

ISOPARAFFINIC AND ISO-OLEFINIC DISTILLATE COMPOSITIONS**FIELD**

[0001] This invention relates to distillate boiling range compositions having high isoparaffin content and methods for forming fuel compositions or fuel blending compositions made from such distillate compositions, including marine fuels and diesel fuels.

BACKGROUND OF THE INVENTION

[0002] The fuel industry is pursuing lower carbon intensity renewable distillate fuels for heavy duty and marine applications. There are multiple high-yield pathways to produce renewable fuels from lipids (animal / vegetable sources) and there are some low-volume commercial options from cellulosic / alternative feedstocks. Both land and marine transportation sectors are seeking to increase their use of renewable fuels, but are interested in utilizing fuels that do not compete with feedstock from food sources (typically animal / vegetable lipid derived). However, development of commercially available drop-in renewable fuels from cellulosic / alternative feedstocks for heavy duty and marine applications are not keeping pace with the needs of the transportation industry. As a result, new lower carbon and renewable fuels from cellulosic/alternative feedstocks are needed to supply both the land and marine sectors.

[0003] U.S. Patent 7,692,049 describe methods for oligomerizing olefins (including C₃ to C₈ olefins) to produce olefins and alkanes that include a high percentage of branched olefins and alkanes. Compositions resulting from the method are described that include C₉ to C₂₀ hydrocarbons. In U.S. Patent 7,692,049, a blend of 25 wt% of one of the compositions with a conventional jet fuel is also described. Sources for the C₃ to C₈ olefins include conversion of methanol to olefins and formation of olefins via steam cracking.

[0004] U.S. Patent 8,318,994, U.S. Patent 7,678,953, and U.S. Patent 7,667,086 also describe methods for oligomerizing olefins and corresponding compositions including branched olefins and alkanes formed via the oligomerization methods.

SUMMARY OF THE INVENTION

[0005] In various aspects, a diesel boiling range composition is provided. The composition includes 1.0 vol% to 75 vol% of a blend component comprising an isoparaffinic blend component, an iso-olefinic blend component, or a combination thereof containing 80 wt% or more of combined isoparaffins and iso-olefins. In some aspects, the composition further

includes 20 vol% to 99 vol% of a mineral distillate boiling range fraction. Additionally or alternately, in some aspects the composition further includes 10 vol% to 99 vol% of a bio-derived component different from the blend component. The composition can have a cetane number of 40 or more, a cloud point that is at least 5.0°C lower than a cloud point of the mineral distillate boiling range fraction and/or bio-derived component, and/or a cloud point of -10°C or less.

[0006] In various aspects, a fuel oil or fuel oil blend component composition is also provided. The composition includes 1.0 vol% to 75 vol% of a blend component comprising an isoparaffinic blend component, an iso-olefinic blend component, or a combination thereof. In some aspects, the composition further includes 25 vol% to 95 vol% of a mineral fraction. Additionally or alternately, in some aspects the composition further includes 5.0 vol% to 50 vol% of a bio-derived component different from the blend component and 15 vol% or more of a mineral fraction. The composition can have a density at 15°C of 0.880 g/cm³ to 0.990 g/cm³, a calculated carbon aromaticity index of 780 or more, a flash point of 60°C or more, and/or a sulfur content of 5000 wppm or less. Optionally, a pour point of the composition can be lower than a pour point of the mineral fraction and/or the bio-derived component.

[0007] In various aspects, a marine distillate or marine distillate blend component composition is also provided. The composition includes 1.0 vol% to 90 vol% of a blend component comprising an isoparaffinic blend component, an iso-olefinic blend component, or a combination thereof. The composition further includes 10 vol% to 99 vol% of a mineral fraction, a bio-derived component different from the blend component, or a combination thereof. The composition can have a density at 15°C of 0.780 g/cm³ to 0.890 g/cm³ or less, a cetane number of 40 or more, and/or a flash point of 43°C or more. Optionally, a pour point of the composition can be at least 5°C lower than a pour point of the mineral fraction, the bio-derived fraction, or the combination thereof.

BRIEF DESCRIPTION OF THE DRAWING

[0008] The Figure shows results from ¹H NMR characterization of iso-olefinic and isoparaffinic blend components.

DETAILED DESCRIPTION OF THE INVENTION

[0009] In various aspects, compositions are provided that include at least a portion of an isoparaffinic blend component, an iso-olefinic blend component, or a combination thereof,

along with a method for making such a blend component. The highly isoparaﬃnic and/or iso-olefinic nature of the blend component can allow a blend component to be used in combination with both conventional / mineral fuel boiling range fractions as well as non-traditional feeds (such as Fischer-Tropsch fractions) to form fuel fractions and/or fuel blending component fractions. Examples of fuels that can be formed by making a blend that includes an isoparaﬃnic and/or iso-olefinic blend component include diesel fuels, marine gas oils, and various types of marine fuel oils (e.g., low sulfur fuel oil, very low sulfur fuel oil, ultra low sulfur fuel oil).

[0010] One of the barriers to reducing the use of distillate fuels derived from mineral fractions is simply a lack of available supply. One option for overcoming this barrier is to synthesize distillate boiling range compounds from a feedstock different from a mineral fraction. Synthesizing distillate boiling range components by oligomerization of olefins can provide such a pathway. For example, the olefins used for oligomerization can be formed by conversion of methanol (and/or other short chain alcohols) to olefins. In this option, the problem of producing non-mineral distillate boiling range compounds is converted into a problem of producing non-mineral methanol for subsequent conversion. (More generally, the olefins for oligomerization can be obtained from any convenient source of olefins, such as olefins formed by pyrolysis, including pyrolysis of a bio-derived feed.) Forming a distillate fuel or distillate fuel blending component from a bio-derived feedstock containing distillate boiling range compounds (or higher boiling range compounds that are converted to jet boiling range) is another example of a pathway for “synthesizing” distillate boiling range compounds.

[0011] With regard to forming distillate fuel or a distillate fuel blending component by synthesis of distillate boiling range compounds from a methanol feedstock, a variety of options are available for producing such methanol. One option can be to use bio-derived methanol. Another option can be to synthesize methanol from CO₂ and H₂. For example, the CO₂ could correspond to CO₂ sequestered from air or another process, while the H₂ can correspond to H₂ formed in a renewable manner, such as by solar-powered electrolysis of water. Because methanol is a readily synthesized feedstock, the source of the methanol (and therefore the source of the resulting olefins) can be modified over time to select an option that provides the highest overall benefits.

[0012] In addition to allowing for production of non-mineral distillate boiling range compounds, the synthesis method for forming the highly isoparaﬃnic and/or iso-olefinic blend component can provide a variety of other advantages. For example, in some aspects, the isoparaﬃnic nature of the blend component can have beneficial cold flow properties. Although

n-paraffins typically have relatively high values for properties such as cloud point or freeze point, various types of isoparaffins generally have much lower values (i.e., cloud points and/or freeze points that correspond to lower temperatures). Iso-olefins also tend to provide improved cold flow properties. The beneficial cold flow properties of the isoparaffinic blend component
5 (and/or iso-olefinic blend component) can be used to balance out another distillate boiling range fraction that may have less favorable properties. For example, Fischer-Tropsch fractions can tend to be primarily composed of n-paraffins, and therefore can tend to have relatively unfavorable cold flow properties. Blending an isoparaffinic blend component with a Fischer-Tropsch fraction can result in a blended synthetic fuel / fuel blending component with sufficient
10 cold flow performance to meet one or more types of distillate fuel specifications while still incorporating a substantial portion of the Fischer-Tropsch fraction.

[0013] As still another example, the isoparaffinic blend component and/or iso-olefinic blend component can have a relatively high energy content (on either a per volume or per weight basis). As a result, such blend components can be a favorable blend components for
15 blending with a variety of other fractions, including sustainable aviation fuel fractions as well as various types of challenged fractions that may have lower energy density and/or less favorable cold flow properties.

[0014] For example, relative to some types of bio-derived distillate fractions, an isoparaffinic and/or iso-olefinic blend component can include a higher content of C₁₇ – C₂₀
20 hydrocarbons, such as a higher content of C₁₇ and/or C₁₈ hydrocarbons. This can be beneficial for improving the energy density of the resulting blend while also providing improved cold flow properties.

[0015] In addition to the above, it has further been discovered that the hydrocarbons in a blend component can have an unexpected distribution of types of carbon atoms, such as an
25 unusual distribution of hydrogens on CH₃ groups relative to hydrogens on CH₂ groups. This can allow for formation of blends that have similarly unexpected distributions of types of carbon atoms in the resulting blend.

DEFINITIONS

[0016] All numerical values within the detailed description and the claims herein are
30 modified by “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0017] In this discussion, if methanol is used as a feedstock for forming olefins, methanol obtained by processing of a bio-derived feedstock and/or methanol obtained by fermentation of a feedstock and/or synthesis of methanol from bio-derived feed components (such as synthesis of methanol for CO and H₂ formed from a bio-derived source) can be referred to as
5 “sustainable” methanol.

[0018] In this discussion, when forming a blend, a “bio-derived component” is defined as any type of bio-derived feed, fraction, or product that is derived from a biological source. For example, fatty acid methyl esters and hydrotreated vegetable oils are both potential bio-derived components that can be used in a blend. Additionally, if biomass or another bio-derived
10 material is used to make synthesis gas, and the synthesis gas is subsequently used in a Fischer-Tropsch process to make a blend component or fraction, such a Fischer-Tropsch component and/or fraction corresponds to a bio-derived component.

[0019] Unless otherwise specified, distillation points and boiling points can be determined according to ASTM D2887. For samples that are not susceptible to
15 characterization using ASTM D2887, D7169 can be used. It is noted that still other methods of boiling point characterization may be provided in the examples. The values generated by such other methods are believed to be indicative of the values that would be obtained under ASTM D2887 and/or D7169.

[0020] In this discussion, the distillate boiling range is defined as 140°C to 370°C. A
20 distillate boiling range fraction is defined as a fraction having a T10 distillation point of 140°C or more and a T90 distillation point of 370°C or less. The diesel boiling range is defined as 170°C to 370°C. A diesel boiling range fraction is defined as a fraction having a T10 distillation point of 170°C or more, a final boiling point of 300°C or more, and a T90 distillation point of 370°C or less. An atmospheric resid is defined as a bottoms fraction having a T10
25 distillation point of 149°C or higher, or 350°C or higher. The vacuum gas oil (VGO) boiling range is defined as 370°C to 565°C. A vacuum gas oil boiling range fraction (also referred to as a heavy distillate) can have a T10 distillation point of 350°C or higher and a T90 distillation point of 538°C or less. A vacuum resid is defined as a bottoms fraction having a T10 distillation point of 500°C or higher, or 538°C or higher, or 565°C or higher. It is noted that the definitions
30 for distillate boiling range fraction, kerosene (or jet fuel) boiling range fraction, diesel boiling range fraction, atmospheric resid, and vacuum resid are based on boiling point only. Thus, a distillate boiling range fraction, diesel fraction, atmospheric resid fraction, vacuum gas oil

fraction, and/or vacuum resid fraction can include components that did not pass through a distillation tower or other separation stage based on boiling point.

[0021] In this discussion, a hydroprocessed fraction refers to a hydrocarbon fraction and/or hydrocarbonaceous fraction that has been exposed to a catalyst having hydroprocessing activity in the presence of 300 kPa-a or more of hydrogen at a temperature of 200°C or more. Examples of hydroprocessed fractions include hydroprocessed distillate fractions (i.e., a hydroprocessed fraction having the distillate boiling range), hydroprocessed kerosene fractions (i.e., a hydroprocessed fraction having the kerosene boiling range) and hydroprocessed diesel fractions (i.e., a hydroprocessed fraction having the diesel boiling range). It is noted that a hydroprocessed fraction derived from a biological source, such as hydrotreated vegetable oil, can correspond to a hydroprocessed distillate fraction, a hydroprocessed kerosene fraction, and/or a hydroprocessed diesel fraction, depending on the boiling range of the hydroprocessed fraction.

[0022] With regard to characterizing properties of diesel / distillate boiling range fractions and/or blends of such fractions with other components to form diesel boiling range fuels, a variety of methods can be used. Density of a blend at 15°C (kg/m^3 or equivalently g/cm^3) can be determined according to ASTM D4052. Sulfur (in wppm or wt%) can be determined according to ASTM D2622, while nitrogen (in wppm or wt%) can be determined according to D4629. Pour point can be determined according to ASTM D5950. Cloud point can be determined according to D2500. Freeze point can be determined according to ASTM D5972. Cetane index can be determined according to ASTM D4737. Cetane number can be determined according to D613. Kinematic viscosity can be determined according to ASTM D445. Aromatics content can be determined according to EN 12916. Flash point can be determined according to ASTM D93.

[0023] For various marine fuels, density (in kg/m^3) can be determined according to ISO 3675. For marine fuel oils, sulfur (in wppm) can be determined according to ISO 8754. For marine fuel oils, kinematic viscosity at 50°C (in cSt) can be determined according to ISO 3104. For marine fuel oils, pour point can be determined according to ISO 3016. For marine fuel oils, sediment can be determined according to ISO 10307-2. CCAI (calculated carbon aromaticity index) can be determined according to Equation F.1 in ISO 8217:2012. Micro carbon residue content can be determined according to ASTM D4530. The content of n-heptane insolubles can be determined according to ASTM D3279. Flash point can be determined according to ASTM D93. The metals content can be determined according to IP 501. Nitrogen

can be determined according to D4629 for lower concentrations and D5762 for higher concentrations, as appropriate.

[0024] In this discussion, the content of n-paraffins, isoparaffins, cycloparaffins, aromatics, and/or olefins can be determined according to test method UOP 990. It is noted that for some of the paraffin, n-paraffin, and isoparaffin contents described below, the contents were determined using gas chromatography according to the Linear Paraffin method. The n-paraffin peaks from a hydrocarbon sample in gas chromatography are well known. The n-paraffin peaks can be separately integrated to determine the n-paraffin content of a sample using gas chromatography. The peaks in a GC spectrum between the n-paraffin peaks can be assigned as isoparaffins with the same carbon number as the lower peak, so that a total amount of paraffins having a given carbon number can be determined. The isoparaffin content for a given carbon number can be determined by subtracting the n-paraffin content from the total paraffin content. It is believed that the values herein determined by the Linear Paraffin method are representative of the values that would be obtained according to UOP 990.

[0025] As noted above, UOP 990 can be used to determine paraffin, naphthene, and aromatics content. It is noted that for some paraffin, naphthene, and/or aromatics contents described herein, supercritical fluid chromatography (SFC) was used. It is believed that the SFC characterization values are representative of what would be obtained according to UOP 990. For SFC characterization, the characterization was performed using a commercial supercritical fluid chromatograph system, and the methodology represents an expansion on the methodology described in ASTM D5186 to allow for separate characterization of paraffins and naphthenes. The expansion on the ASTM D5186 methodology was enabled by using additional separation columns, to allow for resolution of naphthenes and paraffins. The system was equipped with the following components: a high pressure pump for delivery of supercritical carbon dioxide mobile phase; temperature controlled column oven; auto-sampler with high pressure liquid injection valve for delivery of sample material into mobile phase; flame ionization detector; mobile phase splitter (low dead volume tee); back pressure regulator to keep the CO₂ in supercritical state; and a computer and data system for control of components and recording of data signal. For analysis, approximately 75 milligrams of sample was diluted in 2 milliliters of toluene and loaded in standard septum cap autosampler vials. The sample was introduced based via the high pressure sampling valve. The SFC separation was performed using multiple commercial silica packed columns (5 micron with either 60 or 30 angstrom pores) connected in series (250 mm in length either 2 mm or 4 mm ID). Column

temperature was held typically at 35 or 40° C. For analysis, the head pressure of columns was typically 250 bar. Liquid CO₂ flow rates were typically 0.3 ml/minute for 2 mm ID columns or 2.0 ml/minute for 4 mm ID columns. The SFC FID signal was integrated into paraffin and naphthenic regions. In addition to characterizing aromatics according to ASTM D5186, a
5 supercritical fluid chromatograph was used to analyze samples for split of total paraffins and total naphthenes. A variety of standards employing typical molecular types can be used to calibrate the paraffin/naphthene split for quantification.

[0026] Carbon number distribution (CND) is obtained by injecting an appropriate sample of olefin containing reactor product into a hydrogenation GC. The hydrogenation GC is
10 adapted with a zone containing Pt/Al₂O₃ or other suitable hydrogenation catalyst under conditions such that the olefinic material is almost or totally saturated with hydrogen that is co-fed with the sample to the hydrogenation zone prior to entering the GC column. Thus the actual GC measurement is of the corresponding saturate molecules rather than a direct measurement of the olefin species. This provides a more accurate measurement of carbon number by
15 reducing the volatility/retention time scatter that would be found among the various olefinic species.

[0027] Regardless of the specific GC protocol (sample volume injected, specific column and detector, carrier gas type and rate, split levels and other details familiar to those skilled in the art), carbon number is differentiated by the GC retention times of normal linear
20 paraffins. Typically in undertaking this analytical method the selected protocol will be calibrated by feeding a calibration standard containing normal linear paraffins of various carbon numbers of interest, or all of carbon numbers from C5 to C20. An imperfect but reasonably accurate and useful approximation is made that the normal linear paraffin isomer of any given carbon number is the lowest volatility and thus highest retention time of all
25 corresponding carbon number isomers. Thus for example, C8 species are those having a retention time that excludes then immediately follows the peak of n-heptane through and including the peak at n-octane, C9 species are those having a retention time that excludes then immediately follows the peak at n-octane through and including the peak at n-nonane, etc. The imperfection is that certain highly branched paraffins of C_{n+1} may have a retention time that
30 overlaps with the normal linear C_n. For the modest branching level of the molecules produced by the inventive process this is a small error estimated at less than about 5% for any given carbon number.

[0028] An exemplary GC protocol will use an Agilent® 8190 GC instrument adapted with the aforementioned hydrogenation zone at appropriate conditions, sending the saturated material to an Agilent® DB-1 column with dimensions of 100 m x 250 mm x 0.5 mm with a hydrogen, nitrogen or helium carrier gas, an FID detector, and a temperature beginning at about 5 40 °C ramped up to a temperature of about 265 °C at a rate of about 1.5 to 3.5 °C/min, and a typical run will last about 80 minutes.

[0029] In this discussion, the term “paraffin” refers to a saturated hydrocarbon chain. Thus, a paraffin is an alkane that does not include a ring structure. The paraffin may be straight-chain or branched-chain and is considered to be a non-ring compound. “Paraffin” is intended 10 to embrace all structural isomeric forms of paraffins. The term “n-paraffin” has the expected definition of a straight chain alkane (no branches or rings in the carbon chain). The term “isoparaffin” is used herein to refer to any alkane that includes one or more branches in the carbon chain but does not include any ring structures.

[0030] In this discussion, the term “iso-olefin” is analogous to “isoparaffin”, but refers 15 to an alkene rather than an alkane. Thus, an iso-olefin is defined as an alkene that includes at least one branch in the carbon chain but that does not include a ring structure.

[0031] In this discussion, the term “naphthene” refers to a cycloalkane (also known as a cycloparaffin). Therefore, naphthenes correspond to saturated ring structures. The term naphthene encompasses single-ring naphthenes and multi-ring naphthenes. The multi-ring 20 naphthenes may have two or more rings, e.g., two-rings, three-rings, four-rings, five-rings, six-rings, seven-rings, eight-rings, nine-rings, and ten-rings. The rings may be fused and/or bridged. The naphthene can also include various side chains, such as one or more alkyl side chains of 1-10 carbons.

[0032] In this discussion, the term “saturates” refers to all straight chain, branched, and 25 cyclic paraffins. Thus, saturates correspond to a combination of paraffins and naphthenes.

[0033] In this discussion, the term “aromatic ring” means five or six atoms joined in a ring structure wherein (i) at least four of the atoms joined in the ring structure are carbon atoms and (ii) all of the carbon atoms joined in the ring structure are aromatic carbon atoms. Therefore, aromatic rings correspond to unsaturated ring structures. Aromatic carbons can be 30 identified using, for example, ¹³C Nuclear Magnetic Resonance. Aromatic rings having atoms attached to the ring (e.g., one or more heteroatoms, one or more carbon atoms, etc.) but which are not part of the ring structure are within the scope of the term “aromatic ring.” Additionally, it is noted that ring structures that include one or more heteroatoms (such as sulfur, nitrogen,

or oxygen) can correspond to an “aromatic ring” if the ring structure otherwise falls within the definition of an “aromatic ring”.

[0034] In this discussion, the term “non-aromatic ring” means four or more carbon atoms joined in at least one ring structure wherein at least one of the four or more carbon atoms in the ring structure is not an aromatic carbon atom. Non-aromatic rings having atoms attached to the ring (e.g., one or more heteroatoms, one or more carbon atoms, etc.), but which are not part of the ring structure, are within the scope of the term “non-aromatic ring.”

[0035] In this discussion, the term “aromatics” refers to all compounds that include at least one aromatic ring. Such compounds that include at least one aromatic ring include compounds that have one or more hydrocarbon substituents. It is noted that a compound including at least one aromatic ring and at least one non-aromatic ring falls within the definition of the term “aromatics”.

[0036] It is noted that that some hydrocarbons present within a feed or product may fall outside of the definitions for paraffins, naphthenes, and aromatics. For example, any alkenes that are not part of an aromatic compound would fall outside of the above definitions. Similarly, non-aromatic compounds that include a heteroatom, such as sulfur, oxygen, or nitrogen, are not included in the definition of paraffins or naphthenes.

Isoparaffinic Blend Component

[0037] In various aspects, an isoparaffinic blend component and/or iso-olefinic blend component can be used to form blended products that can correspond to distillate fuels and/or distillate fuel blending components. In this discussion, to be either an isoparaffinic blend component or an iso-olefinic blend component, a fraction will contain 50 wt% or more of a combined weight of isoparaffins and iso-olefins, or 60 wt% or more, or 70 wt% or more, or 80 wt% or more, such as up to the fraction substantially being composed of isoparaffins and iso-olefins (i.e., less than 8.0 wt% of other types of hydrocarbons / compounds, or less than 5.0 wt%, or less than 3.0 wt%, or less than 1.0 wt%, such as down to zero).

[0038] In addition to the above, an isoparaffinic blend component refers to a fraction containing less than 5.0 wt% iso-olefins and 80 wt% or more of isoparaffins (relative to the weight of the fraction), or 85 wt% or more, or 90 wt% or more, such as up to having substantially all of the fraction correspond to isoparaffins. An iso-olefinic blend component refers to a fraction that a) satisfies the requirement for the combined amount of iso-olefins and isoparaffins, and b) contains 5.0 wt% or more of iso-olefins, or 25 wt% or more, or 50 wt% or

more, or 70 wt% or more, such as up to having substantially all of the fraction correspond to iso-olefins.

[0039] In some aspects, an isoparaffinic blend component and/or an iso-olefinic blend components can be composed of 80 wt% or more of C₉ to C₂₀ isoparaffins, iso-olefins, or a combination thereof, or 90 wt% or more, or 94 wt% or more, or 97 wt% or more, such as up to substantially all of the composition corresponding to C₉ to C₂₀ components. In other aspects, a blend component can be fractionated prior to use. As an example, one option can be to fractionate a blend component to form a lower boiling fraction having a T90 distillation point of 290°C or less, or 280°C or less, or 270°C or less, or 260°C or less (such as down to 240°C). This fractionation will also form a higher boiling fraction having a T10 distillation point of 260°C or higher, or 270°C or higher, or 280°C or higher, or 290°C or higher (such as up to 310°C). This type of fractionation can be useful for separating an isoparaffinic blend component and/or iso-olefinic blend component into a fraction that is substantially entirely within the jet boiling range and a higher boiling fraction. The higher boiling fraction can be blended into a distillate fuel, such as a diesel fuel or a marine fuel. Such a fraction having a T10 distillation point of 290°C or higher is referred to herein as a 290°C+ fraction.

[0040] In various aspects, an isoparaffinic blend component and/or an iso-olefinic blend component can have one or more of the following properties. In some aspects, 2.0 wt% to 25 wt% of the blend component is composed of C₉ hydrocarbons, or 2.0 wt% to 15 wt%, or 5.0 wt% to 25 wt%, or 5.0 wt% to 15 wt%, or 2.0 wt% to 10 wt%. In some aspects, 1.0 wt% to 15 wt% of the blend component is composed of C₁₇₊ hydrocarbons, or 2.5 wt% to 15 wt%. In some aspects, 1.0 wt% to 15 wt% of the blend component is composed of C₁₇ and/or C₁₈ hydrocarbons, or 2.5 wt% to 15 wt%, or 1.0 wt% to 10 wt%, or 2.5 wt% to 10 wt%. In some aspects, the blend component can contain 5.0 wt% or less of C₁₉₊ hydrocarbons, or 3.0 wt% or less, or 1.0 wt% or less, such as down to having substantially no content of C₁₉₊ hydrocarbons. In some aspects, the blend component can include 5.0 wt% or less of C₈ hydrocarbons, or 3.0 wt% or less, or 1.0 wt% or less, or 0.5 wt% or less, such as down to 0.1 wt% or possibly still lower (i.e., substantially no C₈ content). In some aspects, the blend component has a specific gravity at 15°C of 0.730 g/cm³ to 0.775 g/cm³.

[0041] In some aspects, the blend component can contain 60 wt% to 90 wt% of C₁₁ to C₁₈ isoparaffins, iso-olefins, or a combination thereof, based on the weight of the blend component. Additionally or alternately, the blend component can contain 50 wt% to 75 wt% of C₁₂ to C₁₆ isoparaffins, iso-olefins, or a combination thereof based on the weight of the blend

component. Having high amounts of larger isoparaffins can be beneficial for diesel fuel and/or diesel fuel blend component applications. Having higher amounts of larger isoparaffins / iso-olefins can be beneficial for marine fuel or marine fuel blend component applications.

[0042] In other aspects where the blend component corresponds to a higher boiling fraction (e.g., a higher boiling fraction having a T10 of 260°C or more), an isoparaffinic blend component and/or an iso-olefinic blend component can have one or more of the following properties. In some aspects, 50 wt% to 100 wt% of the blend component is composed of C₁₇+ hydrocarbons, or 50 wt% to 90 wt%, or 60 wt% to 100 wt%, or 60 wt% to 90 wt%. In some aspects, 50 wt% to 90 wt% of the blend component is composed of C₁₇ and/or C₁₈ hydrocarbons, or 50 wt% to 80 wt%. In some aspects, the blend component can contain 2.5 wt% to 50 wt% of C₁₉+ hydrocarbons, or 5.0 wt% to 50 wt%, or 10 wt% to 50 wt%, or 20 wt% to 50 wt%, or 5.0 wt% to 25 wt%, or 10 wt% to 25 wt%. In some aspects, the blend component can include 10 wt% or less of C₁₆- hydrocarbons, or 5.0 wt% or less, or 1.0 wt% or less, or 0.5 wt% or less, such as down to 0.1 wt% or possibly still lower (i.e., substantially no C₁₆- content). In some aspects, the blend component has a specific gravity at 15°C of 0.760 g/cm³ to 0.810 g/cm³.

[0043] In various aspects, the blend component can contain a reduced or minimized amount of aromatics. This can correspond to containing 5.0 wt% or less of aromatics, or 3.0 wt% or less, or 1.0 wt% or less, or 0.5 wt% or less, or 0.1 wt% or less, such as down to having substantially no aromatics content.

[0044] In various aspects, the blend component can have a flash point of 38° C or higher, or 40°C or higher, or 45°C or higher, or 50°C or higher, or 55°C or higher, such as up to 60°C or possibly still higher. Additionally or alternately, the blend component can have a cetane rating of 46.0 to 51.0, or 47.0 to 51.0, or 48.0 to 51.0. Further additionally or alternately, the blend component can have a kinematic viscosity at 40°C of 1.9 cSt to 4.5 cSt, or 2.2 cSt to 4.5 cSt, or 2.5 cSt to 4.5 cSt, or 1.9 cSt to 4.1 cSt, or 2.2 cSt to 4.1 cSt, or 2.5 cSt to 4.1 cSt, or 1.9 cSt to 3.0 cSt, or 2.0 cSt to 3.0 cSt, or 2.2 cSt to 3.0 cSt, or 1.9 cSt to 2.8 cSt, or 2.0 cSt to 2.8 cSt, or 2.2 cSt to 2.8 cSt. Still further additionally or alternately, the blend component can have a cloud point of -40°C or less, or -50°C or less, or -60°C or less, such as down to -100°C or possibly still lower.

[0045] In some aspects, the blend component, prior to adding any additives, can have an electrical conductivity of 10 pS/m or less (according to ASTM Test Method D2624), such as down to having substantially no electrical conductivity. It is noted that an isoparaffinic blend

component as described herein has a good response to conductivity additives. After addition of conventional additives for conductivity, an isoparaffinic blend component can have a conductivity of 50 pS/m to 600 pS/m.

[0046] An example of a suitable process for making an iso-olefinic blend component and/or an isoparaffinic blend component is described in U.S. Patent 7,692,049, which is incorporated by reference herein for the limited purpose of describing how to make the isoparaffinic blend component. Briefly, the blend component can be produced by oligomerizing a feed containing at least one C₃ to C₈ olefin together with an olefinic recycle stream containing no more than 10 wt. % C₁₀+ non-normal olefins over a molecular sieve catalyst such that a) the recycle to fresh feed weight ratio is from about 0.5 to about 2.0 and b) the difference between the highest and lowest temperatures within the reactor is 40°F (22°C) or less. The oligomerization product is then separated into an iso-olefinic stream and at least one light olefinic stream. At least part of the light olefinic stream(s) is then recycled to the oligomerization process. In various aspects, the iso-olefinic stream can be exposed to hydroprocessing conditions to produce an isoparaffinic stream.

[0047] The fresh feed to the oligomerization process can include any single C₃ to C₈ olefin or any mixture thereof in any proportion. Particularly suitable feeds include mixtures of propylene and butylenes having at least 5 wt%, such as at least 10 wt%, for example at least 20 wt%, such as at least 30 wt% or at least 40 wt% C₄ olefin. Also useful are mixtures of C₃ to C₅ olefins having at least 40 wt% C₄ olefin and at least 10 wt% C₅ olefin.

[0048] In one aspect, the olefinic feed is obtained by the conversion of an oxygenate, such as methanol, to olefins over a either silicoaluminophosphate (SAPO) catalyst, according to the method of, for example, U.S. Pat. Nos. 4,677,243 and 6,673,978, or an aluminosilicate catalyst, according to the method of, for example, WO04/18089, WO04/16572, EP 0 882 692 and U.S. Pat. No. 4,025,575. Alternatively, the olefinic feed can be obtained by the catalytic cracking of relatively heavy petroleum fractions, or by the pyrolysis of various hydrocarbon streams, ranging from ethane to naphtha to heavy fuel oils, in admixture with steam, in a well understood process known as “steam cracking”.

[0049] In various aspects, the feed to the oligomerization process also contains an olefinic recycle stream containing no more than 10 wt% C₁₀+ non-normal olefins and/or having a final boiling point of 170°C or less. In some aspects, the olefinic recycle stream can include 30 wt% or less of C₉+ olefins, or 10 wt% or less and/or have a final boiling point of 140°C or less. Additionally or alternately, in some aspects, the olefinic recycle stream contains 30 wt%

or less of C₄ hydrocarbons, or 5.0 wt% or less (therefore roughly corresponding to a de-butanized stream). The amount of olefinic recycle stream fed to the oligomerization process is such that the recycle to fresh feed weight ratio is from about 0.5 to about 2.0. More particularly, the mass ratio of olefinic recycle stream to fresh olefinic feedstock can be at least 0.7 or at least 5 0.9, but generally is no greater than 1.8, or no greater than 1.5 or no greater than 1.3.

[0050] In addition, the feedstock, the recycle or both may comprise other materials, such as an inert diluent, for example, a saturated hydrocarbon, or other hydrocarbon species, such as aromatics or dienes.

[0051] The catalyst used in the oligomerization process can include any crystalline 10 molecular sieve which is active in olefin oligomerization reactions. In one embodiment, the catalyst includes a medium pore size molecular sieve having a Constraint Index of about 1 to about 12. Constraint Index and a method of its determination are described in U.S. Pat. No. 4,016,218, which is incorporated herein by reference. Examples of suitable medium pore size molecular sieves are those having 10-membered ring pore openings and include those of the 15 TON framework type (for example, ZSM-22, ISI-1, Theta-1, Nu-10, and KZ-2), those of the MTT framework type (for example, ZSM-23 and KZ-1), of the MFI structure type (for example, ZSM-5), of the MFS framework type (for example, ZSM-57), of the MEL framework type (for example, ZSM-11), of the MTW framework type (for example, ZSM-12), of the EUO framework type (for example, EU-1) and members of the ferrierite family (for example, ZSM-20 35). In one preferred embodiment, the molecular sieve catalyst comprises ZSM-5.

[0052] Other examples of suitable molecular sieves include those having 12-membered pore openings, such as ZSM-18, zeolite beta, faujasites, zeolite L, mordenites, as well as members of MCM-22 family of molecular sieves (including, for example, MCM-22, PSH-3, SSZ-25, ERB-1, ITQ-1, ITQ-2, MCM-36, MCM-49 and MCM-56).

25 **[0053]** In one embodiment, the crystalline aluminosilicate molecular sieve has an average (d₅₀) crystal size no greater than 0.15 micron. In addition, the molecular sieve is preferably selected so as to have an alpha value between about 100 and about 600, conveniently between about 200 and about 400, or between about 250 and about 350. The alpha value of a molecular sieve is an approximate indication of its catalytic cracking activity compared with a standard 30 silica-alumina catalyst test (with an alpha value of 1). The alpha test is described in U.S. Pat. No. 3,354,078; in the Journal of Catalysis, Vol. 4, p. 527 (1965); Vol. 6, p. 278 (1966); and Vol. 61, p. 395 (1980), each incorporated herein by reference as to that description. The experimental conditions of the test used herein include a constant temperature of 538° C. and

a variable flow rate as described in detail in the Journal of Catalysis, Vol. 61, p. 395. Conveniently the crystalline aluminosilicate molecular sieve having a silica to alumina molar ratio of about 20 to about 300, such as about 20 to about 150, for example about 45 to about 90.

5 **[0054]** The molecular sieve may be supported or unsupported, for example in powder form, or used as an extrudate with an appropriate binder. Where a binder is employed, the binder is conveniently a metal oxide, such as alumina, and is present in an amount such that the oligomerization catalyst contains between about 2 and about 80 wt. % of the molecular sieve.

10 **[0055]** The oligomerization reaction should be conducted at sufficiently high WHSV of fresh feed to the reactor to ensure the desired low level of C₁₇+ oligomers in the reaction product. This can correspond to a WHSV (weight hourly space velocity) of 1.5 or more on a weight of fresh feed versus weight of molecular sieve in the catalyst basis. With regard to the combined fresh olefin feed and recycle to the reactor, the WHSV can be 2.3 or more, again
15 based on the amount of molecular sieve in the oligomerization catalyst.

[0056] The oligomerization process can be conducted over a wide range of temperatures, although generally the temperature within the oligomerization reaction zone should be between about 150°C and 350°C. It is, however, important to ensure that the temperature across the reaction zone is maintained relatively constant so as to produce the desired level of C₄ olefin
20 conversion at a given WHSV and point in the reaction cycle. Thus, as discussed above, the difference between the highest and lowest temperatures within the reactor should be maintained at 40°F (22°C) or less.

[0057] The oligomerization process can be conducted over a wide range of olefin partial pressures, although higher olefin partial pressures are preferred since low pressures tend to
25 promote cyclization and cracking reactions, and are thermodynamically less favorable to the preferred oligomerization reaction. Typical olefin partial pressures of olefins in the combined olefinic feed and light olefinic/recycle stream as total charge to the reactor comprise at least 400 psig (2860 kPa).

[0058] As synthesized, the resulting oligomerized product can correspond to an iso-olefinic blend component. The iso-olefinic blend component can be converted to an isoparaflinic blend component by any convenient olefin saturation process, such as a mild hydrotreatment process. Mild hydroprocessing can generally convert iso-olefins to isoparaflins
30 with a reduced or minimized amount of reduction in the size of the carbon chains in a fraction.

In addition to converting iso-olefins to isoparaffins, hydroprocessing of a kerosene fraction can also be used to remove sulfur, remove nitrogen, saturate olefins, saturate aromatics, and/or for other purposes.

[0059] During hydroprocessing, a feedstock that is partially or entirely composed of a jet fuel boiling range fraction is treated in a hydrotreatment (or other hydroprocessing) reactor that includes one or more hydrotreatment stages or beds. Optionally, the reaction conditions in the hydrotreatment stage(s) can be conditions suitable for reducing the sulfur content of the feedstream, such as conditions suitable for reducing the sulfur content of the feedstream to 500 wppm or less, or 100 wppm or less, or 15 wppm or less, or 10 wppm or less, such as down to 0.5 wppm or possibly still lower. The reaction conditions can include an LHSV of 0.1 to 20.0 hr⁻¹, a hydrogen partial pressure from about 50 psig (0.34 MPag) to about 3000 psig (20.7 MPag), a treat gas containing at least about 50% hydrogen, and a temperature of from about 450°F (232°C) to about 800°F (427°C). Preferably, the reaction conditions include an LHSV of from about 0.3 to about 5 hr⁻¹, a hydrogen partial pressure from about 100 psig (0.69 MPag) to about 1000 psig (6.9 MPag), and a temperature of from about 700°F (371°C) to about 750°F (399°C).

[0060] Optionally, a hydrotreatment reactor can be used that operates at a relatively low total pressure values, such as total pressures of about 200 psig (1.4 MPag) to about 800 psig (5.5 MPag). For example, the pressure in a stage in the hydrotreatment reactor can be at least about 200 psig (1.4 MPag), or at least about 300 psig (2.1 MPag), or at least about 400 psig (2.8 MPag), or at least about 450 psig (3.1 MPag). The pressure in a stage in the hydrotreatment reactor can be about 800 psig (5.5 MPag) or less, or about 700 psig (4.8 MPag) or less, or about 600 psig (4.1 MPa) or less.

[0061] The catalyst in a hydrotreatment stage can be a conventional hydrotreating catalyst, such as a catalyst composed of a Group VIB metal and/or a Group VIII metal on a support. Suitable metals include cobalt, nickel, molybdenum, tungsten, or combinations thereof. Preferred combinations of metals include nickel and molybdenum or nickel, cobalt, and molybdenum. Suitable supports include silica, silica-alumina, alumina, and titania.

[0062] In an embodiment, the amount of treat gas delivered to the hydrotreatment stage can be based on the consumption of hydrogen in the stage. The treat gas rate for a hydrotreatment stage can be from about two to about five times the amount of hydrogen consumed per barrel of fresh feed in the stage. A typical hydrotreatment stage can consume from about 50 SCF/B (8.4 m³/m³) to about 1000 SCF/B (168.5 m³/m³) of hydrogen, depending

on various factors including the nature of the feed being hydrotreated. Thus, the treat gas rate can be from about 100 SCF/B (16.9 m³/m³) to about 5000 SCF/B (842 m³/m³). Preferably, the treat gas rate can be from about four to about five time the amount of hydrogen consumed. Note that the above treat gas rates refer to the rate of hydrogen flow. If hydrogen is delivered
5 as part of a gas stream having less than 100% hydrogen, the treat gas rate for the overall gas stream can be proportionally higher.

Blended Diesel Boiling Range Products

[0063] An isoparaffinic blend component and/or iso-olefinic blend component can be blended with one or more other fractions to form a diesel boiling range product. Examples of
10 fractions that can be blended with an isoparaffinic blend component and/or iso-olefinic blend component include, but are not limited to, conventional diesel fractions, mineral diesel boiling range fractions, and various types of synthetic diesel boiling range fractions, such as hydrotreated vegetable oil, biodiesel (e.g., derived from processing of fatty acid methyl esters), other bio-derived diesel fractions, and/or Fischer-Tropsch fractions. Other challenged fractions
15 where at least a portion of the fraction corresponds to diesel boiling range components can also be blended with an isoparaffinic blend component and/or iso-olefinic blend component.

[0064] In various aspects, a blended product can contain 1.0 vol% or more of an isoparaffinic blend component, or 10 vol% or more, or 20 vol% or more, or 30 vol% or more, or 40 vol% or more, or 60 vol% or more, or 75 vol% or more, such as up to 99 vol% or possibly
20 still higher. In some aspects, such a blended product can include 1.0 vol% to 50 vol% of an isoparaffinic blend component, or 1.0 vol% to 10 vol%, or 1.0 vol% to 30 vol%, or 10 vol% to 50 vol%, or 10 vol% to 30 vol%, or 30 vol% to 50 vol%. In other aspects, such a blended product can include 1.0 vol% to 99 vol% of an isoparaffinic blend component, or 1.0 vol% to 95 vol%, or 1.0 vol% to 70 vol%, or 1.0 vol% to 50 vol%, or 10 vol% to 99 vol%, or 10 vol%
25 to 95 vol%, or 10 vol% to 70 vol%, or 10 vol% to 50 vol%, or 30 vol% to 99 vol%, or 30 vol% to 95 vol%, or 30 vol% to 70 vol%, or 30 vol% to 50 vol%, or 50 vol% to 99 vol%, or 50 vol% to 95 vol%, or 50 vol% to 70 vol%, or 70 vol% to 99 vol%.

[0065] Additionally or alternately, in various aspects, a blended product can contain 1.0 vol% or more of an isoparaffinic blend component, or 10 vol% or more, or 20 vol% or more,
30 or 30 vol% or more, or 40 vol% or more, or 60 vol% or more, or 75 vol% or more, such as up to 99 vol% or possibly still higher. In some aspects, such a blended product can include 1.0 vol% to 50 vol% of an isoparaffinic blend component, or 1.0 vol% to 10 vol%, or 1.0 vol% to 30 vol%, or 10 vol% to 50 vol%, or 10 vol% to 30 vol%, or 30 vol% to 50 vol%. In other

aspects, such a blended product can include 1.0 vol% to 99 vol% of an isoparaffinic blend component, or 1.0 vol% to 95 vol%, or 1.0 vol% to 70 vol%, or 1.0 vol% to 50 vol%, or 10 vol% to 99 vol%, or 10 vol% to 95 vol%, or 10 vol% to 70 vol%, or 10 vol% to 50 vol%, or 30 vol% to 99 vol%, or 30 vol% to 95 vol%, or 30 vol% to 70 vol%, or 30 vol% to 50 vol%, or 50 vol% to 99 vol%, or 50 vol% to 95 vol%, or 50 vol% to 70 vol%, or 70 vol% to 99 vol%.

[0066] In some aspects, the resulting blended product can include an unexpectedly high content of C₁₂-isoparaffins and/or iso-olefins. In such aspects, the resulting blended product can contain 6.0 wt% or more of C₁₂-isoparaffins and/or iso-olefins, or 10 wt% or more, or 15 wt% or more, 20 wt% or more, such as up to 40 wt% or possibly still higher. Additionally or alternately, in some aspects, the resulting blended product can include an unexpectedly high content of C₁₂ isoparaffins and/or iso-olefins. In such aspects, the resulting blended product can include 6.0 wt% or more of C₁₂ isoparaffins and/or iso-olefins, or 10 wt% or more, such as up to 20 wt% or possibly still higher.

[0067] In some aspects, the resulting blended product can have an unexpectedly high content of C₉ hydrocarbons. In such aspects, the resulting blended product can contain 5.0 wt% or more of C₉ hydrocarbons, or 10 wt% or more, or 15 wt% or more, such as up to 25 wt% or possibly still higher.

[0068] In various aspects, the resulting blended product can have a density at 15°C of 0.760 g/cm³ to 0.840 g/cm³. In aspects where the blended product includes less than 50 vol% of conventional and/or mineral diesel fractions, the density at 15°C can be 0.760 g/cm³ to 0.840 g/cm³, or 0.760 g/cm³ to 0.825 g/cm³, or 0.760 g/cm³ to 0.810 g/cm³, or 0.760 g/cm³ to 0.800 g/cm³, or 0.780 g/cm³ to 0.840 g/cm³, or 0.780 g/cm³ to 0.825 g/cm³, or 0.780 g/cm³ to 0.810 g/cm³, or 0.780 g/cm³ to 0.800 g/cm³, or 0.790 g/cm³ to 0.840 g/cm³, or 0.790 g/cm³ to 0.825 g/cm³. In aspects where the blended product includes 50 vol% or more of a conventional and/or mineral diesel fraction, the density at 15°C can be 0.780 g/cm³ to 0.840 g/cm³, or 0.800 g/cm³ to 0.840 g/cm³, or 0.815 g/cm³ to 0.840 g/cm³, or 0.780 g/cm³ to 0.825 g/cm³, or 0.800 g/cm³ to 0.825 g/cm³.

[0069] Additionally or alternately, the resulting blended product can have a flash point of 40°C or higher, or 50°C or higher, or 60°C or higher, such as up to 120°C or possibly still higher.

[0070] In some aspects, when an isoparaffinic blend component and/or an iso-olefinic blend component is blended with a conventional diesel boiling range fraction and/or a mineral

diesel boiling range fraction, the cetane number of the resulting blend can be lower than the cetane number of the conventional diesel boiling range fraction and/or the mineral diesel boiling range fraction. In some aspects, when an isoparaffinic blend component and/or an iso-olefinic blend component is blended with a bio-derived diesel boiling range fraction (e.g.,
5 biodiesel, hydrotreated vegetable oil, diesel derived from fatty acid methyl ester), the cetane number of the resulting blend can be lower than the cetane number of the bio-derived diesel boiling range fraction. In some aspects, the cetane number of the resulting blend can be 54.0 or less, or 53.0 or less, such as down to 52.0, or down to 50.0, or down to 48.0. In some aspects, when an isoparaffinic blend component and/or an iso-olefinic blend component is blended with
10 a Fischer-Tropsch-derived diesel boiling range fraction, the cetane number of the resulting blend can be lower than the cetane number of the Fischer-Tropsch-derived diesel boiling range fraction. In some aspects, the cetane number of the resulting blend can be 54.0 or less, or 53.0 or less, such as down to 52.0, or down to 50.0, or down to 48.0.

[0071] In various aspects, an isoparaffinic blend component and/or iso-olefinic blend
15 component can have favorable cold flow properties relative to other types of blend components. In some aspects where at least 20 vol% (or at least 40 vol%, or at least 60 vol%, such as up to 80 vol%) of an isoparaffinic blend component and/or iso-olefinic blend component is blended with at least 20 vol% (or at least 40 vol%, or at least 60 vol%, such as up to 80 vol%) of conventional / mineral diesel boiling range component, the cloud point of the resulting blend
20 can be lower than the cloud point of the conventional / mineral diesel boiling range fraction by 10°C or more, or 15°C or more, or 20°C or more, such as up to 60°C or possibly still more. In some aspects where at least 20 vol% (or at least 40 vol%, or at least 60 vol%, such as up to 80 vol%) of an isoparaffinic blend component and/or iso-olefinic blend component is blended with at least 20 vol% (or at least 40 vol%, or at least 60 vol%, such as up to 80 vol%) of synthetic
25 diesel boiling range component, the cloud point of the resulting blend can be lower than the cloud point of the synthetic diesel boiling range fraction by 10°C or more, or 15°C or more, or 20°C or more, such as up to 60°C lower or possibly still more.

[0072] In various aspects, the resulting blended product can have a kinematic viscosity at 40°C of 2.0 to 3.5, or 2.0 to 3.2, or 2.0 to 2.8, or 2.0 to 2.4, or 2.0 to 2.2, or 2.2 to 3.5, or 2.2
30 to 3.2, or 2.2 to 2.8, or 2.2 to 2.4.

[0073] In some aspects, the resulting blended product can contain a reduced or minimized amount of aromatics. This can correspond to containing 15 wt% or less of aromatics, or 10 wt% or less, or 5.0 wt% or less, or 3.0 wt% or less, or 1.0 wt% or less, or 0.5 wt% or less, or

0.1 wt% or less, such as down to having substantially no aromatics content. Additionally or alternately, the sulfur content can be 500 wppm or less, or 250 wppm or less, or 100 wppm or less, or 15 wppm or less, or 10 wppm or less, such as down to 0.5 wppm or possibly still lower. Additionally, it is noted that an isoparaffinic blend component and/or iso-olefinic blend component can contain substantially no polyaromatic hydrocarbons. Thus, blends including an isoparaffinic blend component and/or iso-olefinic blend component can have a corresponding reduction in total polyaromatic hydrocarbons (relative to the content of the other blend components).

[0074] In some aspects, the resulting blended product can include at least a portion of one or more conventional diesel fuel(s). A conventional diesel fuel is defined herein as a fraction that already qualifies as a diesel fuel under at least one of ASTM D975 and EN 590. In such aspects, the resulting blended product can include 1.0 vol% to 99 vol% of a conventional diesel fuel fraction, or 1.0 vol% to 90 vol%, or 1.0 vol% to 70 vol%, or 1.0 vol% to 50 vol%, or 1.0 vol% to 30 vol%, or 1.0 vol% to 10 vol%, or 10 vol% to 99 vol%, or 10 vol% to 90 vol%, or 10 vol% to 70 vol%, or 10 vol% to 50 vol%, or 10 vol% to 30 vol%, or 30 vol% to 99 vol%, or 30 vol% to 90 vol%, or 30 vol% to 70 vol%, or 50 vol% to 99 vol%, or 50 vol% to 90 vol%, or 70 vol% to 99 vol%, or 70 vol% to 90 vol%. Thus, the resulting blended product can, in some aspects, include 50 vol% or less of a conventional diesel boiling range fraction, or 30 vol% or less, or 10 vol% or less, such as down to 1.0 vol% or possibly still lower.

[0075] In some aspects, the resulting blended product can include at least a portion of one or more mineral diesel boiling range fraction(s). In such aspects, the resulting blended product can include 1.0 vol% to 99 vol% of a mineral diesel fuel fraction, or 1.0 vol% to 90 vol%, or 1.0 vol% to 70 vol%, or 1.0 vol% to 50 vol%, or 1.0 vol% to 30 vol%, or 1.0 vol% to 10 vol%, or 10 vol% to 99 vol%, or 10 vol% to 90 vol%, or 10 vol% to 70 vol%, or 10 vol% to 50 vol%, or 10 vol% to 30 vol%, or 30 vol% to 99 vol%, or 30 vol% to 90 vol%, or 30 vol% to 70 vol%, or 50 vol% to 99 vol%, or 50 vol% to 90 vol%, or 70 vol% to 99 vol%, or 70 vol% to 90 vol%. Thus, the resulting blended product can, in some aspects, include 50 vol% or less of a mineral boiling range fraction, or 30 vol% or less, or 10 vol% or less, such as down to 1.0 vol% or possibly still lower.

[0076] In some aspects, the resulting blended product can include at least a portion of one or more synthetic diesel boiling range fraction(s), such as bio-derived diesel boiling range fractions and/or Fischer-Tropsch derived diesel boiling range fractions. In such aspects, the

resulting blended product can include 1.0 vol% to 99 vol% of a synthetic diesel boiling range fraction, or 1.0 vol% to 90 vol%, or 1.0 vol% to 70 vol%, or 1.0 vol% to 50 vol%, or 1.0 vol% to 30 vol%, or 1.0 vol% to 10 vol%, or 10 vol% to 99 vol%, or 10 vol% to 90 vol%, or 10 vol% to 70 vol%, or 10 vol% to 50 vol%, or 10 vol% to 30 vol%, or 30 vol% to 99 vol%, or 30 vol% to 90 vol%, or 30 vol% to 70 vol%, or 50 vol% to 99 vol%, or 50 vol% to 90 vol%, or 70 vol% to 99 vol%, or 70 vol% to 90 vol%. Thus, the resulting blended product can, in some aspects, include 50 vol% or less of a synthetic diesel boiling range fraction, or 30 vol% or less, or 10 vol% or less, such as down to 1.0 vol% or possibly still lower.

[0077] It is noted that an isoparaffinic and/or iso-olefinic blend component can be blended with a plurality of different types of fractions. For example, in some aspects, a blended product can include two or more (or three or more) of a conventional diesel fuel fraction, a mineral diesel boiling range fraction, and a synthetic diesel boiling range fraction.

[0078] In some aspects, after blending components together to form a diesel fuel boiling range fraction, it may be desirable to further treat the diesel boiling range fraction for any convenient reason, such as by hydroprocessing the diesel fuel boiling range fraction to reduce or remove heteroatoms such as sulfur, nitrogen and oxygen and/or to improve cold flow properties.

Blended Marine Fuel Products

[0079] In some aspects, an isoparaffinic blend component and/or iso-olefinic blend component can be blended with one or more other fractions to form a marine fuel oil product or marine fuel oil blending component, such as a very low sulfur fuel oil (VLSFO) or an ultra low sulfur fuel oil (ULSFO). In other aspects, an isoparaffinic blend component and/or iso-olefinic blend component can be blended with one or more other fractions to form a marine gas oil product and/or marine gas oil blending component (also referred to as a marine distillate product and/or a marine distillate blending component).

[0080] Examples of fractions that can be blended with an isoparaffinic blend component and/or iso-olefinic blend component include, but are not limited to, conventional fuel oil fractions (including low sulfur fuel oil, VLSFO, and/or ULSFO), mineral fuel oil fractions, renewable fractions, hydroprocessed and/or non-hydroprocessed fractions, and cracked fractions.

[0081] Examples of hydroprocessed fractions include hydroprocessed distillate fractions (i.e., a hydroprocessed fraction having the distillate boiling range) and hydroprocessed resid fractions (i.e., a hydroprocessed fraction having the resid boiling range). It is noted that a

hydroprocessed fraction derived from a biological source, such as hydrotreated vegetable oil, can correspond to a hydroprocessed distillate fraction and/or a hydroprocessed resid fraction, depending on the boiling range of the hydroprocessed fraction.

5 [0082] A cracked fraction refers to a hydrocarbon and/or hydrocarbonaceous fraction that is derived from the effluent of a thermal cracking or catalytic cracking process. A cracked distillate fraction (having the distillate boiling range), such as a light cycle oil from a fluid catalytic cracking process, is an example of a cracked fraction.

[0083] Renewable blending components can correspond to renewable distillate and/or vacuum gas oil and/or vacuum resid boiling range components that are renewable based on one or more attributes. Some renewable blending components can correspond to components that are renewable based on being of biological origin. Examples of renewable blending components of biological origin can include, but are not limited to, fatty acid methyl esters (FAME), fatty acid alkyl esters, biodiesel, biomethanol, biologically derived dimethyl ether, oxymethylene ether, liquid derived from biomass, pyrolysis products from pyrolysis of biomass, products from gasification of biomass, and hydrotreated vegetable oil. Other renewable blending components can correspond to components that are renewable based on being extracted from a reservoir using renewable energy, such as petroleum extracted from a reservoir using an extraction method that is powered by renewable energy, such as electricity generated by solar, wind, or hydroelectric power. Still other renewable blending components can correspond to blending components that are made or processed using renewable energy, such as Fischer-Tropsch distillate that is formed using processes that are powered by renewable energy, or conventional petroleum distillate that is hydroprocessed / otherwise refinery processed using reactors that are powered by renewable energy. Yet other renewable blending components can correspond to fuel blending components formed from recycling and/or processing of municipal solid waste, plastic waste, or another source of carbon-containing waste. An example of processing of waste is pyrolysis and/or gasification of waste, such as pyrolysis of plastic waste or gasification of municipal solid waste.

30 [0084] More generally, isoparaﬃnic blend components and/or iso-olefinic blend components as described herein may be blended with any of the following and any combination thereof in order to form a fuel and/or fuel blending component: low sulfur diesel (sulfur content of less than 500 wppm), ultra low sulfur diesel (sulfur content <10 or <15 ppmw), low sulfur gas oil, ultra low sulfur gasoil, low sulfur kerosene, ultra low sulfur kerosene, hydrotreated straight run diesel, hydrotreated straight run gas oil, hydrotreated straight run kerosene,

- hydrotreated cycle oil, hydrotreated thermally cracked diesel, hydrotreated thermally cracked gas oil, hydrotreated thermally cracked kerosene, hydrotreated coker diesel, hydrotreated coker gas oil, hydrotreated coker kerosene, hydrocracker diesel, hydrocracker gas oil, hydrocracker kerosene, gas-to-liquid diesel, gas-to-liquid kerosene, gas-to-liquid vacuum gas oil,
- 5 hydrotreated vegetable oil, fatty acid methyl esters, non-hydrotreated straight-run diesel, non-hydrotreated straight-run kerosene, non-hydrotreated straight-run gas oil and any distillates derived from low sulfur crude slates, gas-to-liquid wax, and other gas-to-liquid hydrocarbons, non-hydrotreated cycle oil, non-hydrotreated fluid catalytic cracking slurry oil, non-hydrotreated pyrolysis gas oil, non-hydrotreated cracked light gas oil, non-hydrotreated
- 10 cracked heavy gas oil, non-hydrotreated pyrolysis light gas oil, non-hydrotreated pyrolysis heavy gas oil, non-hydrotreated pyrolysis distillate (e.g., kerosene and/or diesel), non-hydrotreated pyrolysis residue, non-hydrotreated thermally cracked residue, non-hydrotreated thermally cracked heavy distillate, non-hydrotreated coker heavy distillates, non-hydrotreated vacuum gas oil, non-hydrotreated coker diesel, non-hydrotreated coker gasoil, non-
- 15 hydrotreated coker vacuum gas oil, non-hydrotreated thermally cracked vacuum gas oil, non-hydrotreated thermally cracked diesel, non-hydrotreated thermally cracked gas oil, hydrotreated fats or oils such as hydrotreated vegetable oil, hydrotreated tall oil, etc., fatty acid methyl ester, Group 1 slack waxes, lube oil aromatic extracts, deasphalted oil, atmospheric tower bottoms, vacuum tower bottoms, steam cracker tar, any residue materials derived from
- 20 low sulfur crude slates, LSFO, RSFO, other LSFO / RSFO blend stocks. A mineral and/or conventional feedstock for blending with an isoparaffinic and/or iso-olefinic blend component can have a sulfur content of 6500 wppm or less, or 5000 wppm or less, or 3000 wppm or less, or 2000 wppm or less, or 1000 wppm or less, or 100 wppm or less, such as down to having substantially no sulfur content (0.1 wppm or less).
- 25 **[0085]** In various aspects for forming a fuel oil product or fuel oil blend component, a blended product can contain 1.0 vol% to 75 vol% of an isoparaffinic blend component and/or iso-olefinic blend component, or 10 vol% to 75 vol%, or 20 vol% to 75 vol%, or 1.0 vol% to 50 vol%, or 10 vol% or more to 50 vol%, or 20 vol% to 50 vol%, or 1.0 vol% to 40 vol%, or 10 vol% to 40 vol%, or 20 vol% to 40 vol%, or 1.0 vol% to 30 vol%, or 10 vol% to 30 vol%,
- 30 or 1.0 vol% to 20 vol%. In some aspects, a blended product can contain 1.0 vol% to 50 vol% of an isoparaffinic blend component, or 10 vol% or more to 50 vol%, or 20 vol% to 50 vol%, or 1.0 vol% to 40 vol%, or 10 vol% to 40 vol%, or 20 vol% to 40 vol%, or 1.0 vol% to 30 vol%, or 10 vol% to 30 vol%, or 1.0 vol% to 20 vol%. In some aspects, a blended product can contain 1.0 vol% to 50 vol% of an iso-olefinic blend component, or 10 vol% or more to 50

vol%, or 20 vol% to 50 vol%, or 1.0 vol% to 40 vol%, or 10 vol% to 40 vol%, or 20 vol% to 40 vol%, or 1.0 vol% to 30 vol%, or 10 vol% to 30 vol%, or 1.0 vol% to 20 vol%.

[0086] In aspects related to forming a marine gas oil or marine gas oil blending component, a blended product can contain 1.0 vol% or more of an isoparaﬃnic blend component and/or iso-olefinic blend component, or 10 vol% or more, or 20 vol% or more, or 30 vol% or more, or 40 vol% or more, or 60 vol% or more, or 75 vol% or more, such as up to 99 vol% or possibly still higher. In some aspects, such a blended product can include 1.0 vol% to 40 vol% of an isoparaﬃnic blend component and/or iso-olefinic blend component, or 1.0 vol% to 20 vol%, or 10 vol% to 40 vol%, or 10 vol% to 20 vol%, or 20 vol% to 40 vol%. In other aspects, such a blended product can include 1.0 vol% to 99 vol% of an isoparaﬃnic blend component and/or iso-olefinic blend component, or 1.0 vol% to 95 vol%, or 1.0 vol% to 80 vol%, or 1.0 vol% to 60 vol%, or 20 vol% to 99 vol%, or 20 vol% to 95 vol%, or 20 vol% to 80 vol%, or 40 vol% to 99 vol%, or 40 vol% to 95 vol%, or 40 vol% to 80 vol%, or 40 vol% to 60 vol%, or 60 vol% to 99 vol%, or 60 vol% to 95 vol%, or 60 vol% to 80 vol%, or 75 vol% to 99 vol%. In still other aspects, such a blended product can include 20 vol% to 80 vol% of an isoparaﬃnic blend component and/or iso-olefinic blend component, or 20 vol% to 60 vol%, or 20 vol% to 40 vol%, or 40 vol% to 80 vol%, or 40 vol% to 60 vol%, or 60 vol% to 80 vol%.

[0087] In some aspects, the resulting blended product can include an unexpectedly high content of C₁₂-isoparaﬃns and/or iso-olefins. In such aspects, the resulting blended product can contain 6.0 wt% or more of C₁₂-isoparaﬃns and/or iso-olefins, or 10 wt% or more, or 15 wt% or more, or 20 wt% or more, such as up to 40 wt% or possibly still higher. Additionally or alternately, in some aspects, the resulting blended product can include an unexpectedly high content of C₁₂ isoparaﬃns and/or iso-olefins. In such aspects, the resulting blended product can include 6.0 wt% or more of C₁₂ isoparaﬃns and/or iso-olefins, or 10 wt% or more, such as up to 20 wt% or possibly still higher.

[0088] In some aspects, the resulting blended product can have an unexpectedly high content of C₉ hydrocarbons. In such aspects, the resulting blended product can contain 5.0 wt% or more of C₉ hydrocarbons, or 10 wt% or more, or 15 wt% or more, such as up to 25 wt% or possibly still higher.

[0089] In various aspects related to a marine fuel oil or marine fuel oil blend component, the resulting blended product can have a density at 15°C of 0.850 g/cm³ to 0.980 g/cm³, or 0.850 g/cm³ to 0.950 g/cm³, or 0.850 g/cm³ to 0.900 g/cm³, or 0.875 g/cm³ to 0.980 g/cm³, or 0.875 g/cm³ to 0.950 g/cm³, or 0.900 g/cm³ to 0.980 g/cm³, or 0.900 g/cm³ to 0.950 g/cm³, or

0.925 g/cm³ to 0.980 g/cm³, or 0.925 g/cm³ to 0.950 g/cm³. Additionally or alternately, the resulting blended product can have a flash point of 60° C or higher, or 70° C or higher, or 80° C or higher, such as up to 180° C or possibly still higher.

[0090] In various aspects related to a marine gas oil or marine gas oil blend component, the resulting blended product can have a density at 15° C of 0.760 g/cm³ to 0.890 g/cm³, or 0.760 g/cm³ to 0.860 g/cm³, or 0.760 g/cm³ to 0.825 g/cm³, or 0.760 g/cm³ to 0.810 g/cm³, or 0.760 g/cm³ to 0.800 g/cm³, or 0.775 g/cm³ to 0.890 g/cm³, or 0.775 g/cm³ to 0.860 g/cm³, or 0.775 g/cm³ to 0.825 g/cm³, or 0.775 g/cm³ to 0.810 g/cm³, or 0.775 g/cm³ to 0.800 g/cm³, or 0.790 g/cm³ to 0.890 g/cm³, or 0.790 g/cm³ to 0.860 g/cm³, or 0.790 g/cm³ to 0.825 g/cm³, or 0.800 g/cm³ to 0.890 g/cm³, or 0.800 g/cm³ to 0.860 g/cm³, or 0.815 g/cm³ to 0.860 g/cm³, or 0.800 g/cm³ to 0.825 g/cm³. Additionally or alternately, the resulting blended product can have a flash point of 43° C or higher, or 50° C or higher, or 60° C or higher, such as up to 120° C or possibly still higher.

[0091] In various aspects, an isoparaffinic blend component and/or iso-olefinic blend component can have favorable cold flow properties relative to other types of blend components. In aspects where the resulting blended product includes a) 10 vol% or more of an isoparaffinic blend component and/or iso-olefinic blend component, and b) 50 vol% or more of a conventional and/or mineral blend component, the resulting blended product can have a cloud point that is lower than the cloud point of the conventional and/or mineral blend component by 10° C or more, or 15° C or more, or 20° C or more, such as up to 60° C lower or possibly still more. In aspects where the resulting blended product includes a) 10 vol% or more of an isoparaffinic blend component and/or iso-olefinic blend component, and b) 40 vol% or more of a synthetic component (different from the isoparaffinic blend component and/or iso-olefinic blend component), the resulting blended product can have a cloud point that is lower than the cloud point of the bio-derived component by 10° C or more, or 15° C or more, or 20° C or more, such as up to 60° C lower or possibly still more. In some aspects, the resulting blended product can have a cloud point of 6° C or less, or 0° C or less, or -6° C or less, or -12° C or less, such as down to -30° C or possibly still lower.

[0092] In various aspects related to a fuel oil or fuel oil blend component, the resulting blended product can have a kinematic viscosity at 50° C of 380 cSt or less, or 200 cSt or less, or 100 cSt or less, or 50 cSt or less, or 20 cSt or less, or 10 cSt or less, such as down to 1.0 cSt or possibly still lower. In some aspects, the resulting blended product can have a kinematic viscosity at 50° C of 20 cSt to 100 cSt, or 20 cSt to 50 cSt. In various aspects related to a marine

gas oil or marine gas oil blend component, the resulting blended product can have a kinematic viscosity at 40°C of 2.0 cSt to 6.0 cSt, or 2.0 cSt to 5.0 cSt, or 3.0 cSt to 6.0 cSt, or 3.0 cSt to 5.0 cSt.

5 [0093] In some aspects, the resulting blended product can have a calculated carbon aromaticity index (CCAI) of 780 to 840, or 790 to 820, or 800 to 840.

[0094] In some aspects related to a fuel oil or fuel oil blend component, an isoparaffinic blend component and/or iso-olefinic blend component can have a favorable estimated cetane number relative to other types of blend components. In aspects where 10 vol% or more of an isoparaffinic blend component and/or iso-olefinic blend component is blended with 50 vol%
10 or more of a conventional fuel oil and/or mineral fuel oil, the resulting blended product can have an estimated cetane number that is higher than the estimated cetane number for the conventional fuel oil and/or mineral fuel oil. In aspects where 10 vol% or more of an isoparaffinic blend component and/or iso-olefinic blend component is blended with 40 vol% or more of a bio-derived component (different from the isoparaffinic and/or iso-olefinic blend
15 component), the resulting blended product can have an estimated cetane number that is higher than the estimated cetane number for the bio-derived component.

[0095] In some aspects related to a fuel oil, an isoparaffinic blend component and/or iso-olefinic blend component can have a favorable estimated energy content relative to other types of blend components. In aspects where 10 vol% or more of an isoparaffinic blend component and/or iso-olefinic blend component is blended with 50 vol% or more of a conventional fuel
20 oil and/or mineral fuel oil, the resulting blended product can have an energy content that is higher than the energy content for the conventional fuel oil and/or mineral fuel oil. In aspects where 10 vol% or more of an isoparaffinic blend component and/or iso-olefinic blend component is blended with 40 vol% or more of a bio-derived component (different from the isoparaffinic and/or iso-olefinic blend component), the resulting blended product can have an
25 energy content that is higher than the energy content for the bio-derived component.

[0096] In various aspects, an isoparaffinic blend component and/or an iso-olefinic blend component can assist with reducing the sulfur content of a resulting blend. Because an isoparaffinic blend component and/or iso-olefinic blend component typically has less than 100
30 wppm of sulfur (or less than 50 wppm, such as down to having substantially no sulfur content), such a blend component can offset a higher sulfur content in other components of a blend. In some aspects, the resulting blended product can have a sulfur content of 5000 wppm or less, or 2500 wppm or less, or 1000 wppm or less, or 500 wppm or less, such as down to 10 wppm or

possibly still lower. It is noted that in aspects where a blended product includes only an isoparaffinic / iso-olefinic blend components mixed with synthetic (e.g., bio-derived, Fischer-Tropsch) blend components, low sulfur contents can be achieved, such as sulfur contents of 100 wppm or less, or 15 wppm or less, or 10 wppm or less, such as down to having substantially
5 no sulfur content (0.1 wppm or less).

[0097] In some aspects, the resulting blended product can include at least a portion of one or more conventional VLSFO fractions, ULSFO fractions, and/or marine gas oil (MGO) fractions. A conventional VLSFO, ULSFO, or MGO is defined herein as a fraction that already qualifies as a VLSFO fuel, ULSFO fuel, or MGO fuel under ISO 8217 (either Table 1 or Table
10 2). In such aspects, the resulting blended product can include 1.0 vol% to 99 vol% of a conventional diesel fuel fraction, or 1.0 vol% to 90 vol%, or 1.0 vol% to 70 vol%, or 1.0 vol% to 50 vol%, or 1.0 vol% to 30 vol%, or 1.0 vol% to 10 vol%, or 10 vol% to 99 vol%, or 10 vol% to 90 vol%, or 10 vol% to 70 vol%, or 10 vol% to 50 vol%, or 10 vol% to 30 vol%, or 30 vol% to 99 vol%, or 30 vol% to 90 vol%, or 30 vol% to 70 vol%, or 50 vol% to 99 vol%,
15 or 50 vol% to 90 vol%, or 70 vol% to 99 vol%, or 70 vol% to 90 vol%.

[0098] In some aspects, the resulting blended product can include at least a portion of one or more mineral distillate boiling range fractions, vacuum gas oil boiling range fractions, and/or resid boiling range fractions. In such aspects, the resulting blended product can include 1.0 vol% to 99 vol% of one or more mineral fraction(s), or 1.0 vol% to 90 vol%, or 1.0 vol%
20 to 70 vol%, or 1.0 vol% to 50 vol%, or 1.0 vol% to 30 vol%, or 1.0 vol% to 10 vol%, or 10 vol% to 99 vol%, or 10 vol% to 90 vol%, or 10 vol% to 70 vol%, or 10 vol% to 50 vol%, or 10 vol% to 30 vol%, or 30 vol% to 99 vol%, or 30 vol% to 90 vol%, or 30 vol% to 70 vol%, or 50 vol% to 99 vol%, or 50 vol% to 90 vol%, or 70 vol% to 99 vol%, or 70 vol% to 90 vol%.

[0099] In some aspects, the resulting blended product can include at least a portion of one or more synthetic fractions (different from the isoparaffinic blend component and/or iso-olefinic blend component), such as bio-derived fractions and/or Fischer-Tropsch derived fractions. In such aspects, the resulting blended product can include 1.0 vol% to 99 vol% of a fraction, or 1.0 vol% to 90 vol%, or 1.0 vol% to 70 vol%, or 1.0 vol% to 50 vol%, or 1.0 vol%
25 to 30 vol%, or 1.0 vol% to 10 vol%, or 10 vol% to 99 vol%, or 10 vol% to 90 vol%, or 10 vol% to 70 vol%, or 10 vol% to 50 vol%, or 10 vol% to 30 vol%, or 30 vol% to 99 vol%, or 30 vol%
30 to 90 vol%, or 30 vol% to 70 vol%, or 50 vol% to 99 vol%, or 50 vol% to 90 vol%, or 70 vol% to 99 vol%, or 70 vol% to 90 vol%.

[00100] It is noted that an isoparaffinic and/or iso-olefinic blend component can be blended with a plurality of different types of fractions. For example, in some aspects, a blended product can include two or more (or three or more) of a conventional fraction, a mineral fraction, and a synthetic fraction.

- 5 [00101] In some aspects, after blending components together to form a marine fuel or fuel blending component, it may be desirable to further treat the resulting blended product for any convenient reason, such as by hydroprocessing the blended product to reduce or remove heteroatoms such as sulfur, nitrogen and oxygen.

Distribution of Carbon Atom Types in Isoparaffinic Blend Component and Resulting Blends

- 10 [00102] In some aspects, an isoparaffinic blend component can be formed according to the synthesis method described herein, where an iso-olefinic blend component is formed via olefin oligomerization, and then exposed to hydrotreating conditions to substantially saturate the olefins, resulting in an isoparaffinic blend component. When an isoparaffinic blend component is formed according to this method, the distribution of types of carbon atoms within
15 the hydrocarbons of the blend component is distinct from a fraction containing isoparaffins that are formed by another method, such as by isomerization of an n-paraffin feed. This difference in the types of carbon atoms can be characterized using various types nuclear magnetic resonance (NMR) analysis, including ¹H NMR and ¹³C NMR.

- [00103] In this discussion, analysis of types of hydrogen atoms within a hydrocarbon-like
20 sample is performed according to the methodology described in a technical paper by Gulder et al. in a SAE Technical Paper Series (892073). The paper is titled "A Rapid Cetane Number Prediction Method for Petroleum Liquids and Pure Hydrocarbons Using Proton NMR".

- [00104] Briefly, ¹H NMR can be used to roughly characterize the amount of hydrogen in a sample that is bonded to various types of carbon atoms. Under the analysis used herein,
25 hydrogens are grouped into 6 categories. "Ha" hydrogens correspond to hydrogen atoms bonded to aromatic rings. "Hα" hydrogens correspond to hydrogens bonded to a carbon atom that is in an "alpha" position relative to an aromatic ring. "Ho" hydrogens correspond to hydrogens bonded to a carbon atom that forms part of an olefinic bond. "Hc₁" hydrogens correspond to hydrogens that are part of a CH group or a CH₂ group that is "beta" to an aromatic
30 ring, and hydrogens that are part of a naphthenic CH group or paraffinic CH group. It is noted that based on the above definitions, hydrogens from a CH group or CH₂ group that is in an "alpha" position relative to an aromatic ring would be included in "Hα", and not as part of "Hc₁". "Hc₂" hydrogens correspond to hydrogens on paraffinic CH₂ groups, naphthenic CH₂

groups, CH₂ groups that are in a "gamma" position or farther away from an aromatic ring, and hydrogens that are part of CH₃ groups that are in a "beta" position relative to an aromatic ring. "Hd" hydrogens correspond to hydrogens that are part of paraffinic CH₃ groups as well as hydrogens that are part of CH₃ groups that are in a "gamma" position or farther away from an aromatic ring. Based on these definitions, the ratio of various types hydrogens in a ¹H NMR spectrum can be characterized. In particular, the peak areas corresponding to each type of hydrogen can be integrated to allow for determination of ratios of one type of hydrogen relative to another. As an example, ¹H NMR can be used to determine the ratio of Hd hydrogens to Hc₂ hydrogens (or roughly the ratio of hydrogens in CH₃ groups to hydrogens in CH₂ groups).

10 **[00105]** In various aspects, an isoparaffinic blend component can have a ratio of Hd hydrogens to Hc₂ hydrogens (as determined based on ¹H NMR) of 1.01 to 1.35, or 1.01 to 1.25, or 1.01 to 1.15, or 1.10 to 1.35, or 1.10 to 1.25, or 0.95 to 1.25, or 0.95 to 1.15. By blending an isoparaffinic blend component with another fraction, a resulting blend can be formed that has a ratio of Hd hydrogens to Hc₂ hydrogens (as determined based on ¹H NMR) of 0.50 to 2.30,
15 or 0.60 to 2.30, or 0.75 to 2.30, or 0.91 to 2.30, or 0.91 to 2.00, or 0.91 to 1.80, or 0.91 to 1.50, or 0.91 to 1.15, or 1.01 to 2.30, or 1.01 to 2.00, or 1.01 to 1.80, or 1.01 to 1.50, or 1.01 to 1.15, or 1.36 to 2.30, or 1.36 to 2.00, or 1.36 to 1.80, or 1.70 to 2.30. It is noted that the ratio of Hd hydrogens to Hc₂ hydrogens can vary depending on the type of fraction that is blended with an isoparaffinic blend component. Directionally, blending an isoparaffinic blend component with
20 a mineral fraction and/or an n-paraffinic fraction will tend to produce blends with a lower ratio of Hd hydrogens to Hc₂ hydrogens. For example, blending an isoparaffinic blend component with a mineral jet boiling range fraction, a mineral distillate boiling range fraction, or a Fischer-Tropsch fraction and/or fraction with a high n-paraffin content, will tend to result in blends having a lower ratio of Hd hydrogens to Hc₂ hydrogens. By contrast, blending an isoparaffinic
25 blend component with a fraction that has been highly isomerized in a catalytic dewaxing / isomerization process will tend to result in blends having a higher ratio of Hd hydrogens to Hc₂ hydrogens.

[00106] In addition to characterizing hydrogen for full samples, ¹³C NMR was used to characterize the quaternary carbon content of the C₁₂ fraction of various samples. For this type
30 of measurement, gas chromatography can be used to separate the C₁₂ compounds present in a sample from the remaining hydrocarbons. A straightforward method that can be used for forming a C₁₂ fraction is the normal paraffin (or linear paraffin) gas chromatograph method. That is, for an appropriate gas chromatograph with a separation column of adequate resolution,

a normal paraffin of a given carbon number is assumed to delineate a peak, above which, species may be assumed to comprise the carbon number of the next higher carbon number normal paraffin peak. For example, all peaks for material eluting in between the peaks for n-decane and n-undecane are assumed to be C₁₁ species.

5 **[00107]** The resulting C₁₂ fraction can then be characterized using ¹³C NMR. It has been discovered that the C₁₂ fraction of an isoparaffinic blend component made according to the methods described herein can have an unexpectedly low content of quaternary carbons relative to a fraction made by catalytic isomerization of n-paraffins. In such aspects, the quaternary carbon content of the C₁₂ fraction of an isoparaffinic blend component can be 1.5% or less of
10 the total carbons present in the C₁₂ fraction, or 1.4% or less, or 1.3% or less, such as down to 1.0% or possibly still lower.

EXAMPLES

Example 1 – Carbon Chain Length Distribution in Isoparaffinic Blend Component

[00108] Several different samples of isoparaffinic blend component were formed using
15 the synthesis methods described herein. Table 1A shows the weight percentage of isoparaffins having various hydrocarbon chain lengths in the resulting isoparaffinic blend components. The samples are referred to as IPB-1, IPB-2, and IPB-3 (for Isoparaffinic Blend Component). For comparison, isoparaffin carbon chain length distributions in a representative hydroprocessed vegetable oil (HVO) sample. The HVO represents a vegetable oil that has been exposed to
20 hydrotreating and some type of hydroisomerization. Although not shown in Table 1A below, it is noted that the HVO sample also included 0.25 wt% of C₇ isoparaffin components, while the IPB samples included no components below C₈.

Table 1A - Isoparaffin Chain Length Distribution

[wt% isopar- affins]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20	C21+
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HVO	0.42	0.49	0.72	0.89	0.83	2.28	8.66	63.16	0.76	0.30
IPB-1	0.4	5	8.7	16.1	31.6	18.7	14	3.8	1.8	
IPB-2	0.3	20	7.3	13.6	26.6	15.7	11.8	3.2	1.5	
IPB-3	0.2	12.6	12.6	14.3	22.8	18.6	13	4.3	1.6	

[00109] As shown in Table 1A, more than 70 wt% of the hydrotreated vegetable oil sample corresponds to C₁₅ – C₁₈ isoparaffins. By contrast, the isoparaffin chain length distribution for the IPB samples peaks at C₁₂, while still retaining a small but noticeable content of C₁₇ – C₂₀ hydrocarbons.

[00110] Tables 1B, 1C, 1D, and 1E show the weight percentage of isoparaffins of various chain lengths that would be incorporated into a blended product that included 70 wt% of an isoparaffinic blend component (Table 1B), 50 wt% (Table 1C), 30 wt% (Table 1D), or 10 wt% (Table 1E). Due to the difference in the peaks for the chain length distributions, even adding 10 wt% of an isoparaffinic (or iso-olefinic) blend component to a hydrotreated vegetable oil can result in substantial changes in the C₁₂ portion of the isoparaffin chain length distribution of the resulting blended product.

Table 1B – Blend Contributions at 70 wt% IPB

[wt% isopar- affins]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20	C21+
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HVO	0.1	0.1	0.2	0.3	0.2	0.7	2.6	18.9	0.2	0.1
IPB-1	0.3	3.5	6.1	11.3	22.1	13.1	9.8	2.7	1.3	0.0
IPB-2	0.2	14.0	5.1	9.5	18.6	11.0	8.3	2.2	1.1	0.0
IPB-3	0.1	8.8	8.8	10.0	16.0	13.0	9.1	3.0	1.1	0.0

Table 1C – Blend Contributions at 50 wt% IPB

[wt% isopar- affins]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20	C21+
HVO	0.2	0.2	0.4	0.4	0.4	1.1	4.3	31.6	0.4	0.1
IPB-1	0.2	2.5	4.4	8.1	15.8	9.4	7.0	1.9	0.9	0.0
IPB-2	0.2	10.0	3.7	6.8	13.3	7.9	5.9	1.6	0.8	0.0
IPB-3	0.1	6.3	6.3	7.2	11.4	9.3	6.5	2.2	0.8	0.0

Table 1D – Blend Contributions at 30 wt% IPB

[wt% isoparaffins]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20	C21+
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HVO	0.3	0.3	0.5	0.6	0.6	1.6	6.1	44.2	0.5	0.2
IPB-1	0.1	1.5	2.6	4.8	9.5	5.6	4.2	1.1	0.5	0.0
IPB-2	0.1	6.0	2.2	4.1	8.0	4.7	3.5	1.0	0.5	0.0
IPB-3	0.1	3.8	3.8	4.3	6.8	5.6	3.9	1.3	0.5	0.0

Table 1E – Blend Contributions at 10 wt% IPB

[wt% isoparaffins]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20	C21+
HVO	0.4	0.4	0.6	0.8	0.7	2.1	7.8	56.8	0.7	0.3
IPB-1	0.0	0.5	0.9	1.6	3.2	1.9	1.4	0.4	0.2	0.0
IPB-2	0.0	2.0	0.7	1.4	2.7	1.6	1.2	0.3	0.2	0.0
IPB-3	0.0	1.3	1.3	1.4	2.3	1.9	1.3	0.4	0.2	0.0

[00111] A similar comparison of isoparaffin content and chain lengths was made relative to a conventional diesel sample. Table 2A shows the isoparaffin contents for the conventional diesel and the three different IPB samples.

Table 2A - Isoparaffin Chain Length Distribution

[wt% isopar- affins]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20	C21+
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Diesel	0.00	0.08	0.40	0.39	0.20	2.83	8.49	2.84	1.33	0.24
IPB-1	0.4	5	8.7	16.1	31.6	18.7	14	3.8	1.8	0
IPB-2	0.3	20	7.3	13.6	26.6	15.7	11.8	3.2	1.5	0
IPB-3	0.2	12.6	12.6	14.3	22.8	18.6	13	4.3	1.6	0

- [00112] As shown in Table 2A, the conventional diesel sample contained relatively few C₁₄-isoparaffins. The C₁₃ – C₁₄ isoparaffins corresponded to less than 3 wt% of the diesel sample, while the C₁₂-isoparaffins corresponded to less than 1.1 wt% of the sample. By contrast, the IPB samples are highly isomerized, so that 95+ wt% or more of the hydrocarbons in the IPB samples correspond to isoparaffins. As a result, the IPB samples include 15 wt% or more of C₁₃ – C₁₄ isoparaffins, 22 wt% or more of C₁₂ isoparaffins, and 30 wt% or more of C₁₁-isoparaffins. This provides an unexpected chain length distribution for a diesel blend component.
- 10 [00113] Tables 2B, 2C, 2D, and 2E show the weight percentage of isoparaffins of various chain lengths that would be incorporated into a blended product that included 70 vol% of an isoparaffinic blend component (Table 2), 50 vol% (Table 3), or 30 vol% (Table 4), with the balance corresponding to the diesel sample. Again, addition of as little as 10 wt% of an isoparaffinic (or iso-olefinic) blend component to a conventional / mineral diesel fraction can
- 15 result in substantial changes in the C₁₂-branched hydrocarbon content of the resulting blended product.

Table 2B – Blend Contributions at 70 wt% IPB

[wt% isopar- affins]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20	C21+
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Diesel	0.0	0.0	0.1	0.1	0.1	0.8	2.5	0.9	0.4	0.1
IPB-1	0.3	3.5	6.1	11.3	22.1	13.1	9.8	2.7	1.3	0.0
IPB-2	0.2	14.0	5.1	9.5	18.6	11.0	8.3	2.2	1.1	0.0
IPB-3	0.1	8.8	8.8	10.0	16.0	13.0	9.1	3.0	1.1	0.0

Table 2C – Blend Contributions at 50 wt% IPB

[wt% isopar- affins]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20	C21+
Diesel	0.0	0.0	0.2	0.2	0.1	1.4	4.2	1.4	0.7	0.1
IPB-1	0.2	2.5	4.4	8.1	15.8	9.4	7.0	1.9	0.9	0.0
IPB-2	0.2	10.0	3.7	6.8	13.3	7.9	5.9	1.6	0.8	0.0
IPB-3	0.1	6.3	6.3	7.2	11.4	9.3	6.5	2.2	0.8	0.0

Table 2D – Blend Contributions at 30 wt% IPB

[wt% isoparaffins]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20	C21+
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Diesel	0.0	0.1	0.3	0.3	0.1	2.0	5.9	2.0	0.9	0.2
IPB-1	0.1	1.5	2.6	4.8	9.5	5.6	4.2	1.1	0.5	0.0
IPB-2	0.1	6.0	2.2	4.1	8.0	4.7	3.5	1.0	0.5	0.0
IPB-3	0.1	3.8	3.8	4.3	6.8	5.6	3.9	1.3	0.5	0.0

Table 2E – Blend Contributions at 10 wt% IPB

[wt% isoparaffins]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20	C21+
Diesel	0.0	0.1	0.4	0.4	0.2	2.5	7.6	2.6	1.2	0.2
IPB-1	0.0	0.5	0.9	1.6	3.2	1.9	1.4	0.4	0.2	0.0
IPB-2	0.0	2.0	0.7	1.4	2.7	1.6	1.2	0.3	0.2	0.0
IPB-3	0.0	1.3	1.3	1.4	2.3	1.9	1.3	0.4	0.2	0.0

Example 2 – Diesel Boiling Range Blends

- 5 **[00114]** Using an empirical blending model, the isoparaffinic blend components corresponding to IPB-1 and IPB-2 in Example 1 were used, in combination with two conventional European diesel fuels and two bio-derived fractions, to produce model blended fuels based on the various fractions. As input for the modeling, a series of measurements were made on IPB-1, IPB-2, two different diesel fuels that meet the requirements of EN 590 (the
- 10 fuels are referred to herein as EPD-1 and EPD-2), the hydrotreated vegetable oil from Example 1, and diesel boiling range fraction based on rapeseed methyl ether (RME). Table 3 shows the measured properties of the various fractions.

Table 3 – Measured Values for Diesel Blend Components

Neat Components	IPB-1	IPB-2	EPD-1	EPD-2	RME	HVO
Test methods	-		-	-	-	
Cetane Number, Value	48.2	47	54.2	51.2	-	-
Density, kg/m ³	767.0	758.0	831.8	842.9	860	784.8
Polyaromatic hydrocarbon, Mass%	0	0	4.8	2.9	-	-
Sulfur, mg/kg	0	0	8.8	5.9	5.0	0.0
Flash Point, °C	58.5	43.3	56.5	78	-	-
Distillation E250, Vol%	80	90	46	29	-	-
Distillation E350, Vol%	100	100	99	97	-	-
Distillation T95, °C	284	272	336	343	-	-
Cloud Point, °C	-80	-62	-10	-5	-	-
Viscosity @ 40 °C, cSt	2.601	1.955	2.286	3.137	4.439	3.13

[00115] As shown in Table 3, the IPB-1 and IPB-2 samples have a cetane number between 47 – 49. This is in contrast to the conventional European diesel samples, which have a cetane number greater than 51. The density of the IPB-1 and IPB-2 samples is also lower than any of the other fractions shown in Table 3. However, the IPB-1 and IPB-2 samples also provide a substantially lower cloud point than the conventional European diesel samples. It is noted that the “Distillation E250” and Distillation E350” rows refer to the volume of a fraction that boils at a temperature of 250°C or 350°C, respectively.

[00116] The measured values in Table 3 were used as the basis for preparing a series of model blends to form potential diesel boiling range fuels. Table 4 shows model blend results for blends formed using 25 vol% of either IPB-1 or IPB-2 in combination with 75 vol% of either EPD-1 or EPD-2.

Table 4 – Blends with Conventional Diesel (Vol%)

Neat Components	25% IPB-1 75% EPD-1	25% IPB-1 75% EPD-2	25% IPB-2 75% EPD-1	25% IPB-2 75% EPD-2
Test methods	-	-	-	-
Cetane Number, Value	51	52.7	50.7	52.4
Density, kg/m ³	815.6	823.9	813.4	821.7

Polyaromatic hydrocarbon, Mass%	3.7	2.2	3.7	2.2
Sulfur, mg/kg	6.7	4.5	6.7	4.5
Flash Point, °C	57	70	52	59
Distillation E250, Vol%	55	42	55	44
Distillation E350, Vol%	99	98	99	98
Distillation T95, °C	331	338	331	338
Cloud Point, °C	-27	-24	-27	-24
Viscosity @ 40 °C, cSt	2.34	2.98	2.20	2.21

[00117] As shown in Table 4, all of the modeled blends including 25 vol% of an isoparaaffinic blend component resulted in cetane numbers greater than 50. Additionally, each of the resulting blends had a cloud point of -20°C or less, so that the cloud point of the resulting blend was more than 15°C lower than the cloud point of the conventional diesel used in the blend.

[00118] Table 5 shows a second series of model blends. In this series of model blends, the first two blends include higher percentages of IPB-2 mixed with EPD-2. The second two blends include IPB-1, EPD-2, and either one or both bio-derived fractions shown in Table 3.

10 **Table 5 – Blends with Higher Content of an Isoparaaffinic Blend Component (Vol%)**

Component Concentrations	30% IPB-1, 70% EPD-2	44% IPB-1, 56% EPD-2	40% IPB-1, 20% RME, 40% EPD-2	33% IPB-1, 20% RME, 10% HVO, 37% EPD-2
Test methods	-	-	-	-
Cetane Number, Value	52.4	50.8	51.9	54.4
Density, kg/m ³	820	800	820	820
Polyaromatic hydrocarbon, Mass%	2.1	1.3	1.2	1.1
Sulfur, mg/kg	4.3	2.7	2.4	2.2
Flash Point, °C	69	64	69	69
Distillation E250, Vol%	45	60	43	38
Distillation E350, Vol%	99	99	97	98
Distillation T95, °C	336	302	343	343
Cloud Point, °C	-25	-31	-27	-26
Viscosity @ 40 °C, cSt	2.96	2.89	3.10	3.15

[00119] As shown in Table 5, an isoparaaffinic blend component can be added to a conventional diesel in quantities of 30 vol% or more, or 40 vol% or more, while still provide a kinematic viscosity at 40°C of greater than 2.0 cSt. With regard to the second two blends where bio-derived components are included, it is noted that bio-derived fractions generally have poor cloud point properties. In spite of the addition of 20 vol% or 30 vol% of bio-derived material, the addition of the IPB-1 was still able to reduce the cloud point of the resulting blend to -27°C or -26°C, so that the cloud point of the resulting blend was more than 15°C lower than the cloud point of the mineral / conventional fraction included in the blend.

[00120] Table 6 shows additional modeled blends where an isoparaaffinic blend component is mixed with one or both of the bio-derived fractions shown in Table 3.

Table 6 – Blends with Bio-Derived Fractions (Vol%)

Component Concentrations	54% IPB-1, 46% RME	50% IPB-1, 50% HVO	40% IPB-1, 20% RME, 40% HVO
Test methods	-	-	-
Cetane Number, Value	51.1	61.9	60.4
Density, kg/m ³	820	776	797
Polyaromatic hydrocarbon, Mass%	0	0	0
Sulfur, mg/kg	2.5	0	2
Flash Point, °C	68	62	66
Distillation E250, Vol%	42	42	38
Distillation E350, Vol%	99	100	98
Distillation T95, °C	344	298	341
Cloud Point, °C	-31	-33	-30
Viscosity @ 40 °C, cSt	3.37	2.85	3.10

[00121] As shown in Table 6, due to the higher cetane number of bio-derived fractions, a greater percentage of the isoparaaffinic blend component could be added to the blended product while still achieving a cetane number of 51 or higher. This also allowed the resulting blended products to have a cloud point of -30°C or lower, which is more than 15°C below the cloud point of either of the bio-derived fractions used for the blends.

Example 3 – Marine Fuel Blends

[00122] The empirical blending model was also used to generate model blends for incorporating isoparaaffinic blend components into various types of marine fuels. Table 7 shows

blends of IPB-1 and IPB-2 with a commercially available VLSFO. The measured properties of the VLSFO are also provided for comparison, along with portions of the specification for RMG 380 (the type of VLSFO) from ISO 8217 Table 2.

Table 7 – Blends with Conventional Fuel Oil (Vol%)

Component Concentrations	ISO 8217 Table 2 (RMG380)	VLSFO (measured)	20% IPB-1, 80% VLSFO	20% IPB-2, 80% VLSFO
Density at 15°C (g/mL)	0.991 Max	0.9628*	0.9236	0.9218
KV50 (cSt)	380.00 Max	217.3*	37.9	34.1
Net energy content (MJ/kg)	-	41.49	41.95	41.96
Estimated Cetane Number	-	20*	26	25
CCAI	870 Max	830	814	814
Sulfur (ppm m/m)	5000 Max	4700*	3919	3927
BMCI	-	64	52.9	52.4
TE	-	40*	40	40
BMCI-TE	-	20	13	12
MCR (wt%)	18.00 Max	6.16*	5.1	5.1
Pour Point (°C)	30 Max	6.0*	-8.7	-9.0
Flash Point (°C)	60 Min	119*	83	66

5 * = Measured values for the VLSFO

[00123] In Table 7, 20 vol% of an isoparaffinic blend component was blended with the VLSFO. This is believed to be near the compatibility limit for maintaining the heavier aromatic cores in the VLSFO in solution in the resulting blend. Based on the modeled results, addition of an isoparaffinic blend component to the VLSFO provided a variety of advantages for the resulting blended product. First, the estimated cetane number of the blended product increased. Additionally, the pour point of the blended product was lower than the pour point of the VLSFO by 10°C or more. The isoparaffinic blend components also reduced the sulfur content of the resulting product relative to the sulfur content of the VLSFO. Additionally, the kinematic viscosity at 50°C was substantially lowered. Finally, a flash point of greater than 60°C was maintained for the resulting blended product.

[00124] Isoparaﬃnic (and/or iso-olefinic) blend components can also be used to make ULSFO fuels or fuel blending components. Table 8 shows modeled examples of blending IPB-1 or IPB-2 with a hydroprocessed vacuum resid fraction. Measured values for the neat hydroprocessed resid (HDP VR) are also shown, along with values for HDME 50, a commercially available ULSFO. Portions of the specification for an RMD80 fuel oil from ISO 8217 Table 2 are also provided.

Table 8 – Blends with Hydroprocessed Vacuum Resid (Vol%)

Component Concentrations	ISO 8217 Table 2 (RMD80)	HDP VR	40% IPB-1, 60% HDP VR	30% IPB-2, 70% HDP VR	HDME50 (Comp. Example)
Density at 15°C (g/mL)	0.975 Max	0.9754*	0.8920	0.9102	0.9082*
KV50 (cSt)	80.00 Max	4300*	24.6	50.1	33.95*
Estimated Cetane Number	-	43*	45	44	66*
CCAI	860 Max	815	790	796	802*
Sulfur (ppm m/m)	1000 Max	1360*	892	1020	720*
BMCI	-	64.0	41.7	46.6	42.0
TE	-	0	0	0	0
BMCI-TE	-	64	42	47	42*
MCR (wt%)	14.00 Max	8.86*	5.8	6.6	0.35*
Pour Point (°C)	30 Max	24*	5.8	10.5	9*
Flash Point (°C)	60 Min	253*	73	61	178*

* = measured values

[00125] As shown in Table 8, blending a hydroprocessed vacuum resid with 30 vol% or 40 vol% of an isoparaﬃnic blend component results in a blended product with substantially lower values for density, kinematic viscosity at 50°C, and pour point. These reductions allow the blended product to have density, KV50, and pour point values that are comparable to the commercially available ULSFO. Also, blending the hydroprocessed resid with the isoparaﬃnic blend component results in an increase in estimated cetane number. It is noted that higher percentages of the isoparaﬃnic blend component (up to 50 vol%) can be added to the

hydroprocessed vacuum resid. Finally, even at 40 vol% (or more) of the isoparaffinic blend component, the resulting blend has a flash point of 60°C or higher.

[00126] Blends of an isoparaffinic blend component (and/or an iso-olefinic blend component) with both renewable fractions and mineral fraction can also be used to form marine fuel oils. Table 9 shows modeled blends of IPB-1 with a higher sulfur content fuel oil (either lightly hydroprocessed or not hydroprocessed). One of the blends corresponds to a 50 vol% / 50 vol% mixture of IPB-1 and the fuel oil (FO). The other blend includes 35 vol% IPB-1, 50 vol% of a fatty acid methyl ester, and 15 vol% of the fuel oil. For comparison, measured values for the neat fuel oil are provided, along with some of the specification for an RMA fuel oil according to ISO 8217 Table 2.

Table 9 – Blends with Fuel Oil and FAME (Vol%)

Component Concentrations	ISO 8217 Table 2 (RMA)	100% FO	35% IPB-1, 50% FAME, 15% FO	50% IPB-1, 50% FO
Density at 15°C (g/mL)	0.920 Max	0.9852*	0.8566	0.8761
KV50 (cSt)	10.00 Max	318.5*	3.5	7.47
Net energy content (MJ/kg)	-	~40.5	~39.9	~42.2
Estimated Cetane Number	-	~15	19	32
CCAI	850 Max	848	803	800
Sulfur (ppm m/m)	5000 Max	8200*	1415	4611
BMCI	-	69.7	32.9	38.9
TE	-	11.5*	12	12
BMCI-TE	-	58	21	27
MCR (wt%)	2.50 Max	10.32*	1.8	5.8
Pour Point (°C)	0 / 6 Max	9.0*	-4.5	-27.8
Flash Point (°C)	60 Min	129*	75	69

* = Measured values

[00127] As shown in Table 9, if the isoparaffinic blend component is formed from a renewable source (such as a renewable methanol source), a blend containing up to 85 vol% of renewable content can be used to make a VLSFO fuel. Additionally, as shown in the final modeled blend in Table 9, up to 50 vol% of an isoparaffinic blend component can be mixed

with a fuel oil while still maintaining a BMCI value that suggests the blend would be compatible for retaining asphaltenes in solution.

[00128] Isoparaﬃnic blend components (and/or iso-olefinic blend components) can also be used for formation of blended products corresponding to marine gas oils or marine gas oil blending components. Table 10 shows modeled blends of 70 vol% of IPB-1 with either 30 vol% of a commercially available MGO or 30 vol% of a fatty acid methyl ester. Measured values for the neat MGO are provided, along with some of the specifications for a DMA marine gas oil under ISO 8217 Table 1.

Table 10 – Marine Gas Oil Blends (Vol%)

Component Concentrations	ISO 8217 Table 1 (DMA)	100% MGO	70% IPB-1, 30% MGO	70% IPB-1, 30% FAME
Test methods	-	-	-	-
Cetane Number, Value	40 Min	*50	48.7	53.4
Density, kg/m ³	-	*855	793.1	801.6
Sulfur, Mass%	1.00 Max	*0.526	0.17	1.5 <wppm>
Flash Point, °C	43.0	*91.8	62	64
Pour Point, °C	Report	*9	-46	-24
Viscosity @ 40 °C, cSt	2.000 Min 6.000 Max	*5.42	3.20	3.02

* = Measured values

[00129] As shown in Table 10, using an isoparaﬃnic blend component to form an MGO fuel or MGO fuel blending component results in a blended product with kinematic viscosity at 40°C between 2.0 and 6.0, a flash point of greater than 50°C, or greater than 60°C, and pour point well below 0°C. Additionally, use of an isoparaﬃnic blend component results in a blended product with a reduced sulfur content (or possibly substantially no sulfur content, if blended with a renewable fraction). The cetane number is reduced relative to the commercially available MGO, but still well above 40. It is noted that the specification for MGO is based on cetane index, rather than cetane number. However, the values of 48.7 and 53.4 shown in Table 10 are sufficiently above 40 that the standard should still be satisfied when measured as cetane index.

Example 4 – ¹H NMR Analysis of Blend Components

[00130] The isoparaﬃnic blend component IPB-1 was formed according to the method described herein, where an iso-olefinic blend component was formed by olefin oligomerization. A portion of the iso-olefinic blend component was then exposed to hydrotreating conditions to saturate the portion, thus forming the IPB-1 sample. Additionally, mixtures were formed

corresponding to 30 wt% iso-olefinic blend component / 70 wt% isoparaffinic blend component and 70 wt% iso-olefinic blend component / 30 wt% isoparaffinic blend component.

[00131] The iso-olefinic blend component, the isoparaffinic blend component, and the two mixtures were characterized using ^1H NMR to characterize the ratio of Hd hydrogens to Hc₂ hydrogens, as determined from the ^1H NMR results. FIG. 3 shows results from the ^1H NMR analysis. In FIG. 3, the first column of data corresponds to data for the substantially fully saturated isoparaffinic blend component (IPB-1 – Column A). The second column and third column show the mixtures corresponding to 70 wt% isoparaffins (column B) and 30 wt% isoparaffins (column C), while the final column corresponds to data for the iso-olefinic blend component (column D), as made from the oligomerization process. As shown in FIG. 3, the isoparaffinic blend component had a ratio of Hd hydrogens to Hc₂ hydrogens of 1.19.

[00132] For comparison with the values shown in FIG. 3, a variety of other types of fractions were also characterized using ^1H NMR to determine the ratio of Hd hydrogens to Hc₂ hydrogens. Table 11 shows the values that were obtained for these various other types of fractions. Where a range is given, this indicates that multiple different samples were characterized, with the range corresponding to the minimum and maximum values.

Table 11 – Ratio of Hd / Hc₂ hydrogens as Determined by ^1H NMR for Other Components

Sample Type	Hd to Hc ₂ Ratio
JET A-1	0.75
Diesel	0.57 – 1.00
Gas Oil	0.54
Primarily Isoparaffin Liquid (formed by catalytic isomerization)	2.50 – 3.21
Primarily N-Paraffin Liquid	0.24 – 0.33
Naphthenic Liquid (Petroleum Distillate)	2.35
Fischer-Tropsch Liquid	0.37

[00133] As shown in Table 6, liquids with high n-paraffin contents tend to have ratios of Hd hydrogens to Hc₂ hydrogens that are well below 1.00. Commercial fuel products generally have ratios below 1.00, although a high isoparaffin content / low aromatic content diesel can

approach 1.00. Fluids containing high contents of naphthenes have ratios of Hd hydrogens to Hc₂ hydrogens above 2.30. Similarly, fractions with high isoparaffin content, where the isoparaffin content is formed by catalytic isomerization, have ratios above 2.30.

Example 5 – Quaternary Carbon Content

5 **[00134]** A sample of IPB-1 was separated using a gas chromatograph to form a C₁₂ fraction. The resulting C₁₂ fraction was analyzed using ¹³C NMR to determine the content of quaternary carbons in the sample. For comparison, C₁₂ fractions were also formed from samples derived from other traditional refinery processes. Table 12 shows the results from analysis of the C₁₂ fractions.

10 **Table 12 – ¹³C NMR Analysis of C₁₂ Fractions**

	C ₁₂ Comparative #1	C ₁₂ Comparative #2	C ₁₂ from IPB-1
Average Carbon Number (by GC)	11.95	11.88	12.0
Naphthenic Content	8	8	0
Number of Branches per Molecule	2.97	2.39	2.78
Quaternaries (% of total number of carbons)	1.64	1.77	1.35

15 **[00135]** As shown in Table 12, the quaternary carbon content of the C₁₂ fraction was substantially lower than the other fractions. For both comparative samples, the C₁₂ fraction had a quaternary carbon content of greater than 1.60% relative to the total number of carbons in the sample, while the C₁₂ fraction from the isoparaffinic blend component has a quaternary carbon content of 1.60% or less, or 1.50% or less, or 1.40% or less, such as down to 1.20% or possibly still lower.

Additional Embodiments

20 **[00136]** Embodiment 1. A diesel boiling range composition comprising: 1.0 vol% to 75 vol% of a blend component comprising an isoparaffinic blend component, an iso-olefinic blend component, or a combination thereof containing 80 wt% or more of combined isoparaffins and iso-olefins, and 20 vol% to 99 vol% of a mineral distillate boiling range fraction, the composition comprising a cetane number of 40 or more and a cloud point that is at least 5.0°C lower than a cloud point of the mineral distillate boiling range fraction.

[00137] Embodiment 2. The composition of Embodiment 1, wherein the composition comprises 1.0 vol% to 75 vol% of an isoparaffinic blend component containing 80 wt% or more of isoparaffins and 5.0 wt% or less of iso-olefins.

5 [00138] Embodiment 3. The composition of Embodiment 1, wherein the composition comprises 1.0 vol% to 75 vol% of an iso-olefinic blend component containing greater than 5.0 wt% iso-olefins and 80 wt% or more of combined isoparaffins and iso-olefins.

[00139] Embodiment 4. The composition of any of Embodiments 1 – 3, wherein the composition comprises 10 vol% to 75 vol% of the blend component.

10 [00140] Embodiment 5. The composition of Embodiment 4, wherein the composition comprises a cetane number of 50 or more.

[00141] Embodiment 6. The composition of Embodiment 4 or 5, wherein the composition comprises a cloud point that is at least 10°C lower than a cloud point of the mineral distillate boiling range fraction.

15 [00142] Embodiment 7. The composition of any of Embodiments 1 - 6, wherein the blend component comprises 10 wt% to 50 wt% of C₁₉₊ hydrocarbons.

[00143] Embodiment 8. The composition of any of Embodiments 1 - 6, wherein the blend component contains 5.0 wt% or less of C₁₉₊ hydrocarbons.

20 [00144] Embodiment 9. The composition of Embodiment 8, wherein the composition comprises 6.0 wt% or more of C₁₂ isoparaffins, or wherein the composition comprises 10 wt% or more of C₁₂ isoparaffins, or a combination thereof.

[00145] Embodiment 10. The composition of any of Embodiments 1 - 9, wherein the composition further comprises 1.0 wt% to 40 wt% of a bio-derived diesel boiling range component, the cloud point of the composition being at least 5°C lower than a cloud point of the bio-derived diesel boiling range component.

25 [00146] Embodiment 11. The composition of any of Embodiments 1 - 10, wherein the composition comprises a) a density of 0.780 g/cm³ or more, b) a flash point of 50°C or more, c) a kinematic viscosity at 40°C of 2.0 cSt to 4.5 cSt, or d) a combination of two or more of a), b), and c).

30 [00147] Embodiment 12. The composition of any of Embodiments 1 - 11, wherein the composition comprises a sulfur content of 15 wppm or less, or wherein the mineral distillate boiling range fraction comprises a sulfur content of 15 wppm or less, or a combination thereof.

[00148] Embodiment 13. The composition of any of Embodiments 1 - 12, wherein a cetane number of the blend component is lower than a cetane number of the mineral distillate boiling range fraction.

5 [00149] Embodiment 14. The composition of any of Embodiment 1 - 13, wherein the mineral distillate boiling range fraction comprises at least one of a mineral diesel boiling range fraction and a conventional diesel fraction.

[00150] Embodiment 15. A diesel boiling range composition comprising: 1.00 vol% to 90 vol% of a blend component comprising an isoparaffinic blend component, an iso-olefinic blend component, or a combination thereof containing 80 wt% or more of combined isoparaffins and
10 iso-olefins, and 10 vol% to 99 vol% of a bio-derived component different from the blend component, the composition comprising a cetane number of 40 or more and a cloud point of -10°C or less.

[00151] Embodiment 16. The composition of Embodiment 15, wherein the composition comprises 10 vol% to 90 vol% of the blend component.

15 [00152] Embodiment 17. The composition of Embodiment 15 or 16, wherein the blend component comprises 10 wt% to 50 wt% of C₁₉₊ hydrocarbons.

[00153] Embodiment 18. The composition of Embodiment 15 or 16, wherein the blend component contains 5.0 wt% or less of C₁₉₊ hydrocarbons.

20 [00154] Embodiment 19. The composition of Embodiment 18, wherein the composition comprises 6.0 wt% or more of C₁₂₋ isoparaffins.

[00155] Embodiment 20. The composition of any of Embodiments 15 – 19, wherein the cloud point of the composition is at least 5.0°C lower than a cloud point of the bio-derived component.

25 [00156] Embodiment 21. The composition of any of Embodiments 15 – 20, wherein the blend component comprises a cetane number less than 50.

[00157] Embodiment 22 The composition of any of Embodiments 15 – 21, wherein the composition comprises 1.0 vol% to 90 vol% of an isoparaffinic blend component containing 80 wt% or more of isoparaffins and 5.0 wt% or less of iso-olefins; or wherein the composition comprises 1.0 vol% to 90 vol% of an iso-olefinic blend component containing greater than 5.0
30 wt% iso-olefins and 80 wt% or more of combined isoparaffins and iso-olefins.

[00158] Embodiment 23. The composition of any of Embodiment 15 – 22, wherein the bio-derived component comprises a bio-derived diesel boiling range component.

[00159] Embodiment 24. A fuel oil or fuel oil blend component composition, comprising: 1.0 vol% to 75 vol% of a blend component comprising an isoparaffinic blend component, an iso-olefinic blend component, or a combination thereof; and 25 vol% to 95 vol% of a mineral fraction, the composition comprising a density at 15°C of 0.880 g/cm³ to 0.990 g/cm³, a
5 calculated carbon aromaticity index of 780 or more, a flash point of 60°C or more, and a sulfur content of 5000 wppm or less, a pour point of the composition being lower than a pour point of the mineral fraction.

[00160] Embodiment 25. The composition of Embodiment 24, wherein the mineral fraction comprises a sulfur content of 2000 wppm or more, the composition comprising 80
10 vol% to 95 vol% of the mineral fraction.

[00161] Embodiment 26. The composition of Embodiment 24 or 25, wherein the composition comprises a kinematic viscosity at 50°C of 380 cSt or less.

[00162] Embodiment 27. The composition of any of Embodiments 24 to 26, wherein the composition further comprises 1.0 vol% to 40 vol% of a bio-derived component different from
15 the blend component.

[00163] Embodiment 28. A fuel oil or fuel oil blend component composition, comprising: 1.0 vol% to 40 vol% of a blend component comprising an isoparaffinic blend component, an iso-olefinic blend component, or a combination thereof; 5.0 vol% to 50 vol% of a bio-derived component different from the blend component; and 15 vol% or more of a mineral fraction, the
20 composition comprising a density at 15°C of 0.880 g/cm³ to 0.990 g/cm³, a calculated carbon aromaticity index of 800 or more, a flash point of 60°C or more, and a sulfur content of 5000 wppm or less, a pour point of the composition being lower than a pour point of the bio-derived component.

[00164] Embodiment 29. The composition of Embodiment 28, wherein the mineral
25 fraction comprises a sulfur content of greater than 5000 wppm.

[00165] Embodiment 30. The composition of Embodiment 28 or 29, wherein the composition comprises a kinematic viscosity at 50°C of 380 cSt or less.

[00166] Embodiment 31. The composition of any of Embodiments 24 – 30, wherein an estimated cetane number of the composition is greater than an estimated cetane number of the
30 mineral fraction, or wherein the estimated cetane number of the composition is greater than an estimated cetane number of the bio-derived fraction, or a combination thereof.

- [00167] Embodiment 32. The composition of any of Embodiments 24 – 31, wherein the composition comprises 2.0 wt% or more of C₁₂- isoparaffins, iso-olefins, or a combination thereof.
- [00168] Embodiment 33. The composition of any of Embodiments 24 – 32, wherein the composition comprises a pour point of 0°C or less.
- [00169] Embodiment 34. The composition of any of Embodiments 24 – 33, wherein the mineral fraction comprises a sulfur content of less than 6500 wppm and the composition comprises a sulfur content of 1000 wppm or less.
- [00170] Embodiment 35. The composition of any of Embodiment 24 – 34, wherein the composition comprises 1.0 vol% to 50 vol% of an isoparaffinic blend component containing 80 wt% or more of isoparaffins and 5.0 wt% or less of iso-olefins; or wherein the composition comprises 1.0 vol% to 50 vol% of an iso-olefinic blend component containing greater than 5.0 wt% iso-olefins and 80 wt% or more of combined isoparaffins and iso-olefins.
- [00171] Embodiment 36. The composition of any of Embodiments 24 – 35, wherein the blend component contains 5.0 wt% or less of C₁₉₊ hydrocarbons, or wherein the blend component comprises 10 wt% to 50 wt% of C₁₉₊ hydrocarbons.
- [00172] Embodiment 37. A marine distillate or marine distillate blend component composition, comprising: 1.0 vol% to 90 vol% of a blend component comprising an isoparaffinic blend component, an iso-olefinic blend component, or a combination thereof; and 10 vol% to 99 vol% of a mineral fraction, a bio-derived component different from the blend component, or a combination thereof, the composition comprising a density at 15°C of 0.780 g/cm³ to 0.890 g/cm³ or less, a cetane number of 40 or more, and a flash point of 43°C or more, a pour point of the composition being at least 5°C lower than a pour point of the mineral fraction, the bio-derived fraction, or the combination thereof.
- [00173] Embodiment 38. The composition of Embodiment 37, wherein the composition comprises a pour point of -10°C or less.
- [00174] Embodiment 39. The composition of Embodiment 37 or 38, wherein the pour point of the composition is at least 10°C lower than the pour point of the mineral fraction, bio-derived component, or combination thereof.
- [00175] Embodiment 40. The composition of any of Embodiments 37 to 39, wherein the composition comprises 1000 wppm or less of sulfur.

[00176] Embodiment 41. The composition of any of Embodiments 37 to 40, wherein the composition comprises 2.0 wt% or more of C₁₂- isoparaffins, iso-olefins, or a combination thereof.

5 [00177] Embodiment 42. The composition of any of Embodiments 37 to 41, wherein the blend component contains 5.0 wt% or less of C₁₉₊ hydrocarbons, or wherein the blend component comprises 10 wt% to 50 wt% of C₁₉₊ hydrocarbons.

[00178] Embodiment 43. The composition of any of Embodiments 15 – 23 or 27 to 42, wherein the bio-derived component a) contains less than 80 wt% of isoparaffins, iso-olefins, or a combination thereof b) has a ratio of Hd hydrogens to Hc₂ hydrogens of 1.6 or more, c) 10 has a ratio of Hd hydrogens to Hc₂ hydrogens of 1.0 or less, d) a combination of a) and b), or e) a combination of a) and c).

[00179] Embodiment 44. The composition of any of the above embodiments, wherein the composition comprises a ratio of Hd hydrogens to Hc₂ hydrogens of 1.01 to 2.00.

15 [00180] Embodiment 45. The composition of any of the above embodiments, wherein the composition comprises a ratio of Hd hydrogens to Hc₂ hydrogens of 1.01 to 1.35.

[00181] Embodiment 46. The composition of any of the above embodiments, wherein the composition comprises a ratio of Hd hydrogens to Hc₂ hydrogens of 1.01 to 2.00.

[00182] Embodiment 47. The composition of any of the above embodiments, wherein the composition comprises a ratio of Hd hydrogens to Hc₂ hydrogens of 1.01 to 1.35.

20 [00183] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

CLAIMS

WHAT IS CLAIMED IS:

1. A fuel oil or fuel oil blend component composition, comprising: 1.0 vol% to 75 vol% of a blend component comprising an isoparaffinic blend component, an iso-olefinic blend component, or a combination thereof; and 25 vol% to 95 vol% of a mineral fraction, the composition comprising a density at 15°C of 0.880 g/cm³ to 0.990 g/cm³, a calculated carbon aromaticity index of 780 or more, a flash point of 60°C or more, and a sulfur content of 5000 wppm or less, a pour point of the composition being lower than a pour point of the mineral fraction.
2. The composition of claim 1, wherein the mineral fraction comprises a sulfur content of 2000 wppm or more, the composition comprising 80 vol% to 95 vol% of the mineral fraction.
3. The composition of claim 1 or 2, wherein the composition comprises a kinematic viscosity at 50°C of 380 cSt or less.
4. The composition of any of claims 1 to 3, wherein the composition further comprises 1.0 vol% to 40 vol% of a bio-derived component different from the blend component.
5. A fuel oil or fuel oil blend component composition, comprising: 1.0 vol% to 40 vol% of a blend component comprising an isoparaffinic blend component, an iso-olefinic blend component, or a combination thereof; 5.0 vol% to 50 vol% of a bio-derived component different from the blend component; and 15 vol% or more of a mineral fraction, the composition comprising a density at 15°C of 0.880 g/cm³ to 0.990 g/cm³, a calculated carbon aromaticity index of 800 or more, a flash point of 60°C or more, and a sulfur content of 5000 wppm or less, a pour point of the composition being lower than a pour point of the bio-derived component.
6. The composition of claim 5, wherein the mineral fraction comprises a sulfur content of greater than 5000 wppm.
7. The composition of claim 5 or 6, wherein the composition comprises a kinematic viscosity at 50°C of 380 cSt or less.

8. The composition of any of claims 1 – 7, wherein an estimated cetane number of the composition is greater than an estimated cetane number of the mineral fraction, or wherein the estimated cetane number of the composition is greater than an estimated cetane number of the bio-derived fraction, or a combination thereof.

9. The composition of any of claims 1 – 8, wherein the composition comprises 2.0 wt% or more of C₁₂- isoparaffins, iso-olefins, or a combination thereof.

10. The composition of any of claims 1 – 9, wherein the composition comprises a pour point of 0°C or less.

11. The composition of any of claims 1 – 10, wherein the mineral fraction comprises a sulfur content of less than 6500 wppm and the composition comprises a sulfur content of 1000 wppm or less.

12. The composition of any of claims 1 – 11, wherein the composition comprises 1.0 vol% to 50 vol% of an isoparaffinic blend component containing 80 wt% or more of isoparaffins and 5.0 wt% or less of iso-olefins; or wherein the composition comprises 1.0 vol% to 50 vol% of an iso-olefinic blend component containing greater than 5.0 wt% iso-olefins and 80 wt% or more of combined isoparaffins and iso-olefins.

13. The composition of any of claims 1 – 12, wherein the blend component contains 5.0 wt% or less of C₁₉₊ hydrocarbons, or wherein the blend component comprises 10 wt% to 50 wt% of C₁₉₊ hydrocarbons.

14. The composition of any of claims 4 – 13, wherein the bio-derived component a) contains less than 80 wt% of isoparaffins, iso-olefins, or a combination thereof b) has a ratio of Hd hydrogens to Hc₂ hydrogens of 1.6 or more, c) has a ratio of Hd hydrogens to Hc₂ hydrogens of 1.0 or less, d) a combination of a) and b), or e) a combination of a) and c).

15. The composition of any of the above claims, wherein the composition comprises a ratio of Hd hydrogens to Hc₂ hydrogens of 1.01 to 2.00.

16. The composition of any of the above claims, wherein the composition comprises a ratio of Hd hydrogens to Hc₂ hydrogens of 1.01 to 1.35.

17. The composition of any of the above claims, wherein the composition comprises a ratio of Hd hydrogens to Hc₂ hydrogens of 1.01 to 2.00.

18. The composition of any of the above claims, wherein the composition comprises a ratio of Hd hydrogens to Hc₂ hydrogens of 1.01 to 1.35.