and/or at least partially desulfurized), diesel boiling range distillate fraction (optionally but preferably at least partially denitrogenated and/or at least partially desulfurized), jet fuel boiling range distillate fraction (optionally but preferably at least partially denitrogenated and/or at least partially desulfurized), kerosene boiling range distillate fraction (optionally but preferably at least partially denitrogenated and/or at least partially desulfurized), and coal liquids. The mineral oil that is included as a part of the feedstock can comprise any one of these example streams or any combination thereof that would be suitable for hydrotreating with the lipid material portion. Preferably, the feedstock does not contain any appreciable asphaltenes. In one embodiment, the mineral oil can be mixed with the lipid material portion and then hydrotreated to form a hydrotreated material. In another embodiment, the mineral oil can be hydrotreated to reduce the nitrogen and/or sulfur content before being mixed with the lipid material portion.

[0042] The mineral oil component can contain nitrogen-containing compounds (abbreviated as “nitrogen”). For example, the mineral oil can contain at least 5 wppm nitrogen, based on total weight of the mineral oil component. Preferably, the mineral oil will contain not greater than 1.0 wt % nitrogen, based on total weight of the mineral oil component. In general, at least a majority of the nitrogen will be in the form of organonitrogen compounds.

[0043] The mineral oil will typically contain sulfur-containing compounds (abbreviated as “sulfur” or “sulfur content”). Such compounds can typically be present in the mineral oil at a sulfur content greater than 500 wppm, or often
greater than 0.1 wt%, based on total weight of the mineral oil. Preferably, the sulfur content of the mineral oil will not be greater than 6 wt%, preferably not greater than 4 wt%, based on total weight of the mineral oil.

In one embodiment, the feedstock can include not greater than 99.5 wt%, for example not greater than 99 wt%, not greater than 98 wt%, not greater than 95 wt%, not greater than 90 wt%, or not greater than 85 wt% mineral oil, based on total weight of the feedstock.

Additionally or alternately, the feedstock can include at least 50 wt% mineral oil, based on total weight of the feedstock. Preferably, the feedstock can include at least 60 wt%, for example at least 70 wt%, at least 75 wt%, at least 80 wt%, or at least 85 wt% mineral oil, based on total weight of the feedstock.

According to one aspect of the invention, the feedstock that is hydrogenated can have an initial boiling point of at least 100° C., preferably at least 150° C., for example at least 180° C. or at least 200° C. The basic test method of determining the boiling points or ranges of such feedstock, as well as the fuel compositions produced according to this invention, can be by performing batch distillation according to ASTM D86-06e1, Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure.

Additionally or alternately, the feedstock can have a final boiling point of not greater than 500° C., preferably not greater than 450° C., for example not greater than 400° C.

The feedstock can preferably be converted to a product by hydrotreating, preferably in a continuous operation process. In one embodiment, hydrotreating can be carried out at a liquid hourly space velocity (LHSV) from 0.1 hr⁻¹ to 20 hr⁻¹, for example from 0.1 hr⁻¹ to 5 hr⁻¹.

Hydroprocessing

The transportation fuel produced according to this invention can advantageously include hydrotreating of the desired feedstock in a hydrotreating zone. Hydroprocessing is a process in which feed material is treated or contacted with hydrogen, optionally but preferably in the presence of a hydroprocessing catalyst. The hydrogen (and/or catalyst) in the process serves to reduce or remove hetero- (non-carbon) atoms from the feed such as nitrogen, sulfur, and oxygen. The hydrogen (and/or catalyst) in the process can also be used to saturate carbon compounds and/or to increase the ratio of isoparaffins to normal paraffins in the product composition. Examples of hydrotreating processes for lipid (bio-) material include, but are not limited to, hydrodeoxygenation, hydrodearomatization, demethylation, deoxygenation, hydrodearomatization, and hydrodeoxygenation. Additional (or alternate) hydrotreating processes for mineral feeds can include hydrodenitrogenation, hydrodesulfurization, and the like.

CO Control

The hydrotreating zone can be maintained during the process at conditions that promote the efficiency of converting the lipid-containing feedstock into transportation fuel. In one embodiment, the hydrotreating zone can be maintained at not greater than 1000 vppm CO (carbon monoxide), for example not greater than 900 vppm CO, not greater than 800 vppm CO, or not greater than 700 vppm CO, based on total vapor content of the hydrotreating zone.

It may also be preferred that, during hydrotreating, a hydrogen-containing stream be added to the hydrotreating zone. Preferably, the hydrogen-containing stream contains greater than 60 vol % H₂, more preferably at least 70 vol % H₂, for example at least 80 vol % H₂ or at least 90 vol % H₂, based on total volume of the hydrogen-containing stream.

The hydrogen-containing stream can also be referred to by other names such as a treated gas stream, a hydrogen stream, or a hydrogen treat gas stream. It is not necessary that the stream be pure H₂, as long as the stream does not contain levels of impurities that would substantially negatively impact hydrotreating of the feedstock to efficiently form transportation fuel.

In one embodiment of the invention, the hydrogen-containing stream added to the hydrotreating zone contains not greater than 200 vppm CO, preferably not greater than 100 vppm CO, for example not greater than 50 vppm CO, not greater than 10 vppm CO, or not greater than 5 vppm CO, based on total volume of the hydrogen-containing stream added to the hydrotreating zone during hydrotreating.

The amount of hydrogen added to the hydrotreating zone should be sufficient to reduce one or more of nitrogen, sulfur, and oxygen atoms in the liquid product portion or fraction by at least a desired amount. In one embodiment, the hydrogen-containing stream added to the hydrotreating zone can be added at volume ratio of hydrogen-containing stream to feedstock (i.e., treat gas rate) from 300 scf/bbl (55 Nm³/m³) to 5000 scf/bbl (890 Nm³/m³). Preferably, the hydrogen-containing treat gas rate can be from 2000 scf/bbl (360 Nm³/m³) to 4000 scf/bbl (710 Nm³/m³).

Hydrodeoxygenation

According to an aspect of the invention, at least a portion of the feedstock can be hydrodeoxygenated during hydrotreating or as a part of the hydrotreating process. Hydrodeoxygenation refers to oxygen reduction and/or removal from a compound by means of hydrogen. Water is typically liberated in the reaction, olefinic (double) bonds may be hydrogenated (saturated), and various sulfur and nitrogen compounds may be removed, if present. Hydrodeoxygenation reactions are typically exothermic.

In one embodiment, hydrodeoxygenation can be carried out in a hydrotreating zone at a pressure from 0.1 MPa to 20 MPa, for example from 1 MPa to 15 MPa. Additionally or alternately, hydrodeoxygenation can be carried out in a hydrotreating zone at a temperature from 100° C. to 500° C., for example from 150° C. to 350° C.

In a preferred embodiment, hydrodeoxygenation can be carried out by treating the feedstock in the presence of a catalyst containing at least one Group VIII metal, at least one Group VII metal, or a combination thereof. In one embodiment, the catalyst can preferably comprise Pt, Pt, Rh, Ni, NiMo, or CoMo metals, for example in the form of a supported catalyst, with a preferred support comprising activated carbon, alumina, silica or a combination thereof.

Preferably, feedstock can be brought into contact or can be treated with the catalyst in the presence of hydrogen at operating temperatures and pressures sufficient to hydrodeoxygenate at least a majority (i.e., more than 50 wt %) of any alcohols and to saturate at least a majority of any olefins present in the feed. The reaction temperature used in the hydrotreating zone can be in the range from 100° C. to 350° C., preferably from 150° C. to 300° C. or from 150° C.
to 275°C. Additionally or alternately, the reaction pressure within the hydrosprocessing zone can be in the range from 5 bara to 150 bara (0.5 MPag to 15 MPag), preferably from 10 bara to 100 bara (1.0 MPag to 10 MPag), for example from 10 bara to 90 bara (1.0 MPag to 9.0 MPag).

Hydrotreating

According to an aspect of the invention, at least a portion of the feedstock can be hydrotreated during hydrosprocessing or as a part of the hydrosprocessing process. Hydrotreating typically results in the reduction and/or removal of hetero- (non-carbon) atoms, such as nitrogen and/or sulfur, from the feedstock.

In one embodiment, hydrotreating can be carried out at a temperature from 400°F to 900°F (204°C to 482°C), for example from 650°F to 850°F (343°C to 454°C). Additionally or alternately, hydrotreating can be carried out at a pressure from 500 psig to 5000 psig (3.5 MPag to 34.6 MPag), for example from 1000 psig to 3000 psig (7.0 MPag to 20.5 MPag).

A preferred hydrotreating catalyst can comprise at least one Group VIIIB metal and at least one Group VIII metal, either as a bulk catalyst or optionally supported on a porous refractory base material. The Groups referred to herein are Groups found in the Periodic Table of the Elements in Hawley’s Condensed Chemical Dictionary, 13th Edition. Examples of such base materials include, but are not limited to, alumina, silica, alumina-silica, zirconia, and combinations thereof. Preferred catalyst metals useful in the process of this invention can include, but are not limited to, cobalt, molybdenum, nickel, nickel-tungsten, cobalt-tungsten, nickel-molybdenum, nickel-cobalt-molybdenum, nickel-cobalt-tungsten, nickel-molybdenum-tungsten, and cobalt-molybdenum-tungsten, optionally but preferably supported with activated carbon, alumina, silica, or a combination thereof.

Hydrocracking

According to an aspect of the invention, at least a portion of the feedstock can be hydrocracked during hydrosprocessing or as a part of the hydrosprocessing process. Hydrocracking is a particular hydrosprocessing process that includes cracking or breaking larger carbon number molecules into smaller carbon number molecules.

In one embodiment, hydrocracking of the feedstock can be carried out in the hydrosprocessing zone at a temperature in the range from 600°F to 900°F (316°C to 482°C), for example from 650°F to 850°F (343°C to 454°C). Additionally or alternately, hydrocracking of the feedstock can be carried out in the hydrosprocessing zone at a pressure in the range from 200 psia to 4000 psia (13 atm to 270 atm, or 1.4 MPa to 27.6 MPa), for example from 500 psia to 3000 psia (34 atm to 200 atm, or 3.4 MPa to 20.7 MPa).

Hydroprocessing can typically be carried out in a hydrosprocessing zone that includes a catalyst capable of carrying out a cracking reaction, which catalyst, in one embodiment, is comprised of an amorphous or zeolitic base and one or more Group VIII and/or Group VIIIB metal hydrogenation components. In another embodiment, the hydrocracking catalyst can comprise a crystalline zeolite cracking base upon which is deposited at least one Group VIII or Group VIIIB metal hydrogenating component. The Groups referred to herein are Groups found in the Periodic Table of the Elements in Hawley’s Condensed Chemical Dictionary, 13th Edition. Examples of Group VIII metals can include Fe, Co, and Ni, preferably Co and/or Ni; examples of Group VIIIB metals include Mo and/or W.

The zeolite cracking bases, which can be used as a component of the hydrocracking catalyst, are also generally referred to as molecular sieves. These materials can be composed of silica, alumina, and one or more exchangeable cations, such as sodium, magnesium, calcium, and one or more rare earth metals.

In one embodiment, a large pore crystalline molecular sieve can be used. Preferably, the crystalline molecular sieve has a Constrain Index of less than 2, more preferably less than 1. The method by which the Constrain Index is determined is fully described in U.S. Pat. No. 4,016,218, which is incorporated herein by reference.

In another embodiment, the hydrocracking catalyst can be comprised of a molecular sieve having a pore size of at least 7 angstroms, preferably at least 7.4 angstroms, for example at least 8 angstroms. Additionally or alternately, the hydrocracking catalyst can be comprised of a molecular sieve having a pore size of not greater than 15 angstroms, for example not greater than 12 angstroms.

Examples of zeolite molecular sieves that can be used in the hydrocracking catalyst can include, but are not limited to, Zeolite Beta, Zeolite X, Zeolite Y, faujasite, Ultrastable Y (USY), Dealuminized Y (Deal Y), Mordenite, ZSM-3, ZSM-4, ZSM-18, ZSM-20, and the like, and combinations thereof.

Typically, the hydrocracking catalyst has at least some acidity. Preferably, the hydrocracking catalyst has an alpha value greater than 1, for example greater than 5 or greater than 10. The alpha value is a measure of zeolite acidic functionality and is described in greater detail in U.S. Pat. No. 4,016,218 and in J. Catalysis, Vol. VI, pages 278-287 (1966).

It is not necessary that the hydrocracking catalyst be highly acidic, although a highly acidic catalyst can be used. In one embodiment, the hydrocracking catalyst has an alpha value of not greater than 200, for example not greater than 100.

Hydrocracking can be carried out under conditions effective for producing the desired fuel product. Preferably, hydrocracking can be carried out at an average reaction temperature from 300°F to 900°F (149°C to 482°C), for example from 550°F to 800°F (289°C to 427°C).

Hydrocracking can also be preferably carried out at an average reaction pressure from 400 psia to 3000 psia (27 atm to 200 atm, or 2.8 MPa to 20.7 MPa), preferably from 500 psia to 2000 psia (34 atm to 136 atm, or 3.5 MPa to 13.8 MPa).

Hydrogenation

According to an aspect of the invention, at least a portion of the feedstock can be hydrogenated during hydrosprocessing or as a part of the hydrosprocessing process. Hydrogenation generally involves saturating unsaturated carbon bonds, including saturating aromatic rings. Preferably, hydrogenation can be carried out in the hydrosprocessing zone at a temperature in the range from 300°F to 900°F (149°C to 427°C), for example from 400°F to 600°F (204°C to 316°C).

In one embodiment, hydrogenation can be carried out in the hydrosprocessing zone at a pressure from 50 psig to
2000 psig (0.34 MPag to 13.8 MPag), for example from 100 psig to 500 psig (0.69 MPag to 3.4 MPag).

[0075] In one embodiment, hydrotreating can be carried out in a hydrotreating zone that includes a catalyst capable of carrying out a hydrogenation reaction. Catalysts that are useful in carrying out hydrotreating reactions are generally also useful in hydrogenation reactions. Exemplary catalysts can include non-sulfided catalysts containing one or more of Pt and Pd, preferably dispersed on a support, such as alumina, silica, silica-alumina, carbon, or the like, or a combination thereof. A particularly preferred support is silica-alumina.

Dewaxing

[0076] According to an aspect of the invention, at least a portion of the feedstock can be dewaxed during hydrotreating or as a part of the hydrotreating process. Dewaxing in this invention refers to catalytic dewaxing in which a heavier hydrocarbon reacts with hydrogen in the presence of a dewaxing catalyst at dewaxing reaction conditions. The catalytic dewaxing process is, in essence, a type of hydrotreating process. Dewaxing is more particularly based on selective hydrocracking of predominantly normal paraffins.

[0077] Dewaxing typically incorporates the use of a molecular sieve-based catalyst in which active hydrocracking sites are accessible to contact with the paraffin molecules and preferably not accessible to aromatic type compounds. The reactions conditions in dewaxing are preferably effective to improve at least one of freeze point, cloud point, pour point, and cold filter plug point of the desired transportation fuel produced according to the invention.

[0078] Any catalyst effective in dewaxing hydrocarbon can be used. In one embodiment, a hydrotreating catalyst can be used as a dewaxing catalyst, particularly those that include one or more of Co, Ni, and Fe, in combination with one or more of Mo or W. In another embodiment, a hydrodehydrogenation catalyst or a hydrogenation catalyst can be used as a dewaxing catalyst, such as Pt and/or Pd noble metals on an acidic support. Additionally or alternatively, the dewaxing catalyst can include an acidic oxide support or carrier. Non-limiting examples of such carrier can include, but are not limited to, silica, alumina, silica-alumina, shape selective molecular sieves, and the like, and combinations thereof. Preferably, the carrier can be combined with at least one catalytic component such as titania, zirconia, vanadia, other Group IIa, IVB, VB, or VIB oxides, ferricrete, mordenite, ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-22 (also known as theta one or TON), ZSM-48, silicoaluminophosphates (SAPOs) including SAPO-11, -36, -37 and -40, zeolite Y sieves such as ultrastable Y, and the like, as well as combinations thereof. If striping is not available prior to dewaxing and/or if the sulfur content of the hydrotreated and separated heavy fraction is high enough to result in dewaxing catalyst activity reduction or loss, zeolites containing framework transition metals having improved sulfur resistance (see, e.g., U.S. Pat. Nos. 5,185,136, 5,185,137, and 5,185,138) may be employed.

[0079] The dewaxing can be carried out at reaction conditions which include an average hydrotreating zone temperature from 300° F. to 900° F. (149° C. to 482° C.), for example from 550° F. to 800° F. (289° C. to 427° C.). Dewaxing can also be carried out at any reaction pressure from 400 psia to 2000 psia (27 atm to 136 atm, or 2.8 MPa to 13.8 MPa). Dewaxing can also be carried out at reaction conditions which include an average hydrotreating zone temperature from 300° F. to 900° F. (149° C. to 482° C.), for example from 550° F. to 800° F. (289° C. to 427° C.). Dewaxing can also be carried out at any reaction pressure from 400 psia to 2000 psia (27 atm to 136 atm, or 2.8 MPa to 13.8 MPa).

Hydroisomerization

[0080] According to an aspect of the invention, at least a portion of the feedstock can be hydroisomerized during hydrotreating or as a part of the hydrotreating process. The terms “hydroisomerize,” “hydroisomerized,” and “hydroisomerization,” as used herein, all refer to a catalytic process in which feedstock is contacted with catalyst in the presence of hydrogen and in which a substantial portion of waxy paraffin compounds in the feedstock is converted to non-waxy (e.g., branched and/or iso-) paraffins, while at the same time minimizing conversion of normal paraffins (n-paraffins) by cracking. Hydroisomerization can effectively increase the volume of transportation fuel formed in the overall process. In particular, a hydrotreating process in which at least a portion of the feedstock is hydroisomerized can reduce the heavier portion of the feedstock by transforming that component into an additional volume of transportation fuel.

[0081] Hydroisomerization can be carried out using a shape selective molecular sieve catalyst. Large pore crystalline molecular sieves or intermediate pore molecular sieves are particularly effective.

[0082] Large pore crystalline molecular sieves useful in the hydroisomerization aspect this invention preferably have a Constraint Index of less than 2. Intermediate pore crystalline molecular sieves useful in the hydroisomerization step of this invention preferably have a Constraint Index of at least 2. The method by which the Constraint Index is determined is fully described in U.S. Pat. No. 4,016,218, which is incorporated herein by reference.

[0083] In one embodiment, the molecular sieves used in the hydroisomerization aspect of this invention have an alpha value of less than 100. The alpha value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst. The alpha test gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time) of the test catalyst relative to the standard catalyst which is taken as an alpha of 1 (Rate Constant=0.016 sec⁻¹). The alpha test is described in U.S. Pat. No. 3,354,078 and in J. Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980), to which reference is made for a description of the test. The experimental conditions of the test used to determine the alpha values referred to in this specification include a constant temperature of 538° C. and a variable flow rate as described in detail in J. Catalysis, 61, 395 (1980).

[0084] Non-limiting examples of large pore molecular sieve catalysts can include, but are not limited to, molecular sieves selected from the group consisting of zeolite beta, mordenite, zeolite Y, ZSM-20, ZSM-4 (omega), zeolite L, VPI-5, SAPO-37, MeAPO-37, AIPO-8, cloverite, and combinations thereof. Non-limiting examples of intermediate pore molecular sieves can include, but are not limited to, ZSM-22, ZSM-23, ZSM-48, SAPO-11, SAPO-5, MeAPO-11, MeAPO-5, and combinations thereof; and an example of a non-intersecting two-dimensional intermediate pore molecular sieve is ZSM-35 (synthetic ferrierte).

[0085] Catalysts useful in the hydroisomerization step preferably contain a hydrogenation metal, which can be one or more noble metals, one or more non-noble metals, or a combination thereof. Suitable noble metals include Group VIII noble metals, such as platinum and other members of the platinum group, such as iodine, palladium, and rhodium, and combinations of these metals. Suitable non-noble metals include those of Groups VB, VIB, and (the non-noble metals of) VIII of the Periodic Table. Preferred non-noble metals include, but are not limited to, chromium, molybdenum, tungsten, cobalt, nickel, and combinations of these metals,
including cobalt-molybdenum, nickel-tungsten, nickel-molybdenum, cobalt-nickel-molybdenum, nickel-molybdenum-tungsten, cobalt-molybdenum-tungsten, and cobalt-nickel-tungsten. The non-noble metals can be pre-sulfided prior to use by exposure to a sulfur-containing gas such as hydrogen sulfide at an elevated temperature to effect conversion (e.g., of the oxide form) to the corresponding sulfide form of the metal.

In one embodiment, the metal can be incorporated into the catalyst by any suitable method or combination of methods, such as by impregnation or ion exchange into the zeolite. The metal can be incorporated in the form of a cationic, anionic, or neutral complex. Cationic complexes of the type Pt(NH₃)₄⁺⁺ can be used for exchanging metals onto the zeolite. Anionic complexes such as the molybdate or metatungstate ions can also be useful for impregnating metals into the catalysts.

In one embodiment, the hydroisomerization catalyst can comprise a zeolite and a hydrogenation metal. In one preferred embodiment, the catalyst can comprise from 0.01 wt % to 20 wt %, for example from 0.1 wt % to 15 wt %, of hydrogenation metal, based on total weight of the catalyst.

The molecular sieve, in one embodiment, can include a binder (or matrix) material. Binder materials are preferably metal oxides. Non-limiting examples of metal oxide binders can include, but are not limited to, alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia-zirconia, and the like, and combinations thereof. In one embodiment, the catalysts are ZSM-23, ZSM-48 or SAPO-11, and zeolite beta, which are combined with alumina, and formed into a useable shape by methods such as extrusion or tabletting.

Hydroisomerization can be carried out in the presence of hydrogen gas under hydroprocessing conditions of elevated temperature and pressure. Particular reaction conditions for hydroisomerization can depend on the feedstock used, the catalyst used, whether or not the catalyst is sulfided, the desired yield, and the desired properties of the desired product, inter alia. Conditions under which the hydroisomerization process of this invention can be carried out include temperatures from 600°F to 750°F (315°C to 399°C), for example from 600°F to 700°F (315°C to 371°C), and pressures from 1.7 atm to 204 atm (25 psia to 3000 psia, or 170 kPa to 20.7 MPa), for example 6.8 atm to 17 atm (100 psia to 2500 psia, or 1.4 MPa to 17.3 MPa). Hydroisomerization processes in this context refer to the hydrogen partial pressure within the hydroisomerization reactor, although the hydrogen partial pressure is the same as or substantially the same as the total pressure when the treat gas is 100% or substantially 100% hydrogen. However, the total pressure will be greater than the hydrogen partial pressure when the treat gas contains hydrogen and other usually relatively inert gases.

Hydrofinishing

In one embodiment, at least a portion of the feedstock can be hydrofinishing during hydroprocessing or as a part of the hydroprocessing process. Hydrofinishing can refer to treating the feedstock with hydrogen to saturate at least a portion of the feedstock for improved (oxidative) stability.

Hydroprocessing catalysts that can accomplish a hydrofinishing aspect can include catalysts containing at least one Group VII metal and at least one Group VIII metal. Such a catalyst can include at least one noble metal having a strong hydrogenation function, such as platinum and/or palladium. A mixture of metals can be present as bulk metal catalysts, wherein the amount of metal is 50 wt % or greater, for example 60 wt % or greater or 70 wt % or greater, based on the catalyst. Suitable metal oxide supports, when present, can include relatively low acidic oxides, such as silica, alumina, silica-alumina, titania, and combinations thereof, preferably at least including alumina. Non-noble metal content of the catalyst can be up to 20 wt %, but is preferably not greater than about 1 wt %.

In one embodiment, the catalyst can be a mesoporous material belonging to the M41S class or family of catalysts. Examples can include, but are not limited to, MCM-41, MCM-48, MCM-50, and the like, and combinations thereof. The term “mesoporous” refers to catalysts having pore sizes ranging from 15 to 100 angstroms. The mesoporous materials can include a metal hydrogenation component, which can be at least one Group VIII metal. Preferred are noble Group VIII metals, particularly Pt and/or Pd.

In one embodiment, the hydrofinishing aspect can be carried out at a temperature in a range from 150°C to 350°C, for example 180°C to 250°C. Total pressure in the hydroprocessing zone can be in a range from 400 psig to 3000 psig (2.8 MPag to 20.7 MPag).

Separation of Liquid and Gas Streams Formed in Hydroprocessing

Hydroprocessing the feedstock in this invention can advantageous produce a hydroprocessed product comprised of a liquid fraction and a gas fraction. The gas fraction can be separated from the liquid fraction, with at least a portion of the liquid fraction preferably forming a transportation fuel. Separation can be accomplished by any suitable means. Such means can include, but are not limited to, flash separation, distillation, and the like.

Treatment of Gas Stream to Form Hydrogen Stream

In one embodiment, the separated gas fraction can be further processed to remove CO or to reduce the CO content in order to form a treated gas fraction. Preferably, the hydrogen-containing stream added to the hydroprocessing zone can comprise at least a portion of this treated gas fraction.

In one particular embodiment, a gas fraction can be separated from the hydroprocessed product and can then be treated or contacted with a membrane or an adsorbent to remove at least a majority (i.e., at least 50%) of the CO from the gas stream to form a treated gas stream. Treatment/contact/adsorption can be carried out to recover a treated gas stream comprised of not greater than 50 vppm CO, preferably not greater than 20 vppm CO, for example not greater than 10 vppm CO or not greater than 5 vppm CO, based on total volume of the treated gas stream.

In one embodiment, at least a portion of the gas fraction of the hydroprocessed product can be contacted with a membrane to remove at least a portion of the CO from the gas stream. The membrane can preferably be a membrane preferential for permeation of hydrogen gas over carbon monoxide (and optionally carbon dioxide). Examples of such membranes can include, but are not limited to, membranes comprised of silicon rubber, butyl
rubber, polycarbonate, poly(phenylene oxide), nylon 6.6, polystyrene, polysulfones, polyamides, polyimides, polyethers, polyarylene oxides, polyurethanes, polyesters, and combinations and copolymers thereof. In one preferred embodiment, the hydrogen gas permeation membrane can be of hollow fiber construction.

In a particular embodiment, at least a portion of the gas fraction of the hydrossociated product can be contacted with the preferential hydrogen gas permeation membrane at a pressure at which the non-permeate pressure can remain sufficiently high to allow downstream use without further compression. Preferably, at least a portion of the gas fraction of the hydrossociated product can be passed along or across the preferential hydrogen gas permeation membrane at a pressure in the range from 500 psig to 2000 psig (34 atm to 140 atm, or 3.4 MPag to 13.8 MPag), for example from 800 psig to 1200 psig (54 atm to 82 atm, or 5.5 MPag to 8.3 MPag). A hydrogen-rich gas can permeate through the membrane, and the permeate can generally experience a pressure drop in the range from about 300 psig to 700 psig (2.1 MPag to 4.7 MPag) as it passes through the membrane. After membrane separation, the permeate can generally be at a pressure in the range from 200 psig to 1500 psig (1.4 MPag to 10.3 MPag).

In another embodiment of the invention, an adsorbent material can be used to remove at least a majority of the CO from the gas stream to form the treated gas stream. In this embodiment, the adsorbent material can be an adsorbent having a greater affinity for carbon monoxide (and optionally also a greater affinity for carbon dioxide and/or methane) than for hydrogen. The adsorbent material may be a molecular sieve, activated carbon, or a combination thereof. Alternatively, or additionally, one or more of calcium and sodium aluminosilicate zeolites can be employed. Carbon molecular sieves and silica molecular sieves can additionally be used. Suitable zeolite sieves can include, but are not limited to, types 5A, 10X, and 13X zeolite molecular sieves, mordenites, and the like. Preferred zeolite sieves can include type 5A zeolite sieves and molecular sieves with comparable pore size and molecular attraction affinity.

In another embodiment, the adsorbent material can be an adsorbent having a greater affinity for carbon monoxide than for hydrogen, carbon dioxide, and methane. Non-limiting examples of such materials can include copper-exchanged Y-type aluminosilicate zeolite molecular sieves, copper-exchanged alumina, copper-exchanged activated carbon, and combinations thereof. In one particular embodiment, the adsorbent material can be or include copper aluminosilicate zeolite molecular sieve material, such as commercially available under the tradename NKK type adsorbent from Nippon Kokan K.K. of Tokyo, Japan.

According to an aspect of the invention, adsorption of the CO from the gas stream can be carried out in a pressure swing adsorption system. In a pressure swing adsorption system, a gas stream can be passed through a bed of an adsorbent material which selectively adsorbs one or more of the components of the gas stream. Treated gas, enriched in the unadsorbed gaseous component(s), can then be withdrawn from the bed and either further treated or in some other way recycled or utilized.

A pressure swing adsorption system typically employs at least two adsorbent beds operated on cycles that are sequenced to be out of phase with one another, so that, when at least one bed is in the adsorption or production step, at least one other bed can be in a regeneration step. Multiple adsorption beds may be connected in series or in parallel. Generally, series arrangements of beds are preferred for obtaining a high purity gas product, with parallel arrangements of beds typically being preferred for purifying a large quantity of a gaseous mixture in a short time cycle.

In a preferred embodiment, adsorption of the CO from the gas stream is carried out in a rapid cycle pressure swing adsorption system. Rapid cycle pressure swing adsorption (RCPSA) is primarily characterized relative to standard or conventional pressure swing adsorption (PSA) by relatively shorter, or more rapid, cycles. For example, RCPSA cycle times are typically less than a minute, preferably not greater than 30 seconds, for example not greater than 15 seconds, not greater than 10 seconds, or not greater than 5 seconds, while PSA cycle times are typically 2-4 minutes or greater. Hardware (e.g., valves, piping, configuration of vessels) to perform these cycles also tends to differ considerably, and commercial vendors of equipment for both PSA and RCPSA exist.

An example of an RCPSA apparatus that can be used according to this invention is described in U.S. Patent Publication Application No. 2009/0071332. In an embodiment, the CO can be removed using an RCPSA having a rotary valving system to conduct the gas flow through a rotary sorber module that contains a number of separate adsorbent beds or “tubes,” each of which can be successively cycled through the sorption and desorption steps as the rotary module completes the cycle of operations. In this embodiment, the rotary sorber module can preferably be comprised of multiple tubes held between two seal plates on either end of the rotary sorber module, which seal plates can be in contact with a stator comprised of separate manifolds, wherein the inlet gas can be conducted to the RCPSA tubes, and wherein processed purified product gas and the tail gas exiting the RCPSA tubes can be conducted away from the rotary sorber module. By suitable arrangement of the seal plates and manifolds, a number of individual compartments or tubes may pass through the characteristic steps of the complete cycle at any one time.

In RCPSA, flow and pressure variations required for the sorption/desorption cycle can change in a number of separate increments on the order of seconds per cycle, which can smooth out the pressure and flow rate pulsations encountered by the compression and valving machinery. In this form, the RCPSA module can include valving elements angularly spaced around the circular path taken by the rotating sorption module, so that each compartment can be successively passed to a gas flow path in the appropriate direction and pressure to achieve one of the incremental pressure/flow direction steps in the complete RCPSA cycle. Example RCPSA modules and valving arrangements that can be used according to this invention are described in U.S. Reissue Patent Nos. RE 40,006 and RE 38,493.

Without being limited by theory, one significant advantage of the RCPSA technology includes a highly efficient use of the adsorbent material. The quantity of adsorbent required with RCPSA technology is typically a fraction of that required for standard PSA technology to achieve the same separation quantities and qualities. RCPSA technology also tends to have a small foot print, which allows technology to be deployed closer to the hydrossociation units in an efficient manner. Because of the relatively fast cycle times, RCPSA technology can also exhibit added capability to pro-
duce treat gas hydrogen with low CO content in a steady manner (i.e., steady state can be achieved relatively quickly, e.g., in less than about an hour).

Acid Gas Treating

[0107] According to an aspect of the invention, the gas stream separated from the hydroprocessed product can be acid gas treated. Acid gas treatment refers to treating a gas stream to remove or to lower acid gas components. Acid gas components can include one or more acid gases, such as those selected from the group consisting of CO₂, H₂S, SO₂, CS₂, HCN, COS, and mercaptans.

[0108] Acid gas treatment can preferably comprise contacting the gas stream containing at least one of the acid gas components with an organic solvent or an aqueous solution of an organic solvent in a gas scrub or a liquid-liquid extraction. The solvent can be a physical solvent or a chemical solvent. Physical solvents generally rely on a physical absorption process. In such a process the acid gases can dissolve in a physical solvent. Examples of physical solvents can include, but are not limited to, cyclohexamethylene sulfonate (sulfone) and its derivatives, aliphatic acid amides, NMP (N-methylpyrrolidone), N-alkylated pyrrolidones and corresponding piperidones, methanol, mixtures of dialkylethers of polyethylene glycols (e.g., SELEXOL® from Union Carbide of Danbury, Conn.), and combinations thereof.

[0109] Chemical solvents can tend to work on the basis of chemical reactions in which the acid gases are converted into compounds that are simpler to remove. Examples of such chemical solvents can include aqueous solutions of one or more amines, preferably alkanolamines. Preferred amines include those that form salts when acid gases pass through a solution containing the amine. These salts can then preferably be decomposed by heating or stripping and can be re-used. Preferred alkanolamines can include, but are not limited to, monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropylamine (DIPA), aminoethoxyethanol (AEE), methyldiethanolamine (MDEA), and combinations thereof.

Reactor Type

[0110] Any reactor or catalyst arrangement suitable for hydroprocessing the feedstock of this invention can be used. For example, the feedstock can be provided to a hydroprocessing zone so as to contact a fixed bed of catalyst, a fluidized bed, or an ebullating bed. An example of one type of configuration includes a trickle-bed operation in which a liquid feedstock trickles through a stationary fixed bed. Another example of a reactor configuration includes a countercurrent process, i.e., the hydrocarbon feed flows down over a fixed catalyst bed while H₂ flows in the upward (opposite) direction.

Transportation Fuel Recovery

[0111] Light or heavy fractions of the hydroprocessed product (typically a liquid portion of the hydroprocessed product) can be removed to produce or recover the desired transportation fuel. In one embodiment, separation of light or heavy components or fractions of the hydroprocessed product can be carried out to positively affect fuel quality; and in particular to provide at least one jet fuel or diesel fuel having high quality characteristics. Separation can be carried out using any appropriate means. Fractionation or distillation may be preferred. Atmospheric distillation, vacuum distillation, or a combination thereof can be used.

Additional Embodiments

[0112] Additionally or alternatively, the invention includes one or more of the following embodiments.

[0113] Embodiment 1. A method for producing transportation fuel, comprising: providing a feedstock containing lipid material and mineral oil, wherein the lipid material is selected from the group consisting of triglycerides, fatty acid alkyl esters, and combinations thereof; and hydroprocessing the feedstock in a hydroprocessing zone to produce the transportation fuel, wherein the hydroprocessing zone is maintained at not greater than 1000 ppm CO, based on total vapor content of the hydroprocessing zone.

[0114] Embodiment 2. The method of embodiment 1, wherein a hydrogen-containing stream that contains not greater than 200 ppm CO, based on total volume of the hydrogen-containing stream, is added to the hydroprocessing zone during hydroprocessing, which hydrogen-containing stream optionally contains greater than 60 vol % H₂, based on total volume of the hydrogen-containing stream.

[0115] Embodiment 3. The method of embodiment 1 or embodiment 2, wherein the hydroprocessing zone contains a CoMo or a NiMo hydroprocessing catalyst.

[0116] Embodiment 4. The method of any of the previous embodiments, wherein the hydroprocessing produces a hydroprocessed product comprised of a liquid fraction and a gas fraction, and the gas fraction is separated from the liquid fraction, with at least a portion of the liquid fraction forming the transportation fuel, wherein the separated gas fraction is optionally treated or contacted with a membrane or an adsorbent to remove at least a majority of the CO from the gas stream to form a treated gas stream.

[0117] Embodiment 5. The method of embodiment 4, wherein (i) the separated gas fraction is treated or contacted with an adsorbent that is contained in a pressure swing adsorption system or a rapid cycle pressure swing adsorption system to form the treated gas stream, (ii) at least a portion of the treated gas stream is added to the hydroprocessing zone during hydroprocessing, or (iii) both (i) and (ii).

[0118] Embodiment 6. The method of embodiment 4 or embodiment 5, wherein at least a portion of the separated gas fraction is acid gas treated.

[0119] Embodiment 7. The method of any of the previous embodiments, wherein (i) the feedstock includes at least 0.05 wt % lipid material, based on total weight of the feedstock, (ii) the lipid material portion of the feedstock is comprised of at least 20 wt % fatty acid alkyl ester, based on total weight of the lipid material in the feedstock, or (iii) both (i) and (ii).

[0120] Embodiment 8. A process for producing a transportation fuel, comprising: providing a feedstock containing lipid material and mineral oil; hydroprocessing the feedstock in a hydroprocessing zone to produce a hydroprocessed product comprised of a liquid fraction and a gas fraction; separating at least a portion of the gas fraction from the hydroprocessed product; removing at least a majority of CO contained in the separated gas fraction to form a treated gas stream; providing at least a portion of the treated gas stream to the hydroprocessing zone; and recovering at least a portion of the liquid fraction as the transportation fuel.
Embodyment 9. The method of embodiment 8, wherein at least a portion of the gas fraction separated from the hydrotreated product is acid gas treated prior to removing the CO.

Embodyment 10. The method of embodiment 8 or embodiment 9, wherein the hydrotreating zone is maintained at not greater than 1000 ppm CO, based on total vapor content of the hydrotreating zone.

Embodyment 11. The method of any one of embodiments 8-10, wherein (i) the separated gas fraction is treated or contacted with an adsorbent that is contained in a pressure swing adsorption system or a rapid cycle pressure swing adsorption system to form the treated gas stream, (ii) at least a portion of the treated gas stream is added to the hydrotreating zone during hydrotreating, or (iii) both (i) and (ii).

Embodyment 12. The method of any one of embodiments 8-11, wherein the hydrotreating zone contains a CoMo or a NiMo hydrotreating catalyst.

Embodyment 13. The method of any one of embodiments 8-12, wherein (i) the feedstock includes at least 0.05 wt% lipid material selected from the group consisting of triglycerides, fatty acid alkyl esters, and combinations thereof, based on total weight of the feedstock, (ii) the lipid material portion of the feedstock is comprised of at least 20 wt% fatty acid alkyl ester, based on total weight of the lipid material in the feedstock, or (iii) both (i) and (ii).

EXAMPLES

Example 1

A feedstock was prepared, with about 1.5 wt% of the total feedstock being comprised of a fatty acid methyl ester and the remainder being a light gas oil. The feedstock was hydrotreated over a reactor containing about 100 cm³ of a CoMo hydrotreating catalyst at a liquid hourly space velocity of about 0.76 hr⁻¹. The reaction was carried out at a reactor temperature of about 630° F. (about 322° C.) and a reactor pressure of about 230 psig (about 1.6 MPag), with the reactor operating over a period of several days. At about 26.6-29.2 days of operation, hydrogen gas was added to the reactor. The gas contained about 80% H₂, and was added at a relative gas rate (TGR) of about 370 scf/bbl (about 300 scf/bbl of H₂). The result of the run is shown in the FIGURE as Case A.

At about 32.8-35.6 days, the gas was changed to contain about 60% H₂, and was added at a rate of about 550 scf/bbl (about 330 scf/bbl of H₂). The result of the run is shown in the FIGURE as Case B.

Comparing Case A to Case B in the FIGURE, it can be seen that Case B produces substantially greater CO and CO₂ relative to Case A.

Example 2

A Run 2A is performed as in Example 1, except that the hydrogen treat gas contains 100% H₂ to obtain a base case run.

A Run 2B is performed as in Run 2A, except that the hydrogen treat gas contains 200 vppm CO, with the remainder of the treat gas being H₂.

A Run 2C is performed as in Run 2A, except that the hydrogen treat gas contains 1000 vppm CO, with the remainder of the treat gas being H₂.

An analysis of the gas phase of the hydrotreated product of Run 2B should show a reduction in catalyst activity, as compared to Run 2A.

An analysis of the gas phase of the hydrotreated product of Run 2C should show a significant reduction in catalyst activity, relative to Runs 2A and 2B.

The above Examples indicate that the H₂ and/or CO content of a treat gas to a hydrotreating zone can significantly impact the conversion of feedstock to fuel product when the feedstock contains even a small amount of lipid material. In one embodiment, a combination of membranes, adsorbents, or both can be utilized to increase H₂ purity to a desired, predetermined amount, as well as to selectively adsorb CO to thereby reduce the CO content of the treat gas to a desired, predetermined amount.

The principles and modes of operation of this invention have been described above with reference to various exemplary and preferred embodiments. As understood by those of skill in the art, the overall invention, as defined by the claims, may encompass other embodiments not specifically enumerated herein.

What is claimed is:

1. A method for producing transportation fuel, comprising: providing a feedstock containing lipid material and mineral oil, wherein the lipid material is selected from the group consisting of triglycerides, fatty acid alkyl esters and combinations thereof; and hydrotreating the feedstock in a hydrotreating zone to produce the transportation fuel, wherein the hydrotreating zone is maintained at not greater than 1000 ppm CO, based on total vapor content of the hydrotreating zone.

2. The method of claim 1, wherein a hydrogen-containing stream that contains not greater than 200 vppm CO, based on total volume of the hydrogen-containing stream, is added to the hydrotreating zone during hydrotreating.

3. The method of claim 1, wherein the hydrogen-containing stream that is added to the hydrotreating zone during hydrotreating contains greater than 60 vol% H₂, based on total volume of the hydrogen-containing stream.

4. The method of claim 1, wherein the hydrotreating zone contains a CoMo or a NiMo hydrotreating catalyst.

5. The method of claim 1, wherein the hydrotreating produces a hydrotreated product comprised of a liquid fraction and a gas fraction, and the gas fraction is separated from the liquid fraction, with at least a portion of the liquid fraction forming the transportation fuel.

6. The method of claim 5, wherein the separated gas fraction is treated or contacted with a membrane or an adsorbent to remove at least a majority of the CO from the gas stream to form a treated gas stream, with the treated gas stream containing greater than 60 vol% H₂ and not greater than 200 vppm CO, based on total volume of the treated gas stream.

7. The method of claim 6, wherein the separated gas fraction is treated or contacted with an adsorbent that is contained in a pressure swing adsorption system or a rapid cycle pressure swing adsorption system to form the treated gas stream.

8. The method of claim 6, wherein at least a portion of the treated gas stream is added to the hydrotreating zone during hydrotreating.

9. The method of claim 5, wherein at least a portion of the separated gas fraction is acid gas treated.
10. The method of claim 1, wherein the feedstock includes at least 0.05 wt % lipid material, based on total weight of the feedstock.

11. The method of claim 1, wherein the lipid material portion of the feedstock is comprised of at least 20 wt % fatty acid alkyl ester, based on total weight of the lipid material in the feedstock.

12. A process for producing a transportation fuel, comprising:
   providing a feedstock containing lipid material and mineral oil;
   hydroprocessing the feedstock in a hydroprocessing zone to produce a hydroprocessed product comprised of a liquid fraction and a gas fraction;
   separating at least a portion of the gas fraction from the hydroprocessed product;
   removing at least a majority of CO contained in the separated gas fraction to form a treated gas stream;
   providing at least a portion of the treated gas stream to the hydroprocessing zone; and
   recovering at least a portion of the liquid fraction as the transportation fuel.

13. The method of claim 12, wherein at least a portion of the gas fraction separated from the hydroprocessed product is acid gas treated prior to removing the CO.

14. The method of claim 12, wherein the hydroprocessing zone is maintained at not greater than 1000 vppm CO, based on total vapor content of the hydroprocessing zone.

15. The method of claim 12, wherein the separated gas fraction is treated or contacted with a membrane or an adsorbent to remove the CO and form the treated gas stream, with the treated gas stream containing greater than 60 vol % H₂ and not greater than 200 vppm CO, based on total volume of the treated gas stream.

16. The method of claim 15, wherein the separated gas fraction is treated or contacted with an adsorbent that is contained in a pressure swing adsorption system or a rapid cycle pressure swing adsorption system to form the treated gas stream.

17. The method of claim 12, wherein the lipid material is selected from the group consisting of triglycerides, fatty acid alkyl esters, and combinations thereof.

18. The method of claim 12, wherein the hydroprocessing zone contains a CoMo or a NiMo hydroprocessing catalyst.

19. The method of claim 12, wherein the feedstock includes at least 0.05 wt % lipid material, based on total weight of the feedstock.

20. The method of claim 12, wherein the lipid material portion of the feedstock is comprised of at least 20 wt % fatty acid alkyl ester, based on total weight of the lipid material in the feedstock.

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