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(54) **HIGH-OCTANE, UNLEADED AVIATION FUEL COMPOSITIONS**

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C10L 1/19	(2006.01)

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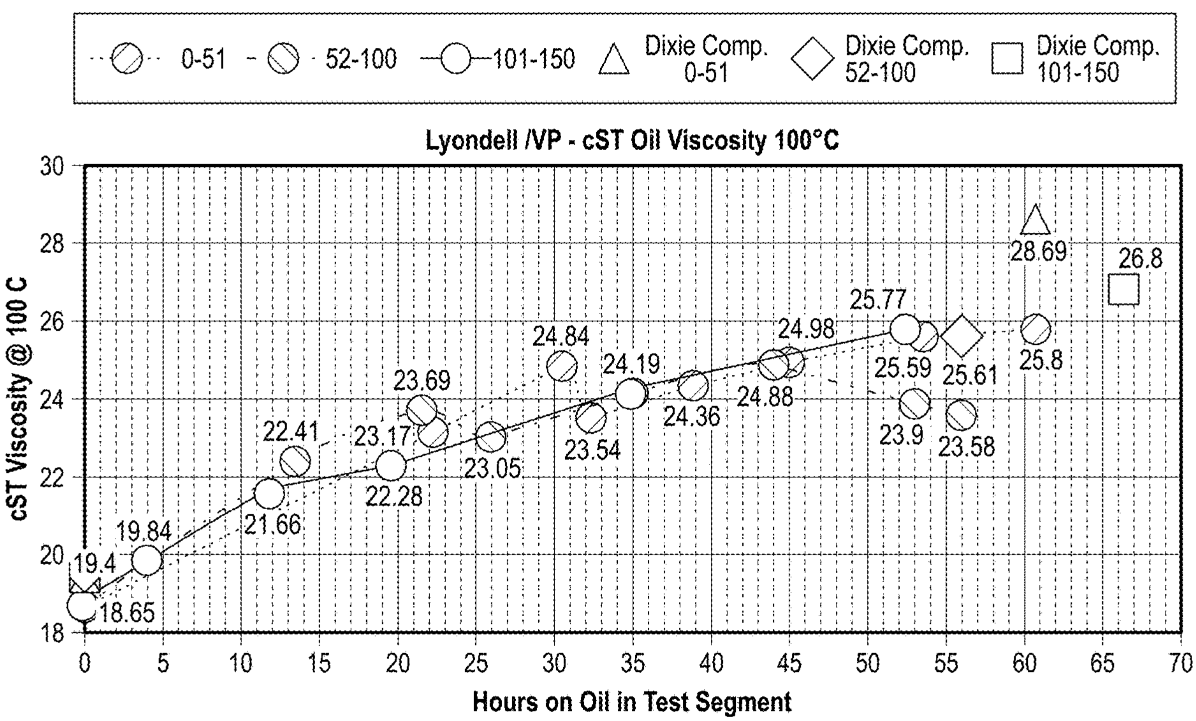
(57) **ABSTRACT**

In some embodiments, a composition includes isooctane in an amount of about 81 vol % to about 87 vol %. The composition further includes a dialkyl ether compound in an amount of about 10 vol % to about 18 vol %, wherein the dialkyl ether compound is selected from the group consisting of ethyl-tert-butyl-ether, methyl-tert-butyl-ether, and combinations thereof. The composition further includes methanol in an amount of about 1.5 vol % or less. The total oxygen content present in the composition comprises about 3.2 wt % or less of the composition. The figures illustrate comparative testing including compositions of the disclosure.



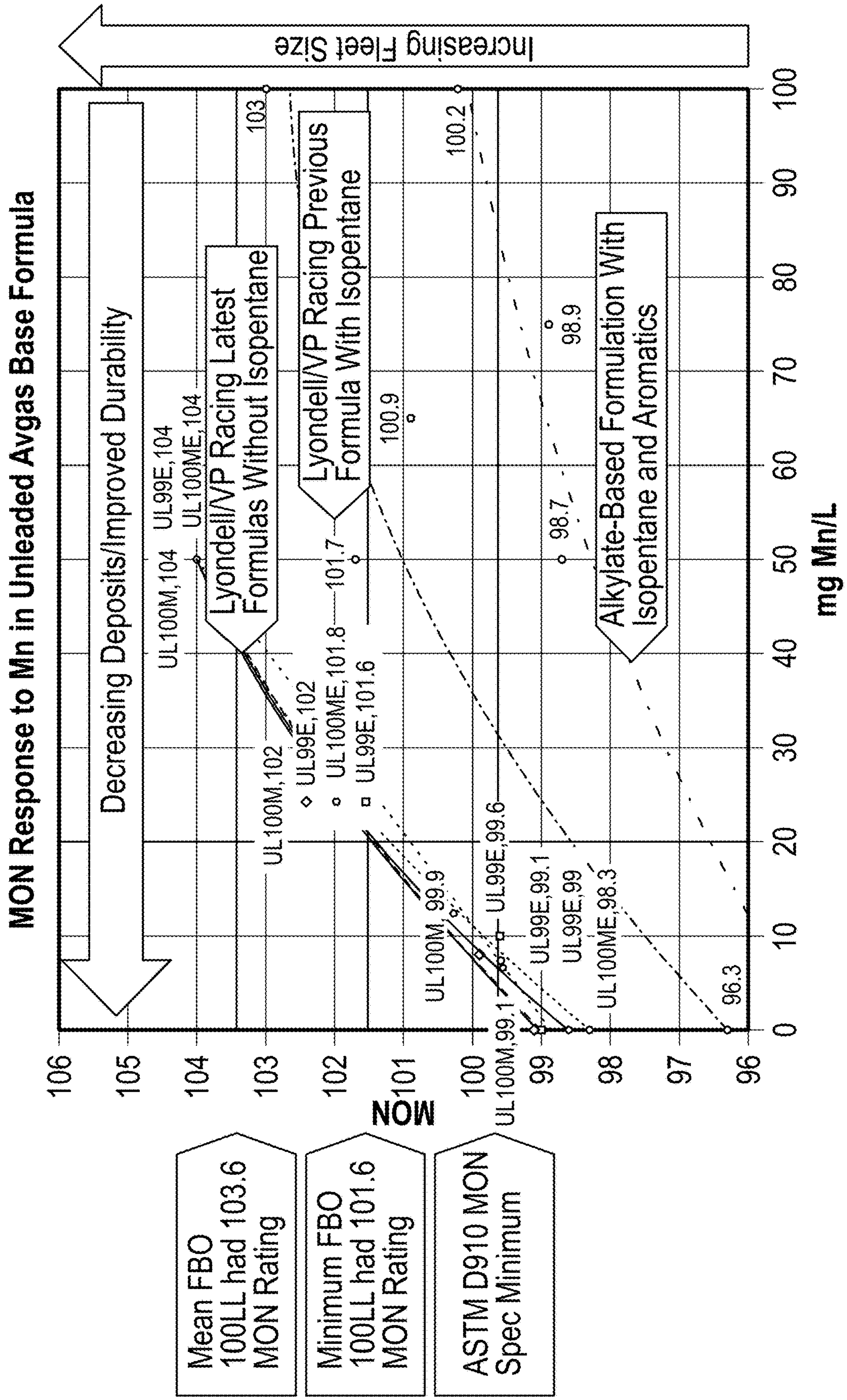
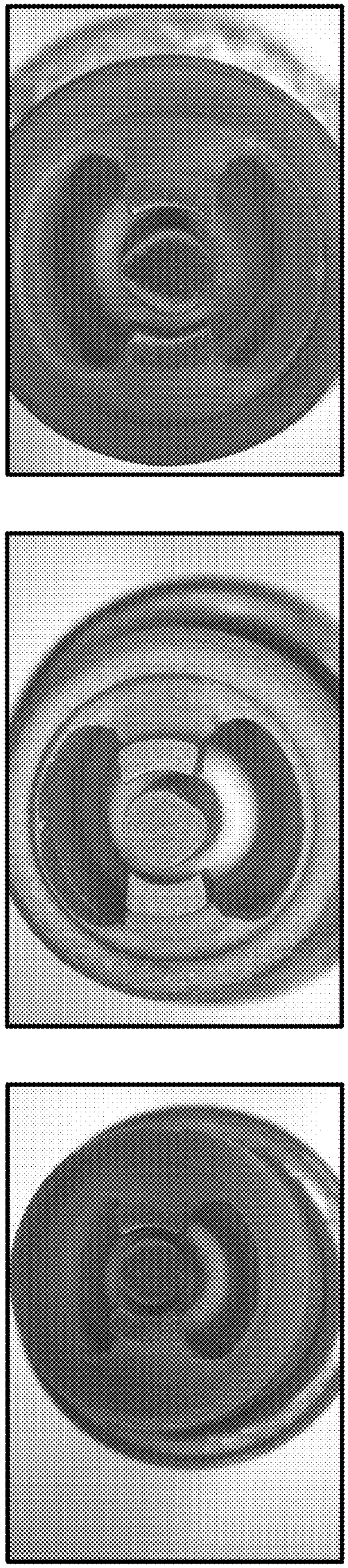

MON Response to Mn in Unleaded Avgas Base Formula
Increasing Fleet Size
Decreasing Deposits/Improved Durability
Lyondell/VP Racing Latest Formulas Without Isopentane
Lyondell/VP Racing Previous Formula With Isopentane
Alkylate-Based Formulation With Isopentane and Aromatics
Mean FBO 100LL had 103.6 MON Rating
Minimum FBO 100LL had 101.6 MON Rating
ASTM D910 MON Spec Minimum
UL100M,102
UL99E,102
UL100ME,101.8
UL99E,101.6
UL100M,104
UL99E,104
UL100ME,104
UL100M,99.9
UL99E,99.6
UL99E,99.1
UL99E,99
UL100ME,98.3
UL100M,99.1
96.3
98.7
98.9
100.2
100.9
101.7
103
MON
mg Mn/L
106
105
104
103
102
101
100
99
98
97
96
0
10
20
30
40
50
60
70
80
90
100

FIG. 1



50 Hours

100 Hours
Cleaned

150 Hours

FIG. 2

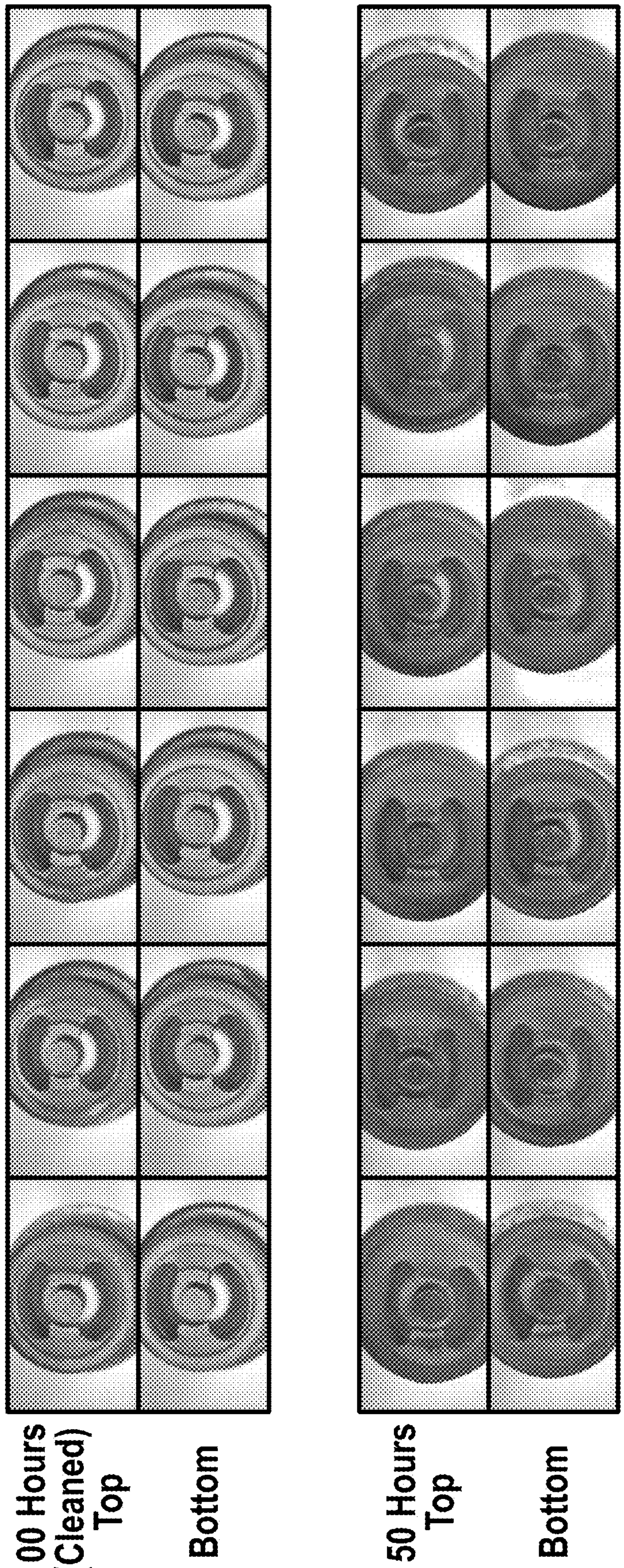


FIG. 3

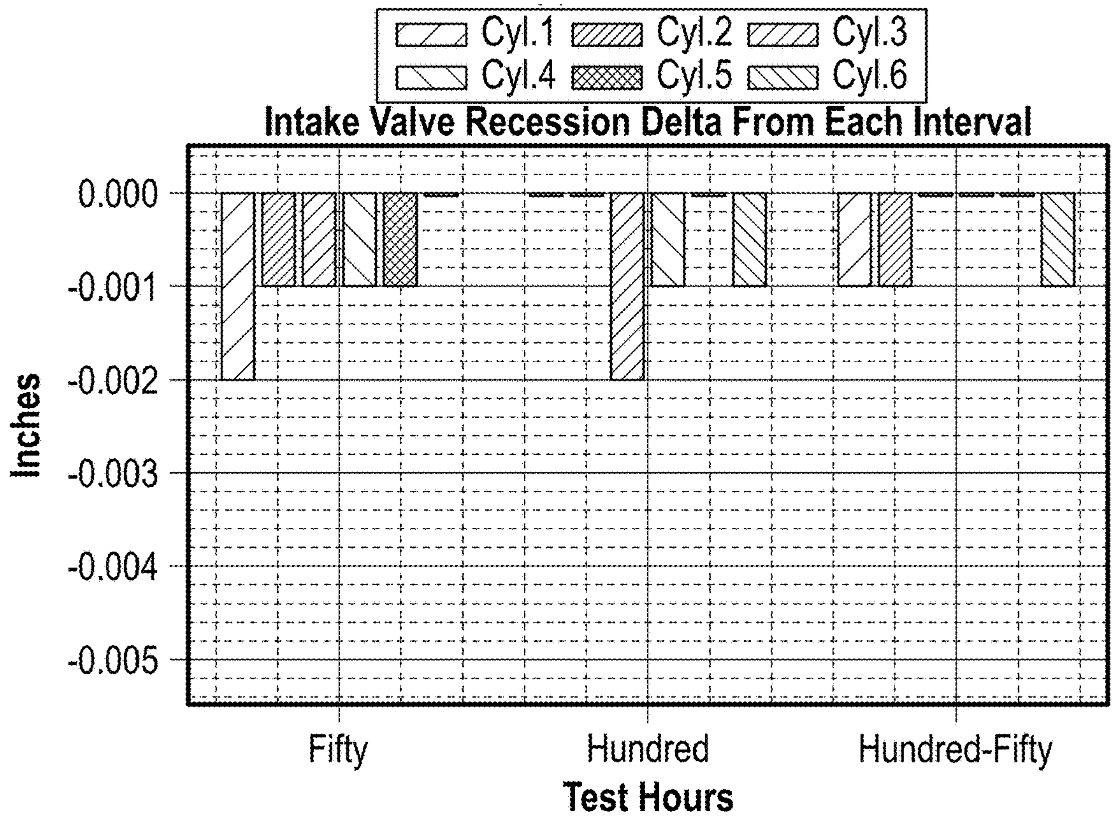

Cyl.1
Cyl.2
Cyl.3
Cyl.4
Cyl.5
Cyl.6
Intake Valve Recession Delta From Each Interval
0.000
-0.001
-0.002
-0.003
-0.004
-0.005
Inches
Fifty
Hundred
Hundred-Fifty
Test Hours

FIG. 4A

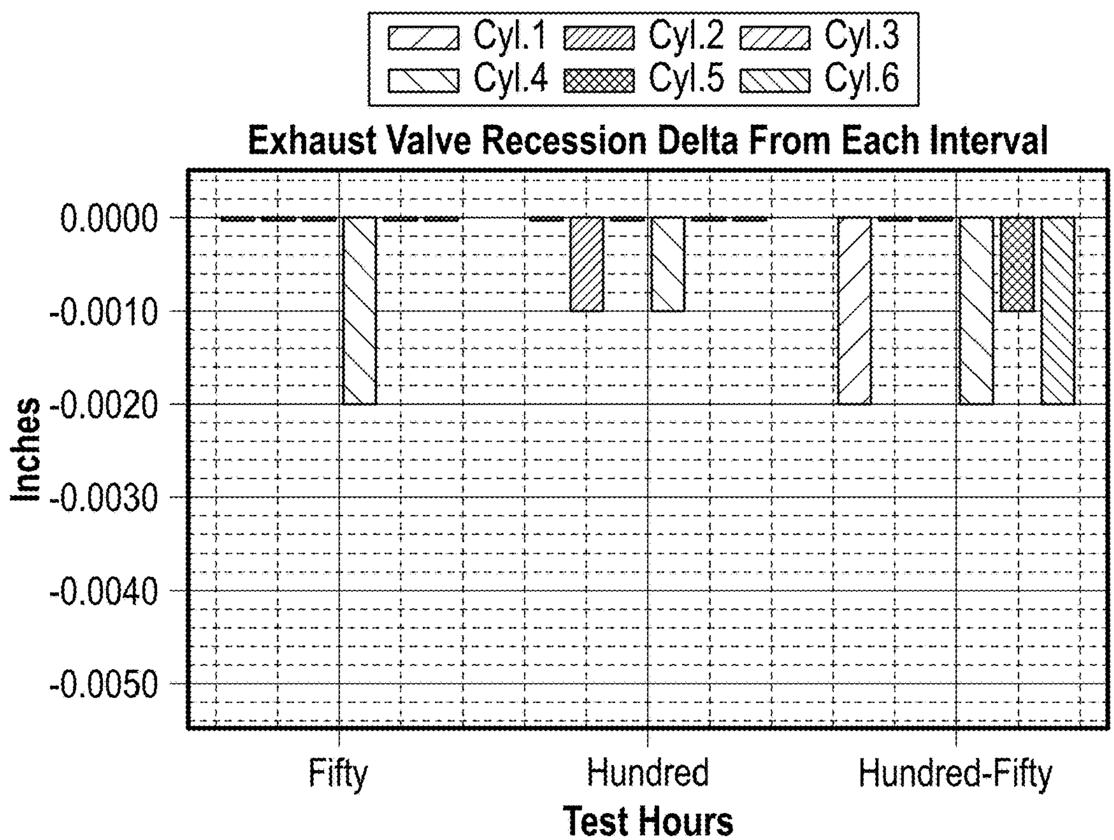

Cyl.1
Cyl.2
Cyl.3
Cyl.4
Cyl.5
Cyl.6
Exhaust Valve Recession Delta From Each Interval
0.0000
-0.0010
-0.0020
-0.0030
-0.0040
-0.0050
Inches
Fifty
Hundred
Hundred-Fifty
Test Hours

FIG. 4B

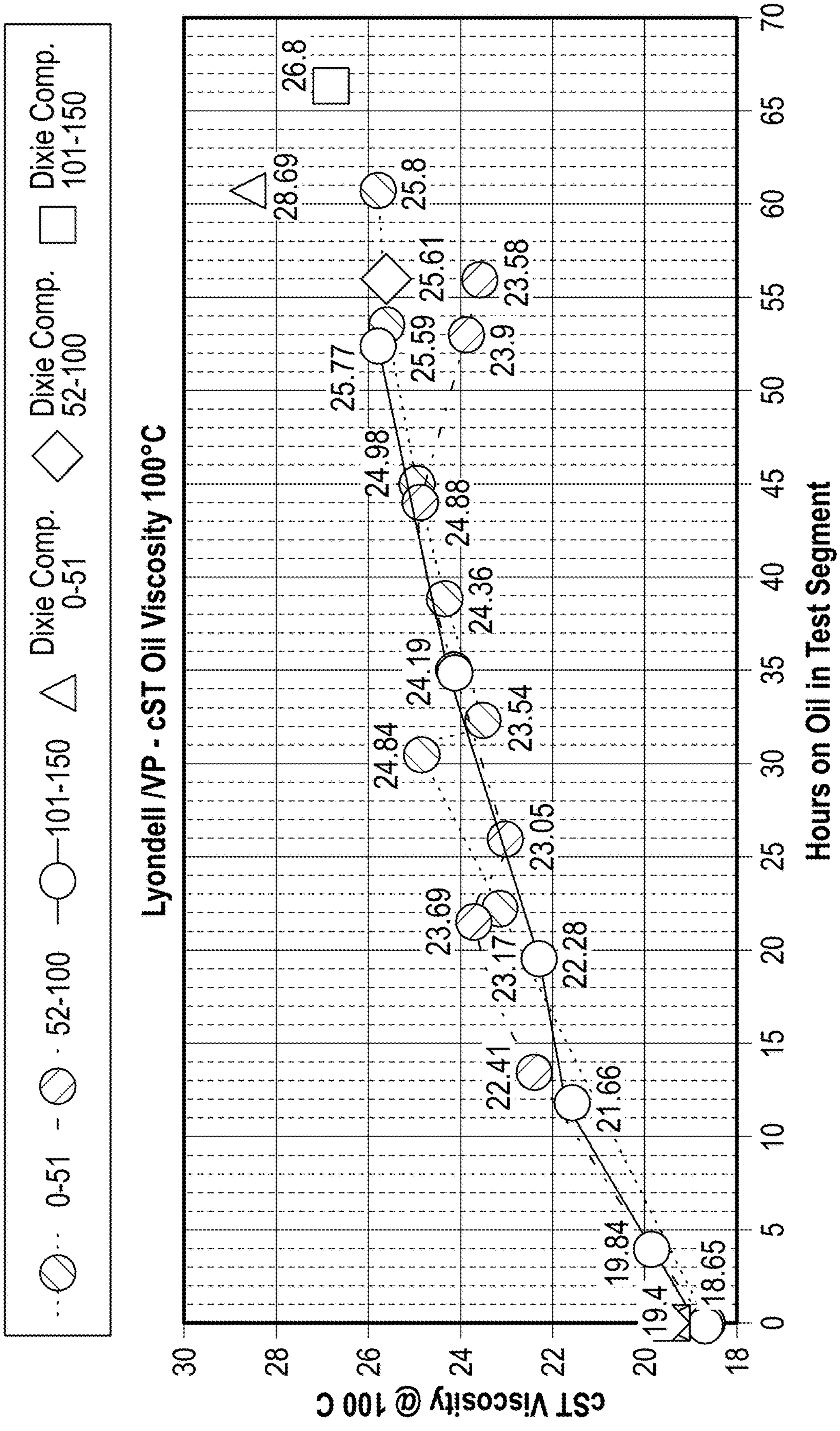

Lyondell /VP - cST Oil Viscosity 100°C
0-51
52-100
101-150
Dixie Comp. 0-51
Dixie Comp. 52-100
Dixie Comp. 101-150
cST Viscosity @ 100 C
Hours on Oil in Test Segment
18.65
19.4
19.84
21.66
22.41
22.28
23.17
23.69
23.05
24.84
23.54
24.19
24.36
24.88
24.98
25.77
25.59
23.9
25.61
23.58
25.8
28.69
26.8

FIG. 5

HIGH-OCTANE, UNLEADED AVIATION FUEL COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The application claims the benefit of priority to U.S. Provisional Patent Application No. 63/553,041 filed on Feb. 13, 2024, which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] This disclosure relates to high-octane, unleaded aviation gasoline compositions for piston aircraft.

INTRODUCTION

[0003] Given the rise in climate and public health concerns, current market and regulatory trends continue to push towards the development of improved renewable, efficient, and cleaner-burning fuel sources for deployment within the global economy. Yet, despite advances in technology and engineering, many economic sectors have found difficulty in developing and integrating such fuel sources due to stringent operating requirements and the variety of engine types and technologies in the existing fleet. One such sector is General Aviation (GA) which is composed of 220,000 aircraft powered by piston engines that run on leaded aviation gasoline (AVGAS). These engines run almost exclusively on 100LL (low-lead) because most GA airports only have one AVGAS tank and the fuel must be suitable for the entire GA fleet. Aviation is also a transportation platform that is not well suited to electrification due to the high weight of the batteries involved to power EV engines. Replacing 220,000 gasoline-powered aircraft would also be impractical.

[0004] The fuel currently used by the vast majority of general aviation aircraft is 100LL whose properties and composition are specified in ASTM D910. In addition, the U.S. Environmental Protection Agency (EPA) made a final determination that emissions from aircraft that operate on leaded fuel cause or contribute to air pollution which might be anticipated to endanger public health and welfare under the Clean Air Act. Consequently, the EPA has issued an endangerment finding from lead emissions. With this finding, EPA is now obligated to propose and promulgate regulatory standards for lead emissions from certain aircraft engines. Under certain regulations, the Federal Aviation Administration (FAA) must develop standards that address the composition, chemical, or physical properties of an aircraft fuel or fuel additive to control or eliminate aircraft lead emissions. The development of unleaded AVGAS that meets all the specifications and performance requirements of 100LL has been the goal of the Piston Aircraft Fuel Initiative (PAFI) program, launched by Federal Aviation Administration in 2014. Despite best efforts, all potential fuel source solutions fell short for a multitude of reasons, including poor compatibility with aircraft and engines materials, insufficient detonation resistance (octane), and incompatibility with 100LL. Additionally, many of these fuel compositions lacked the ability to integrate into the current market and aviation fleet due to compatibility and cost considerations, as well as engine compatibility detriments.

[0005] There is a need to develop new, unleaded fuel compositions that meet the parameters for general aviation, without the use of tetraethyl-lead or other harmful or toxic additives, to boost octane. In addition, the new fuel compositions should be able to be easily integrated within and/or compatible with current fuel streams (e.g., 100LL) such that a seamless transition can occur between the fuel sources of the fleet. Additionally, the newly developed fuel compositions should meet storage and stability standards currently employed by the aviation industry. Finally, the new fuels should meet as many of the specifications in ASTM D910 as possible and provide the safety margins specified by the engine and pilot operating manuals for as much as the existing fleet as possible, without modifications to the aircraft's equipment, operation, or maintenance.

SUMMARY

[0006] This disclosure relates to unleaded aviation fuel compositions that are "drop-in" substitutes for 100LL for a large portion (>85%) of the GA fleet.

[0007] In some embodiments, a composition includes isooctane in an amount of about 81 vol % to about 87 vol %. The composition further includes a dialkyl ether compound in an amount of about 10 vol % to about 18 vol %, wherein the dialkyl ether compound is selected from the group consisting of ethyl-tert-butyl-ether, methyl-tert-butyl-ether, and combinations thereof. The composition further includes methanol in an amount of about 1.5 vol % or less. The total oxygen content present in the composition comprises about 3.2 wt % or less of the composition.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. **1** is a graph illustrating the octane response to manganese for several unleaded AVGAS formulations, according to an embodiment.

[0009] FIG. **2** is images illustrating spark plugs throughout 150 hours of continuous operation with alternating rich and lean conditions with interruptions every 50 hours, first to weigh the spark plugs and change the oil, then to clean the spark plugs at 100 hours, according to an embodiment.

[0010] FIG. **3** is images illustrating spark plugs throughout 150 hours of continuous operation with alternating rich and lean conditions with an interruption at 100 hours to weigh the spark plugs, change the oil, and then clean the spark plugs, according to an embodiment.

[0011] FIG. **4**A is a graph illustrating results of the valve seat recession test on the intake valve after 150 hours of continuous operation, at 50 hour intervals, according to an embodiment.

[0012] FIG. **4**B is a graph illustrating results of the valve seat recession test on the exhaust valve after 150 hours of continuous operation, at 50 hour intervals, according to an embodiment.

[0013] FIG. **5** is a graph illustrating engine oil viscosity after 150 hours of continuous operation, at 50 hour increments, according to an embodiment.

DETAILED DESCRIPTION

[0014] Compositions of the present disclosure generally include (1) isooctane, (2) a dialkyl ether compound selected from ethyl-tert-butyl-ether (ETBE), methyl-tert-butyl-ether (MTBE), or combinations thereof, and (3) methanol. Compositions may include a manganese-based octane booster.

[0015] The present disclosure relates to substantially lead-free aviation fuel compositions compatible with current piston-aircraft and aviation fuels. The performance of aviation fuel compositions disclosed herein are comparable to that of the current piston-aircraft aviation fuel (e.g., 100LL), but can be substantially or entirely free of lead content and still have adequate detonation resistance (octane rating) and power output for the vast majority (>85%) of engines and aircraft in the GA fleet without any modifications or changes in operations. In at least one embodiment, the remainder of the fleet can accommodate the fuel's reduced detonation resistance with changes in the operating conditions or mechanical modifications such as adjusting the timing of spark ignition.

[0016] In one or more embodiments, the aviation fuel compositions presented herein are compositionally compatible with current 100LL and are shown to be viable "drop-in" additions to or replacements for such compositions (e.g., 100LL). As such, aviation fuel compositions of the present disclosure can be readily implemented into current fuel streams and/or integrated directly into the current private aviation aircraft fleet with minimal need for new equipment/engines or modifications of those currently in operation. Additionally, the aviation fuel compositions disclosed herein offer increased photostability over the photostability of 100LL, the principal aviation fuel used in aircrafts with spark-ignited internal combustion engines, and other manganese-based unleaded gasolines described in the art.

[0017] Aviation fuel compositions of the present disclosure offer vapor pressure values suitable for engine cold starts and in-flight engine operation, while also reducing the amount of light iso-alkane (e.g., isopentane) components present therein, to minimize the risk of vapor-lock, simplify manufacturing, lower costs, and improve storage stability. Such aviation fuel compositions can offer an easily-produced, compositionally-consistent, economical, storage-stable, "drop-in", substantially lead-free fuel replacement for the current AVGAS (100LL).

[0018] In some embodiments, the use of isooctane (2,2,4 trimethylpentane from isobutylene dimerization and hydrogenation of the isooctene intermediate) may be the hydrocarbon blendstock for several reasons, including, the isooctane provides: (1) high motor octane number (MON), (2) affordability, (3) ease of manufacture, storage, and transportation, (4) consistent quality and purity compared to aviation alkylate and other refinery streams, (5) compatibility with engine and aircraft materials, and (6) low density and high gravimetric energy content.

[0019] In at least one embodiment, the incorporation of ETBE provides a number of advantages over all-hydrocarbon formulations including: (1) improved combustion and lower exhaust emissions of volatile organic compounds (VOCs), particulate matter (PM), and air toxics, (2) reduced carbonaceous deposits vs. aromatic-containing fuels, (3) improved anti-icing properties without the need for added Fuel System Icing Inhibitors (FSII) such as isopropyl alcohol (IPA) and di(ethylene glycol) methyl ether methacrylate (DEGMA), (4) lower density than aromatics, and (5) renewable content and lower CO_2 emissions.

[0020] In at least one embodiment, the total amount of ETBE (or MTBE) added is less than about 18 vol. % to prevent over-leaning the fuel. Higher amounts provide some octane boost but reduce detonation resistance under turbocharged conditions. This may ultimately require higher fuel flow to cool the engine and reduces the aircraft's range and increase fuel costs per flown mile. As such, the ether content in some embodiments is from about 12 vol. % to about 15 vol. %, thereby potentially boosting octane without substantially impacting the stoichiometric air-to-fuel (AFR) ratio or reducing the fuel's gravimetric energy content (Lower heating value in MJ/KG).

[0021] In some embodiments, the incorporation of a small amount of methanol can provide a Reid Vapor Pressure (RVP) boost for low-temperature startups and restarts without requiring the addition of isopentane. Methanol also expands the combustion range of the fuel, which helps improve ignition and combustion properties over a broader range of operational conditions. This can improve fuel ignitability, combustion, storage stability and simplifies the manufacturing process. In some embodiments, the methanol content can range from about 0.5 vol. % to about 1.0 vol. %. More than 1.0 vol. % starts negatively impacting the Stoichiometric AFR and water sensitivity of the fuel. Less than 0.5 vol. % does not provide sufficient RVP boost for cold startups and restarts. Substituting MTBE for ETBE can also boost RVP without negatively affecting other fuel properties.

[0022] The addition of a manganese-based octane booster such as MMT is unnecessary for safe operations in the majority (greater than about 80%) of the GA fleet. However, the base fuels described above without manganese might not have sufficient detonation margin for safe operation under all operating conditions, especially in turbocharged engines under cruise conditions at altitude. However, there are a number of modifications that can be made to the operating conditions, as well as mechanical modifications, that can be made to prevent detonation. These can include changes to the engine operating manual and POH to operate at lower cylinder heat temperatures or critical altitudes or mechanical modifications to the engine such as adjusting the ignition timing, intercooling, or lowering the compression ratio. There are several aftermarket options for adjusting the ignition timing including fully automatic digital electronic control (FADEC) and electronic magneto (E-mag) ignition, and electronic fuel injection.

[0023] That said, addition of small amounts of manganese (MMT; e.g., but not limited to, 5-50 mg Mn/L) can be useful to boost octane and detonation margins, adjust octane to meet minimum specification limits, and reduce the potential for valve seat recession. In some embodiments, the maximum amount used is dictated by the amount of manganese oxide deposits that buildup on the sparkplugs, cylinder walls, valves, pistons, lubricating oil, and other internal engine parts. The rate of deposit accumulation is also impacted by the aircraft operation mode, especially how rich fuel a mixture is used. Deposit accumulation on spark plugs is problematic because it can prevent sparking, causing misfires and loss of power. Accumulation of deposits in the lubricating oil can cause viscosity increases resulting in poor flow, valve sticking, and piston ring adhesion. Deposits may also lead to pre-ignition events which, over time, can ultimately lead to catastrophic engine failure. This is also a problem with leaded fuels which is mitigated with periodic oil changes (every 50 hours is standard) and spark plug cleanings (50-100 hours depending on the richness of the fuel-air mixture). (Flight schools typically run full rich and involve more frequent maintenance intervals.)

[0024] Testing has shown that the fuel compositions of the present disclosure can display unusually strong octane response to manganese content and require less MMT to boost octane than other compositions, especially those containing aromatics. These results are illustrated in FIG. **1**.

[0025] The antagonistic response of aromatic compounds on MON response to manganese has been previously reported (CRC Report No. AV-7-07) but the negative response to isopentane was not expected. For example, the blends containing only isooctane, ETBE or MTBE, and methanol exhibit consistently superior response to manganese compared to blends with either toluene or isopentane. The octane response was similar whether the ether was ETBE or MTBE with a slight benefit with ETBE. The benefit of strong octane response to manganese is that less manganese can be used for the application, resulting in lower deposits.

[0026] In some embodiments, compositions of the present disclosure can have a total oxygen content, as provided by all oxygenated compounds, of about 3.2 wt % or less to prevent over-leaning the fuel and reducing the detonation resistance especially in turbocharged engines. Lean fuels can also cause increases in cylinder head and exhaust gas temperatures (CHT and EGT) which can adversely impact the longevity of the engine, cause exhaust valve seat recession, and involve higher fuel flows to cool the engine. Higher fuel flows can be detrimental to the operational range of the aircraft and an increase in operational costs.

[0027] In addition, use of MTBE can be beneficial for compositions of the present disclosure operating in cold environments as MTBE increases the fuel vapor pressure and ignitability. In some embodiments, ETBE and/or MTBE can include residual alcohols retained from the production of such ethers (e.g., methanol, ethanol, tertiary butyl alcohol, and the like) as such impurities in the ETBE and/or MTBE feed streams are beneficial to the performance of fuel compositions of the present disclosure. For instance, such compounds are known to increase the fuel vapor pressure and ignitability, which is beneficial for engine startup in frigid environments.

[0028] In addition, such compounds also can act as anti-icing agents, thereby preventing fuel compositions from freezing in frigid environments. In fact, in at least one embodiment, one or more fuel compositions of the present disclosure exhibit greater anti-icing performance than commercial fuels having traditionally used anti-icing agents such as isopropanol or diethylene glycol monomethyl ether (DEGME). In addition, an aviation fuel of the present disclosure can be substantially or completely free of anti-static agent(s) since the alcohols already present substantially reduce the fuel's resistivity (as expressed in pS/m) and the risk of static discharge during refueling and transfer operations.

[0029] In addition, it has been found that aviation fuels including methanol and MTBE rather than light alkylates or isopentane, allow for comparable fuel properties at reduced Reid vapor pressure (RVP) range and higher octane for improved detonation resistance. As such, aviation fuel compositions of the present disclosure that may include methanol offer a vapor pressure value suitable for engine cold starts and in-flight engine operation. Additionally, including methanol rather than light alkylates or isopentane to boost RVP, simplifies aviation fuel manufacturing because volatile fuel components like isopentane require pressurized storage and may evaporate from the finished AVGAS during extended storage, limiting the shelf life of the fuel. Surprisingly, addition of small amounts of methanol in addition to the alcohols contained in production of ETBE or MTBE did not result in any detectable increase in water sensitivity as measured by ASTM D1094 (Water Reaction).

[0030] In some embodiments, isooctane produced by dimerization of isobutylene followed by hydrogenation of the intermediate di-isobutylene may be preferred for the following reasons: isooctane provides higher octane than light alkylate and can be produced in higher purity and less compositional variability than light alkylate, which is a refinery stream. The higher octane of isooctane also obviates the need to add toluene or other aromatics, which are harder on elastomers, increase fuel density, and increase combustion deposits, exhaust hydrocarbons and fine particulate emissions. Highly symmetrical aromatics such as benzene and mesitylene (1,3,5-trimethylbenzene) are also susceptible to crystallization at low temperatures which can cause an undesirable increase in viscosity of the fuel and/or precipitation. Aromatics are also more carbon-intensive in their production and combustion than isooctane and ethers, which increase the CO_2 footprint of the finished gasolines that contain them. For these and other reasons, it can be desirable to produce aviation gasolines that are substantially free of aromatic compounds yet still have acceptable octane numbers and detonation resistance.

[0031] In addition, compositions of the present disclosure may include a valve seat recession additive (VSRA). Unleaded fuels have lower lubricity than leaded fuels and may cause excessive wear of the exhaust valve seat, ultimately resulting in loss of compression in a cylinder. Manganese compounds help prevent valve seat recessions, but in some fuels (such as those that do not contain manganese compounds), it can be helpful to have small amounts of one or more VSRAs to reduce valve seat wear. Without being bound by theory, such compounds are effective in preventing valve seat recession by cleaning abrasive carbonaceous deposits, which may accumulate on fuel exhaust valves.

[0032] Overall, while aviation fuels of the present disclosure may include one or more additives (e.g., anti-static agents, corrosion inhibiting agents, anti-icing agents, biocidal agents, metal deactivating agents, thermal stability improvement agents, and the like), such additive agents can be considered as optional and/or unnecessary to adequate stability, properties, combustion and proper long term aircraft operation. Advantageously, aviation fuel compositions disclosed herein are designed/composed to include components therein that are believed to cause little to no particulate formation, static buildup, and/or thermal instability during and throughout storage, transport, or aircraft operation. As such, the additive agents combating such deleterious effects are deemed optional. For example, exclusion of aromatic compounds and isopentane from aviation fuel compositions disclosed herein can allow for (1) fuel composition simplification and (2) reduced production cost, 3) improved materials compatibility, and 4) reduced propensity of carbonaceous deposit formation. Exclusion of aromatic compounds decreases deposit formation and exclusion of isopentane increases MON of fuel compositions. While isopentane is commonly implemented to increase the RVP of aviation fuel compositions, isopentane is a highly volatile component that can present challenges in compositional stability during long-term storage and transport. Without being bound by theory, it is believed that the aviation fuel compositions of the present disclosure provide, at least, adequate combustion and vapor pressure necessary for proper aircraft engine operation including cold starts and re-starts.

[0033] In addition, compositions of the present disclosure can provide lowered vapor pressure (e.g., lower than the minimum of 38 kPa specified in ASTM D910) for an all-hydrocarbon fuel without compromising safety and is desirable if it results in other benefits such as higher octane, production simplicity, and storage stability.

[0034] As used herein, "additive" refers to a gasoline component added in small (e.g., <1 wt. %) amounts that improves properties of the fuel such as lubricity, deposit control, VSR and icing control.

[0035] As used herein, "aviation fuel" refers to a gasoline composition possessing specific properties suitable for fueling aircraft powered by reciprocating spark ignition engines.

[0036] The term "composition" or "blend" as used herein refers to a mixture of two or more components, such as components of a fuel and/or gasoline. A composition can include the components of the compositions and/or reaction product(s) of two or more of the components. Blends may be produced by, for example, batch or in-line solution blending.

[0037] As used herein, "fuel component" refers to any compound or a mixture of compounds that are used to formulate a fuel composition.

[0038] As used herein, "aliphatic ether" refers to a compound or compounds composed of carbon, hydrogen, and oxygen, wherein the oxygen is bonded to two carbon atoms.

[0039] As used herein, "MMT" means "methylcyclopentadienyl manganese tricarbonyl" which is an oil-soluble organometallic complex of manganese used to increase fuel octane.

[0040] As used herein, "oxygenate" refers to an oxygen-containing ashless organic compound, such as an alcohol or ether, which may be used as fuel or a fuel component.

[0041] As used herein, "corrosion inhibitors" refers to a compound or compounds that conform to MIL-PRF-25017F, which may be added to a fuel composition.

[0042] As used herein, "anti-icing additive" refers to a compound or compounds that inhibit a fuel composition from freezing or water from crystallizing in the fuel at low temperatures.

[0043] As used herein, "vapor pressure" refers to the measure of the tendency of the more volatile components of an aviation gasoline to evaporate. Fuels having a vapor pressure no higher than 45 kPa (6.5 psi) will be free of vapor-locking tendencies under operating conditions of the aircraft developed for such fuels.

[0044] As used herein, "distillation" and/or "distillation temperatures" refer to a measure of a fuel's volatility profile.

[0045] As used herein, "existent gum" refers to the amount of non-volatile organic residue remaining after evaporation by a high temperature air jet.

[0046] As used herein, "potential gum" refers to an estimate regarding fuel stability in storage and the effectiveness of the oxidation inhibitors therein.

[0047] As used herein, "dyes" refers to one or more inert colorants, which may be added to aviation fuels to differentiate between grades.

[0048] As used herein, "MON" means "motor octane number" which refers to a set of numbers indicating the grade of aviation gasoline being identified (e.g., 91/96 and 100LL). The first number indicates the motor octane rating (MON as measured by ASTM D2700) of the fuel when tested to "aviation lean" standards, which is one component of the "pump rating" associated with automobile gasoline in the United States of America (the other being the Research Octane Number as measured by ASTM D2699). The second number, however, indicates the octane rating of the fuel when tested to the "aviation rich" standard simulating a supercharged condition with a rich mixture, elevated temperatures, and high manifold pressures.

[0049] As used herein, "vapor pressure" or "Reid vapor pressure" of a fuel is a measure of the vapor pressure of the fuel in pounds per square inch at 100° F. It is an indication of the volatility of the fuel. Reid vapor pressure of a fuel can be measured according to ASTM D5191 specification.

[0050] As used herein, "Research Octane Number" or "RON" refers to the octane number of a fuel determined by running the fuel through a specific test engine with a variable compression ratio under controlled conditions, and comparing these results with those for mixtures of isooctane and n-heptane. RON can be measured according to ASTM D2699 specification.

[0051] As used herein, "heat of combustion" of a compound is the energy released as heat when the compound undergoes complete combustion with oxygen. Heat of combustion of a liquid fuel can be measured according to ASTM D4809 specification.

[0052] As used herein, "iso-alkane" refers to a branched alkane. For example, "iso-alkane" may include a substance and/or compounds produced by dimerizing two isobutylene molecules followed by hydrogenation of the product diisobutylene (DIB or 2,2,4-trimethyl-1-pentene) to a composition containing mostly 2,2,4-trimethlypentane (isooctane).

[0053] As used herein, "valve seat recession additive or VSRA" refers to an oil-soluble organometallic, salt, or ashless substance that reduces the abrasion and recession of exhaust valve seats.

Aviation Fuel and Components Thereof

[0054] For the preparation of the aviation fuel according to the present disclosure, blending and/or mixing of the components thereof may occur in any order as long as the components are mixed sufficiently. In order to satisfy other parameters, the aviation fuel according to the disclosure may contain one or more additives which a person skilled in the art may choose to add from standard additives used in aviation fuel.

[0055] In one or more embodiments, an aviation fuel can include one or more of an iso-alkane, an ether, an alcohol, a manganese containing compound, a VSRA, an alkanoic acid, an antioxidant, an anti-icing agent, an antistatic agent, a corrosion inhibitor, a dye, and/or a combination thereof.

[0056] In some embodiments, an aviation fuel includes one or more iso-alkane compounds. In one or more embodiments, the at least one iso-alkane compound is selected from C_4-C_{12} hydrocarbons, such as isooctane (2,2,4-trimethylpentane), aliphatic compounds (saturated or partially unsaturated), and combinations thereof. In at least one embodiment, the iso-alkane is isooctane.

[0057] In some embodiments, an aviation fuel includes about 75 vol % to about 95 vol % iso-alkane, such as about 80 vol % to about 89 vol %, such as about 81 vol % to about 87 vol %. In one or more alternative embodiments, an aviation fuel includes about 80 vol % to about 90 vol % iso-alkane, alternatively about 85 vol % to about 88 vol %, alternatively about 82 vol % to about 86 vol %, alternatively about 82 vol % to about 85 vol %.

[0058] In some embodiments, an aviation fuel includes about 75 vol % to about 95 vol % isooctane, such as about 80 vol % to about 89 vol %, such as about 81 vol % to about 87 vol %. In one or more alternative embodiments, an aviation fuel includes about 80 vol % to about 90 vol % isooctane, alternatively about 85 vol % to about 87 vol %, alternatively about 82 vol % to about 85 vol %, alternatively about 82 vol % to about 86 vol %.

[0059] In some embodiments, an aviation fuel includes one or more oxygenates to improve detonation resistance (octane rating) and help the fuel burn more completely, such as one or more esters, ethers, carbonates, and combinations thereof. Including ether-containing compounds into aviation fuels can reduce the amount of lead components therein, while maintaining an acceptable level of octane and reducing exhaust emissions associated with consuming such fuel sources. In one or more embodiments, the ether-containing compound can include one or more dialkyl ether compounds. In one or more embodiments, the one or more dialkyl ether compounds can include one or more alkyl-tertiary-butyl ether (e.g., ethyl-tert-butyl-ether and/or methyl-tert-butyl-ether). Such ether-containing components, when present in an aviation fuel, act as "octane boosters" and increase octane ratings of aviation fuels. Both ethyl-tert-butyl-ether (ETBE) and methyl-tert-butyl-ether (MTBE) containing fuels are approved for use in aircraft certificated for motor gasoline use by the US Federal Aviation Administration (FAA). (See (1) FAA Advisory Circular (AC) 23.1521-IB; and (2) Dec. 1, 1995, FAA Memorandum approving ETBE as an additive for use in Autogas Supplemental Type Certificates (STCs)).

[0060] In some embodiments, an aviation fuel includes one or more dialkyl ether compounds in an amount of about 10 vol % to about 20 vol %, such as about 12 vol % to about 18 vol %, such as about 12 vol % to about 15 vol %, alternatively about 15 vol % to about 18 vol %. In at least one embodiment, the one or more dialkyl ether compounds can include ethyl-tert-butyl-ether (ETBE), methyl-tert-butyl-ether (MTBE), and combinations thereof.

[0061] In some embodiments, an aviation fuel includes ETBE in an amount of about 10 vol % to about 20 vol %, such as about 12 vol % to about 18 vol %, such as about 12 vol % to about 15 vol %, alternatively about 15 vol % to about 18 vol %. In some embodiments, an aviation fuel includes MTBE in an amount of about 9 vol % to about 18 vol %, such as about 11 vol % to about 16 vol %, such as about 11 vol % to about 14 vol %, alternatively about 14 vol % to about 16 vol %. In some embodiments, an aviation fuel includes MTBE in an amount of 4.0 vol % to about 8.0 vol % and ETBE in the amount of 6.0 vol % to about 12.0 vol %. The total ether content should not exceed 18 vol % to prevent over-leaning the fuel. More importantly, the fuel's total oxygen content (ASTM D4815), as provided by all oxygenated compounds, should not exceed about 3.2 wt. % to prevent over-leaning the fuel and reducing detonation resistance especially in turbocharged engines.

[0062] The use of MTBE can be beneficial for fuels operating in cold environments as it increases the fuel vapor pressure and ignitability. In addition, ETBE and/or MTBE can include residual alcohols retained from the production of such ether containing compounds (e.g., methanol, ethanol, isomers of butyl alcohol, and the like). However, such impurities in the ETBE and/or MTBE feed streams may be beneficial to the performance of fuel compositions disclosed herein. For instance, such compounds are known to increase the fuel vapor pressure and ignitability, which is beneficial for engine startup in frigid environments. In addition, such compounds also can act as anti-icing agents, thereby preventing fuel compositions from freezing in frigid environments or ice crystal formation which can interfere with fuel flow. In fact, in at least one embodiment, one or more fuel compositions disclosed herein exhibit greater anti-icing performance than commercial fuels having traditionally used anti-icing agents.

[0063] In some embodiments, an aviation fuel includes one or more alcohol-containing compounds in an amount of about 0.4 vol % to about 1.2 vol %, such as about 0.5 vol % to about 1 vol %, such as 0.5 vol % to about 0.8 vol %, such as about 0.8 vol % to about 1 vol %. In one or more embodiments, the one or more alcohol containing compounds can include methanol, ethanol, propanols, butanols, and combinations thereof. Without being bound by theory, providing the aviation fuel with one or more alcohol containing compounds increases the vapor pressure (e.g., Reid vapor pressure) to a level for an engine to start efficiently, without resorting to more volatile components (e.g., isopentane). The use of isopentane is detrimental to detonation resistance and is replaced with methanol and MTBE to boost vapor pressure and octane in these embodiments when an aircraft is stored in frigid environments. Additionally, the alcohol helps with fuel combustion and reduces the potential for fuel icing. As such, in some embodiments wherein methanol is used as the alcohol, added methanol should not exceed about 1.0 vol % to prevent over-leaning or introducing water sensitivity. In addition, the presence of the alcohol in aviation fuels of the present disclosure renders anti-static agents merely optional in aviation fuels. For example, an aviation fuel of the present disclosure can be substantially or completely free of anti-static agent(s) since the alcohols substantially reduce the fuel's resistivity (as expressed in pS/m) and the risk of static buildup and fires during refueling and transfer operations.

[0064] In some embodiments, an aviation fuel composition includes an alcohol content and an ether content, wherein the total oxygen content should not exceed about 3.2 wt % of the aviation fuel composition. In one or more embodiments, the aviation fuel includes a total ether content of about 18 vol % or less. In one or more embodiments, the aviation fuel includes a total alcohol content of about 1.5 vol % or less.

[0065] In some embodiments, an aviation fuel includes base components of one or more alcohol compounds, one or more ether compounds, and isooctane. In some embodiments, an aviation fuel composition includes an ether content of about 10 vol % to about 18 vol %, such as about 10 vol % to about 15 vol %. In some embodiments, the ether content may include ETBE, MTBE, or a combination thereof. In some embodiments, an aviation fuel composition includes an alcohol content of less than about 1.5 vol %, such as less than about 1 vol %. In some embodiment, the alcohol content may include methanol. In some embodiments, the aviation fuel composition includes isooctane, wherein the vol % isooctane present in the aviation fuel composition is determined by the vol % occupied by the ether and alcohol content such that the total sum of the ether, alcohol, and isooctane content is 100 vol %. In some embodiments, the aviation fuel composition includes isooctane in an amount of about 80.5 vol % to about 90 vol %, such as about 81 vol % to about 90 vol %, such as about 81 vol % to about 87 vol %. In some embodiments, the total oxygen content of the aviation fuel composition does not exceed 3.2 wt %.

[0066] Previous aviation fuel compositions included base fuel based on light alkylate, which is a complex mixture of hydrocarbons including lights. Such aviation fuel compositions laid the groundwork for the development of ASTM D910, a generalized specification for fuels commonly used in the aviation industry. However, these light alkylate fuel compositions include volatile components which can cause vapor locking during aircraft operation in warm conditions. For example, excessively volatile fuels (e.g., that which is outside and/or near the upper boundary of the range for Reid vapor pressure as outlined in ASTM D910) can cause vapor-locking when at increased altitudes and/or higher engine operating temperatures. In contrast, it has been found that aviation fuels including methanol and MTBE rather than light alkylates or isopentane, allow for comparable fuel properties at reduced Reid vapor pressure (RVP) range and higher octane for improved detonation resistance. As such, aviation fuel compositions of the present disclosure, which include methanol, offer a vapor pressure value suitable for engine cold starts and in-flight engine operation. Additionally, including methanol rather than light alkylates or isopentane to boost RVP, simplifies aviation fuel manufacturing because fuel components like isopentane require pressurized storage and may evaporate from the finished AVGAS during extended storage, impacting the properties of the fuel. Instead of light alkylate, isooctane produced by dimerization of isobutylene followed by hydrogenation of the intermediate di-isobutylene can be preferred for the following reasons: isooctane provides higher octane than light alkylate and can be produced in higher purity and less compositional variability than light alkylate, which is a refinery stream. The higher octane of isooctane also obviates the need to add toluene or other aromatics, which are harder on elastomers, increase fuel density, and increase combustion deposits, exhaust hydrocarbons and fine particulate emissions. Aromatics are also more carbon-intensive in their production and combustion than isooctane and ethers, which increase the CO_2 footprint of the finished gasolines that contain them.

[0067] In some embodiments, an aviation fuel includes one or more manganese containing compounds, such as manganese carbonyls (e.g., Mn(I) compounds). In one or more embodiments, the manganese carbonyl(s) is present in the aviation fuel in an amount of about 5 mg manganese per liter (Mn/L) to about 100 mg Mn/L, such as about 5 mg Mn/L to about 85 mg Mn/L, such as about 5 mg Mn/L to about 75 mg Mn/L, such as about 5 mg Mn/L to about 25 mg Mn/L. In one or more embodiments, an aviation fuel can include methylcyclopentadienyl manganese tricarbonyl (MMT), manganese naphthenate, cymantrene (cyclopentadienyl manganese tricarbonyl) and/or any substituted derivative thereof, or any combination thereof. In at least one embodiment, an aviation fuel includes MMT in an amount of about 5 mg manganese per liter (Mn/L) to about 100 mg Mn/L, such as about 5 mg Mn/L to about 85 mg Mn/L, such as about 5 mg Mn/L to about 75 mg Mn/L, such as about 5 mg Mn/L to about 25 mg Mn/L. In some embodiments, the one or more manganese containing compounds are an optional additive to the aviation fuel, and are not present while still achieving the proper combustion for proper aircraft operation.

[0068] Manganese carbonyls (e.g., MMT and substituted derivatives of cymantrene) are photosensitive compounds, which can produce manganese oxides when exposed to light. The production of manganese oxide within an aviation fuel might be detrimental to aircraft operations as manganese oxide lacks solubility within such fuel compositions causing precipitates that can ultimately accumulate on fuel filters and interfere with fuel flow. Additionally, manganese oxide deposits can cause the fuel to ignite prematurely in areas (e.g., pistons, valve heads, and the like) that are not easily cleaned via manual cleaning methods (unlike spark plugs). Thus, it would be advantageous to increase the photo-stability of such manganese carbonyl compounds, thereby increasing the storage stability of such fuel compositions. It has been discovered that including an oil-soluble alkanoic acid within an aviation fuel composition increases the photostability of such manganese carbonyl compounds therein without substantially affecting the overall performance of the fuel. In fact, such aviation fuel compositions are comparable to currently available fuels meeting 100LL parameters.

[0069] In some embodiments, an aviation fuel includes one or more oil-soluble alkanoic acid compounds. In one or more embodiments, the one or more oil-soluble alkanoic acid compounds is selected from 2-ethylhexanoic acid, 2-methylhexanoic acid, 3-ethylhexanoic acid, 3-methylhexanoic acid, 4-methylhexanoic acid, 4-ethylpentanoic acid, 4-ethylpentanoic acid, combinations thereof, and the like. In at least one embodiment, the oil-soluble alkanoic acid is 2-ethylhexanoic acid. In some embodiments, an aviation fuel can include an oil-soluble alkanoic acid in an amount relative to the amount of manganese present in the fuel composition, such as about one part by weight to about fifteen parts alkanoic acid per fifteen parts by weight manganese.

[0070] In some embodiments, an aviation fuel includes a weight ratio of oil-soluble alkanoic acid to manganese of about 1:15 to about 1:1, such as about 1:10 to about 1:1, such as about 1:5 the about 1:1. In at least one embodiment, an aviation fuel includes a weight ratio of 2-hexylalkanoic acid to manganese of about 1:15 to about 1:1, such as about 1:10 to about 1:1, such as about 1:5 the about 1:1.

[0071] In some embodiments, an aviation fuel of the present disclosure does not have the level of tetraethyl lead (TEL) used in currently available commercial aviation fuels. In fact, in some embodiments, an aviation fuel of the present disclosure eliminates the need for such material altogether. In one or more embodiments, an aviation fuel includes TEL in an amount of less than 0.013 g/L. In at least one embodiment, an aviation fuel includes TEL in an amount of about 0.0002 g/L to about 0.013 g/L, such as about 0.0002 g/L to about 0.001 g/L.

[0072] In some embodiments, an aviation fuel includes one or more dyes in order to differentiate fuel compositions of different grades. Service experience has indicated that only some dyes in specified amounts can be tolerated without manifestation of induction system deposition (e.g., deposit formation on an engine intake port or valve). In one or more embodiments, an aviation fuel includes one or more dyes in an amount of about 1.5 mg/L to about 3 mg/L, such as about 1.5 mg/L to about 2.5 mg/L, such as about 1.5 mg/L to about 2 mg/L.

[0073] In some embodiments, an aviation fuel includes one or more antioxidants/oxidation inhibitors selected from 2,6-ditertiary-butyl-phenol, 2,6-ditertiary-butyl-4-methylphenol, 2,4-dimethyl-6-tertiary-butyl-phenol, 2,6-ditertiary-butyl-phenol, tertiary and tritertiary-butyl-phenols, 2,4-dimethyl-6-tertiary-butyl-phenol, 4-methyl-2,6-ditertiary-butyl phenol, dimethyl-tertiary-butyl-phenols, 2,4-dimethyl-6-tertiary-butyl-phenol, tertiary-butyl-methyl-phenols, tertiary-butyl-dimethyl-phenols, 2,6-ditertiary-butyl-4-methyl-phenol, methyl tertiary-butyl-phenols, ethyl tertiary-butyl-phenols, dimethyl tertiary-butyl-phenols, 2,4-di-tertiary butyl-phenol, tertiary-butyl-phenol, butylated ethyl-phenols, butylated methyl-phenols, butylated dimethyl-phenols, di-isopropyl-phenols, tri-isopropyl-phenols, di-tertiary butyl-phenols, tri-tertiary butyl-phenols, N,N' di-secondary butyl-para phenylenediamine, N,N' di-isopropyl-para-phenylenediamine, N-secondary butyl, N'-phenyl ortho-phenylenediamine, dimethylcyclohexylamine, p-phenylenediamine, and combinations thereof. In one or more embodiments, an antioxidant or combination thereof is present in an aviation fuel in an amount of no more than 12 mg of antioxidant per liter of fuel.

[0074] In some embodiments, an aviation fuel includes a valve seat recession additive (VSRA). Unleaded fuels have lower lubricity than leaded fuels and may cause excessive wear of the exhaust valve seat, ultimately resulting in loss of compression in a cylinder. Manganese compounds help prevent valve seat recessions, but in fuels that do not contain manganese compounds, it can be helpful to have small amounts of one or more VSRAs to reduce valve seat wear. In some embodiments, oil-soluble sodium and potassium-based compounds can be effective VSRAs in amounts as low as about 10 mg Na/L and/or K/L. Without being bound by theory, such compounds are effective in preventing valve seat recession by cleaning abrasive carbonaceous deposits, which may accumulate on fuel exhaust valves. In at least one embodiment, a VSRA of the present disclosure can include one or more of zinc, iron, sodium, calcium, vanadium, potassium, and/or phosphorus salts of oil-soluble alkanoic acids. In some embodiments, aviation fuels of the present disclosure can include VSRAs made up of, at least, sodium and potassium salts of alkanoic acids such as 2-ethyl-hexanoic acid. In one or more embodiments, aviation fuels of the present disclosure include potassium 2-ethylhexyl hexanoate and/or sodium 2-ethylhexyl hexanoate for use as a VSRA in an amount of about 50 mg/L to about 100 mg/L, such as about 60 mg/L to about 90 mg/L, such as about 70 mg/L to about 80 mg/L. In at least one embodiment, an aviation fuel includes potassium 2-ethylhexyl hexanoate in an amount of about 10 mg K/L to about 20 mg K/L, such as about 12 mg K/L to about 18 mg K/L, such as about 14 mg K/L to about 16 mg K/L. In at least one embodiment, an aviation fuel includes sodium 2-ethylhexyl hexanoate in an amount of about 6 mg Na/L to about 12 mg Na/L, such as about 7 mg Na/L to about 11 mg Na/L, such as about 8 mg Na/L to about 10 mg Na/L. In some embodiments, aviation fuel compositions can pass a 150 hour+ valve seat recession test (a general engine durability test), as described in the Examples section below.

[0075] In addition, because of a lack of corrosive components in aviation fuels of the present disclosure, added corrosion inhibitors are merely optional in the aviation fuels. For example, an aviation fuel can be substantially free or entirely free of corrosion inhibitors.

[0076] In addition, because of the presence of alcohol in aviation fuels of the present disclosure, added anti-icing additives are merely optional in the aviation fuels. For example, an aviation fuel can be substantially free or entirely free of fuel system icing inhibitors (FSII) additives.

[0077] Overall, while aviation fuels of the present disclosure may include one or more additives (e.g., anti-static agents, corrosion inhibiting agents, anti-icing agents, biocidal agents, metal deactivating agents, thermal stability improvement agents, and the like), such additive agents can be considered as optional and/or unnecessary to the achievement of adequate stability, properties, combustion and proper long term aircraft operation. Advantageously, aviation fuel compositions disclosed herein are designed/composed to include components therein that are believed to cause little to no particulate formation, static buildup, and/or thermal instability during and throughout storage, transport, or aircraft operation. As such, the additive agents combating such deleterious effects are deemed optional. Additionally, aviation fuel compositions disclosed herein are free of and/or substantially free of aromatic compounds (e.g., 0 wt % to 0.1 wt %, such as 0 wt %) and isopentane (e.g., 0 wt % to 0.1 wt %, such as 0 wt %), components commonly used in aviation fuel compositions. The removal of aromatic compounds and isopentane from aviation fuel compositions disclosed herein allow for (1) fuel composition simplification; (2) reduced production cost; 3) improved materials compatibility; and 4) reduced propensity for carbonaceous deposit formation and emissions. As is well understood, aromatic compounds are generally considered as reactive and can form secondary aerosols during the combustion process which can lead to particulate formation and carbonaceous deposits. Such deposit formation is detrimental to proper engine performance. Furthermore, aromatic compounds swell elastomers within the engine assembly and fuel distribution system. Additionally, removing isopentane increases the MON of fuel compositions and the MON-response to manganese. While isopentane is commonly included to increase the RVP of aviation fuel compositions, isopentane is a highly volatile component that can present challenges in compositional stability during long-term storage and transport. Without being bound by theory, it is believed that the aviation fuel compositions of the present disclosure provide, at least, adequate combustion and vapor pressure necessary for proper aircraft engine operation.

[0078] In some embodiments, an aviation fuel can include one or more detergents. Generally, the amount of the detergent additive is less than 10,000 ppm, such as less than 1,000 ppm, such as less than 100 ppm, such as less than 10 ppm, based on the total weight of the fuel or fuel composition. Some non-limiting examples of suitable detergents include polyolefin substituted succinimides or succinamides of polyamines, for instance polyisobutylene succinimides or polyisobutylene amine succinamides, aliphatic amines, Mannich bases or amines, and polyolefin (e.g., polyisobutylene) maleic anhydrides. In at least one embodiment, the detergent is a polyolefin substituted succinimide, such as polyisobutylene succinimide. In one or more embodiments, the one or more detergents is present in the aviation fuel in an amount of about 0.1 vol % to about 5 vol %, such as about 0.1 vol % to about 1 vol %, such as about 0.1 vol % to about 0.5 vol %.

[0079] In some embodiments, an aviation fuel includes at least one iso-alkane compound, at least one dialkyl ether compound, at least one alcohol containing compound, and at least one manganese containing compound. In one or more embodiments, the at least one iso-alkane compound is selected from C_4-C_{12} hydrocarbons, such as isooctane (2,2,4-trimethylpentane). In at least one embodiment, the iso-alkane compound is isooctane. In one or more embodiments, the at least one dialkyl ether compound is selected from one or more esters, ethers, carbonates, C_5-C_7 cycloalkanes, and combinations thereof. In at least one embodiment, the at least one dialkyl ether compound is ethyl-tert-butyl-ether, methyl-tert-butyl-ether, or a combination thereof. In one or more embodiments, the at least one alcohol containing compound is selected from methanol, ethanol, propanol, butanol, and combinations thereof. In at least one embodiment, the at least one alcohol containing compound is methanol. In one or more embodiments, the at least one manganese containing compound is selected from MMT, manganese naphthenate, cymantrene and/or a substituted derivative of cymantrene, and combinations thereof. In at least one embodiment, the at least one manganese containing compound is MMT. In one or more embodiments, the aviation fuel includes the at least one iso-alkane compound in an amount of about 81 vol % to about 87 vol % (such as about 81 vol % to about 84 vol %, alternatively about 84 vol % to about 87 vol %), the at least one dialkyl ether compound in an amount of about 10 vol % to about 18 vol %, the at least one alcohol containing compound in an amount of about 0.5 vol % to about 1 vol %, and the at least one manganese containing compound in an amount of about 5 mg Mn/L to about 60 mg Mn/L, wherein the total vol % of the aviation fuel is equal to 100 vol %.

[0080] In some embodiments, an aviation fuel includes at least one iso-alkane compound, at least one dialkyl ether compound, at least one alcohol containing compound, and at least one VSRA. In one or more embodiments, the at least one iso-alkane compound is selected from C_4-C_{12} hydrocarbons, such as isooctane. In at least one embodiment, the iso-alkane compound is isooctane. In one or more embodiments, the at least one dialkyl ether compound is selected from one or more esters, ethers, carbonates, C_5-C_7 cycloalkanes, and combinations thereof. In at least one embodiment, the at least one dialkyl ether compound is ethyl-tert-butyl-ether, methyl-tert-butyl-ether, or a combination thereof. In one or more embodiments, the at least one alcohol containing compound is selected from methanol, ethanol, propanol, butanol, and combinations thereof. In at least one embodiment, the at least one alcohol containing compound is methanol. In one or more embodiments, the at least one VSRA is selected from potassium 2-ethylhexyl hexanoate, sodium 2-ethylhexyl hexanoate, or a combination thereof. In at least one embodiment, the at least one VSRA is potassium 2-ethylhexyl hexanoate. In one or more embodiments, the aviation fuel includes the at least one iso-alkane compound in an amount of about 81 vol % to about 87 vol % (such as about 81 vol % to about 84 vol %, alternatively about 84 vol % to about 87 vol %), the at least one dialkyl ether compound in an amount of about 10 vol % to about 18 vol %, the at least one alcohol containing compound in an amount of about 0.5 vol % to about 1 vol %, and the at least one VSRA in an amount of about 50 mg/L to about 100 mg/L, wherein the total vol % of the aviation fuel is equal to 100 vol %.

[0081] Aviation fuel compositions disclosed herein exhibit compositional compatibility with already existing and commercially available aviation fuel compositions. For example, the aviation fuel compositions of the present disclosure can be formulated and/or designed to be a "drop-in" replacement fuel for 100LL, where the aviation fuel compositions of the present disclosure meet various parameters set forth in ASTM D910 (e.g., MON, RVP, density, and the like). As such, aviation fuel compositions disclosed herein can be readily integrated into the fuel stream currently available for use in various commercial and private aircrafts, such as aircrafts having a spark-ignition engine and/or a reciprocating aviation engine (e.g., Cessna T-303 and Cessna Model 172R aircrafts). Additionally, aviation fuel compositions disclosed herein have little to no observable effects on various components of an aircraft's fuel system (e.g., connections, tubes, gaskets, seals, etc.). Such compatibility of aviation fuels disclosed herein as replacement for or alongside those previously available allow for simple integration within the current aircraft fleet.

Additive Packages

[0082] In some embodiments, an aviation fuel may be prepared via mixing an aviation base fuel with one or more additive packages. As such, an aviation base fuel may include a high-grade aviation unleaded iso-alkane having a selected MON. In one or more embodiments, an aviation fuel may be provided by mixing an unleaded aviation gasoline base fuel (e.g., high-grade aviation iso-alkane, commercial isooctane, or a combination thereof) with an additive package using any method known to one of ordinary skill in the art. The simplicity of such processes further exemplifies the easy integration of such aviation fuel compositions into the already existing aviation fuel stream as a "drop-in" replacement fuel for 100LL.

[0083] In some embodiments, an additive package may include one or more of a manganese containing compound, an oil-soluble alkanoic acid, a VSRA, an additive compound, or a combination thereof. In at least one embodiment, the at least one manganese containing compound is selected from MMT, manganese naphthenate, cymantrene and/or a substituted derivative of cymantrene, and combinations thereof. In at least one embodiment, the at least one oil-soluble alkanoic acid is selected from 2-ethylhexanoic acid, 2-methylhexanoic acid, 3-ethylhexanoic acid, 3-methylhexanoic acid, 4-methylhexanoic acid, 4-ethylpentanoic acid, 4-ethylpentanoic acid, and combinations thereof. In some embodiments, an additive package can include an oil-soluble alkanoic acid in an amount relative to the amount of manganese present in the fuel composition, such as about one part by weight alkanoic acid per fifteen parts by weight manganese, such as about one part alkanoic acid to about one part by weight manganese. In one or more embodiments, an additive package includes at least one additive compound in an amount of about 0.1 vol % to about 5 vol %, such as about 0.1 vol % to about 1 vol %, such as about 0.1 vol % to about 0.5 vol %. In at least one embodiment, the at least one additive compound is selected from any one or more antioxidants/oxidation inhibitors, solvents, dyes, anti-static agents, corrosion inhibitors, anti-icing additives, biocides, thermal stability improvement agents, detergents, and combinations thereof.

Methods of Manufacturing Fuels

[0084] In some embodiments, a method for manufacturing an aviation fuel includes providing an additive package to an unleaded aviation gasoline base fuel, and mixing the two components by any suitable method known to one of ordinary skill in the art. More generally, in at least one embodiment, such an unleaded aviation gasoline base fuel may include a high grade iso-alkane having a selected motor octane number (MON) of at least 96;

[0085] Additionally, or alternatively, in some embodiments, the unleaded aviation gasoline base fuel includes one or more of a dialkyl ether compound, an alcohol compound, and combinations thereof. In one or more embodiments the unleaded aviation gasoline base fuel includes at least one dialkyl ether compound in an amount of about 10 vol % to about 40 vol %, such as about 10 vol % to about 30 vol %, such as about 10 vol % to about 20 vol %. In at least one embodiment, the at least one dialkyl ether compound is ethyl-tert-butyl-ether, methyl-tert-butyl-ether, or a combination thereof. In one or more embodiments the unleaded aviation gasoline base fuel includes at least one alcohol containing compound in an amount of about 0.1 vol % to about 5 vol %, such as about 0.25 vol % to about 5 vol %, such as about 0.5 vol % to about 1 vol %. In at least one embodiment, the at least one alcohol containing compound is selected from methanol, ethanol, propanol, butanol, and combinations thereof. The alcohol containing compound may be deliberately added as a pure compound or be a residual component of the manufacture of a fuel ether such as ETBE or MTBE. Such residual components include methanol, ethanol, and tert-butanol which is the product of the reaction of isobutylene and water contained in the alcohol raw material.

Aviation Fuel Properties

[0086] Aviation fuel should meet the power demands and detonation resistance for the selected aviation engines in which the fuel is consumed. The MON is a standard measure of the performance of a fuel. A reciprocating aviation engine uses a fuel of sufficient octane rating to prevent uncontrolled premature combustion known as engine knocking or detonation. The higher the MON, the more compression the fuel can withstand before detonating. In broad terms, fuels with a higher motor octane rating are most useful in high-compression engines that generally have higher performance. The MON is a measure of how the fuel behaves when under load applied by the engine. ASTM D2700 describes MON testing using a test engine with a preheated fuel mixture, 900 rpm engine speed, and variable ignition timing to stress the fuel's knock resistance. The MON of an aviation gasoline fuel can be used as a guide to the amount of knock-limiting power that may be obtained in a full-scale engine under take-off, climb and cruise conditions.

[0087] Various MON ratings are considered base values for aircraft use, depending on the type of engine and other factors. In some embodiments, an aviation fuel of the present disclosure has a MON greater than 99.6, such as greater than 100.6, such as greater than 101.6. In some embodiments, an aviation fuel of the present disclosure has a MON of about 99.6 to about 105.6, such as about 99.6 to about 104.6, such as about 99.6 to about 103.6.

[0088] The vapor pressure of an aviation fuel is another important factor, which should be considered. Aircraft engines operate in wide ranges of temperatures and atmospheric pressures (e.g., altitudes), and the fuels must start and provide sufficient combustion characteristics throughout those ranges. Lower vapor pressure levels are desirable in avoiding vapor lock during summer heat and/or flying at high altitudes, and higher levels of vaporization are desirable for winter starting and operation. Fuel cannot be pumped when there is vapor in the fuel line (summer) and winter starting ("cold start") will be more difficult when liquid gasoline in the combustion chambers has not vaporized. Vapor pressure is critically important for aviation gasolines, affecting starting, warm-up, and tendency to vapor lock with high operating temperatures or high altitudes. However, the upper limit of vapor pressure is safety critical whereas the lower limit is not. So the minimum limit of 38 kPa specified in ASTM D910 for an all-hydrocarbon fuel can be lowered for a fuel of different composition without compromising safety and is desirable if it results in other benefits such as higher octane, production simplicity, and storage stability.

[0089] The ability of an aviation gasoline to satisfy the foregoing property recommendation may be assessed based on the RVP. The RVP is the absolute vapor pressure exerted by a liquid as determined by the test method ASTM D4953, ASTM D5191, and/or ASTM D5482. In some embodiments, the aviation fuel has a RVP greater than 30 kPa, such as greater than 32.5 kPa, such as greater than 35 kPa. In some embodiments, the aviation fuel has a RVP less than 45 kPa, such as less than 42.5 kPa, such as less than 40 kPa. In some embodiments, the aviation fuel has a RVP of about 30 kPa to about 45 kPa, such as about 32.5 kPa to about 42.5 kPa, such as about 35 kPa to about 40 kPa.

[0090] The energy content of an aviation fuel can usually be predicted by fuel density, which is also a function of fuel composition. Generally, less dense aviation fuels have a higher gravimetric energy content, and more dense aviation fuels have a higher volumetric energy content. The density of an aviation fuel can be determined by ASTM D1298 and/or ASTM D4052. In some embodiments, an aviation fuel has a density less than 6 lbs/gal, such as less than 5.5 lbs/gal, such as less than 5 lbs/gal. In some embodiments, the aviation fuel has a density of about 6 lbs/gal to about 5 lbs/gal, such as about 6 lbs/gal to about 5.25 lbs/gal, such as about 6 lbs/gal to about 5.5 lbs/gal.

Additional Aspects

[0091] The present disclosure provides, among others, the following embodiments, each of which may be considered as optionally including any alternate embodiments.

Clause 1A. A composition, comprising:

- **[0092]** an iso-alkane compound;
- **[0093]** a dialkyl ether compound;
- **[0094]** an alcohol compound; and
- **[0095]** optionally at least one of:
  - **[0096]** a manganese containing compound; or
  - **[0097]** an oil-soluble sodium or potassium-based valve seat recession additive (VSRA).

Clause 1B. A composition, consisting essentially of:

- **[0098]** an iso-alkane compound;
- **[0099]** a dialkyl ether compound;
- **[0100]** an alcohol compound; and
- **[0101]** optionally at least one of:
  - **[0102]** a manganese containing compound; or
  - **[0103]** an oil-soluble sodium or potassium-based valve seat recession additive (VSRA).

Clause 1C. A composition, consisting of:

- **[0104]** an iso-alkane compound;
- **[0105]** a dialkyl ether compound;
- **[0106]** an alcohol compound; and
- **[0107]** optionally at least one of:
  - **[0108]** a manganese containing compound; or
  - **[0109]** an oil-soluble sodium or potassium-based valve seat recession additive (VSRA).

Clause 2. The composition of one of clauses 1A, 1B, or 1C, wherein the iso-alkane compound is present in the composition at about 82 vol % to about 90 vol %.

Clause 3. The composition of one of clauses 1A, 1B, 1C, or 2, wherein the dialkyl ether compound is present in the composition at about 10 vol % to about 18 vol %.

Clause 4. The composition of one of clauses 1A, 1B, 1C, or 2-3, wherein the alcohol compound is present in the composition at about 0.5 vol % to about 1 vol %.

Clause 5. The composition of one of clauses 1A, 1B, 1C, or 2-4, wherein the manganese containing compound is present in the composition at about 5 mg manganese per liter fuel (mg Mn/L) to about 60 mg Mn/L.

Clause 6. The composition of one of clauses 1A, 1B, 1C, or 2-5, wherein the iso-alkane compound is one or more C_4-C_{12} hydrocarbons.

Clause 7. The composition of one of clauses 1A, 1B, 1C, or 2-6, wherein the iso-alkane compound is isooctane (2,2,4-trimethylpentane).

Clause 8. The composition of one of clauses 1A, 1B, 1C, or 2-7, wherein the dialkyl ether compound is ethyl-tert-butyl-ether, methyl-tert-butyl-ether, or a combination thereof.

Clause 9. The composition of one of clauses 1A, 1B, 1C, or 2-8, wherein the dialkyl ether compound is ethyl-tert-butyl-ether.

Clause 10. The composition of one of clauses 1A, 1B, 1C, or 2-9, wherein the dialkyl ether compound is methyl-tert-butyl-ether.

Clause 11. The composition of one of clauses 1A, 1B, 1C, or 2-10, wherein the dialkyl ether compound is a combination of ethyl-tert-butyl-ether and methyl-tert-butyl-ether.

Clause 12. The composition of one of clauses 1A, 1B, 1C, or 2-11, wherein the alcohol containing compound is selected from methanol, ethanol, propanol, butanol, and combinations thereof.

Clause 13. The composition of one of clauses 1 A, 1B, 1C, or 2-12, wherein the alcohol containing compound is methanol.

Clause 14. The composition of one of the clauses 1A, 1B, 1C, or 2-13, wherein the VSRA is potassium 2-ethylhexanoate.

Clause 15. The composition of one of clauses 1A, 1B, 1C, or 2-13, wherein the manganese containing compound is selected from methylcyclopentadienyl manganese tricarbonyl (MMT), manganese naphthenate, cymantrene and/or a substituted derivative of cymantrene, and combinations thereof.

Clause 16. The composition of one of clauses 1A, 1B, 1C, or 2-14, wherein the manganese containing compound is methylcyclopentadienyl manganese tricarbonyl (MMT).

Clause 17. The composition of one of clauses 1A, 1B, 1C, or 2-15, wherein the composition further comprises an oil-soluble alkanoic acid.

Clause 18. The composition of clause 16, wherein the oil-soluble alkanoic acid is present in the composition in an amount of about one part by weight to about fifteen parts alkanoic acid per fifteen parts by weight manganese.

Clause 19. The composition of one of clauses 16-17, wherein the oil-soluble alkanoic acid is selected from 2-ethylhexanoic acid, 2-methylhexanoic acid, 3-ethylhexanoic acid, 3-methylhexanoic acid, 4-methylhexanoic acid, 4-ethylpentanoic acid, 4-ethylpentanoic acid, and combinations thereof.

Clause 20. The composition of one of clauses 16-18, wherein the oil-soluble alkanoic acid is 2-ethylhexanoic acid.

Clause 21. The composition of one of clauses 1A, 1B, 1C, or 2-19, wherein the composition further comprises an additive compound.

Clause 22. The composition of clause 20, wherein the additive compound is present in the composition in an amount of about 0.1 vol % to about 5 vol %.

Clause 23. The composition of one of clauses 20-21, wherein the additive compound is selected from any one or more antioxidants/oxidation inhibitors, solvents, dyes, anti-static agents, corrosion inhibitors, anti-icing additives, biocides, thermal stability improvement agents, detergents, and combinations thereof.

Clause 27. The composition of one of clauses 24-25, wherein the composition further comprises one or more dyes.

Clause 28. The composition of one of clauses 1A, 1B, 1C, or 2-27, wherein the composition comprises a motor octane number (MON) of greater than about 99.6, as determined in accordance with ASTM D2700.

Clause 29. The composition of one of clauses 1A, 1B, 1C, or 2-28, wherein the composition comprises a motor octane number (MON) of about 99.6 to about 105.6, as determined in accordance with ASTM D2700.

Clause 30. The composition of one of clauses 1A, 1B, 1C, or 2-28, wherein the composition comprises a motor octane number (MON) of greater than about 100.6, as determined in accordance with ASTM D2700.

Clause 31. The composition of one of clauses 1A, 1B, 1C, or 2-30, wherein the composition comprises a motor octane number (MON) of about 100.6 to about 105.6, as determined in accordance with ASTM D2700.

Clause 32. The composition of one of clauses 1A, 1B, 1C, or 2-31, wherein the composition comprises a motor octane number (MON) of greater than about 101.6, as determined in accordance with ASTM D2700.

Clause 33. The composition of one of clauses 1A, 1B, 1C, or 2-32, wherein the composition comprises a motor octane number (MON) of about 101.6 to about 105.6, as determined in accordance with ASTM D2700.

Clause 34. The composition of one of clauses 1A, 1B, 1C, or 2-33, wherein the composition comprises a Reid vapor pressure (RVP) of about 30 kPa to about 45 kPa, as determined in accordance with ASTM D4953, ASTM D5191, and/or ASTM D5482.

Clause 35. The composition of one of clauses 1A, 1B, 1C, or 2-34, wherein the composition comprises a Reid vapor pressure (RVP) of about 32.5 kPa to about 42.5 kPa, as determined in accordance with ASTM D4953, ASTM D5191, and/or ASTM D5482.

Clause 36. The composition of one of clauses 1A, 1B, 1C, or 2-35, wherein the composition comprises a Reid vapor pressure (RVP) of about 35 kPa to about 40 kPa, as determined in accordance with ASTM D4953, ASTM D5191, and/or ASTM D5482.

Clause 37. The composition of one of clauses 1A, 1B, 1C, or 2-36, wherein the composition comprises a density of about 6 lbs/gal to about 5 lbs/gal, as determined in accordance to ASTM D1298 and/or ASTM D4052.

Clause 38. The composition of one of clauses 1A, 1B, 1C, or 2-37, wherein the composition comprises a density of about 6 lbs/gal to about 5.25 lbs/gal, as determined in accordance to ASTM D1298 and/or ASTM D4052.

Clause 39. The composition of one of clauses 1A, 1B, 1C, or 2-38, wherein the composition comprises a density of about 6 lbs/gal to about 5.5 lbs/gal, as determined in accordance to ASTM D1298 and/or ASTM D4052.

Clause 40. A method, comprising:

[0110] providing a first component to a second component, wherein the first component is an unleaded aviation gasoline base fuel and the second component is an additive package;

[0111] mixing the first component with the second component to provide an aviation fuel composition.

Clause 41. The method of clause 40, wherein the unleaded aviation gasoline base fuel comprises a high grade aviation iso-alkane; Clause 42. The method of clause 41, wherein the high grade aviation iso-alkane comprises a motor octane number (MON) of at least 96.

Clause 43. The method of one of clauses 40-42, wherein the vapor pressure of the unleaded aviation gasoline base fuel is about 38 kPa to about 49 kPa.

Clause 44. The method of one of clauses 40-43, wherein the unleaded aviation gasoline base fuel further comprises a dialkyl ether compound and an alcohol compound.

Clause 45. The method of clause 44, wherein the dialkyl ether compound is present in the unleaded aviation gasoline base fuel at about 10 vol % to about 18 vol %.

Clause 46. The method of one of clauses 44-45, wherein the alcohol compound is present in the unleaded aviation gasoline base fuel at about 0.1 vol % to about 5 vol %.

Clause 47. The method of one of clauses 44-46, wherein the dialkyl ether compound is ethyl-tert-butyl-ether, methyl-tert-butyl-ether, or a combination thereof.

Clause 48. The method of one of clauses 44-47, wherein the dialkyl ether compound is ethyl-tert-butyl-ether.

Clause 49. The method of one of clauses 44-48, wherein the dialkyl ether compound is methyl-tert-butyl-ether.

Clause 50. The method of one of clauses 44-50, wherein the dialkyl ether compound is a combination of ethyl-tert-butyl-ether and methyl-tert-butyl-ether.

Clause 51. The method of one of clauses 44-51, wherein the alcohol containing compound is selected from methanol, ethanol, propanol, butanol, and combinations thereof.

Clause 52. The method of one of clauses 44-52, wherein alcohol containing compound is methanol.

Clause 53. The method of one of clauses 40-53, wherein the additive package comprises:

[0112] an oil-soluble VSRA. (Potassium 2-ethylhexanoate (K2HE) at 10 mg K/L fuel or 50 mg K2HE/L).

Clause 54. The method of one of clauses 40-53, wherein the additive package comprises:

[0113] a manganese containing compound; and

[0114] an oil-soluble alkanoic acid.

Clause 55. The method of clause 54, wherein the manganese containing compound is present in the additive package at about 50 vol % to about 94 vol %.

Clause 56. The method of one of clauses 54-55, wherein the oil-soluble alkanoic acid is present in the additive package in an amount of about one part by weight to about fifteen parts by weight alkanoic acid per fifteen parts by weight manganese.

Clause 57. The method of one of clauses 54-56, wherein the manganese containing compound is selected from methylcyclopentadienyl manganese tricarbonyl (MMT), manganese naphthenate, cymantrene and/or a substituted derivative of cymantrene, and combinations thereof.

Clause 58. The method of one of clauses 54-57, wherein the manganese containing compound is methylcyclopentadienyl manganese tricarbonyl (MMT).

Clause 59. The method of one of clauses 54-58, wherein the oil-soluble alkanoic acid is selected from 2-ethylhexanoic acid, 2-methylhexanoic acid, 3-ethylhexanoic acid, 3-methylhexanoic acid, 4-methylhexanoic acid, 4-ethylpentanoic acid, 4-ethylpentanoic acid, and combinations thereof.

Clause 60. The method of one of clauses 54-59, wherein the oil-soluble alkanoic acid is 2-ethylhexanoic acid.

Clause 61. The method of one of clauses 54-60, wherein the additive package further comprises an additive compound.

Clause 62. The method of clause 61, wherein the additive compound is present in the additive package in an amount of about 0.1 vol % to about 5 vol %.

Clause 63. The method of one of clauses 61-62, wherein the additive compound is selected from any one or more antioxidants/oxidation inhibitors, solvents, dyes, anti-static agents, corrosion inhibitors, anti-icing additives, biocides, thermal stability improvement agents, detergents, and combinations thereof.

Clause 64. The method of one of clauses 39-63, wherein the aviation fuel composition comprises a motor octane number (MON) of greater than about 99.6, as determined in accordance with ASTM D2700.

Clause 65. The method of one of clauses 39-64, wherein the aviation fuel composition comprises a motor octane number (MON) of about 99.6 to about 105.6, as determined in accordance with ASTM D2700.

Clause 66. The method of one of clauses 39-65, wherein the additive package comprises a motor octane number (MON) of greater than about 100.6, as determined in accordance with ASTM D2700.

Clause 67. The method of one of clauses 39-66, wherein the aviation fuel composition comprises a motor octane number (MON) of about 100.6 to about 105.6, as determined in accordance with ASTM D2700.

Clause 68. The method of one of clauses 39-67, wherein the aviation fuel composition comprises a motor octane number (MON) of greater than about 101.6, as determined in accordance with ASTM D2700.

Clause 69. The method of one of clauses 39-68, wherein the aviation fuel composition comprises a motor octane number (MON) of about 101.6 to about 105.6, as determined in accordance with ASTM D2700.

Clause 70. The method of one of clauses 39-69, wherein the aviation fuel composition comprises a Reid vapor pressure (RVP) of about 30 kPa to about 45 kPa, as determined in accordance with ASTM D4953, ASTM D5191, and/or ASTM D5482.

Clause 71. The method of one of clauses 39-70, wherein the aviation fuel composition comprises a Reid vapor pressure (RVP) of about 32.5 kPa to about 42.5 kPa, as determined in accordance with ASTM D4953, ASTM D5191, and/or ASTM D5482.

Clause 72. The method of one of clauses 39-71, wherein the aviation fuel composition comprises a Reid vapor pressure (RVP) of about 35 kPa to about 45 kPa, as determined in accordance with ASTM D4953, ASTM D5191, and/or ASTM D5482.

Clause 73. The composition of one of clauses 39-72, wherein the aviation fuel composition comprises a density of about 6 lbs/gal to about 5 lbs/gal, as determined in accordance to ASTM D1298 and/or ASTM D4052.

Clause 74. The method of one of clauses 39-73, wherein the aviation fuel composition comprises a density of about 6 lbs/gal to about 5.25 lbs/gal, as determined in accordance to ASTM D1298 and/or ASTM D4052.

Clause 75. The method of one of clauses 39-74, wherein the aviation fuel composition comprises a density of about 6 lbs/gal to about 5.5 lbs/gal, as determined in accordance to ASTM D1298 and/or ASTM D4052.

Clause 76A. A composition, comprising:

[0115] isooctane in an amount of about 81 vol % to about 87 vol %;

[0116] a dialkyl ether compound in an amount of about 10 vol % to about 18 vol %; and

[0117] alcohol compounds in an amount of less than about 1.5 vol %.

Clause 76B. A composition, consisting essentially of:

[0118] isooctane in an amount of about 81 vol % to about 87 vol %;

[0119] a dialkyl ether compound in an amount of about 10 vol % to about 18 vol %; and

[0120] alcohol compounds in an amount of less than about 1.5 vol %.

Clause 76C. A composition, consisting of:

[0121] isooctane in an amount of about 81 vol % to about 87 vol %;

[0122] a dialkyl ether compound in an amount of about 10 vol % to about 18 vol %; and

[0123] alcohol compounds in an amount of less than about 1.5 vol %.

Clause 77. The composition of one of clauses 76A, 76B, or 76C, wherein the composition further comprises a manganese containing compound.

Clause 78. The composition clause 77, wherein the composition comprises about 5 mg manganese per liter (mg Mn/L) to about 25 mg Mn/L.

Clause 79. The composition of one of clauses 77-78, wherein the manganese containing compound comprises methylcyclopentadienyl manganese tricarbonyl (MMT).

Clause 80. The composition of clause 79, wherein the composition comprises about 5 mg manganese per liter (mg Mn/L) to about 25 mg Mn/L.

Clause 81. The composition of one of clauses 77-80, wherein the composition further comprises an oil-soluble alkanoic acid.

Clause 82. The composition of clause 81, wherein the oil-soluble alkanoic acid is selected from 2-ethylhexanoic acid, 2-methylhexanoic acid, 3-ethylhexanoic acid, 3-methylhexanoic acid, 4-methylhexanoic acid, 4-ethylpentanoic acid, 4-ethylpentanoic acid, and combinations thereof.

Clause 83. The composition of one of clauses 77-82, wherein the composition comprises about one part by weight of the oil soluble alkanoic acid per fifteen parts by weight manganese to about one part by weight alkanoic acid per one part by weight manganese.

Clause 84. The composition of one of clauses 76A, 76B, 76C, or 77-83, wherein the composition further includes an oil-soluble valve seat recession additive (VSRA).

Clause 85. The composition of clause 84, wherein the oil-soluble VSRA is selected from potassium 2-ethylhexyl hexanoate, sodium 2-ethylhexyl hexanoate, and combinations thereof.

Clause 86. The composition of one of clauses 84-85, wherein the oil-soluble VSRA comprises potassium 2-ethylhexyl hexanoate and is present in the composition in an amount of about 10 mg potassium per liter (mg K/L) to about 20 mg K/L.

Clause 87. The composition of one of clauses 76A, 76B, 76C, or 77-86, comprising about 0.5 vol % to about 1 vol % of methanol.

Clause 88. The composition of one of clauses 76A, 76B, 76C, or 77-87, comprising about 12 vol % to about 15 vol % of the dialkyl ether compound.

Clause 89. The composition of one of clauses 76A, 76B, 76C, or 77-88, comprising about 81 vol % to about 84 vol % of the isooctane.

Clause 90. The composition of one of clauses 76A, 76B, 76C, or 77-89, wherein the composition has a motor octane number (MON; as determined in accordance to ASTM D2700) greater than 99.6.

Clause 91. The composition of one of clauses 76A, 76B, 76C, or 77-90, wherein the composition has a motor octane number (MON; as determined in accordance to ASTM D2700) of about 99.6 to about 105.6.

Clause 92. The composition of one of clauses 76A, 76B, 76C, or 77-91, wherein the composition is substantially free of aromatic compounds and isopentane.

Clause 93. The composition of one of clauses 76A, 76B, 76C, or 77-92, wherein:

[0124] the dialkyl ether compound is present in an amount of about 10 vol % to about 18 vol %;

[0125] the alcohol compound is methanol; and

[0126] the methanol is present in an amount of about 1.5 vol % or less.

Examples

[0127] Example 1. Compositions and Octane: Five different aviation fuels were prepared, each including 84 vol % isooctane, 15 vol % dialkyl ether, 1 vol % methanol, a manganese content, and an oil-soluble alkanoic acid content. Three of the five aviation fuel compositions implemented methylcyclopentadienyl manganese tricarbonyl (MMT) as the manganese content at different concentrations thereof, such as (1) 0 mg Mn/L, (2) 6.5-7.8 mg Mn/L, (3) 25 mg Mn/L. Additionally, three of the five aviation fuel compositions incorporated 2-ethylhexanoic acid as the oil-soluble alkanoic acid in an amount relative to the amount of manganese present in each of the aviation fuel formulations. As such, three aviation formulation incorporated 2-ethylhexanoic acid in an amount of 15 parts alkanoic acid per fifteen parts by weight manganese. Each of the aviation fuel formulations were tested in accordance to ASTM D2700 to determine the effects different manganese contents have on motor octane number (MON) of such aviation fuel formulations. The results are summarized in Table 1.

TABLE 1

MON values of aviation fuel compositions having different manganese content	
Mn concentration in the fuel composition	MON
MTBE or ETBE blend with 0-12 mg Mn/L	~99.6
MTBE or ETBE blend with 15-20 mg Mn/L	~100.6
MTBE or ETBE blend with 25-30 mg Mn/L	~101.6
MTBE or ETBE blend with 35-40 mg Mn/L	~102.6
MTBE or ETBE blend with 45-55 mg Mn/L	~103.6

[0128] As is apparent from the results provided in Table 1, an increase in manganese content provides a corresponding increase in MON. Additionally, it is important to note that the aviation fuels of the present disclosure exhibit increased photostability as compared to other aviation fuels of similar manganese content and composition. Without being bound by theory, this photostability is presumed to be due to the oil-soluble alkanoic acid providing increased solubility of the manganese compound within the aviation fuel composition and stabilization of intermediate photodecomposition products.

[0129] Example 2. A fuel was prepared with no added manganese (Grade UL100E) with 84 vol % isooctane, 15 vol % ETBE, and 1.0 vol. % methanol. The fuel was tested in triplicate according to ASTM D910 and the results are summarized in Table 2.

TABLE 2

Detailed properties for manganese-free UL100E unleaded aviation fuel vs. ASTM D910 specifications for 100LL.

Properties		ASTM D910 Specification	Grade UL100E			ASTM Test Method
Combustion						
Neat heat of combustion, MJ/Kg	min	43.5	42.9	42.9	42.6	D4809
Knock value, lean mixture, Motor method octane number	min	99.6	100.0	100.0	99.7	D2700
Aviation Lean Rating, Performance number, rich mixture	min	100.0	101.1	101.1	100.2	D2700
Supercharge Number	min	130	>130	>130	>130	D909
Composition						
Lead content g/L	max	0.013	<0.005	<0.005	<0.005	D5059
Manganese content mg/L			None detected	None detected	None detected	D3831 & D5059
Sulfur, mass %	max	0.05	0.0003	0.0002	0.0003	D2622
Total combined alcohols, wt. %			1.2	1.2	1.6	D6733
Combined ethers and alcohols, wt. %,			15.5	15.4	17.6	D6733
Aromatic content, wt. %			0.3	0.3	0.5	D6733
Volatility						
Vapor pressure 38° C., kPa	min	38	30.9	30.3	32.9	D5191
	max	49				
Initial Boiling Point, ° C.	Report		61.5	60.5	60.0	D86
Fuel Evaporated						
10 volume % at ° C.	max	85	87.5	87.5	84.5	D86
40 volume % at ° C.	min	75	94.5	94.0	93.5	D86
50 volume % at ° C.	max	105	96.0	95.5	95.0	D86
90 volume % at ° C.	max	135	108.0	107.5	107.5	D86
Final Boiling point, ° C.	max	180	178.5	180.0	178.5	D86
Sum of 10% + 50% evaporated Boiling Points	min	135	183.5	183.0	179.5	D86
Recovery, volume %	min	97	98.5	98.5	98.0	D86
Residue, volume %	max	1.5	1.3	1.1	1.3	D86
Loss, volume %	max	1.5	0.2	0.4	0.7	D86
Other Properties						
Water reaction, volume change, mL	max	2	1.0	1.0	1.0	D1094
Density at 15° C., kg/m^3	report		707.7	707.6	709.2	D4052
Freezing point, ° C.	max	−58	<−70	<−70	<−70	D2386
Electrical conductivity, pS/m	max	600	39	67	185	D2624
Corrosion, copper strip (3 h at 50° C.)	max	No. 1	1a	1a	1a	D130
Potential gum (5-h aging) mg/100 mL	max	6	2	2	4	D873

[0130] Example 3. A fuel was prepared from Grade UL100E described in example 2 and 10 mg/L manganese added as an MMT package with 8 mg/L 2-ethyhexanoic acid. The fuel was tested in triplicate according to ASTM D910 and the results are summarized in Table 3.

TABLE 3

Detailed properties for UL100E unleaded aviation fuel with 10 mg/L manganese vs. ASTM D910 specifications for 100LL.

Properties		ASTM D910 Specification	Grade UL100E			ASTM Test Method
Combustion						
Neat heat of combustion, MJ/Kg	min	43.5	42.9	42.9	42.9	D4809
Knock value, lean mixture, Motor method octane number	min	99.6	100.4	100.3	100.4	D2700
Aviation Lean Rating, Performance number, rich mixture	min	100.0	102.1	101.9	102.1	D2700
Supercharge Number	min	130	>138	>138	>138	D909
Composition						
Lead content g/L	max	0.013	<0.005	<0.005	<0.005	D5059
Manganese content mg/L			16, 15	10, 9	13, 16	D3831 & D5059
Sulfur, mass %	max	0.05	0.0003	0.0002	0.0003	D2622
Total combined alcohols, wt. %			1.1	1.2	1.6	D6733
Combined ethers and alcohols, wt. %,			15.6	15.4	16.2	D6733
Aromatic content, wt. %			0.3	0.3	0.3	D6733
Volatility						
Vapor pressure 38° C., kPa	min	38	30.6	31.2	30.2	D5191
	max	49				
Initial Boiling Point, ° C.	Report		61.0	60.5	61.0	D86
Fuel Evaporated						
10 volume % at ° C.	max	85	87.0	87.0	87.5	D86
40 volume % at ° C.	min	75	94.0	94.5	94.0	D86
50 volume % at ° C.	max	105	95.5	96.0	95.5	D86
90 volume % at ° C.	max	135	108.0	107.0	107.5	D86
Final Boiling point, ° C.	max	180	178.0	179.5	179.0	D86
Sum of 10% + 50% evaporated Boiling Points	min	135	182.5	183.0	183.0	D86
Recovery, volume %	min	97	98.0	98.0	98.0	D86
Residue, volume %	max	1.5	1.2	1.0	1.3	D86
Loss, volume %	max	1.5	0.8	1.0	0.7	D86
Other Properties						
Water reaction, volume change, mL	max	2	1.0	1.0	1.0	D1094
Density at 15° C., kg/m^3	report		707.7	707.6	709.2	D4052
Freezing point, ° C.	max	−58	<−70	<−70	<−70	D2386
Electrical conductivity, pS/m	max	600	69	51	88	D2624
Corrosion, copper strip (3 h at 50° C.)	max	No. 1	1a	1a	1a	D130
Potential gum (5-h aging) mg/100 mL	max	6	5	2	4	D873

[0131] The fuels described in Examples 2 and 3 met all but three D910 specifications for leaded fuel, none of which are critical to the performance of the aviation fuel in piston engines and aircraft. Net heat of combustion is just a measure of gravimetric energy content. It is indirectly related to fuel efficiency but is not a critical performance property for the fuel as it is less than 2% lower than all-hydrocarbon 100LL.

[0132] The vapor pressure of the fuel is about 1 psi lower than the minimum value specified in D910, but it is unclear if this lower RVP limit was chosen based on the normal composition of 100LL or is a critical performance property. The UL100E fuels ignite under all normal ambient conditions as well as cold conditions. The RVP is also well below the upper limit of 49 kPa suggesting a low potential for vapor lock. This was confirmed in a hot-fuel flight test in a Robinson R44 helicopter and cold starting in a Lycoming engine test cell. There were also no issues starting engines with UL100E fuels suggesting that a 2.9% exceedance of the 10% evaporation temperature specification in D910 does not interfere with normal operation of the engine.

[0133] Materials compatibility testing—The effect of the fuel of Example 2 was compared to commercial FBO 100LL on a variety of metallic and non-metallic materials described in ASTM D7826. There were no significant differences between the two fuels.

[0134] Engine testing—The detonation margin of the fuels described in Examples 2 and 3 were tested per FAA ETP-003 in a turbocharged Continental TSIO-520-VB engine. Similar fuels with MTBE instead of ETBE and with 25 mg Mn/L were also tested under the same conditions:

TABLE 4

Fuel compositions.					
Fuel Label	Stoich AFR	Density @ 59° F. (lb/gal)	Comment	MMT (mg/L)	Oxygenate
Lyondell UL100E0	14.643	5.87	15% ETBE, zero MMT	0	ETBE
Lyondell UL 100M0	14.516	5.89	15% MTBE, zero MMT	0	MTBE
Lyondell UL101E10	14.594	5.90	15% ETBE, 6.5 mg/L MMT	6.5	ETBE
Lyondell UL101M10	14.518	5.93	15% MTBE, 7.8 mg/L MMT	7.8	MTBE
Lyondell UL101M25	14.518	5.91	15% MTBE, 25 mg/L MMT	25	MTBE
Isooctane	15.152	5.775	Isooctane for reference		

[0135] All five fuels had adequate detonation margins for that engine under all three conditions tested. Higher manganese content increased the detonation margin and ETBE-based fuels had slightly better detonation margins than MTBE fuels although within experimental variability range.

TABLE 5

Detonation margins of fuel compositions at various conditions.													
			Mass Fuel Flow (lb/hr)										
			Min	Lyondell U100E0		Lyondell UL100M0		Lyondell UL101E10		Lyondell UL101M10		Lyondell UL101M25	
Altitude (ft)	RPM Table	MAP_ETP	AFMF (lb/hr)	Rich Full	Det Onset	Rich Full	Det Onset	Rich Full	Det Onset	Rich Full	Det Onset	Rich Full	Det Onset
0	2700	39	197.1	205.0	159.2	206.4	160.4	204.7	152.5	206.1	152.9		0.0
12,000	2700	39	188.2	197.5	181.6	197.6	181.6	197.4	178.1	199.4	178.1	197.7	173.4
16,000	2300	30.3	99.6	118.0	94.4	118.4	96.5						

[0136] Altitude was simulated between sea level and 16,000 feet. All fuels showed detonation onsets below the minimum allowable fuel mass flow (AFMF) for that engine under the conditions selected.

[0137] The fuel of Example 3 was then tested for durability in a turbocharged Continental TSIO-550K engine per FAA Part 33.49 durability testing. The test consists of 150 hours of continuous operation with alternating rich and lean conditions with interruptions every 50 hours, first to weigh the spark plugs and change the oil, then to clean the spark plugs at 100 hours, as shown in FIG. **2** and FIG. **3**.

TABLE 6

Summarized results from the engine durability test. Durability Test Schedule Propeller Test Cell Continental TSIO-550-K Engine								
FAR Event 33.49	Hours Alternating (hr)	RPM ± 3%	Engine OBHP (−0/+5)	Fuel Vol. Flow (GPH)	MAP (−0/+0.25) (Inch Hg)	Temp Limits	Event Length (hr)	Mixture
(b)(7)	2.5	2500	—	40-40.4	36.5	High	20	Full Rich[3]
	2.5	2500	262	—	—	Norm		Lean (ROP)[4]
(b)(6)	1.5	2500	—	40-40.4	36.5	High	20	Full Rich[3]
	0.5	2300	158	—	—	Norm		Lean (LOP)[5]
(b)(5)	1.5	2500	—	40-40.4	36.5	High	20	Full Rich[3]
	0.5	2400	189	—	—	Norm		Lean (LOP)[5]
(b)(2)	1.5	2500	—	40-40.4	36.5	Norm	20	Full Rich[3]
	0.5	2500	232	—	—	Norm		Lean (ROP)[4]

TABLE 6-continued

Summarized results from the engine durability test.
Durability Test Schedule
Propeller Test Cell
Continental TSIO-550-K Engine

FAR Event 33.49	Hours Alternating (hr)	RPM ± 3%	Engine OBHP (−0/+5)	Fuel Vol. Flow (GPH)	MAP (−0/+0.25) (Inch Hg)	Temp Limits	Event Length (hr)	Mixture
(b)(3)	1.5	2500	—	40-40.4	36.5	Norm	20	Full Rich[3]
	0.5	2400	220	—	—	Norm		Lean (ROP)[4]
(b)(4)	1.5	2500	—	40-40.4	36.5	Norm	20	Full Rich[3]
	0.5	2400	205	—	—	Norm		Lean (LOP)[5]
(b)(1)	5 min	2500	—	40-40.4	36.5	High	30	Full Rich[3]
	5 min	2500	262	—	—	Norm		Lean (ROP)[4]

[3]Mixture may be leaned to maintain the Fuel Vol. Flow within the specified limits of 40-40.5 GPH.

[4]For Lean - Rich of Peak (ROP) mixture settings, or whenever Lean - Lean of Peak (LOP) conditions (see Note 5) cannot be stabilized while using a dynamometer, manually, and without undo delay, lean the engine while observing EGT indications to identify the first cylinder to peak. Note the temperature at which this EGT peaks. Enrichen the mixture without undo delay until the EGT indication for the first cylinder to peak is 75-125° F. cooler than peak. CAUTION - When leaning, DO NOT exceed 460° F. CHT on any cylinder. In the event the external cylinder cooling air blower system cannot maintain the normal CHT temp limits, continue to enrichen the mixture until within CHT limits.

[5]For Lean - Lean of Peak (LOP) mixture settings, manually, and without undo delay, lean the engine while observing both TIT indications to identify the last TIT to peak. Note the temperature at which this TIT peaks then further lean the mixture without undo delay until the last TIT to peak is 50-75° F. lean of peak. When leaning, do not exceed 460° F. CHT on any cylinder or 1850 OF TIT at any time. Do not exceed 1750° F. TIT for more than 30 seconds. In the event the external cylinder cooling air blower system cannot maintain the normal CHT temp limits, continue to lean the mixture until within CHT limits.

[0138] The spark plugs, valves, piston, and turbines showed orange manganese oxide deposits, but the engine operated normally without abnormal misfires or power loss. The spark plugs cleaned easily at 100 hours.

[0139] Surprisingly, the deposit accumulation rate on the spark plugs decreased ten-fold after the first cleaning. Spark plug function was normal throughout the test as was appearance (compared to 100LL) operation after 150 hours.

[0140] Intake and exhaust valve seats were measured before and after the test (FIG. **4**A and FIG. **4**B) and showed very little valve seat recession. Over the 150 hour test, both the intake and exhaust valves saw an average recession of 0.002 inches. The greatest loss of material was found on Cylinder 4's exhaust valve (0.005 inches).

[0141] The properties of the engine oil were also evaluated before and after each 50-hour interval, as illustrated in FIG. **5**. Oil viscosity, flash point, and metals content were tested and showed little impact from the test fuel.

[0142] The oil viscosity increased between 5 and 7 centistokes after 50 hours of operation, showed no signs of dilution, and flash points decreased between 3 and 14° C. (1-5% decrease) which confirms that little dilution had occurred.

[0143] These tests demonstrate that the fuels are "drop-in replacements" for 100LL in turbocharged piston engines and meet all critical ASTM D910 parameters.

[0144] Overall, the present disclosure provides aviation fuel compositions comparable to that of current market fuels (e.g., 100LL), but without the need for lead content. The aviation fuel compositions presented herein are formulated to be compositionally compatible with 100LL, such that the aviation fuel compositions discussed herein are considered "drop-in" replacements for 100LL. Additionally, the aviation fuel compositions disclosed herein offer increased photostability over that of 100LL. Such aviation fuel compositions offer an easily substituted, lead-free replacement for the current aviation fleet.

[0145] The phrases, unless otherwise specified, "consists essentially of" and "consisting essentially of" do not exclude the presence of other steps, elements, or materials, whether or not, specifically mentioned in this specification, so long as such steps, elements, or materials, do not affect the basic and novel characteristics of the present disclosure, additionally, they do not exclude impurities and variances normally associated with the elements and materials used.

[0146] Numerical ranges used herein include the numbers recited in the range. For example, the numerical range "from 1 wt % to 10 wt %" includes 1 wt % and 10 wt % within the recited range.

[0147] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0148] All numerical values within the detailed description herein are modified by "about" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0149] All documents described herein are incorporated by reference herein, including any priority documents and or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the present disclosure have been illustrated and described, various modifications can be made without departing from the spirit and scope of the present disclosure. Accordingly, it is not intended that the present disclosure be limited thereby. Likewise, the term "comprising" is considered synonymous with the term "including" for purposes of United States law. Likewise, whenever a composition, an element or a group of elements is preceded with the transitional phrase "comprising," it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of," "selected from the group of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

[0150] While the present disclosure has been described with respect to a number of embodiments and examples, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope and spirit of the present disclosure.

1. A composition, comprising:
- about 81 vol % to about 87 vol % of isooctane;
- about 10 vol % to about 18 vol % of a dialkyl ether compound, wherein the dialkyl ether compound is selected from ethyl-tert-butyl-ether, methyl-tert-butyl-ether, and combinations thereof; and
- about 1.5 vol % or less of methanol;
- about 1.8-3.2 wt % total oxygen content as determined in accordance to ASTM D4815.

2. The composition of claim **1**, wherein the composition further comprises a manganese containing compound.

3. The composition of claim **2**, wherein the composition comprises about 5 mg manganese per liter (mg Mn/L) to about 25 mg Mn/L of the manganese containing compound of.

4. The composition of claim **2**, wherein the manganese containing compound comprises methylcyclopentadienyl manganese tricarbonyl (MMT).

5. The composition of claim **4**, wherein the composition comprises about 5 mg manganese per liter (mg Mn/L) to about 25 mg Mn/L of MMT.

6. The composition of claim **2**, wherein the composition further comprises an oil-soluble alkanoic acid.

7. The composition of claim **6**, wherein the oil-soluble alkanoic acid is selected from 2-ethylhexanoic acid, 2-methylhexanoic acid, 3-ethylhexanoic acid, 3-methylhexanoic acid, 4-methylhexanoic acid, 4-ethylpentanoic acid, 4-ethylpentanoic acid, and combinations thereof.

8. The composition of claim **6**, wherein the composition comprises about one part by weight of the oil-soluble alkanoic acid per fifteen parts by weight manganese to about one part by weight alkanoic acid per one part by weight manganese.

9. The composition of claim **1**, wherein the composition further includes an oil-soluble valve seat recession additive (VSRA).

10. The composition of claim **9**, wherein the oil-soluble VSRA is selected from potassium 2-ethylhexyl hexanoate, sodium 2-ethylhexyl hexanoate, and combinations thereof.

11. The composition of claim **10**, wherein the oil-soluble VSRA comprises about 10 mg potassium per liter (mg K/L) to about 20 mg K/L potassium 2-ethylhexyl hexanoate.

12. The composition of claim **1**, comprising about 0.5 vol % to about 1 vol % of methanol.

13. The composition of claim **1**, comprising about 12 vol % to about 15 vol % of the dialkyl ether compound.

14. The composition of claim **1**, comprising about 81 vol % to about 84 vol % of the isooctane.

15. The composition of claim **1**, wherein the composition has a motor octane number (MON; as determined in accordance to ASTM D2700) greater than 99.6.

16. The composition of claim **1**, wherein the composition has a motor octane number (MON; as determined in accordance to ASTM D2700) of about 99.6 to about 105.6.

17. The composition of claim **2**, wherein the composition has a motor octane number (MON; as determined in accordance to ASTM D2700) greater than 99.6.

18. The composition of claim **1**, wherein the composition is substantially free from aromatic compounds and isopentane.

19. A composition, consisting essentially of:
- about 81 vol % to about 87 vol % of isooctane;
- about 10 vol % to about 18 vol % of a dialkyl ether compound, wherein the dialkyl ether compound is selected from ethyl-tert-butyl-ether, methyl-tert-butyl-ether, and combinations thereof; and
- about 1.5 vol % or less of methanol;
- about 1.8-3.2 wt % total oxygen content as determined in accordance to ASTM D4815.

20. A composition, consisting of:
- about 81 vol % to about 87 vol % of isooctane;
- about 10 vol % to about 18 vol % of a dialkyl ether compound, wherein the dialkyl ether compound is selected from ethyl-tert-butyl-ether, methyl-tert-butyl-ether, and combinations thereof; and
- about 1.5 vol % or less of methanol;
- about 1.8-3.2 wt % total oxygen content as determined in accordance to ASTM D4815.

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