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(54) **Title:** RENEWABLE FUELS FOR DISTLLATE AND RESIDUAL MARINE FUEL BLEND COMPOSITIONS

		Type	Biodiesel Bottoms	Biodiesel Bottoms	Biodiesel Bottoms	Biodiesel Bottoms	Undistilled Biodiesel	Undistilled Biodiesel	Undistilled Biodiesel	Biodiesel
Test Description	Test Method	Unit								
Viscosity @ 50 °C	D445-11/ASV	cSt	62.45	39.7	17.8	33.56				3.734
Density @ 15 °C	B3942/PGC	kg/m3	935	931	928	922	882	837	878	0.8807
Acid Number	D664-5/ASV	mg KOH/g	18.41	0.89	0.76	6.6	0.23	4.38	6.64	~0.3
Sulfur	D2622-1/CLN	mg/kg	237	63.3	41.6	245	19.6	20.4	27.4	~7
Carbon residue	D4530/ASV	Mass %	3.45	1.54	0.78	2.3	0.06			
Total Sediment Existent (TSE)	ISO 10307-1	Mass %	0.21	0.13	0.07	0.06				<det. limit
SIMDIST (T10)	M1567/ASV	°C	368	357	355	355		332	334	342
SIMDIST (T50)	M1567/ASV	°C	516	571	455	510		340	355	348
SIMDIST (T90)	M1567/ASV	°C	641	612	585			359	363	355
Pour Point	D5950-1/GAS	°C	1	9	9	18		19	N/A	6
Ash	D482	wt%	0.385	0.215	0.011	0.643				<det. limit
Vanadium	D5158-MOD	mg/kg		0	0	<1				
Aluminum	D5158-MOD	mg/kg	52	0	2	25		0	1	
Silicon		mg/kg	8	9	5	4		0	0	
Calcium		mg/kg	440	52	0	121		0	18	
Zinc		mg/kg	15	0	0	<1		0	1	
Phosphorus		mg/kg	700	44	2	442		0	27	<1
Magnesium		mg/kg	28	28	0			0	1	
Iron		mg/kg	1000	7	1			4	39	
Potassium		mg/kg	300		0	109		7	15	
Sodium			21	9	42	174		0		<1
Chlorine	ASTM D7536	wt%	11.3	3.5	14.4			2.9	3.6	

FIG. 1

(57) **Abstract:** A marine fuel or fuel blending composition that includes a renewable component that can be blended into heavy residual fuel oil or marine gasoil to meet statutory limits for sulfur. The renewable component may comprise biodiesel distillation tower bottoms and/or renewable diesel comprising at least 70% n-paraffins. The marine fuel composition may also include a biodiesel. Alternatively, the renewable component may comprise unrefined biodiesel, wherein the unrefined biodiesel has been separated to remove glycerol but has not been subject to further upgrading or purification. The marine fuel composition may also exhibit increased solvency.

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RENEWABLE FUELS FOR DISTLLATE AND RESIDUAL MARINE FUEL BLEND COMPOSITIONS

FIELD

[0001] The present disclosure relates generally to marine fuels and marine fuel blending compositions.

BACKGROUND OF THE INVENTION

[0002] Ocean transport vessels that burn marine fuel oil have historically represented a significant source of CO_2 emissions, as well as being a source of emissions of SOx and NOx. In an effort to reduce carbon emissions, the International Maritime Organization (IMO) has agreed on a target to cut the shipping sectors' overall CO_2 output by 50% by 2050 compared to 2008.

[0003] In January 2020, the International Maritime Organization (IMO) set a new limit for the sulfur content for marine fuels. Known as IMO 2020, this rule limits the sulfur content in fuel oil used onboard marine vessels which are not outfitted with exhaust gas scrubbers to no more than 0.5 wt.% sulfur in order to reduce sulfur oxide (SOx) emissions, a substantial reduction from the prior sulfur limit of 3.5 wt.%. In some coastal areas, known as Emission Control Areas (ECAs), which include the Baltic Sea area, the North Sea area, the North American area (covering designated coastal areas off the United States and Canada), and the United States Caribbean Sea area (covering coastal areas around Puerto Rico and the United States Virgin Islands), the sulfur limit is 0.1% wt.%. In order to meet the requirements of IMO 2020, marine vessels must either use a fuel oil which is inherently low enough in sulfur and/or install an appropriate exhaust gas cleaning system.

[0004] Refineries may blend fuel oil that has a high (i.e., non-compliant) sulfur content with fuel components and distillates that have a sulfur content lower than the required sulfur content to achieve a compliant fuel oil composition. Additives may be added to enhance other properties of the fuel oil or fuel oil blend composition, such as pour point depressant.

[0005] Air pollutants may also be limited by installing exhaust gas cleaning systems (i.e., "scrubbers") to meet the sulfur limit requirements. These scrubbers are designed to remove sulfur oxides from the marine vessel's engine and boiler exhaust gases. Based thereon, a marine vessel fitted with a scrubber can use a non-compliant marine fuel or heavy fuel oil, since the sulfur oxides emissions will be reduced to a level equivalent to the required fuel oil sulfur limit.

[0006] Before the limits of IMO 2020 were imposed, it was common for marine vessels to use heavy fuel oil (also known as "heavy residual fuel oil" or HFO). Derived as a residue from crude oil distillation, heavy fuel oil has a much higher sulfur content which, following combustion in the engine, ended up in a marine vessel's emissions. At present, many marine vessels use very low sulfur fuel oil (VLSFO) to comply with the requirements of IMO 2020 and other tighter pollution control standards.

[0007] Very low sulfur marine fuels (VLSFO) are often a blend of heavy residual fuel oil (HFO) and distillate fuels and or residual fuels to meet the ISO 8217 fuel standards for marine distillate fuels and marine residual fuels and statutory requirements for sulfur, including IMO 2020 which sets the sulfur limit at no more than 0.5 wt.%.

[0008] Marine fuel markets also have an interest in the use of renewable fuels, such as biodiesel and renewable diesel, to blend with residual fuel oil to reduce carbon emissions.

[0009] While biodiesel and renewable diesel can be blended with HFO, MGO, and other marine fuels to decrease the carbon impact and/or reduce the sulfur content of the overall fuel, there is some concern related to the use of biodiesel for marine applications due to competition with on-road heavy duty transportation organizations for supply.

[0010] To reduce this competition with on-road heavy duty transportation organizations, it is desirable to explore other renewable products that can be blended into HFO, MGO, and other marine fuels to reduce sulfur and carbon impact and meet statutory requirements, including IMO 2020.

SUMMARY OF THE INVENTION

[0011] In one embodiment, a marine fuel or fuel blending composition is described that includes a renewable component that can be blended into heavy residual fuel oil or marine gasoil to reduce lifecycle carbon emissions.

[0012] In one embodiment a renewable component is blended into a compliant fuel oil to increase the renewable content of the marine fuel or fuel blending composition.

[0013] In one embodiment, a marine fuel or fuel blending composition is described comprising a blend of heavy residual fuel oil and one or more of:

a) biodiesel distillation tower bottoms, and

b) renewable diesel comprising at least 70% n-paraffins, wherein the marine fuel or fuel blending composition contains less than 3.5 wt.% sulfur.

[0014] In one embodiment, the marine fuel or fuel blending composition further comprises a biodiesel.

[0015] In one embodiment, the marine fuel or fuel blending composition comprises unrefined biodiesel that has been separated to remove glycerol but has not been subject to further upgrading or purification.

[0016] In one embodiment, the marine fuel or fuel blending composition comprises the biodiesel distillation tower bottoms, wherein the biodiesel distillation tower bottoms have a viscosity of greater than 6 cSt at 40°C, a pour point of 10°C or higher, and an ASTM color value of at least 3 according to ASTM D1500.

[0017] In one embodiment, the marine fuel or fuel blending composition comprises the renewable diesel, wherein the renewable diesel comprises up to 95% n-paraffins.

[0018] In one embodiment, a marine fuel or fuel blending composition is described comprising marine gasoil and renewable diesel comprising at least 70% n-paraffins.

[0019] In one embodiment, a method of using biodiesel distillation tower bottoms in a marine fuel composition is described, in which the biodiesel distillation tower bottoms have a viscosity of greater than 6 cSt at 40°C, a pour point of 10°C or higher, and an ASTM color value of at least 3 according to ASTM D1500,

wherein the biodiesel distillation tower bottoms are blended with heavy residual fuel oil, wherein the biodiesel distillation tower bottoms are present in the marine fuel at a concentration of up to 30% by weight.

[0020] In one embodiment, a method of using renewable diesel comprising at least 70% n-paraffins in a marine fuel composition is described,

wherein the renewable diesel comprising the majority of n-paraffins are blended with heavy residual fuel oil or marine gasoil, wherein the renewable diesel is present in the marine fuel at a concentration of up to 30% by weight.

BRIEF DESCRIPTION OF THE FIGURES

[0021] FIG. 1 shows a comparison of properties of various biodiesel distillation tower bottoms samples with various biodiesel samples.

[0022] FIG. 2 shows ester contents for the biodiesel distillation tower bottoms samples and biodiesel samples from FIG. 1.

DETAILED DESCRIPTION OF THE INVENTION

[0023] As used herein, "a," "an," and "the" refer to both singular and plural referents unless the context clearly dictates otherwise.

[0024] As used herein, the terms "about" or "approximately" refer to a measurable value such as a parameter, an amount, a temporal duration, and the like and is meant to include variations of +/-15% or less, preferably variations of +/-10% or less, more preferably variations of +/-5% or less, even more preferably variations of +/-1% or less, and still more preferably variations of +/-0.1% or less of and from the particularly recited value, in so far as such variations are appropriate to perform herein. Furthermore, it is also to be understood that the value to which the modifier "about" refers is itself specifically disclosed herein.

[0025] As used herein, the terms "comprises" and/or "comprising," specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

[0026] As used herein, the term "substantially-free" or "essentially-free" if not otherwise defined herein for a particular element or compound means that a given element or compound is not detectable by ordinary analytical means that are well known to those skilled in the art.

[0027] As used herein, the term "substantially meets" in the context of a fuel standard means that the fuel or fuel component does not meet each and every requirement of the fuel standard such that the fuel or fuel component may not meet one or more of the requirements of the fuel standards but meets the remaining requirements of the fuel standard.

[0028] Where reference is made to an ASTM, EN, or the standard herein, the standard is expected to be the latest standard as of the filing of the application if not otherwise defined.

[0029] As used herein the term "heavy residual fuel oil" (HFO) refers to a residual fuel incurred during the distillation of crude oil and is mainly used as a marine fuel. The quality of the residual fuel depends on the quality of the crude oil and processing techniques. To achieve various specifications and quality levels, these residual fuels are fluxed with lighter fuels such as marine gasoil or marine diesel oil. Heavy fuel oil is defined either by a density of greater than 900 kg/m³ at 15°C or a kinematic viscosity of more than 10 mm²/s at 50°C. Heavy fuel oils have large percentages of heavy molecules such as long-chain hydrocarbons, multi-ring aromatic hydrocarbons, and aromatics with long-branched side chains.

[0030] As used herein the term "marine gasoil" (MGO) refers to a fuel composed of various blends of distillates, the components of crude oil that evaporate in fractional distillation and are condensed from the gas phase into liquid fractions.

[0031] As used herein, the term "renewable fuel" refers to a fuel or fuel composition derived from one or more renewable fuel blending components. Renewable fuel blending components can be derived from naturally-replenishing energy sources, such as biomass, vegetable oils, animal fats, and electricity produced from hydropower, wind, solar, or geothermal sources.

[0032] As used herein, the term "renewable diesel" refers to a hydrocarbon fuel that is chemically similar to petroleum diesel but made from fats and renewable oils. The renewable diesel may be formed at least in part by conversion (i.e. hydrotreating or F-T synthesis) of a renewable feedstock, such as, but not limited to, canola oil, palm oil, palm oil mill effluent, rapeseed oil, corn oil, soybean oil, tallow, cooking oil (i.e., vegetable cooking oil), used cooking oil (i.e., used vegetable cooking oil) and combinations of one or more of the foregoing.

[0033] As used herein the term "biodiesel" refers to a fuel comprised of fatty acid alkyl esters (FAAE) of long chain fatty acids derived from fats and oils. Biodiesel as used herein may also contain a minority of "impurities" or compounds other than FAAE.

[0034] As used herein, the term "fatty acid alkyl ester" (FAAE) refers to long chain fatty acids derived from fats and oils, which may also include fatty acid methyl esters (FAME).

[0035] As used herein, the terms "fuel blending component" or "fuel fraction", which terms may be used interchangeably, refer to a liquid fraction that can be used to form a fuel, which may be derived from renewable or conventional sources. In some cases, fuel blending components may possess the appropriate properties for use in a combustion device without further modification. Fuel blending components may be combined (blended) with fuels, other fuel blending components, or fuel additives to form a finished fuel or fuel composition that possesses the appropriate properties for use in a combustion device.

[0036] As used herein, the term "conventional fuel" refers to a fuel or fuel composition derived from one or more conventional fuel blending components. Conventional fuel blending components are derived from conventional hydrocarbon sources such as crude oil, natural gas, liquid condensates, heavy oil, shale oil, and oil sands, as described in ASTM D4175.

[0037] It will be understood that if a composition is stated to include "Cx -Cy hydrocarbons," such as C7 -C12 n-paraffins, this means the composition includes one or more paraffins with a carbon number falling in the range from x to y.

[0038] As used herein, the term "ester" is used to refer to organic esters wherein a fatty acid moiety is bound to an alcohol moiety by an ester linkage, including mono-esters, di-esters, tri-esters, and more generally multi-esters.

[0039] As used herein, the term "biodiesel distillation tower bottoms" is used to refer the portion of a crude biodiesel that is removed when the crude biodiesel is converted to a purified biodiesel. More generally, BDTB is formed by distilling the effluent resulting from a transesterification process. The bottoms from such a distillation corresponds to BDTB.

[0040] As used herein, the term "distillation bottoms" refers to the less volatile, or bottoms, product from the distillation of biodiesel wherein biodiesel is the intended distillate and distillation is used to purify the crude biodiesel.

[0041] As used herein the term "major amount" or "majority" as it relates to components included within the fuel compositions of the specification and the claims means greater than or equal to 50 wt.%, or greater than or equal to 60 wt.%, or greater than or equal to 70 wt.%, or greater than or equal to 80 wt.%, or greater than or equal to 90 wt.% based on the total weight of the fuel. Alternatively, the term "major amount" or "majority" may refer to vol.% instead of wt.% such that it means greater than or equal to 50 vol.%, or greater than or equal to 60 vol.%, or greater than or equal to 70 vol.%, or greater than or equal to 80 vol.%, or greater than or equal to 90 vol.% based on the total volume of the fuel.

[0042] As used herein the term "minor amount" or "minority" as it relates to components included within the fuel compositions of the specification and the claims means less than 50 wt.%, or less than or equal to 40 wt.%, or less than or equal to 30 wt.%, or greater than or equal to 20 wt.%, or less than or equal to 10 wt.%, or less than or equal to 5 wt.%, or less than or equal to 2 wt.%, or less than or equal to 1 wt.%, based on the total weight of the fuel. Alternatively, the term "minor amount" or "minority" may refer to vol.% instead of wt.% such that it means less than 50 vol.%, or less than or equal to vol.%, or less than or equal to 30 vol.%, or less than or equal to 20 vol.%, or less than or equal to 10 vol.%, or less than or equal to 5 vol.%, or less than or equal to 2 vol.%, or less than or equal to 1 vol.%, based on the total volume of the fuel.

[0043] In one embodiment, the present disclosure relates generally to marine fuel or fuel blending composition comprising: a blend of heavy residual fuel oil and one or more of:

a) biodiesel distillation tower bottoms, and

b) renewable diesel comprising at least 70% n-paraffins, wherein the marine fuel or fuel blending composition contains less than 3.5 wt.% sulfur. In one embodiment, the marine fuel or fuel blending composition contains less than 3.0 wt.% sulfur or less than 2.5 wt.% sulfur, or less than 2.0 wt.% sulfur or less than 1.5 wt.% sulfur, or less than 1.0 wt.5 sulfur or less than 0.5 wt.% sulfur.

[0044] In one embodiment, the present disclosure relates generally to marine fuel or fuel blending composition comprising:

a blend of very low sulfur fuel oil and one or more of:

a) biodiesel distillation tower bottoms, and

b) renewable diesel comprising at least 70% n-paraffins, wherein the marine fuel or fuel blending composition contains less than 3.5 wt.% sulfur. In one embodiment, the marine fuel or fuel blending composition contains less than 3.0 wt.% sulfur or less than 2.5 wt.% sulfur, or less than 2.0 wt.% sulfur or less than 1.5 wt.% sulfur, or less than 1.0 wt.% sulfur or less than 0.5 wt.% sulfur.

[0045] Heavy residual fuel oil (HFO) refers to a residual fuel incurred during the distillation of crude oil that is mainly used as a marine fuel and that optionally may contain a lower density and viscosity flux to adjust properties. The quality of the residual fuel depends on the quality of the crude oil. Heavy fuel oil is defined either by a density of greater than 900 kg/m³ at 15°C or a kinematic viscosity of more than 10 mm²/s at 50°C. Heavy fuel oils have large percentages of heavy molecules such as long-chain hydrocarbons, multi-ring aromatic hydrocarbons, and aromatics with long-branched side chains.

[0046] Very low sulfur fuel oil (VLSFO) generally contain less than 1.0 wt.% sulfur and in order to meet the requirements for ISO 8217, must contain less than 0.5 wt.% sulfur. However, the addition of BDTB or renewable diesel comprising a majority of n-paraffins can further reduce the sulfur content of the marine fuel or fuel blending composition.

[0047] Biodiesel distillation tower bottoms (BDTB) are the residual bottoms that are produced when biodiesel suppliers distill their biodiesel to upgrade their FAME product. BDTB is typically darker in color, more viscous, higher density, and has a higher pour point than typical biodiesel. However, this fuel, when blended appropriately with VLFSO to increase renewable content, does not negatively impact the finished blend's density, viscosity, and total sediment potential (TSP).

[0048] Biodiesel distillation tower bottoms (BDTB) are also known as heavy esters, bioesters, methyl ester distillation residue, pitch, bio-residual oil, industrial fuel, and bio-fuel oil. BDTB is commonly produced from fats and oils such as used cooking oil, distillers corn oil, animal fat and vegetable oil. BDTB is the biodiesel equivalent of No. 6 fuel oil (also known as

Residual Fuel Oil) and is made up of high molecular weight esters, monoglycerides, diglycerides, triglycerides, sterols, free fatty acids, glycerin, and similar types of molecules left over after the refining of biodiesel. Due to the higher molecular weight components, 20 wt% or more of a BDTB can have a boiling point of 550°C or higher, or 25 wt% or more, such as up to 50 wt% or possibly still higher. Additionally or alternately, due to the higher molecular weight components, 20 wt% or more of a BDTB can have a boiling point of 550°C or higher, or 575°C or higher, or 600°C or higher, such as up to 20 wt% or more having a boiling point of 725°C or higher. It is noted that crude biodiesel prior to distillation can typically contain 2.0 wt% or less of 550°C+ components. The boiling profile of a sample can be determined according to ASTM D7169 and/or a method that provides results equivalent to ASTM D7169.

[0049] Biodiesel can be purified/refined using various techniques so that unsaponifiables can be recovered. For example, biodiesel may be purified/refined by distillation to separate the unsaponifiable material and impurities by concentrating them in the BDTB as described, for example, in U.S. Pat. Pub. No. 2021/0363431 to White et al.

[0050] The BDTB may contain a significant amount of unsaponifiable material from which valuable chemicals such as tocopherols, sterols, steryl esters, terpenes, sulfolipids, proteins, hydroxycinnamic acids, fatty acid myricyl esters, waxes, flavonoids, carotenoids, and other valuable chemicals can be recovered.

[0051] In some aspects, the BDTB can correspond to a disadvantaged fraction when considered for use as a fuel blending component. For example, in some aspects the BDTB can have an ash content of 0.15 wt% or more, or 0.20 wt% or more, or 0.25 wt% or more, or 0.35 wt% or more, such as up to 1.0 wt% or possibly still higher. It is noted that for very low sulfur fuel oils, under ISO 8217, the maximum ash content is 0.1 wt% or less. As another example, in some aspects the BDTB can have an elevated metals content. In some aspects, this can correspond to the BDTB having a combined sodium plus potassium content of 50 wppm or more (such as up to 2000 wppm), or having a combined calcium plus magnesium content of 50 wppm or more (such as 2000 wppm or more, or having a phosphorus content of 50 wppm or more (such as up to 2000 wppm). In other aspects, this can correspond to the BDTB containing 50 wppm or more of sodium (such as up to 2000 wppm), or 50 wppm or more of potassium (such as up to 2000 wppm), or 50 wppm or more of calcium (such as up to 2000 wppm), or 50 wppm or more of magnesium (such as up to 2000 wppm), or 50 wppm or more of phosphorus (such as up to 2000 wppm), or a combination thereof.

[0052] Additionally or alternately, in some aspects, BDTB can be blended with a disadvantaged mineral fraction (a disadvantaged heavy residual fuel oil) for formation of a very low sulfur fuel oil have a sulfur content of 1.0 wt% or less. In such aspects, the disadvantaged heavy residual fuel oil can have a sulfur content of 1.1 wt% or more, or 1.2 wt% or more, or 1.5 wt% or more, such as up to 2.0 wt% or possibly still higher.

[0053] The biodiesel distillation tower bottoms (BDTB) fraction in the present embodiment comprises C20+ fatty acid alkyl esters (FAAE), unconverted glycerides (mono-, di-, and triglycerides), and unsaponifiables described previously in this disclosure. In some embodiments, the BDTB comprises at least 15 wt.% C20+ fatty acid FAAE. In some embodiments, the BDTB C20+ FAAE content is between 15 and 90 wt.%. In some aspects, the BDTB can contain 40 wt% or less of FAAE of any chain length, such as 15 wt% to 40 wt%, or 15 wt% to 30 wt%, or 25 wt% to 40 wt%. In some aspects where the BDTB contains 40 wt% or less of fatty acid alkyl esters, a blend of heavy residual fuel oil with BDTB can contain 1.0 wt% to 10 wt% of BDTB. Additionally or alternately, in some aspects where the BDTB contains 40 wt% or less of fatty acid alkyl esters, a blend of heavy residual fuel oil and BDTB can contain 90 wt% or more of a combined amount of the heavy residual fuel oil and the BDTB, or 95 wt% or more, such as up to being substantially composed of heavy residual fuel oil and BDTB. In other words, such a blend can contain 10 wt% or less of components other than heavy residual fuel oil and BDTB, or 5 wt% or less, such as down to having substantially no components other than heavy residual fuel oil and BDTB.

[0054] In one embodiment, the marine fuel or fuel blending composition comprises unrefined biodiesel that has been separated to remove glycerol but has not been subject to further upgrading or purification. In this instance, the BDTB may be present in a biodiesel sample derived from the crude esterification process or processes that has not been subjected to further upgrading or purification in order to produce a higher quality alkyl-ester composition. This would essentially allow a producer to create a FAAE that would typically be distilled to produce a product that meets or substantially meets ASTM D6751 or EN 14214 biodiesel regulations. However, the product that meets or substantially meets ASTM D6751 or EN14214 biodiesel regulations and the BDTB could be kept together. The unrefined biodiesel that has been separated to remove glycerol but has not been subject to further upgrading or purification can then be blended with heavy residual fuel oil.

[0055] In this instance, the marine fuel or fuel blending composition comprises a blend of heavy residual fuel oil and unrefined biodiesel that has been separated to remove glycerol but has not been subject to further upgrading or purification.

[0056] In one embodiment, the BDTB has a viscosity of greater than 6 cSt at 40°C, or greater than 8 cSt at 40°C, or greater than 10 cSt at 40°C, or greater than 20 cSt at 40°C, or greater than 30 cSt at 40°C, or greater than 40 cSt at 40°C, or greater than 50 cSt at 40°C and up to 80 cSt at 40°C , or up to 90 cSt at 40°C, or up to 100 cSt at 40°C.

[0057] In one embodiment, the BDTB has a pour point of 10°C or higher, or a pour point of 12°C or higher or a pour point of 15°C or higher.

[0058] In one embodiment, the BDTB has an ASTM color value of at least 3.0, or at least 3.5, or at least 4.0, at least 4.5 or least 5 or at least 5.5 or at least 6 or at least 6.5 according to the ASTM D1500 color scale.

[0059] It is noted that BDTB can have a substantially lower carbon intensity than other bio-derived fuel fractions. When determining the carbon intensity for a bio-derived fuel or fuel blending component, the various carbon emissions associated with growing, harvesting, and processing biomass are assigned to the primary fuel product. By contrast, biodiesel distillation tower bottoms are considered a residue, so the carbon emissions from production are not assigned to the BDTB product. Thus, the only carbon intensity associated with BDTB is any intensity due to transportation and/or end use.

[0060] Renewable diesel is an on-road fuel that can be blended with HFO to reduce sulfur and carbon intensity in producing a VLSFO. Renewable diesel is a bio-mass derived transportation fuel suitable for use in compression ignition engines, including diesel engines, and that is designed to meet or substantially meet the EN 15940 specification.

[0061] Renewable diesel differs from biodiesel in how it is produced. Renewable diesel is a hydrocarbon that may be produced by processes such as hydrotreating or via F-T synthesis, pyrolysis, and other biochemical and thermochemical technologies. Renewable diesel molecules are predominantly hydrocarbons, thus making them chemically identical to molecules contained in petroleum diesel. Because it is hydrogenated and isomerized, renewable diesel does not contain significant amounts of oxygen (but may contain trace levels of oxygen) and avoids the challenges biodiesel presents relating stability and impurities. Cold flow of the renewable diesel depends at least in part on isomerization which also affects the cloud point of the renewable diesel. On the other hand, biodiesel is a mono-alkyl ester produced via transesterification. In one embodiment, the biodiesel meets or substantially meets ASTM D6751 specifications.

[0062] Petroleum No. 2 diesel, which is often used to blend with HFO, typically contains a variety of hydrocarbon species with carbon numbers from C10-C22. Renewable diesel is primarily comprised of C14 to C22 n- and iso-paraffins. The most common feedstocks for renewable diesel are triglycerides, FAME, and free fatty acids.

[0063] Triglycerides are typically the most common feedstocks for renewable diesel. Often, the production of on-road renewable diesel necessitates a two-step process of triglycerides, which entails first hydrotreating and then isomerization. The amount of isomerization of the paraffins can be tuned to produce a resultant renewable diesel that has a wide range of cold flow qualities (i.e., cloud point of < -50°C to ~ 25°C).

[0064] To generate renewable diesel with low cloud points necessary for on-road use, typically deeper isomerization processing conditions is necessary and can contribute to the fuels having a higher carbon impact. However, renewable diesel that contains a majority of n-paraffins (HNRD) and little isomerization may have cloud/pour points in the range of 15 to 25°C. These types of lower carbon intensity HNRD are not well-suited for on-road applications due to their tendency to gel and elevated cold flow temperatures, resulting in vehicle operability issues such as filter plugging. However, these HNRD's can be blended into marine residual fuels and marine distillate fuels to meet ISO 8217 standards. This allows marine vessels to utilize a lower carbon intensity HNRD that does not compete with on-road markets. Marine vessels utilize heated fuel tanks to mitigate the risk of using fuels with elevated cold-flow temperatures.

[0065] In addition to producing a high cloud point HNRD, one could also distill the high temperature boiling range fraction from a HNRD sample to improve its low temperature performance. The high temperature boiling range fraction from HNRD samples may also be blended into distillate and residual marine fuels.

[0066] In one embodiment, the majority of n-paraffins comprise greater than 50% n-paraffins, or greater than 60% n-paraffins, or greater than 70% n-paraffins and may comprise up to 95% n-paraffins. In one embodiment, the content of n-paraffins in the HNRD is between 70-90% n-paraffins.

[0067] In one embodiment, the marine fuel or fuel blending composition contains both the BDTB and the HNRD. The presence of the BDTB may provide a synergistic effect with respect to solvency and allow for greater blending of the HNRD in the marine fuel or fuel blending composition as the BDTB helps to offset and enable the HNRD.

[0068] In one embodiment, the marine fuel or fuel blending composition also comprises a biodiesel or biodiesel fuel blend component. The biodiesel or biodiesel fuel blend component may meet or at least substantially meet ASTM D6751 specifications and/or EN14214 specifications. The use of such biodiesel or biodiesel fuel blending components is beneficial for the marine residual fuels disclosed herein because they can potentially reduce particulate matter within the combustion process and increases the renewable content of the fuel.

[0069] ASTM D6751 establishes specifications for a biodiesel blend stock for middle distillate fuels and is intended for the biodiesel component that is to be blended to produce biodiesel/diesel fuel blends. Since 2012, the ASTM D6751 standard has defined two grades of biodiesel: grade 2-B (identical to biodiesel defined by earlier versions of the standard) and grade 1-B with tighter controls on monoglycerides and cold soak filterability.

[0070] ASTM D6751 defines biodiesel as mono-alkyl esters of long chain fatty acids derived from vegetable oils and animal fats. The type of alcohol used is not specified. Thus mono-alkyl esters could be produced with any alcohol (methanol, ethanol, etc.) so long as it meets or substantially meets the detailed requirements outlined in the fuel specification. These fatty acid alkyl esters (FAAE) include fatty acid methyl esters (FAME). By requiring that the fuel be mono-alkyl esters of long chain fatty acids, other components, with the exception of additives, are inherently excluded.

[0071] The European biodiesel specification, EN 14214, is more restrictive and applies only to mono-alkyl esters made with methanol, fatty acid methyl esters (FAME). The minimum ester content is specified at 96.5%. The addition of components that are not fatty acid methyl esters, other than additives, is not allowed.

[0072] By using these biodiesel and biodiesel fuel blending components as at least a partial replacement for conventional marine fuel, the particulate emissions can potentially be reduced by potentially 2% or more, or 5% or more, 10% or more, 20% or more, 30% or more, 40% or more, or 50% or more, or possibly still more. In terms of visual observation, by using such biodiesel fuel blending components at least a partial replacement for conventional marine fuel, particulate emissions which are observable to the human eye may potentially be reduced by a sufficient amount such that the particulate matter emissions are difficult to detect by the human eye, or possibly still more, such that they are no longer visually detectable by the human eye.

[0073] Potential PM emissions reduction depends on multiple factors related to the fuel composition and marine vessel hardware and operation, such as (1) the blend level of renewable blending components as a percentage of the marine residual fuel final blend, (2) the chemical composition of the renewable blending components such as whether the renewable blending components contain hydrocarbon, oxygenate, or other chemical species, and (3) engine hardware design and engine load conditions, so variation in the magnitude of the potential PM emissions reduction may be possible.

[0074] The biodiesel generally comprises fatty acid alkyl esters (FAAE) of long chain fatty acids derived from fats and oils, which may also include fatty acid methyl esters (FAME). Biodiesel as used herein may also contain a minority of "impurities" or compounds other than FAAE.

[0075] In some embodiments, the one or more fatty acid alkyl esters can have a BMCI value of 50 or less, a SBN value of 55 or more, or a combination thereof. Optionally, the SBN value of the one or more fatty acid alkyl esters can be higher than the SBN value of the resid-containing fraction. In some embodiments, a fatty acid alkyl ester can include an alkyl group containing between 1 carbon (fatty acid methyl ester) to 10 carbons (fatty acid decyl ester), or 1 to 8 carbons, or 1 to 6 carbons, or 1 to 4 carbons. In some embodiments, a fatty acid alkyl ester fraction can include a blend of two or more types of fatty acid alkyl esters. The fatty acid alkyl esters in a blend of fatty acid alkyl esters can correspond to a blend of esters with different fatty acids, a blend of esters with different alkyl groups, or a blend of esters including both different fatty acid and different alkyl groups. In some embodiments, a fatty acid alkyl ester fraction can correspond to a fatty acid methyl ester fraction that meets or substantially meets the requirements provided in EN 14214. In some embodiments, a fatty acid alkyl ester fraction can correspond to a fraction that meets or substantially meets the requirements described in ASTM D6751. In some embodiments, a fatty acid alkyl ester fraction can be a fraction formed at least in part by transesterification of a renewable feedstock selected from the group consisting of canola oil, palm oil, palm oil mill effluent, rapeseed oil, corn oil, soybean oil, tallow, cooking oil (i.e., vegetable cooking oil), used cooking oil (i.e., used vegetable cooking oil) and combinations of one or more of the foregoing.

[0076] In one embodiment, the marine fuel or fuel blending composition comprises the heavy residual fuel oil (or the VLSFO) and biodiesel distillation tower bottoms (BDTB), wherein the BDTB are present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.%.

[0077] In another embodiment, the marine fuel or fuel blending composition comprises the heavy residual fuel oil (or the VLSFO) and biodiesel distillation tower bottoms (BDTB), wherein the BDTB are present in composition in an amount of 1.0 vol.% to 75 vol.%, or 10 vol.% to 75 vol.%, or 20 vol.% to 75 vol.%, or 1.0 vol.% to 50 vol.%, or 10 vol.% to 50 vol.%, or 20 vol.% to 50 vol.%, or 1.0 vol.% to 30 vol.%, or 10 vol.% to 30 vol.%.

[0078] In one embodiment, the marine fuel or fuel blending composition comprises the heavy residual fuel oil (or the VLSFO) and the renewable diesel (HNRD), wherein the HNRD is present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.%.

[0079] In one embodiment, the marine fuel or fuel blending composition comprises the heavy residual fuel oil (or the VLSFO), the BDTB, and the biodiesel, where the BDTB are present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.% and the biodiesel is present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.% or up to 35 vol.% or up to 40 vol.% or up to 45 vol.% or up to 50 vol.%. Optionally, higher amounts of BDTB can be present, such as 1.0 vol.% to 75 vol.%, or 10 vol.% to 75 vol.%, or 20 vol.% to 75 vol.%, or 1.0 vol.% to 50 vol.%, or 10 vol.% to 50 vol.%, or 20 vol.% to 50 vol.%, or 1.0 vol.% to 30 vol.%, or 10 vol.% to 30 vol.%.

[0080] In embodiment, the marine fuel or fuel blending composition comprises the heavy residual fuel oil and unrefined biodiesel that has been separated to remove glycerol but has not been subject to further upgrading or purification, where the unrefined biodiesel is present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.% or up to 35 vol.% or up to 40 vol.% or up to 45 vol.% or up to 50 vol.%.

[0081] In one embodiment, the marine fuel or fuel blending composition comprises the heavy residual fuel oil (or the VLSFO), the HNRD, and the biodiesel, where the HNRD is present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.% and the biodiesel is present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.% .% or up to 35 vol.% or up to 40 vol.% or up to 45 vol.% or up to 50 vol.%..

[0082] In one embodiment, the marine fuel or fuel blending composition comprises the heavy residual fuel oil (or the VLSFO) and both the BDTB and the HNRD, where each of the BDTB and the HNRD are independently present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.%. In other words, the composition may independently include up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.% of the BDTB and up to 10 vol.% or up to 15 vol.% or up to

20 vol.% or up to 25 vol.% or up to 30 vol.% of the HNRD. Optionally, higher amounts of BDTB can be present, such as 1.0 vol.% to 75 vol.%, or 10 vol.% to 75 vol.%, or 20 vol.% to 75 vol.%, or 1.0 vol.% to 50 vol.%, or 10 vol.% to 50 vol.%, or 20 vol.% to 50 vol.%, or 1.0 vol.% to 30 vol.%, or 10 vol.% to 30 vol.%.

[0083] In one embodiment, the marine fuel or fuel blending composition comprises the heavy residual fuel oil (or the VLSFO), the BDTB, the HNRD, and the biodiesel where each of the BDTB, the HNRD, and the biodiesel are each independently present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.%. In other words, the composition may independently include up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.% of the BDTB, up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.% of the renewable diesel, and up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.% of the biodiesel. Optionally, higher amounts of BDTB can be present, such as 1.0 vol.% to 75 vol.%, or 10 vol.% to 75 vol.%, or 20 vol.% to 75 vol.%, or 1.0 vol.% to 50 vol.%, or 10 vol.% to 50 vol.%, or 20 vol.% to 50 vol.%, or 1.0 vol.% to 30 vol.%, or 10 vol.% to 30 vol.%.

[0084] In another embodiment, the present disclosure relates generally to a marine fuel or fuel blending composition comprising marine gasoil and renewable diesel (HNRD) comprising at least 70% n-paraffins.

[0085] Marine gasoil (MGO) describes marine fuels that consist essentially of a blend of various distillates. Marine gasoil is also known as marine distillate fuel and is formulated to meet or substantially meet ISO 8217 standards. The MGO can be combined with renewable diesel comprising at least 70% n-paraffins described above to provide a marine fuel or fuel blending composition.

[0086] In one embodiment, the marine fuel or fuel blending composition comprises the marine gasoil and the HNRD, wherein the renewable diesel is present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.%.

[0087] In one embodiment, the marine fuel or fuel blending composition also comprises a biodiesel or a biodiesel fuel blend component. The biodiesel or biodiesel fuel blend component may meet or at least substantially meet ASTM D6751 specifications and/or EN14214 specifications. The use of such biodiesel or biodiesel fuel blending components is beneficial for the marine residual fuels disclosed herein because they can potentially reduce particulate matter within the combustion process.

[0088] In one embodiment, the marine fuel or fuel blending composition comprises the marine gasoil, the HNRD, and the biodiesel, where the renewable diesel is present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.% and the biodiesel is present in composition in an amount of up to 10 vol.% or up to 15 vol.% or up to 20 vol.% or up to 25 vol.% or up to 30 vol.%.

[0089] In one embodiment, the present invention also relates generally to a method of using the BDTB in a marine fuel composition, wherein the BDTB have a viscosity of greater than 6 cSt at 40°C, a pour point of 10°C or higher, and an ASTM color value of 3 or more according to ASTM D1500. The BDTB are blended with heavy residual fuel oil (or VLSFO), wherein the BTBD are present in the marine fuel at a concentration of up to 30% by volume.

[0090] As discussed above, the marine fuel or fuel blending composition may also include renewable diesel comprising at least 70% n-paraffins and/or a biodiesel.

[0091] In one embodiment, the present invention also relates generally to the use of renewable diesel comprising at least 70% n-paraffins in a marine fuel composition, wherein the renewable diesel comprising the majority of n-paraffins are blended with heavy residual fuel oil or marine gasoil, wherein the renewable diesel is present in the marine fuel at a concentration of up to 30% by volume.

[0092] As discussed above, the marine fuel or fuel blending composition may also include a biodiesel or biodiesel fuel blend component.

[0093] The fuel composition may have a BMCI value of 70 or less, 65 or less, 60 or less, or 55 or less, or 50 or less, such as down to 30 or possibly still lower. Additionally or alternately, the fuel composition can have a BMCI – TE difference value of 30 or less, or 20 or less, or 15 or less, or 12 or less, or 10 or less, such as down to -20 or possibly still lower. Further additionally or alternately, a fuel composition can have an S_{BN}-I_N difference value of 20 or more, or 25 or more, or 30 or more, such as up to 60 or possibly still higher. An S_{BN}-I_N difference value of 20 or more generally indicates a compatible blend.

[0094] In some embodiments, the fuel compositions and fuel blending compositions described herein may exhibit a kinematic viscosity at 50°C between 2 cSt and 380 cSt, or between 2 cSt and 180 cSt, or between 2 cSt and 80 cSt, or between 2 cSt and 60 cSt, or between 2 cSt and 30 cSt, or between 4.5 cSt and 380 cSt, or between 4.5 cSt and 180 cSt, or between 4.5 cSt and 80 cSt, or between 4.5 cSt and 60 cSt, or between 4.5 cSt and 30 cSt, or between 4.5 cSt and 10 cSt, or between 8 cSt and 380 cSt, or between 8 cSt and 180 cSt, or between 8 cSt and 80 cSt, or between 8 cSt and 60 cSt, or between 8 cSt and 30 cSt, or between 10 cSt and 380 cSt, or between 10 cSt and 180 cSt, or between 10 cSt and 80 cSt, or between 10 cSt and 60 cSt, or between 10 cSt and 30 cSt.

[0095] In some embodiments, the fuel compositions and fuel blending compositions described herein may exhibit a micro carbon residue of 0.5 wt.% or more, or 1 wt.% or more, or 2 wt.% or more, or 5 wt.% or more, or 10 wt.% or more, or 15wt% or more, such as up to 18 wt.%; an asphaltene content of 0.5 wt.% or more, or 1 wt.% or more, or 1.5 wt.% or more, or 2 wt.% or more, or 3 wt.% or more, or 5 wt.% or more, or 10 wt.% or more or possibly still higher.

[0096] In some embodiments, the fuel compositions and fuel blending compositions described herein may exhibit; a density at 15°C of between 0.87 and 1.05 g/cm^3, or between 0.89 and 1.05 g/cm^3, or between 0.90 and 1.05 g/cm^3, or between 0.92 and 1.05 g/cm^3, or between 0.96 and 1.05 g/cm^3, or between 0.975 and 1.05 g/cm^3, or between 0.87 and 1.00 g/cm^3, or between 0.87 and 0.991 g/cm^3, or between 0.87 and 0.975 g/cm^3, or between 0.87 and 0.96 g/cm^3, or between 0.87 and 0.92 g/cm^3, or between 0.89 and 0.991 g/cm^3, or between 0.89 and 0.975 g/cm^3, or between 0.90 and 0.991 g/cm^3, or between 0.90 and 0.975 g/cm^3.

[0097] In some embodiments, the fuel compositions and fuel blending compositions described herein exhibit a sulfur content of 10,000 wppm or less, or 5000 wppm or less (such as 1500 wppm to 5000 wppm, or 4000 wppm to 5000 wppm), or 1000 wppm or less (such as 800 wppm to 1000 wppm), such as down to 10 wppm or possibly still lower. In some embodiments, the fuel compositions disclosed herein can have a sulfur content of 500 wppm or more, or 800 wppm or more, or 1000 wppm or more, or 2000 wppm or more, or 4000 wppm or more, such as up to 1000 wppm or 5000 wppm.

[0098] The fuel compositions and fuel blending compositions described herein can also have a low sediment content and/or a favorable value for the spot test cleanliness rating according to ASTM D4740. In some embodiments, the fuel compositions disclosed herein can have a sediment content according to ISO 10307-2 Procedure A or B of 0.1 wt.% or less, or 0.07 wt.% or less, or 0.05 wt.% or less, or 0.02 wt.% or less, such as down to having substantially no sediment (less than 0.01 wt.%). Additionally or alternately, the fuel compositions disclosed herein can have a spot test cleanliness rating (according to ASTM D4740) of 1 or 2.

[0099] Any other convenient type of blend component (also referred to as a secondary flux) can also be included in the marine fuel or fuel blending composition of the disclosure so long as the sulfur content of the marine fuel or fuel blending composition contains no more than 0.5 wt.% sulfur, or no more than 0.1 wt.% sulfur. Thus, the marine fuel or fuel blending composition may be blended with any of one or more of the following: low sulfur diesel (sulfur content of less than 500 wppm), ultra-low sulfur diesel (sulfur content <10 wppm or <15 wppm), 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, 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 cracked heavy gas oil, non-hydrotreated pyrolysis light gas oil, non-hydrotreated pyrolysis heavy gas oil, 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-hydrotreated coker vacuum gas oil, non-hydrotreated thermally cracked vacuum gas oil, non-hydrotreated thermally cracked diesel, non-hydrotreated thermally cracked gas oil, synthetic renewable hydrocarbons such as gas-to-liquid hydrocarbons from renewable synthesis gas (from gasification of biomass, municipal solid waste, or other renewable feedstocks), hydrotreated natural fats or oils (such as hydrotreated vegetable oils including soy oil, canola oil, rapeseed oil, etc., or hydrotreated animal oils and fats such as fish oils, chicken fat or beef tallow), hydrotreated waste cooking oils, hydrotreated tall oil, oxygenates such as ethers (diethyl ether, methyl t-butyl ether) or alcohols (methanol, ethanol) or esters or acids or carboxylic acids (fatty acids, resin acids) or cyclic oxygenates (sugars, C6 lignin derivatives) or combinations thereof; Group 1 slack waxes, lube oil aromatic extracts, deasphalted oil, atmospheric tower bottoms, vacuum tower bottoms, steam cracker tar, any residue materials derived from low sulfur crude slates, ultra-low sulfur fuel oils (ULSFO) with sulfur level up to 0.1wt%, very low sulfur fuel oil (VLSFO) with sulfur level up to 0.5 wt.%, low sulfur fuel oils (LSFO) with sulfur level up to 1wt%, regular sulfur fuel oil (RSFO; also called heavy fuel oil, HFO) with sulfur level up to 3.5wt%, other ULSFO/VLSFO/LSFO/RSFO blend stocks.

[0100] As needed, the fuel compositions or fuel blending component fractions disclosed herein may also include one or more fuel additives, including one or more fuel additives selected from the group consisting of pour point improver, combustion improver, flocculant, dispersant, H2S scavenger, antioxidant, stability improver, compatibility improver, etc., and combinations thereof at concentrations ranging from 5 vppm to up to 1 vol%, or 5 vppm to up to 0.8 vol%, or 5 vppm to up to 0.6 vol%, or 5 vppm to up to 0.4 vol%, or 5 vppm to up to 0.3 vol%, or 5 vppm to up to 2000 vppm, or 100 vppm to up to 1.0 vol%, or 500 vppm to up to 1.0 vol%, or 1000 vppm to up to 1.0 vol%, or 2000 vppm to up to 1.0 vol%, or 0.3 vol% to up to 1.0 vol%, 0.4 vol% to up to 1.0 vol%, 0.5 vol% to up to 1.0 vol%, or 50 vppm to 0.8 vol%, or 500 vppm to 0.6 vol%, or 1000 vppm to 0.4vol%, to improve properties of the marine fuel or fuel blending composition and/or meet local specifications.

The following are examples of the present disclosure and are not to be construed as limiting.

EXAMPLES

Test Methods

[0101] The Bureau of Mines Correlation Index (BMCI) provides a method for characterizing the properties of a fuel oil (or another petroleum fraction). The BMCI index can provide an indicator of the ability of a fuel oil fraction to maintain solubility of compounds such as asphaltenes. The BMCI index can be calculated based on Equation (1):

[0102](1) $BMCI = \frac{48640}{VABP} + (473.7 \times d_{60}) - 456.8$

[0103] In Equation (1), VABP refers to the volume average boiling point (in degrees Kelvin) of the fraction, which can be determined based on the fractional weight boiling points for distillation of the fraction at roughly 10 vol % intervals from ~10 vol % to ~90 vol %. The "d_{60}" value refers to the density in g/cm^3 of the fraction at ~60° F. (~16° C.). While this definition does not directly depend on the nature of the compounds in the fraction, the BMCI index value is believed to provide an indication of the ability of a fuel oil fraction to solvate asphaltenes. An additional/alternative method of characterizing the solubility properties of a fuel oil (or other petroleum fraction) can correspond to the toluene equivalence (TE) of a fuel oil, based on the toluene equivalence test as described, for example, in U.S. Pat. No. 5,871,634, which is incorporated herein by reference with regard to the definitions for and descriptions of toluene equivalence, solubility number (S_{BN}), and insolubility number (I_N).

[0104] For the toluene equivalence test, the procedure specified in AMS 79-004 and/or as otherwise published (e.g., see Griffith, M. G. and Siegmund, C. W., "Controlling Compatibility of Residual Fuel Oils," *Marine Fuels, ASTM STP* 878, C. H. Jones, Ed., American Society for Testing and Materials, Philadelphia, 1985, pp. 227-247, which is hereby incorporated by reference herein) is defined as providing the procedure. Generally, a convenient volume ratio of oil to a test liquid mixture can be selected, such as about 2 grams of fuel oil (with a density of about 1 g/ml) to about 10 ml of test liquid mixture. Then various mixtures of the test liquid mixture can be prepared by blending n-heptane and toluene in various known proportions. Each of these can be mixed with the fuel oil at the selected volume ratio of oil to test liquid mixture. A determination can then be made for each oil/test liquid mixture to determine if the asphaltenes are soluble or insoluble. Any convenient method might be used. One possibility can be to observe a drop of the blend of test liquid mixture and oil between a glass slide and a glass cover slip using transmitted light with an optical microscope at a magnification from ~50× to ~600×. If the asphaltenes are in solution, few, if any, dark particles will be observed. If the asphaltenes are insoluble, many dark, usually brownish, particles, usually ~0.5 microns to ~10 microns in size, can be observed. Another possible method can be to put a drop of the blend of test liquid mixture and oil on a piece of filter paper and let it dry. If the asphaltenes are insoluble, a dark ring or circle will be seen about the center of the yellow-brown spot made by the oil. If the asphaltenes are soluble, the color of the spot made by the oil will be relatively uniform in color. The results of blending oil with all of the test liquid mixtures can then be ordered according to increasing percent toluene in the test liquid mixture. The desired TE value can be between the minimum percent toluene that dissolves asphaltenes and the maximum percent toluene that precipitates asphaltenes. Depending on the desired level of accuracy, more test liquid mixtures can be prepared with percent toluene amounts in between these limits. The additional test liquid mixtures can be blended with oil at the selected oil to test liquid mixture volume ratio, and determinations can be made whether the asphaltenes are soluble or insoluble. The process can be continued until the desired value is determined within the desired accuracy. The final desired TE value can be taken as the mean of the minimum percent toluene that dissolves asphaltenes and the maximum percent toluene that precipitates asphaltenes.

[0105] The above test method for the toluene equivalence test can be expanded to allow for determination of a solubility number (S_{BN}) and an insolubility number (I_N) for a fuel oil sample. If it is desired to determine S_{BN} and/or I_N for a fuel oil sample, the toluene equivalence test described above can be performed to generate a first data point corresponding to a first volume ratio R_1 of fuel oil to test liquid at a first percent of toluene T_1 in the test liquid at the TE value. After generating the TE value, one option can be to determine a second data point by a similar process but using a different oil to test liquid mixture volume ratio. Alternatively, a percent toluene below that determined for the first data point can be selected and that test liquid mixture can be added to a known volume of the fuel oil until asphaltenes just begin to precipitate. At that point the volume ratio of oil to test liquid mixture, R_2, at the selected percent toluene in the test liquid mixture, T_2, can be used the second data point. Since the accuracy of the final numbers can increase at greater distances between the data points, one option for the second test liquid mixture can be to use a test liquid containing 0% toluene or 100% n-heptane. This type of test for generating the second data point can be referred to as the heptane dilution test.

[0106] Based on the toluene equivalence test and heptane dilution test (or other test so that R_1, R_2, T_1, and T_2 are all defined), the insolubility and solubility numbers for a sample can be calculated based on Equations (2) and (3).

[0107] (2) $I_N = T_2 - \left[\frac{T_2 - T_1}{R_2 - R_1}\right] R_2$

[0108] (3) $S_{BN} = I_N\left[1 + {}^{1}/_{R_2}\right] - {}^{T_2}/_{R_2}$

[0109] U.S. Pat. No. 5,871,634, the subject matter of which is herein incorporated by reference in its entirety, describes alternative methods are available for determining the solubility number of a fuel oil that has an insolubility number of zero.

[0110] Tables 1-7 below depict examples of potential blends that can be generated with HFO and VLSFO blended with BDTB and HNRD. Both the BDTB and HNRD are renewable fuel candidates that do not typically meet on-road fuel needs and be used to produce the marine fuels and marine fuel blending compositions described herein.

[0111] The example blends include a low bookend at 5% and a high bookend at 15%. There is also a high-biofuel concentration blend that is 47.5% of a high-cloud point biodiesel and 2.5% BDTB to maximize biofuel blending. Lastly, there is a blend with HNRD with a high-cloud MGO at 10% and 20% blend concentrations.

[0112] The TSP compatibility testing for all of the examples for all of the examples is at 0.01 wt.% or below. This is an excellent compatibility value that is well below the 0.1 wt.% limit.

[0113] Table 1 compares the properties of the two residual fuels (heavy fuel oil and marine gasoil) to be blended with BDTB and the renewable diesel comprising the majority of n-paraffins along with very low sulfur fuel oil. The Heavy Fuel Oil (HFO) is used in the examples below is a Marine fuel oil that at least substantially complies with ISO 8217:2017 and is available from Exxon Mobil Corporation. The Very Low Sulfur Fuel Oil (VLSFO) used in the examples below is available from Exxon Mobil Corporation under the tradename EMF.5™. The Marine Gas Oil used in the examples below is available from Exxon Mobil Corporation under the tradename HDME 50™.

Table 1: Neat Properties of Marine Fuels

Method	Description	Unit	Heavy Fuel Oil (HFO)	Very Low Sulfur Fuel Oil (VLSFO)	Marine Gas Oil (MGO)
D4052	Density, 15 ºC	g/mL	0.986	0.942	0.9083
D445	Viscosity @ 40 ºC	cSt	740.4	255.3	-
D341-Extrapolated	Viscosity @ 50 ºC	cSt	*372.6	*84.00	40.84
D7042	Viscosity @ 100 ºC	cSt	35.41	18.01	-
D664	Acid Number	mg KOH/g	<0.05	0.40	<0.05
D2622	Sulfur	Mass%	3.27	0.469	0.039
See above	BMCI	Value	69.8	53.7	41.5
ISO8217	CCAI	Value	847.1	813.8	798
ISO 10307-2	Total Sediment Potential	Mass%	<0.01	<0.01	†0.01
D5949	Pour Point	ºC	6	15	17
D4530	Carbon Residue	Mass%	13.5	5.66	0.16
D482	Ash	Mass%	0.027	0.016	-
D7169	High Temp SIMDIST (T0.5)	ºC	**162.28	182.25	270
D2887	SIMDIST (T10)	ºC	**278.97	**298.13	369
D2887	SIMDIST (T50)	ºC	**550.12	**488.24	446
D2887	SIMDIST (T88)	ºC	**729.33	-	-
D2887	SIMDIST (T90)	ºC	-	**689.82	534
D2887	SIMDIST (T98)	ºC	-	**732.83	-
D2887	SIMDIST (T99.5)	ºC	-	-	610
AM-S 79-004	TE	Value	41.25		
E1999-2/CLN	S_{BN}	Value	103		

Method	Description	Unit	Heavy Fuel Oil (HFO)	Very Low Sulfur Fuel Oil (VLSFO)	Marine Gas Oil (MGO)
E1999-2/CLN	I_N	Value	52		
E1999-2/CLN	S_{BN}/I_N	Value	1.98		

*Estimated Value
**High-Temp SIMDIST Method per the method of D7169
†Total Sediment Accelerated method

[0114] Table 2 describes the neat test properties of the various blend components – (1) biodiesel distillation tower bottoms (BDTB), (2) biodiesel (or FAME), and (3) renewable diesel comprising a majority of n-paraffins (HNRD).

Table 2: Neat Properties BDTB, FAME, and HNRD

Method	Description	Unit	BDTB	FAME	HNRD
D4052	Density, 15 ºC	g/mL	*0.922	0.8787	*0.787
D445	Viscosity @ 50 ºC	cSt	33.56	-	2.853
D1500	ASTM Color	Value	>8	<2	-
D664	Acid Number	mg KOH/g	6.6	0.30	<0.05
D5453	Sulfur	mg/kg	7.8	7.3	-
D2622	Sulfur	mg/kg	-	-	<5
D2887	T0.5/Initial Boiling Point	ºC	**316.82	-	†146.1
D2887	T10	ºC	**355.14	-	†270.8
D2887	T50	ºC	**510.45	-	†302.9
D2887	T82	ºC	**728.07	-	-
D2887	T90	ºC	-	-	†319.5
D2887	% (V/V) Recovered at 250 ºC	% (V/V)	**0%	-	†<10
D2887	% (V/V) Recovered at 350 ºC	% (V/V)	**<10	-	†<90
D2887	T99.5/Final boiling point	ºC	**>728.07	-	†476.8
See above	BMCI	Value	42.4	-	0.8
ISO8217	CCAI	Value	814.7	-	740

Method	Description	Unit	BDTB	FAME	HNRD
D4530	Carbon Residue (Micro)	Mass%	2.30	-	<0.01
D482	Ash	Wt%	0.643	-	-
D5773	Cloud Point	ºC	-	8	18
D7501	Cold Soak Filtration Test	sec	-	122	-
D6371	Cold Filter Plugging Point	ºC	-	4	14
D5949	Pour Point	ºC	18	7	16
EN 14103	Ester Content	Wt%	-	>96.8%	-
D6584	Free Glycerin	Wt%	-	0.010	-
D6584	Total Glycerin	Wt%	-	0.115	-
D6584	Monoglycerides	Wt%	-	<0.25	-
D6584	Diglycerides	Wt%	-	<0.121	-
D6584	Triglycerides	Wt%	-	<0.22	-
ISO 10307-1	Total Sediment Existent	Mass%	0.06	-	-
UOP 990	2D GC (C9-C28 iso-paraffins)	Wt.%			3.05
UOP 990	2D GC (C7-C27 n-paraffins)	Wt.%			92.42

*Estimated Value
**High-Temp SIMDIST Method per the method of D7169
†SIMDIST by D2887

[0115] Table 3 depicts the properties of two different marine fuel blend compositions containing various concentrations of very low sulfur fuel oil (VLSFO) and renewable diesel comprising a majority of n-paraffins (HNRD). As seen in Table 3, the addition of a larger concentration of HNRD reduced the amount of sulfur in the fuel composition.

Table 3: Blends of 0.5% Sulfur VLSFO with HNRD

Method	Description	Unit	5% HNRD with 95% 0.5% S VLSFO	15% HNRD with 85% 0.5% S VLSFO
D4052	Density, 15 ºC	g/mL	0.9324	0.9172
D445	Viscosity @ 50 ºC	cSt	97.12	56.07
IP 541	ECN	Value	>40	>40
D664	Acid Number	mg KOH/g	0.25	0.24
D2622	Sulfur	Mass%	*0.450	*0.410
See above	BMCI	Value	*51.1	*45.8
ISO8217	CCAI	Value	809	802
ISO 10307-2	Total Sediment Potential	Mass%	<0.01	<0.01
D5949	Pour Point	ºC	12	9
D4530	Carbon Residue	Mass%	*5.43	*4.95
D482	Ash	Mass%	-	0.012
IP 501	Vanadium	mg/kg	10	9
IP 501	Sodium	mg/kg	29	25
IP 501	Aluminum + Silicon	mg/kg	2	2
IP 501	Aluminum	mg/kg	1	1
IP 501	Silicon	mg/kg	1	1
IP 501	Calcium	mg/kg	1	1
IP 501	Zinc	mg/kg	<1	<1
IP 501	Phosphorus	mg/kg	<1	<1
IP 501	Magnesium	mg/kg	<1	<1
IP 501	Iron	mg/kg	9	9
IP 501	Nickle	mg/kg	9	8
IP 501	Potassium	mg/kg	1	1

IP 501	Lead	mg/kg	<1	<1

*Estimated Value

[0116] Table 4 depicts the properties of two different marine fuel blend compositions containing various concentrations of heavy residual fuel oil and BDTB as well as composition containing 50% HFO and 50% BDTB and biodiesel (FAME). As seen in Table 5, the addition of a larger concentration of BDTB reduced the amount of sulfur in the fuel composition. Furthermore, the addition of both biodiesel (FAME) and BDTB reduced the amount of sulfur in the fuel composition by a significant amount.

Table 4: Blends of 3.5% Sulfur HFO with BDTB

Method	**Description**	**Unit**	**5% BDTB with 95% 3.5% S HFO**	**15% BDTB with 85% 3.5% S HFO**	**50% 3.5% S HFO and 47.5% FAME and 2.5% BDTB**
D4052	Density, 15 ºC	g/mL	0.9834	0.9762	0.9342
D445	Viscosity @ 50 ºC	cSt	367.1	225.3	19.78
IP 541	ECN	Value	28.8	27.3	>40
D664	Acid Number	mg KOH/g	0.8	1.76	0.57
D2622	Sulfur	Mass%	*3.12	*2.81	*1.73
See above	BMCI	Value	*68.4	*65.7	*54.4
ISO8217	CCAI	Value	845	843	836
ISO 10307-2	Total Sediment Potential	Mass%	0.01	0.01	<0.01
D5949	Pour Point	ºC	3	3	-6
D4530	Carbon Residue	Mass%	*13.0	*11.9	7.54
D482	Ash	Mass%	*0.056	*0.114	0.041
IP 501	Vanadium	mg/kg	66	51	33
IP 501	Sodium	mg/kg	31	43	18

Method	Description	Unit	5% BDTB with 95% 3.5% S HFO	15% BDTB with 85% 3.5% S HFO	50% 3.5% S HFO and 47.5% FAME and 2.5% BDTB
IP 501	Aluminum + Silicon	mg/kg	11	14	5
IP 501	Calcium	mg/kg	14	21	6
IP 501	Zinc	mg/kg	<1	<1	<1
IP 501	Phosphorus	mg/kg	21	50	9
IP 501	Magnesium	mg/kg	113	325	59
IP 501	Iron	mg/kg	26	35	18
IP 501	Nickle	mg/kg	19	21	12
IP 501	Potassium	mg/kg	9	14	2
IP 501	Lead	mg/kg	<1	<1	<1

*Estimated Value

[0117] Table 5 depicts the properties of two different marine fuel blend compositions containing various concentrations of VLSFO and BTDB. As seen in Table 6, the addition of a larger concentration of BDTB reduced the amount of sulfur in the fuel composition. Furthermore, the addition of both biodiesel (FAME) and BDTB reduced the amount of sulfur in the fuel composition by a significant amount.

Table 5: Blends of 0.5% VLSFO with BDTB

Method	Description	Unit	5% BDTB with 95% 0.5% S VLSFO	15% BDTB with 85% 0.5% VLSFO	50% 0.5% S VLSFO and 47.5% FAME and 2.5% BDTB
D4052	Density, 15 ºC	g/mL	0.9390	0.9374	0.9108
D445	Viscosity @ 50 ºC	cSt	117.7	96.13	14.55
IP 541	ECN	Value	>40	>40	>40

Method	**Description**	**Unit**	**5% BDTB with 95% 0.5% S VLSFO**	**15% BDTB with 85% 0.5% VLSFO**	**50% 0.5% S VLSFO and 47.5% FAME and 2.5% BDTB**
D664	Acid Number	mg KOH/g	0.75	1.76	0.55
D2622	Sulfur	Mass%	*0.447	*0.404	*0.243
See above	BMCI	Value	53.1	52.0	46.3
ISO8217	CCAI	Value	813	814	819
ISO 10307-2	Total Sediment Potential	Mass%	<0.01	0.01	<0.01
D5949	Pour Point	ºC	9	15	3
D4530	Carbon Residue	Mass%	*5.50	*5.17	3.17
D482	Ash	Mass%	*0.047	*0.108	0.037
IP 501	Vanadium	mg/kg	10	9	5
IP 501	Sodium	mg/kg	34	50	19
IP 501	Aluminum + Silicon	mg/kg	4	8	2
IP 501	Calcium	mg/kg	7	17	3
IP 501	Zinc	mg/kg	<1	<1	<1
IP 501	Phosphorus	mg/kg	17	55	9
IP 501	Magnesium	mg/kg	120	369	61
IP 501	Iron	mg/kg	15	22	6
IP 501	Nickle	mg/kg	10	9	5
IP 501	Potassium	mg/kg	5	15	2
IP 501	Lead	mg/kg	<1	<1	<1

*Estimated Value

[0118] Table 6 depicts the properties of two different marine fuel blend compositions containing various concentrations of MGO and HNRD. As seen in Table 7, the addition of HNRD reduced the amount of sulfur in the fuel composition.

Table 6: Blend of MGO with HNRD

Method	Description	Unit	90% MGO and 10% HNRD	80% MGO and 20% HNRD
D4052	Density, 15 ºC	g/mL	0.8845	0.8966
D445	Viscosity @ 50 ºC	cSt	26.43	18.45
D445	Viscosity @ 40 ºC	cSt	44.35	28.55
IP 541	ECN	Value	>40	>40
D664	Acid Number	mg KOH/g	0.04	0.03
D2622	Sulfur	Mass%	*0.036	*0.032
See above	BMCI	Value	*37.4	*33.4
ISO8217	CCAI	Value	781	800
ISO 10307-1	Total Sediment Existent	Mass%	<0.01	<0.01
D975	Pour Point	ºC	15	15
D4530	Carbon Residue	Mass%	*0.15	*0.13
D482	Ash	Mass%	<0.010	<0.010

*Estimated Value

[0119] It has been discovered that biodiesel distillation tower bottoms have an unexpectedly high compatibility for blending with resid fractions. Biodiesel distillation tower bottoms can typically have BMCI values of around 45 or less. This is similar to the BMCI values of around 30 that are typical of various types of hydrotreated distillate fractions that are commonly used as distillate flux for blending with resid fractions to form marine fuel oils (and/or fuel blending components). However, it has been unexpectedly discovered that biodiesel distillation tower bottoms have substantially greater compatibility for blending with resid fractions while reducing or minimizing formation of sediment and/or sludge. The unexpected compatibility of biodiesel distillation tower bottoms for blending with resid fractions can be further seen in the unexpected difference between BMCI values and solubility blending numbers for biodiesel distillation tower bottoms fractions. It has been discovered that biodiesel distillation tower bottoms fractions have unexpectedly high solubility blending numbers (S_{BN}) relative to the corresponding BMCI values. As a result, when forming a blend of a resid-containing fraction with a BDTB fraction, the resulting blend can have an unusually high S_{BN}. In some aspects, using a biodiesel distillation tower bottoms fraction as a flux for a resid-containing fraction can provide the unexpected combination of reducing the density, kinematic viscosity, and optionally sulfur content of a blend while also maintaining or increasing the compatibility. This is in contrast to the expected behavior of a blend where flux is added. Conventionally, addition of flux to a resid-containing fraction can reduce one or more of density, kinematic viscosity, and sulfur, but with a corresponding reduction in compatibility. Without being bound by any particular theory, it is believed that the paraffinic, oxygenated nature of a BDTB fraction contributes to the unexpected benefits of BDTB relative to the BMCI value of a BDTB fraction. Traditionally, BMCI serves as a proxy for ability to solvate asphaltenes due to the differing density of chain-like compounds and ring-based compounds. However, it is believed that the oxygenated nature of the BDTB provides for increased aromatic solubility in spite of the BDTB having an otherwise paraffin-like profile with regard to the factors for calculating BMCI.

[0120] In general residual fuel oils contain asphaltenes, the heaviest and most polar class of hydrocarbons, which require a certain solvency (as measured in S_{BN}) from the fuel to keep them in solution. If the solvency is disrupted by blending or adding a component, the asphaltenes may fall out of solution forming sediment or sludge. Sediment will block fuel filters in a marine vessel, causing a disruption of fuel flow. Without a fuel supply, a marine engine may stall, and the marine vessel may lose power, which is a serious safety concern.

[0121] The residual fuel oil sample has a solvency value (SBN) of 103, whereas the biodiesel distillation tower bottoms has a SBN of 104. Based on known blending rules, a blend of the residual oil and biodiesel distillation tower bottoms would be expected to have a SBN between 103 and 104. However, an unexpected result was discovered when the SBN of a 5 vol.% and 15 vol.% blend of biodiesel distillation tower bottoms in the residual fuel oil was measured. The blended composition had SBN values of 116 and 152 respectively, which were much higher than the SBN values of the fuel oil and biodiesel distillation tower bottoms components separately. These SBN values of the blend surprisingly demonstrated an increase in the solubility number (SBN) of at least 5 or at least 10 or at least 15 or at least 20 or at least 25 or at least 30 as compared with the solubility number of the heavy residual fuel oil and biodiesel distillation tower bottoms components separately. Without wishing to be bound by theory, it is believed that the observed increased in solvency may come from an interaction of the BDTB and residual fuel oil, yet the required solvency of asphaltenes (as measured by IN) does not change. The blend IN values are 39-41 versus 41 in the residual fuel oil. These results are provided below in Table 7:

Table 7. Solubility Data

Sample	**Residual Fuel Oil**		**15 vol.% BDTB with Residual Fuel Oil**		**5 vol.% BDTB with 95 vol.% Residual Fuel Oil**		**BDTB**
		+/-		+/-		+/-	
Density at 15°C (g/ml)	0.984				0.9809		*0.922
T50 °C	550						510
BMCI	69		65		67		42.3
S_{BN}	103	6	152	9	116	7	103.7
I_N	52	2	58	3	54	2	0
TE	41.25	1.25	38.75	1.25	41.25	1.25	0
HD	5	0.2	8.2	0.2	5.8	0.2	
Implied S_{BN} of BDTB			430	60	363	140	

*Estimated Value

Characterization of Biodiesel Distillation Tower Bottoms

[0122] Additional samples of biodiesel distillation tower bottoms and various samples of biodiesel were characterized in order to illustrate the differences in properties between the samples. FIG. 1 and FIG. 2 shows the results from these additional characterizations.

[0123] In FIG. 1, compositional data, including impurity data, is provided for various biodiesel distillation tower bottoms samples and various biodiesel samples. As shown in FIG. 1, there are a number of differences between biodiesel distillation tower bottoms and either biodiesel prior to distillation or a distilled biodiesel. For example, the density at 15°C of BDTB is typically greater than 900 kg/m^3, while undistilled biodiesel or a distilled biodiesel fractions have a density at 15°C of 890 kg/m^3 or less. The kinematic viscosity at 50°C of BDTB is also substantially higher than the kinematic viscosity at 50°C of a biodiesel fraction. The higher density and kinematic viscosity of BDTB is consistent with the higher boiling point profile of BDTB relative to biodiesel (either prior to distillation or after distillation).

[0124] Additionally, biodiesel distillation tower bottoms typically have substantially higher contents of impurities than biodiesel fractions. As shown in FIG. 1, BDTB can have an ash content of greater than 0.1 wt% and/or elevated metal impurity levels. The ash content and/or content of metal impurities for a BDTB fraction can be improved by further processing, but such further processing can be costly relative to the end value use of the BDTB.

[0125] FIG. 2 provides additional information about the various BDTB and biodiesel fractions with regard to ester content in the fractions. As shown in FIG. 2, BDTB fractions can have a wide range of ester content. The ester content depends in part on the nature of the distillation that is used to form a biodiesel fraction and the corresponding bottoms fraction. During a distillation, while it is desirable to increase the amount of biodiesel that is recovered, the distillation also needs to be performed so that the resulting biodiesel satisfies a desired specification with regard to boiling range and impurity levels. As a result, the bottoms fraction typically includes at least some esters, and the ester content can be relatively high depending on the quality of the distillation. Thus, the ester content of BDTB can range from 10 wt% to 45 wt%, or 10 wt% to 40 wt%, or 15 wt% to 45 wt%, or 15 wt% to 40 wt%, or 20 wt% to 40 wt%. This is in contrast to either undistilled biodiesel or biodiesel after distillation, where the ester content can be 99 wt% or more.

[0126] In addition to the values shown in FIG. 1 and FIG. 2, the appearance of BDTB fractions is also different from conventional biodiesel. Biodiesel samples typically have a visual appearance of clear and bright. By contrast, BDTB samples are typically opaque. Due to the opaque nature of BDTB, in some aspects BDTB samples can have an ASTM D1500 color value of 3.0 or more, or 5.0 or more, such as up to 8.0.

PCT/EP Clauses: [0127] Clause 1. A marine fuel or fuel blending composition comprising: a blend of heavy residual fuel oil and one or more of (a) biodiesel distillation tower bottoms, and (b) renewable diesel comprising at least 70% n-paraffins, wherein the marine fuel or fuel blending composition contains less than 3.5 wt.% sulfur.

[0128] Clause 2. The marine fuel or fuel blending composition according to clause 1, wherein the fuel or fuel blending composition further comprises a biodiesel.

[0129] Clause 3.The marine fuel or fuel blending composition according to clause 1 or 2, wherein the fuel or fuel blending composition comprises the biodiesel distillation tower bottoms, wherein the biodiesel distillation tower bottoms have a viscosity of greater than 6 cSt at 40°C, a pour point of 10°C or higher, and an ASTM color value of at least 3 according to ASTM D1500.

[0130] Clause 4. The marine fuel or fuel blending composition according to clause 3, wherein the biodiesel distillation tower bottoms are present in the fuel composition at a concentration of up to 30% by volume.

[0131] Clause 5. The marine fuel or fuel blending composition according to claim 3, wherein the marine fuel or fuel blending composition exhibits an increases in solubility number (S_{BN}) of at least 5 or at least 10 or at least 15 or at least 20 or at least 25 or at least 30 as compared with the solubility number of the heavy residual fuel oil and biodiesel distillation tower bottoms components separately.

[0132] Clause 6. The marine fuel or fuel blending composition according to any of clause 1-4, wherein the fuel or fuel blending composition comprises the renewable diesel, wherein the renewable diesel comprises up to 95% n-paraffins.

[0133] Clause 7. The marine fuel or fuel blending composition according to clause 3, wherein the renewable diesel is present in the fuel composition at a concentration of up to 30% by volume.

[0134] Clause 8. The marine fuel or fuel blending composition according to clause 1, wherein the fuel or fuel blending composition comprises the biodiesel distillation tower bottoms and the renewable diesel.

[0135] Clause 9. The marine fuel or fuel blending composition according to clause 8, wherein each of the biodiesel distillation tower bottoms and the renewable diesel is present in the fuel composition at a concentration of up to 30% by volume.

[0136] Clause 10. The marine fuel or fuel blending composition according to clause 8 or clause 9, wherein the fuel or fuel blending composition further comprises a biodiesel.

[0137] Clause 11. A marine fuel or fuel blending composition comprising marine gasoil and renewable diesel comprising at least 70% n-paraffins.

[0138] Clause 12. The marine fuel according to clause 11, wherein the fuel or fuel blending composition further comprises a biodiesel.

[0139] Clause 13. A marine fuel or fuel blending composition comprising a blend of heavy residual fuel oil and unrefined biodiesel, wherein the unrefined biodiesel has been separated to remove glycerol but has not been subject to further upgrading or purification.

[0140] Clause 14. A method of using biodiesel distillation tower bottoms in a marine fuel composition, the biodiesel distillation tower bottoms have a viscosity of greater than 6 cSt at 40°C, a pour point of 10°C or higher, and an ASTM color value of 3 or more according to ASTM D1500, wherein the method comprises the step of blending the biodiesel distillation tower bottoms with heavy residual fuel oil, wherein the biodiesel distillation tower bottoms are present in the marine fuel at a concentration of up to 30% by weight.

[0141] Clause 15. The method according to clause 14, wherein the marine fuel composition further comprises renewable diesel comprising at least 70% n-paraffins.

[0142] Clause 16. The method according to clause 14 or clause 15, wherein the marine fuel composition further comprises a biodiesel.

[0143] Clause 17. A method using renewable diesel comprising at least 70% n-paraffins in a marine fuel composition, wherein the method comprises the step of blending the renewable diesel comprising the majority of n-paraffins with heavy residual fuel oil or marine gasoil, wherein the renewable diesel is present in the marine fuel at a concentration of up to 30% by volume.

[0144] Clause 18. The method according to clause 17, wherein the marine fuel composition further comprises a biodiesel.

[0145] Clause 19. A method of improving solvency of a marine fuel or fuel blending composition, the method comprising the steps of: blending at least 1% by volume biodiesel distillation tower bottoms with heavy residual oil to produce the marine fuel or fuel blending composition, wherein the marine fuel or fuel blending composition exhibits improved solvency.

[0146] Clause 20. The method according to claim 19, wherein the marine fuel or fuel blending composition exhibits an increase in solubility number (S_{BN}) of at least 5 or at least 10 or at least 15 or at least 20 or at least 25 or at least 30 as compared with the solubility number of the heavy residual fuel oil and biodiesel distillation tower bottoms components separately.

[0147] Clause 21. The method according to claim 19, wherein the marine fuel or fuel blending composition comprises at least 5% by volume biodiesel distillation tower bottoms.

[0148] Clause 22. The method according to claim 20 or claim 21, wherein the marine fuel or fuel blending composition comprises at least 15% and up to 30% by volume biodiesel distillation tower bottoms.

[0149] Clause 23. A marine fuel or fuel blending composition comprising: a blend of heavy residual fuel oil and biodiesel distillation tower bottoms, wherein the composition comprises less than 3.5 wt.% sulfur, wherein the composition comprises 1.0 vol.% to 70 vol% of the biodiesel distillation tower bottoms.

[0150] Clause 24. The marine fuel or fuel blending composition of Clause 23, wherein 20 wt% or more of the biodiesel distillation tower bottoms has a boiling point of 550°C or higher.

[0151] Clause 25. The marine fuel or fuel blending composition of Clause 23 or 24, wherein the biodiesel distillation tower bottoms comprise an ash content of 0.2 wt% or more.

[0152] Clause 26. The marine fuel or fuel blending composition of any of Clauses 23 to 25, wherein the biodiesel distillation tower bottoms comprises i) a combined content of sodium and potassium of 50 wppm or more; ii) a combined content of calcium and magnesium of 50 wppm or more; iii) 50 wppm or more of phosphorus; iv) or a combination of two or more of i), ii), and iii).

[0153] Clause 27. The marine fuel or fuel blending composition of any of Clauses 23 to 26, wherein the composition comprises less than 5.0 wt% of fatty acid alkyl esters.

[0154] Clause 28. The marine fuel or fuel blending composition of any of Clauses 23 to 27, wherein the biodiesel distillation tower bottoms comprise 40 wt% or less of fatty acid alkyl esters.

[0155] Clause 29. The marine fuel or fuel blending composition of Clause 28, wherein the composition comprises 10 vol% or less of biodiesel distillation tower bottoms.

[0156] Clause 30. The marine fuel or fuel blending composition of any of Clauses 23 to 29, wherein the composition comprises a sulfur content of 1.0 wt% or less, the composition comprising 90 wt% or more of a combined amount of the heavy residual fuel oil and biodiesel distillation tower bottoms, the heavy residual sulfur fuel oil comprising a sulfur content of 1.5 wt% or more.

[0157] Clause 31. The marine fuel or fuel blending composition of any of Clauses 23 to 30, wherein a fatty acid alkyl ester content of the composition is lower than a fatty acid alkyl ester content of the biodiesel distillation tower bottoms.

[0158] Applicants have attempted to disclose all embodiments and applications of the disclosed subject matter that could be reasonably foreseen. However, there may be unforeseeable, insubstantial modifications that remain as equivalents. While the present disclosure has been described in conjunction with specific, exemplary embodiments thereof, it is evident that many alterations, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description without departing from the spirit or scope of the present disclosure. Accordingly, the present disclosure is intended to embrace all such alterations, modifications, and variations of the above detailed description.

[0159] All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent with this disclosure and for all jurisdictions in which such incorporation is permitted.

CLAIMS

1. A marine fuel or fuel blending composition comprising: a blend of heavy residual fuel oil and one or more of: a) biodiesel distillation tower bottoms, and b) renewable diesel comprising at least 70% n-paraffins, wherein the marine fuel or fuel blending composition contains less than 3.5 wt.% sulfur.

2. The marine fuel or fuel blending composition according to claim 1, wherein the fuel or fuel blending composition further comprises a biodiesel.

3. The marine fuel or fuel blending composition according to claim 1, wherein the fuel or fuel blending composition comprises the biodiesel distillation tower bottoms, wherein the biodiesel distillation tower bottoms have a viscosity of greater than 6 cSt at 40°C, a pour point of 10°C or higher, and an ASTM color value of at least 3 according to ASTM D1500.

4. The marine fuel or fuel blending composition according to claim 3, wherein the biodiesel distillation tower bottoms are present in the fuel composition at a concentration of up to 30% by volume.

5. The marine fuel or fuel blending composition according to claim 3, wherein the marine fuel or fuel blending composition exhibits an increase in solubility number (S_{BN}) of at least 5 or at least 10 or at least 15 or at least 20 or at least 25 or at least 30 as compared with the solubility number of the heavy residual fuel oil and biodiesel distillation tower bottoms components separately.

6. The marine fuel or fuel blending composition according to claim 1, wherein the fuel or fuel blending composition comprises the renewable diesel, wherein the renewable diesel comprises up to 95% n-paraffins.

7. The marine fuel or fuel blending composition according to claim 3, wherein the renewable diesel is present in the fuel composition at a concentration of up to 30% by volume.

8. The marine fuel or fuel blending composition according to claim 1, wherein the fuel or fuel blending composition comprises the biodiesel distillation tower bottoms and the renewable diesel.

9. The marine fuel or fuel blending composition according to claim 8, wherein each of the biodiesel distillation tower bottoms and the renewable diesel is present in the fuel composition at a concentration of up to 30% by volume.

10. The marine fuel or fuel blending composition according to claim 8, wherein the fuel or fuel blending composition further comprises a biodiesel.

11. A marine fuel or fuel blending composition comprising marine gasoil and renewable diesel comprising at least 70% n-paraffins.

12. The marine fuel according to claim 10, wherein the fuel or fuel blending composition further comprises a biodiesel.

13. A marine fuel or fuel blending composition comprising a blend of heavy residual fuel oil and unrefined biodiesel, wherein the unrefined biodiesel has been separated to remove glycerol but has not been subject to further upgrading or purification.

14. A method of using biodiesel distillation tower bottoms in a marine fuel composition, the biodiesel distillation tower bottoms have a viscosity of greater than 6 cSt at 40°C, a pour point of 10°C or higher, and an ASTM color value of 3 or more according to ASTM D1500, wherein the method comprises the step of blending biodiesel distillation tower bottoms with heavy residual fuel oil, wherein the biodiesel distillation tower bottoms are present in the marine fuel at a concentration of up to 30% by volume.

15. The method according to claim 14, wherein the marine fuel composition further comprises renewable diesel comprising at least 70% n-paraffins.

16. The method according to claim 14, wherein the marine fuel composition further comprises a biodiesel.

17. A method using renewable diesel comprising at least 70% n-paraffins in a marine fuel composition, wherein the method comprises the step of blending the renewable diesel comprising the majority of n-paraffins with heavy residual fuel oil or marine gasoil, wherein the renewable diesel is present in the marine fuel at a concentration of up to 30% by volume.

18. The method according to claim 17, wherein the marine fuel composition further comprises a biodiesel.

19. A method of improving solvency of a marine fuel or fuel blending composition, the method comprising the steps of: blending at least 1% by volume biodiesel distillation tower bottoms with heavy residual oil to produce the marine fuel or fuel blending composition, wherein the marine fuel or fuel blending composition exhibits improved solvency.

20. The method according to claim 19, wherein the marine fuel or fuel blending composition exhibits an increase in solubility number (S_{BN}) of at least 5 or at least 10 or at least 15 or at least 20 or at least 25 or at least 30 as compared with the solubility number of the heavy residual fuel oil and biodiesel distillation tower bottoms components separately.

21. The method according to claim 19, wherein the marine fuel or fuel blending composition comprises at least 5% by volume biodiesel distillation tower bottoms.

22. The method according to claim 21, wherein the marine fuel or fuel blending composition comprises at least 15% and up to 30% by volume biodiesel distillation tower bottoms.

23. A marine fuel or fuel blending composition comprising: a blend of heavy residual fuel oil and biodiesel distillation tower bottoms, wherein the composition comprises less than 3.5 wt.% sulfur, wherein the composition comprises 1.0 vol.% to 70 vol% of the biodiesel distillation tower bottoms.

24. The marine fuel or fuel blending composition of claim 23, wherein 20 wt% or more of the biodiesel distillation tower bottoms have a boiling point of 550°C or higher.

25. The marine fuel or fuel blending composition of claim 23, wherein the biodiesel distillation tower bottoms comprise an ash content of 0.2 wt% or more.

26. The marine fuel or fuel blending composition of claim 23, wherein the biodiesel distillation tower bottoms comprises i) a combined content of sodium and potassium of 50 wppm or more; ii) a combined content of calcium and magnesium of 50 wppm or more; iii) 50 wppm or more of phosphorus; iv) or a combination of two or more of i), ii), and iii).

27. The marine fuel or fuel blending composition of claim 23, wherein the composition comprises less than 5.0 wt% of fatty acid alkyl esters.

28. The marine fuel or fuel blending composition of claim 23, wherein the biodiesel distillation tower bottoms comprise 40 wt% or less of fatty acid alkyl esters.

29. The marine fuel or fuel blending composition of claim 28, wherein the composition comprises 10 vol% or less of biodiesel distillation tower bottoms.

30. The marine fuel or fuel blending composition of claim 23, wherein the composition comprises a sulfur content of 1.0 wt% or less, the composition comprising 90 wt% or more of a combined amount of the heavy residual fuel oil and biodiesel distillation tower bottoms, the heavy residual sulfur fuel oil comprising a sulfur content of 1.5 wt% or more.

31. The marine fuel or fuel blending composition of claim 23, wherein a fatty acid alkyl ester content of the composition is lower than a fatty acid alkyl ester content of the biodiesel distillation tower bottoms.

		Type	Biodiesel Bottoms	Biodiesel Bottoms	Biodiesel Bottoms	Biodiesel Bottoms	Undistilled Biodiesel	Undistilled Biodiesel	Undistilled Biodiesel	Biodiesel
Test Description	Test Method	Unit								
Viscosity @ 50 °C	D445-11/ASV	cSt	62.45	39.7	17.8	33.56				3.734
Density @ 15 °C	B3942/PGC	kg/m3	935	931	928	922	882	837	878	0.8807
Acid Number	D664-5/ASV	mg KOH/g	18.41	0.89	0.76	6.6	0.23	4.38	6.64	~0.3
Sulfur	D2622-1/CLN	mg/kg	237	63.3	41.6	245	19.6	20.4	27.4	~7
Carbon residue	D4530/ASV	Mass %	3.45	1.54	0.78	2.3	0.06			
Total Sediment Existent (TSE)	ISO 10307-1	Mass %	0.21	0.13	0.07	0.06				<det. limit
SIMDIST (T10)	M1567/ASV	°C	368	357	355	355		332	334	342
SIMDIST (T50)	M1567/ASV	°C	516	571	455	510		340	355	348
SIMDIST (T90)	M1567/ASV	°C	641	612	585			359	363	355
Pour Point	D5950-1/GAS	°C	1	9	9	18		19	N/A	6
Ash	D482	wt%	0.385	0.215	0.011	0.643				<det. limit
Vanadium	D5158-MOD	mg/kg		0	0	<1				
Aluminum	D5158-MOD	mg/kg	52	0	2	25		0	1	
Silicon		mg/kg	8	9	5	4		0	0	
Calcium		mg/kg	440	52	0	121		0	18	
Zinc		mg/kg	15	0	0	<1		0	1	
Phosphorus		mg/kg	700	44	2	442		0	27	<1
Magnesium		mg/kg	28	28	0			0	1	
Iron		mg/kg	1000	7	1			4	39	
Potassium		mg/kg	300		0	109		7	15	
Sodium			21	9	42	174		0		<1
Chlorine	ASTM D7536	wt%	11.3	3.5	14.4			2.9	3.6	

FIG. 1

		Type	Biodiesel Bottoms	Biodiesel Bottoms	Biodiesel Bottoms	Biodiesel Bottoms	Undistilled Biodiesel	Undistilled Biodiesel	Undistilled Biodiesel	Biodiesel
Test Description	Test Method	Unit								
Ester content	EN 14103	wt%	14.6	37.2	43.6			>99	>99	
Linolenic acid Methyl ester	EN 14103	wt%	<0.1	0.4	1.5			0.1	0.2	
Free glycerin	ASTM D6584	wt%	0.001	0.03	0.002			0.061	0.054	0.005
Monoglycerides	ASTM D6584	wt%	0.402	0.994	0.503			0.005	0.299	0.427
Diglycerides	ASTM D6584	wt%	1.996	7.903	0.389			<0.001	0.247	0.103
Triglycerides	ASTM D6584	wt%	7.209	20.696	0.094			<0.001	0.069	0.016
Total glycerin	ASTM D6584	wt%	1.15	3.624	0.2			0.062	0.175	0.132

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/027260

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10L1/02 C10L1/16 C10L1/08
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10L C10G

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2022/169934 A1 (GUAY LISA M [US] ET AL) 2 June 2022 (2022-06-02) paragraphs [0002], [0010], [0127]; claims paragraphs [0038], [0107] - [0127]; examples; tables -----	1-5,7-10
X	US 2013/014431 A1 (JIN HONG [US] ET AL) 17 January 2013 (2013-01-17) paragraphs [0016], [0017], [0031], [0035], [0036], [0040] - [0043], [0048], [0051] - [0053] -----	1-5,7-10
X	US 2022/033717 A1 (KIISKI ULLA [FI] ET AL) 3 February 2022 (2022-02-03) paragraphs [0079] - [0082]; claims 1-15 -----	1,2,6, 8-10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 October 2023	08/12/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Bertin, Séverine

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2023/027260

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims;; it is covered by claims Nos.:
1-10----------------

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-10

   A low sulfur marine fuel or fuel blending composition comprising a blend of heavy residual fuel oil and renewable diesel derived fraction

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2. claims: 11, 12

   A marine fuel or fuel blending composition comprising marine gasoil and renewable paraffinic diesel

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3. claim: 13

   A marine fuel or fuel blending composition comprising a blend of heavy residual fuel oil and unrefined biodiesel

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4. claims: 14-16

   A method of using a defined biodiesel distillation tower bottoms in a marine fuel composition by blending in certain given concentrations

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5. claims: 17, 18

   A method using renewable paraffinic diesel in a marine fuel composition, wherein the method comprises the step of blending the renewable diesel with heavy residual fuel oil or marine gasoil in a given concentration

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6. claims: 19-22

   A method of improving solvency of a marine fuel or fuel blending composition

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7. claims: 23-31

   A low sulfur marine fuel or fuel blending composition comprising: a blend of heavy residual fuel oil and biodiesel distillation tower bottoms

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2023/027260

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2022169934 A1	02-06-2022	CA 3200308 A1	02-06-2022
		EP 4251718 A1	04-10-2023
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		WO 2020109653 A1	04-06-2020