

HYDROPROCESSING OF PYROLYSIS OIL AND ITS USE AS A FUEL

FIELD OF THE INVENTION

[0001] This invention is directed to the hydroprocessing of pyrolysis oils. In particular, this invention is directed to the production of fuels from hydroprocessed pyrolysis oils.

BACKGROUND OF THE INVENTION

[0002] Pyrolysis oil, the liquid product of a particular hydrocarbon heat treatment process, is known to have limited use as a low grade or heavy fuel composition. The type of fuel use is limited as a consequence of the relatively low quality fuel characteristics that are common to pyrolysis oils. For example, pyrolysis oils can contain undesirable amounts of water, which can have a negative impact on catalysts used to upgrade fuel base or blend stock components. Pyrolysis oils are also typically relatively high in oxygen content, which limits their use in higher quality diesel, jet, or gasoline fuels. In addition, typical pyrolysis oils contain significant amounts of relatively unstable compounds such as aldehydes, ketones and carboxylic acids, which can have adverse effects on the oil composition over a period of time.

[0003] A variety of hydroprocessing steps have been proposed to treat pyrolysis oil to increase the fuel quality of the oil. The proposed steps, however, are generally quite complex and costly.

[0004] U.S. Patent Application Publication No. 2009/0253948 discloses a process for producing naphtha, aviation, and/or diesel fuel, blending components, or related products from pyrolysis oil. The pyrolysis oil is treated in a partial deoxygenation zone generating a partially deoxygenated stream. Water, gases, and light ends are removed, and the remainder of the partially deoxygenated stream is further treated in a full deoxygenation zone to produce a deoxygenated product stream. The deoxygenated product stream comprises hydrocarbon compounds that, when fractionated, are useful as gasoline and naphtha, aviation fuel, or as additives to, or blending components of, one or both products. The product stream can also be upgraded to produce a diesel fuel, blending component, or additive. Furthermore, the product stream can serve as a source of chemicals or chemical feedstocks.

[0005] U.S. Patent No. 7,425,657 discloses a method of hydrodeoxygenation of pyrolysis or bio-oil. The bio-oil and hydrogen are reacted over a catalyst comprising Pd at a temperature of more than 200°C. Typically, the method is conducted in the presence of water; with the bio-oil comprising 5-50 mass % water. The bio-oil can be a single-phase or

multi-phase liquid. In preferred embodiments, water is removed during the step of reacting the bio-oil and hydrogen over a catalyst. The method is further characterized by a bio-oil deoxygenation of at least 50% and/or a yield of liquid oil of at least 60%. The bio-oil comprises acetic acid, and at least 30% of the acetic acid in the bio-oil is converted to ethanol during the process.

[0006] U.S. Patent No. 4,308,411 discloses a process for converting a pyrolysis product of a cellulosic fraction derived from municipal solid waste into a hydrocarbon. The solid waste is separated into an inorganic fraction and an organic fraction. The organic fraction is comminuted to a particle size of less than 8 mesh and dried preferably to a moisture content of less than about 20%. The dried organic fraction is then pyrolyzed in the presence of an inert carrier gas, *i.e.*, a carrier gas which is nondeleteriously reactive with the pyrolysis products, and a heat source, for example a carbon containing residue of pyrolysis of the organic fraction of solid waste or a particulate inorganic solid heat source, which may be formed from the decarbonization of said carbon-containing residue of pyrolysis. The inorganic heat source that may be the carbon-containing solid residue of pyrolysis or a decarbonized inorganic solid derived therefrom is separated, along with any solid carbon-containing residue, from the “pyrovapor.” The “pyrovapor” is deoxygenated after separation from the carbon-containing solid residue of pyrolysis and/or the inorganic heat source by contacting with a crystalline aluminosilicate zeolite catalyst to convert the oxygenated hydrocarbons into hydrocarbon product. The hydrocarbon product is gasoline.

[0007] If pyrolysis oils are to be viable as fuels, negative characteristics associated with the oils, such as high water content, high oxygen content, and stability of components within the oils need to be further addressed. As the technology currently stands, only highly complex, intensive treatment processes have been suggested for treating pyrolysis oils, so that such oils can be used as viable high quality fuels.

SUMMARY OF THE INVENTION

[0015] One aspect of the invention relates to a process for producing a reduced sulfur fuel, comprising: hydroprocessing pyrolysis oil in the presence of a non-aluminum support catalyst and hydrogen at a hydrogen to pyrolysis oil ratio of not greater than about 1000 SCF/bbl (about $170 \text{ Nm}^3/\text{m}^3$) to produce a hydroprocessed product; and combining at least a portion of the hydroprocessed product with a base fuel in which the base fuel has a sulfur content in excess of that of the hydroprocessed product to produce the reduced sulfur fuel.

[0016] Another aspect of the invention relates to a process for producing a reduced sulfur fuel, comprising: pyrolyzing a hydrocarbon feedstock to produce a pyrolysis oil; hydroprocessing the pyrolysis oil in the presence of a non-aluminum support catalyst and hydrogen at a hydrogen to pyrolysis oil ratio of not greater than about 1000 SCF/bbl (about $170 \text{ Nm}^3/\text{m}^3$) to produce a hydroprocessed product; and combining at least a portion of the hydroprocessed product with a base fuel in which the base fuel has a sulfur content in excess of that of the hydroprocessed product to produce the reduced sulfur fuel.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Introduction

[0017] The present invention relates to processes for providing reduced sulfur fuels. The low sulfur fuels are preferably produced as a blend that includes a hydroprocessed pyrolysis oil product and a base fuel in which the base fuel has a higher sulfur content than that of the hydroprocessed pyrolysis oil product. In this manner, a pyrolysis oil can be hydroprocessed to reduce its sulfur content, so that a higher sulfur hydrocarbon, *e.g.*, a base fuel that is off-spec for high sulfur content, can be used as an on-spec fuel blend composition.

[0018] Due to the innate chemistry of pyrolysis oils, *e.g.*, typically a relatively high water content, the hydroprocessed pyrolysis oil product can advantageously be produced using a catalyst that can tolerate that chemistry (*e.g.*, water content). Additionally or alternately, the pyrolysis oil can be hydroprocessed under relatively low severity conditions, *e.g.*, to limit additional water formation and/or to make the pyrolysis oil more stable (*i.e.*, to reduce the content of higher reactivity compounds, preferably in favor of lower reactivity compounds). For instance, the pyrolysis oil can be converted to a more stable product by converting at least a majority of the aldehydes, ketones, and/or carboxylic acids in the pyrolysis oil to more highly stable partially deoxygenated compounds (*e.g.*, alcohols) and/or completely deoxygenated hydrocarbons. The hydroprocessed pyrolysis oil product can also be relatively very low in sulfur content and can thus be particularly suited as a blend component for a variety of fuels, or in certain rare circumstances as a fuel composition by itself. Examples of preferred fuels for blending with the hydroprocessed pyrolysis oil product can include, but are not limited to, distillate fuels that include diesel fuel, home heating oil, industrial heating and boiler oil, marine fuels such as bunker fuel, and the like, and combinations thereof.

Pyrolysis Oil

[0019] In general, pyrolysis is a thermal degradation process in which large hydrocarbon molecules are broken or cracked into smaller molecules in the presence of little if any (*e.g.*, substantially no) reactive gas component such as oxygen. A wide variety of hydrocarbon materials can be pyrolyzed to produce vapor, liquid, and often solid hydrocarbon materials. The portion of the pyrolysis product that is liquid at about 25°C and about 101 kPaa (about 14.7 psia, about 1.0 atm) absolute pressure, is also referred to herein as pyrolysis oil. According to the present invention, the pyrolysis oil can be hydroprocessed under predetermined (effective hydroprocessing) conditions to produce a hydroprocessed product, and optionally but preferably at least a portion of the product can be combined or blended with higher sulfur hydrocarbons, *e.g.*, an off-spec high sulfur content base fuel, to produce a lower sulfur fuel, such as an on-spec sulfur content fuel composition.

[0020] A wide range of feedstocks of various types, sizes, and moisture contents can be pyrolyzed to produce a pyrolysis oil that can be processed according to the present invention. Feedstocks that can be used in the pyrolysis step can comprise any hydrocarbon that can be thermally decomposed or transformed. In a preferred embodiment, the feedstock can comprise biomass, preferably at least 10 wt%, for example at least 30 wt%, at least 50 wt%, at least 70 wt%, or at least 90 wt% biomass, based on total weight of feedstock processed/supplied to the thermal/pyrolysis reactor.

[0021] The term “biomass,” for the purposes of this invention, is considered any material not derived from fossil/mineral resources and comprising at least carbon, hydrogen, and oxygen. Examples of biomass can include, but are not limited to, plant and plant-derived material, vegetation, agricultural waste, forestry waste, wood waste, paper waste, animal-derived waste, poultry-derived waste municipal solid waste, cellulose, carbohydrates or derivatives thereof, charcoal, and the like, and combinations/mixtures thereof. The feedstock can additionally or alternately comprise pyrolyzable components other than biomass, such as fossil/mineral fuels (*e.g.*, coal, petroleum, crude oil-derived fuels, shale oil-derived fuels, and the like, and combinations/mixtures thereof).

[0022] Further examples of biomass that can additionally or alternately be present as feedstock components can include, but are not limited to, timber harvesting residues, softwood chips, hardwood chips, tree branches, tree stumps, leaves, bark, sawdust, off-spec paper pulp, corn, corn cob, corn stover, wheat straw, rice straw, sugarcane bagasse, switchgrass, miscanthus, animal manure, municipal garbage, municipal sewage, commercial

waste, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, grass pellets, hay pellets, wood pellets, cardboard, paper, plastic, cloth, and the like, and combinations/mixtures thereof.

[0023] The biomass to be pyrolyzed can optionally but preferably be ground prior to pyrolyzing. For example, the biomass can be ground in a mill until a desired particle size is achieved. In one embodiment, the particle size of the biomass to be pyrolyzed is sufficiently ground to pass through a 30 mm screen, for example through a 20 mm screen, through a 10 mm screen, through a 5 mm screen, or through a 1 mm screen.

[0024] Pyrolysis can preferably be carried out in a relatively inert atmosphere, which means that there are few if any (*e.g.*, substantially no) reactive components to react with the pyrolysis feed material. Such reactive components can include hydrocarbon reactive gases, such as reactive oxygen compounds, sulfur compounds, and various reactive hydrogen compounds. Preferably, pyrolysis can be carried out in an environment (*e.g.*, in the pyrolysis reactor) having a hydrocarbon reactive gas (*e.g.*, oxygen, sulfur, and/or hydrogen) content of not greater than about 10 vol%, for example not greater than about 5 vol%, not greater than about 1 vol%, or not greater than about 0.1 vol%. In a continuous process, this reactive gas content can be based on total volume of gas, *e.g.*, fluidizing gas, supplied to the pyrolysis reactor during continuous operation.

[0025] In one embodiment where reactive oxygen (*i.e.*, oxygen that is not covalently bonded to pyrolysis hydrocarbon feedstock) is present in the hydrocarbon reactive gas(es), it can advantageously be present in an amount less than the stoichiometric amount required for complete combustion. Additionally or alternately, pyrolysis can be carried out in an environment (*e.g.*, in the pyrolysis reactor) having an oxygen content of less than about 40%, less than about 30%, less than about 20%, less than about 10%, less than about 5%, less than about 1%, less than about 0.5%, less than about 0.1%, or less than about 0.01% of the stoichiometric amount of oxygen required for complete combustion of the feedstock. Further additionally or alternately, pyrolysis can be carried out in the absence of (added) reactive oxygen.

[0026] Pyrolysis conditions can preferably include those that reduce and/or minimize non-condensable gas formation and/or solid/char formation. Additionally or alternately, the pyrolysis conditions can preferably include those that lead to condensable gas and/or liquid formation. See, for example, Czernik and Bridgwater, *Energy & Fuels*, 18:590-598, 2004; see also Mohan et al., *Energy & Fuels*, 20:848-889, 2006.

[0027] In one embodiment, pyrolyzed product exits the pyrolysis reactor as a vapor, preferably passing through a filter to separate solids from the more desirable portion of the product. In this embodiment, the filtered vapors can then be condensed to form one or more liquid pyrolysis products.

[0028] Condensation can be carried out using any equipment suitable for such purpose, *e.g.*, a condensation train to collect the desired products. The condensation train can comprise at least one chilled water condenser, at least one electrostatic precipitator, at least one coalescence filter, or a combination thereof.

[0029] Pyrolysis temperature should be high enough to convert a sufficient quantity of feed to desired product, but not so high to produce undesirably high quantities of non-condensable gas and/or solid products. In a preferred embodiment, feed can be pyrolyzed at a temperature from about 200°C to about 600°C, for example from about 300°C to about 600°C or from about 400°C to about 500°C.

[0030] Pyrolysis pressure should be within a range that reduces and/or minimizes formation of non-condensable gas and/or solid products. The pressure can range from about 0 psig (about 0 MPag) to about 1000 psig (about 6.9 MPag), for example from about 5 psig (about 35 kPag) to about 500 psi (about 3.5 MPag) or from about 10 psig (about 69 kPag) to about 200 psig (about 1.4 MPag).

[0031] Pyrolysis can advantageously be carried out for a period of time that enables a substantial or desired quantity of feed to be converted into condensable vapor and/or liquid products. This time window can range widely and can be rather broad, depending upon pressure, temperature, type of reactor used, and other considerations. For example, pyrolysis conditions can be implemented for a period of time from about 0.1 seconds to about 24 hours, for example from about 0.1 seconds to about 1 hour, from about 0.5 seconds to about 4 hours, from about 1 second to about 6 hours, from about 0.1 seconds to about 6 hours, from about 0.5 seconds to about 1 hour, from about 1 second to about 4 hours, or from about 1 second to about 1 hour. If only for sheer economic reasons, shorter times can be particularly advantageous, such as from about 0.1 seconds to about 1 minute, from about 0.1 seconds to about 30 seconds, from about 0.1 seconds to about 10 seconds, from about 0.5 seconds to about 1 minute, from about 0.5 seconds to about 30 seconds, from about 0.5 seconds to about 10 seconds, from about 1 second to about 1 minute, from about 1 second to about 30 seconds, or from about 1 second to about 10 seconds.

[0032] In some embodiments, fast pyrolysis can be used. Fast pyrolysis is a relatively high-temperature process in which feedstock is relatively rapidly heated, in some embodiments in the absence of oxygen. The feedstock can decompose to generate predominantly vapor and solid (*i.e.*, char) products. The vapor product can preferably be cooled and condensed to form one or more liquid products. Multiple steps of heating and cooling can be carried out to produce intermediate pyrolysis liquid products. Fast pyrolysis processes can produce from about 60 wt% to about 75 wt% condensable gas and liquid products, from about 15 wt% to about 25 wt% solid char, and from about 10 wt% to about 20 wt% non-condensable gas products, but these percentages can vary greatly depending on the particular composition of the feedstock.

[0033] Additionally or alternately, slow pyrolysis can be used. In slow pyrolysis, the feedstock can be heated to not greater than about 600°C for a period ranging from about 1 minute to about 24 hours, for example from about 1 minute to about 60 minutes. Vapor product typically does not escape as rapidly in slow pyrolysis as it does in fast pyrolysis. Thus, vapor products may react more with each other as solid char and any liquid are being formed. As the name would imply, rate of heating in slow pyrolysis is typically slower than that used in fast pyrolysis. In slow pyrolysis, a feedstock can be held at constant temperature or can be relatively slowly heated. Vapors can be removed (*e.g.*, continuously) as they are formed.

[0034] Further additionally or alternately, vacuum pyrolysis can be used. In vacuum pyrolysis, the feedstock can be heated at less than atmospheric pressure (less than about 0 kPag, or less than about 100 kPaa). Vacuum conditions can be used to decrease the boiling point and/or to avoid, reduce, and/or minimize adverse chemical reactions.

[0035] As mentioned above, pyrolysis product can contain water. As an example, condensed pyrolysis product can contain from about 10 wt% to about 30 wt% water. Optionally but preferably, the water can be removed prior to hydroprocessing using any appropriate means, such as by flashing, decanting, distillation, membrane separation, or the like, or any combination thereof. Thus preferably, prior to hydroprocessing, water can be removed from (water content can be reduced in) the pyrolysis product to produce a pyrolysis oil hydroprocessing feedstock having not greater than about 20 wt%, preferably not greater than about 10 wt%, for example not greater than about 5 wt% water or not greater than about 3 wt% water, based on total weight of the pyrolysis oil hydroprocessing feedstock.

[0036] The pyrolysis oil used as feedstock for hydroprocessing can unfortunately contain components that can be relatively unstable over time. Such components can include, but are not necessarily limited to, one or more of aldehydes, ketones, and carboxylic acids.

[0037] In one embodiment, the pyrolysis oil hydroprocessing feedstock can comprise at least about 1.0 wt% aldehydes, for example at least about 1.5 wt% aldehydes, from about 1.5 wt% to about 20 wt% aldehydes, or from about 2 wt% to about 15 wt% aldehydes, based on total weight of the pyrolysis oil hydroprocessing feedstock.

[0038] Additionally or alternately, the pyrolysis oil hydroprocessing feedstock can comprise at least about 0.8 wt% ketones, for example at least about 1 wt% ketones, from about 1 wt% to about 10 wt% ketones, or from about 1.5 wt% to about 8 wt% ketones, based on total weight of the pyrolysis oil hydroprocessing feedstock.

[0039] Further additionally or alternately, the pyrolysis oil hydroprocessing feedstock can comprise at least about 1.2 wt% carboxylic acids, for example at least about 1.5 wt% carboxylic acids, from about 1.5 wt% to about 25 wt% carboxylic acids, or from about 2 wt% to about 20 wt% carboxylic acids, based on total weight of the pyrolysis oil hydroprocessing feedstock.

Hydroprocessing Catalyst and Conditions

[0040] Hydroprocessing refers to processes or treatments that expose at least a portion of a feedstock (in this case, the pyrolysis product) to hydrogen in the presence of a hydroprocessing catalyst to facilitate the reaction. Such processes can include, but are not limited to, hydrodeoxygenation, hydrodenitrogenation, hydrodesulfurization, hydrotreating, hydrocracking, hydroisomerization, hydrodewaxing, and the like, and combinations thereof. For examples of such processes, see U.S. Patent Nos. 7,513,989, 7,435,335, 7,288,182, 7,288,181, 7,244,352 and 7,220,352, the relevant contents of which are hereby incorporated by reference. Specifically with regard to the pyrolysis oil, hydroprocessing can primarily involve the conversion of oxygen-containing hydrocarbons to non-aromatic alcohols and/or paraffins.

[0041] Pyrolysis oil can be hydroprocessed according to this invention to produce a hydroprocessed product reduced in one or more of aldehyde, ketone, and carboxylic acid content and optionally but preferably increased in alcohol content. In a particularly preferred embodiment, the pyrolysis product can be reduced in each of aldehyde, ketone, and carboxylic acid content and can be simultaneously increased in alcohol content.

[0042] Hydroprocessing catalysts suitable for use with a pyrolysis oil-based feedstock according to the present invention can preferably be able to tolerate at least a relatively low level moisture content within the hydroprocessing environment or reaction vessel, as there will generally be some amount of water included with the pyrolysis oil, and additional water can form as a byproduct during hydroprocessing.

[0043] Thus, in an effort to maintain catalytic activity and/or catalyst life, the hydroprocessing catalyst and hydroprocessing conditions can advantageously be maintained to limit/minimize water formation during hydrolysis, while reducing at least one of aldehyde, ketone, and carboxylic acid content in the hydroprocessed pyrolysis oil product. Preferably, water formation can be limited/minimized during hydroprocessing, while a majority (*i.e.*, at least 50%) of the combined aldehyde, ketone, and carboxylic acid components (*e.g.*, as measured by the ratio of the pre-hydroprocessing collective content to the post-processing collective content) are converted, *e.g.*, to alcohol components.

[0044] Hydroprocessing catalysts whose support(s) contain substantially no aluminum (usually, but not necessarily, in oxide form) can be preferred. For instance, non-aluminum-containing supported catalysts can include at least one metal from Groups 8-10 of the Periodic Table of the Elements, designated according to the IUPAC System. Examples of such metals can include, but are not limited to, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, and combinations thereof. In a particularly preferred embodiment, palladium and/or platinum is present.

[0045] In the aforementioned hydroprocessing catalysts, the total content of metals from Groups 8-10 can be at least about 0.1 wt%, for example at least about 0.3 wt%, at least about 0.5 wt%, at least about 1.0 wt%, at least about 2.0 wt%, or at least about 3.0 wt%. Additionally or alternately, the total content of metals from Groups 8-10 can be about 40 wt% or less, for example about 30 wt% or less, about 25 wt% or less, about 20 wt% or less, about 15 wt% or less, about 10 wt% or less, or about 5.0 wt% or less.

[0046] Hydroprocessing catalyst support materials can include, but are not limited to, carbon (*e.g.*, relatively high surface area graphitized carbon, graphite, activated carbon, or the like, or a combination thereof) and silica supports, with a preference for support materials that are porous particulate solids and that contain substantially no aluminum (alumina). Examples of carbon and silica supports are described in U.S. Patent No. 5,149,680, the relevant contents of which are hereby incorporated by reference.

[0047] When the catalyst comprises a carbon support material, the support can advantageously have a relatively high BET surface area, for example at least about 100 m²/g, at least about 200 m²/g, or at least about 300 m²/g. Additionally or alternately, the BET surface area is typically not greater than about 1000 m²/g, for example not greater than about 750 m²/g.

[0048] A preferred carbon support, such as an activated carbon support, can be prepared by heat treating a carbon-containing starting material, which can comprise/be any suitable carbon material, such as an oleophilic graphite, a carbon black, or the like.

[0049] Additionally or alternately, the carbon support material can be at least partially oxidized, for example at a temperature from about 300°C to about 1200°C for an appropriate period of time to sufficiently oxidize the support material, prior to use. In such an embodiment, the carbon support can be heated, *e.g.*, in an inert atmosphere at a temperature from about 900°C to about 3300°C, and the heated carbon can be oxidized, *e.g.*, at a temperature from about 300°C to about 1200°C. Further in such an embodiment, the oxidized material can optionally be heated, *e.g.*, in an inert atmosphere (such as nitrogen) at a temperature from about 900°C to about 3000°C.

[0050] Examples of oxidizing agents can include, but are not limited to, steam, carbon dioxide, gases containing molecular oxygen (*e.g.*, air), or the like, or a combination thereof. In one embodiment, oxidation can be carried out to give a carbon weight loss of at least about 10 wt%, for example at least about 15 wt%, based on weight of carbon subjected to the oxidation step. Additionally or alternately, the carbon weight loss due to such oxidation can be not greater than about 40 wt%, for example not greater than about 25 wt%, of the carbon subjected to the oxidation step. The rate of supply of oxidizing agent can be such that the desired weight loss takes place over at least about 2 hours, for example over at least about 4 hours.

[0051] Preferred silica supports are those having a relatively high surface area, for example greater than about 50 m²/g, greater than about 75 m²/g, or greater than about 100 m²/g.

[0052] In the hydroprocessing reaction, it can be preferred to limit the amount of hydrogen used in the process, *e.g.*, to limit any water that can be formed as a co-product. In one embodiment, hydroprocessing can be carried out at a hydrogen to pyrolysis oil treat gas ratio of not greater than about 1000 SCF/bbl (about 170 Nm³/m³), for example not greater

than about 900 SCF/bbl (about $150 \text{ Nm}^3/\text{m}^3$) or not greater than about 800 SCF/bbl (about $140 \text{ Nm}^3/\text{m}^3$).

[0053] Hydroprocessing can be carried out over a wide range of pressures, *e.g.*, from about 3.4 MPaa (about 500 psia) to about 21 MPaa (about 3000 psia), from about 3.4 MPaa (about 500 psia) to about 14 MPaa (about 2000 psia), from about 3.4 MPaa (about 500 psia) to about 12 MPaa (about 1800 psia), from about 3.4 MPaa (about 500 psia) to about 9.0 MPaa (about 1300 psia), or from about 3.4 MPaa (about 500 psia) to about 6.2 MPaa (about 900 psia).

[0054] Hydroprocessing can also be carried out over a wide range of temperatures, for example from about 200°C to about 500°C , from about 200°C to about 400°C , or from about 300°C to about 375°C .

[0055] Space velocity through the reaction vessel in which hydroprocessing is carried out should be high enough to avoid over-reacting through high residence times. In one embodiment, hydroprocessing can be carried out at a liquid hourly space velocity (LHSV) of at least about 0.1 hr^{-1} , for example at least about 0.5 hr^{-1} , at least about 1.0 hr^{-1} , or at least about 1.5 hr^{-1} . Additionally or alternately, the LHSV can be about 10 hr^{-1} or less, for example about 5.0 hr^{-1} or less, about 3.0 hr^{-1} or less, about 2.0 hr^{-1} or less, or about 1.5 hr^{-1} or less.

Hydroprocessed Product

[0056] The hydroprocessed product produced according to the present invention can advantageously be reduced in one or more of aldehyde, ketone, and carboxylic acid content and optionally but preferably can be increased in alcohol content. In a particularly preferred embodiment, the pyrolysis product can be reduced in each of aldehyde, ketone, and carboxylic acid content and can be simultaneously increased in alcohol content.

[0057] In one embodiment, the hydroprocessed product can comprise less than about 1.5 wt% aldehydes, for example less than about 1 wt% aldehydes or less than about 0.5 wt% aldehydes, based on total weight of the hydroprocessed product. Additionally or alternately, the hydroprocessed product can comprise less than about 1 wt% ketones, for example less than about 0.5 wt% ketones or less than about 0.1 wt% ketones, based on total weight of the hydroprocessed product. Further additionally or alternately, the hydroprocessed product can comprise less than about 1.5 wt% carboxylic acids, for example less than about 1 wt% carboxylic acids or less than about 0.5 wt% carboxylic acids, based on total weight of the

hydroprocessed product. Still further additionally or alternately, the hydroprocessed product can comprise at least about 10 wt% non-aromatic alcohols, for example at least about 15 wt% non-aromatic alcohols, at least about 20 wt% non-aromatic alcohols, or at least about 25 wt% non-aromatic alcohols, based on total weight of the hydroprocessed product.

[0058] The hydroprocessed product can also advantageously be relatively low in sulfur content, for example comprising less than about 2.0 wt% sulfur, less than about 1.0 wt% sulfur, less than about 5000 wppm sulfur, less than about 2000 wppm sulfur, less than about 1000 wppm sulfur, less than about 500 wppm sulfur, less than about 200 wppm sulfur, less than about 100 wppm sulfur, less than about 50 wppm sulfur, less than about 30 wppm sulfur, less than about 20 wppm sulfur, less than about 15 wppm sulfur, less than about 10 wppm sulfur, or less than about 5 wppm sulfur, based on total weight of the hydroprocessed product.

[0059] If desired, water in the hydroprocessed product can be removed prior to combining or blending with base fuel to produce the low sulfur fuel. Removal of water can be accomplished using any appropriate means, such as by flashing, decanting, distillation, membrane separation, or the like, or a combination thereof. In one embodiment, prior to combining or blending with base fuel, water can be removed to produce a hydroprocessed product having a water content of not greater than about 2 wt%, for example not greater than about 1 wt% or not greater than about 0.5 wt%.

Reduced Sulfur Fuel

[0060] The hydroprocessed product produced according to the present invention can be useful as a fuel or as a component of a fuel product. The fuel that is produced can generally be a heavier fuel, typically referred to as a bunker fuel, and can be particularly advantageous in its reduction in sulfur content relative to current bunker fuels.

[0061] Thus, in one embodiment, a fuel is provided that is a blend product of hydroprocessed product and a base fuel. At least a portion of the hydroprocessed product can be combined or blended with the base fuel to produce a higher quality fuel and/or to meet strict governmental and/or product fuel specifications. In particular, the fuel that is produced can have a sulfur content of not greater than about 5 wt%, for example not greater than about 4 wt%, not greater than about 3 wt%, not greater than about 2 wt%, not greater than about 1 wt%, not greater than about 5000 wppm, not greater than about 2000 wppm, not greater than about 1000 wppm, not greater than about 500 wppm, not greater than about 200 wppm, not greater than about 100 wppm, not greater than about 50 wppm, not greater than about 30

wppm, not greater than about 20 wppm, not greater than about 15 wppm, or not greater than about 10 wppm, based on at least one of ISO 8754 or ISO 14596 test methods.

[0062] Base fuels that can be combined or blended with the hydroprocessed product can generally comprise, consist essentially of, or be any heavier refinery fraction. Such fractions are typically heavier than gasoline or a majority of gasoline blend stocks. Examples of base fuels include, but are not limited to, gas oil, heavy fuel oil, atmospheric resid, vacuum resid, heavy cycle oil, and the like, and mixtures thereof.

[0063] The base fuel combined or blended with the hydroprocessed product can typically have an overall sulfur content in excess of that of the hydroprocessed product, such that the blend can thereby produce a reduced sulfur fuel. In one embodiment, the hydroprocessed product can be combined or blended with a base fuel having a sulfur content in excess of the hydroprocessed product to produce a reduced sulfur fuel, *e.g.*, the base fuel having a sulfur content that is at least 10% in excess of that of the hydroprocessed product, for example at least 50% in excess, at least 100% in excess, at least 200% in excess, or at least 400% in excess.

[0064] Additionally or alternately, the fuel produced according to the present invention can be reduced in viscosity relative to typical base (heavy) fuels. For example, the fuel that is produced can have a kinematic viscosity at ~50°C of not greater than about 800, *e.g.*, not greater than about 600, not greater than about 400, or not greater than about 200, based on ISO 3104 test method.

[0065] Further additionally or alternately, the fuel produced according to the present invention can be increased in flash point relative to typical base (heavy) fuels. For example, the fuel that is produced can have a flash point of at least about 40°C, *e.g.*, at least about 50°C or at least about 60°C, based on ISO 2719 test method.

[0066] Still further additionally or alternately, the fuel produced according to the present invention can be reduced in water content relative to typical base (heavy) fuels. For example, the fuel that is produced can have a water content of not greater than about 0.5 vol%, *e.g.*, not greater than about 0.4 vol% or not greater than about 0.3 vol%, based on ISO 3733 test method.

[0067] Specific examples of fuels produced according to the present invention can include, but are not limited to, diesel fuels, home heating oil, industrial heater and boiler fuel, and marine fuel, preferably marine fuels of the distillate type (*e.g.*, gas oil or marine gas oil), intermediate type (*e.g.*, marine diesel fuel or intermediate fuel oil), and resid type (*e.g.*, fuel

oil or residual fuel oil). Examples of marine distillate fuels can include, but are not limited to, DM designated fuel grades (*e.g.*, DMX, DMA, DMB, and DMC). Examples of intermediate marine fuels can include, but are not limited to, IF fuel grades (*e.g.*, IFO 180 and 380). Examples of resid fuel types can include, but are not limited to, RM designated fuel grades (*e.g.*, RMA to RML).

[0068] Additionally or alternately, the present invention can include one or more of the following embodiments.

[0069] Embodiment 1. A process for producing a reduced sulfur fuel, comprising: hydroprocessing pyrolysis oil in the presence of a non-aluminum support catalyst and hydrogen at a hydrogen to pyrolysis oil ratio of not greater than about 1000 SCF/bbl (about 170 Nm³/m³) to produce a hydroprocessed product; and combining at least a portion of the hydroprocessed product with a base fuel in which the base fuel has a sulfur content in excess of that of the hydroprocessed product to produce the reduced sulfur fuel.

[0070] Embodiment 2. A process for producing a reduced sulfur fuel, comprising: pyrolyzing a hydrocarbon feedstock to produce a pyrolysis oil; hydroprocessing the pyrolysis oil in the presence of a non-aluminum support catalyst and hydrogen at a hydrogen to pyrolysis oil ratio of not greater than about 1000 SCF/bbl (about 170 Nm³/m³) to produce a hydroprocessed product; and combining at least a portion of the hydroprocessed product with a base fuel in which the base fuel has a sulfur content in excess of that of the hydroprocessed product to produce the reduced sulfur fuel.

[0071] Embodiment 3. The process of embodiment 1 or embodiment 2, wherein the hydrocarbon feedstock comprises biomass.

[0072] Embodiment 4. The process of any one of the previous embodiments, wherein the non-aluminum-containing support catalyst comprises at least one metal from Groups 8-10 of the Periodic Table of Elements.

[0073] Embodiment 5. The process of any one of the previous embodiments, wherein the non-aluminum-containing support comprises a carbon support or a silica support.

[0074] Embodiment 6. The process of embodiment 5, wherein the non-aluminum-containing support catalyst comprises at least one of palladium and platinum.

[0075] Embodiment 7. The process of any one of the previous embodiments, wherein the pyrolysis oil is comprised of one or more of aldehydes, ketones, and carboxylic acids.

[0076] Embodiment 8. The process of any one of the previous embodiments, wherein the base fuel includes at least one gas oil, heavy fuel oil, or resid oil component.

[0077] Embodiment 9. The process of any one of the previous embodiments, wherein the hydroprocessed product comprises at least 10 wt% non-aromatic alcohols, based on total weight of the hydroprocessed product.

[0078] Embodiment 10. The process of any one of the previous embodiments, wherein the reduced sulfur fuel comprises a diesel fuel, a home heating oil, an industrial heater or boiler fuel, a marine fuel, or a combination thereof.

[0079] Embodiment 11. The process of any one of the previous embodiments, wherein the pyrolysis oil is a liquid fraction of a pyrolysis product.

[0080] 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, encompasses other preferred embodiments not specifically enumerated herein.

CLAIMS:

1. A process for producing a reduced sulfur fuel, comprising:
hydroprocessing pyrolysis oil in the presence of a non-aluminum support catalyst and hydrogen at a hydrogen to pyrolysis oil ratio of not greater than about 1000 SCF/bbl (about $170 \text{ Nm}^3/\text{m}^3$) to produce a hydroprocessed product; and
combining at least a portion of the hydroprocessed product with a base fuel in which the base fuel has a sulfur content in excess of that of the hydroprocessed product to produce the reduced sulfur fuel.
2. A process for producing a reduced sulfur fuel, comprising:
pyrolyzing a hydrocarbon feedstock to produce a pyrolysis oil;
hydroprocessing the pyrolysis oil in the presence of a non-aluminum support catalyst and hydrogen at a hydrogen to pyrolysis oil ratio of not greater than about 1000 SCF/bbl (about $170 \text{ Nm}^3/\text{m}^3$) to produce a hydroprocessed product; and
combining at least a portion of the hydroprocessed product with a base fuel in which the base fuel has a sulfur content in excess of that of the hydroprocessed product to produce the reduced sulfur fuel.
3. The process of claim 1 or claim 2, wherein the hydrocarbon feedstock comprises biomass.
4. The process of any one of the previous claims, wherein the non-aluminum-containing support catalyst comprises at least one metal from Groups 8-10 of the Periodic Table of Elements.
5. The process of any one of the previous claims, wherein the non-aluminum-containing support comprises a carbon support or a silica support.
6. The process of claim 5, wherein the non-aluminum-containing support catalyst comprises at least one of palladium and platinum.
7. The process of any one of the previous claims, wherein the pyrolysis oil is comprised of one or more of aldehydes, ketones, and carboxylic acids.
8. The process of any one of the previous claims, wherein the base fuel includes at least one gas oil, heavy fuel oil, or resid oil component.

9. The process of any one of the previous claims, wherein the hydroprocessed product comprises at least 10 wt% non-aromatic alcohols, based on total weight of the hydroprocessed product.
10. The process of any one of the previous claims, wherein the reduced sulfur fuel comprises a diesel fuel, a home heating oil, an industrial heater or boiler fuel, a marine fuel, or a combination thereof.
11. The process of any one of the previous claims, wherein the pyrolysis oil is a liquid fraction of a pyrolysis product.