

TITLE OF THE INVENTION

METHODS AND SYSTEMS USING 1,1-DIFLUOROPROPENE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application 63/527,179 filed July 17, 2023, and U.S. Provisional Application 63/565,030 filed March 14, 2024, the disclosure of each of which is incorporated herein by reference in its entirety.

FIELD

[0002] The present invention is directed to compositions containing 1,1-difluoropropene for use in automobile heat pumps for electric vehicles.

BACKGROUND

[0003] The automotive industry is going through an architecture platform rejuvenation from using an internal combustion engine (ICE) for propulsion to using electric motors for propulsion. This platform rejuvenation is severely limiting the size of the internal combustion engine (ICE) in hybrid, plug-in hybrid vehicles or possibly eliminating the ICE altogether in pure electric vehicles. Some vehicles still maintain an ICE and are noted as hybrid electric vehicle (HEV) or plug-in hybrid electric vehicles (PHEV) or mild hybrid electric vehicles (MHEV). Vehicles which are fully electric and have no ICE are denoted as full electric vehicles (EV), including battery electric vehicles (BEV). All HEV, PHEV, MHEV and EVs use at least one electric motor, where the electric motor provides some form of propulsion for the vehicles normally provided by the internal combustion engine (ICE) found in gasoline/diesel powered vehicles.

[0004] In electrified vehicles, the ICE is typically reduced in size (HEV, PHEV, or MHEV) or eliminated (EV) to reduce vehicle weight thereby increasing the electric drive-cycle. While the ICE's primary function is to provide vehicle propulsion, it also provides heat to the passenger cabin as a secondary function. Typically, heating is required when ambient conditions are 10°C or lower. In a non-electrified vehicle, there is excess heat from the ICE, which can be scavenged and used to heat the

passenger cabin. It should be noted that the ICE may take some time (several minutes) to heat up and generate heat. Therefore, in electrified vehicles, ICE size reduction or elimination is creating a demand for effective alternative heating of the passenger cabin. In current EVs, with no ICE, positive temperature coefficient (PTC) heaters are currently being used. Use of a heat pump for cooling and heating can replace or reduce dependency on the PTC heater and allow more efficient cooling and heating. In addition to heating and cooling of the passenger cabin, electrified vehicles also introduce the need for heating and cooling of vehicle components, such as the battery, power electronics, and electric motors.

[0005] Due to environmental pressures, HFC-134a, a hydrofluorocarbon or HFC, has been phased out for automobile air conditioning in favor of lower global warming potential (GWP) HFO-1234yf with GWP < 150. While HFO-1234yf, a hydrofluoro-olefin, meets the low GWP requirement (GWP =4 per Pappadimitriou and GWP <1 per AR5), it has lower refrigeration capacity and efficiency compared to R-134a and may not fully meet the heating requirements at low temperatures (e.g., lower than -10°C).

[0006] Therefore, there is a need in this art for new refrigerants that meet evolving regulations as well as provide heat transfer and thermodynamic characteristics that meet or exceed the effectiveness of conventional refrigerants, and extend the operating window to lower ambient temperatures for further reduction in the dependency on lower efficiency PTC heaters. There is a need for low GWP heat pump type fluids to meet the ever-increasing needs of hybrid, mild hybrid, plug-in hybrid and electric vehicles, electrified mass transit, and residential and commercial structures for thermal management which can provide both cooling and heating.

[0007] The instant invention solves certain problems associated with conventional refrigerants and provides compositions which meet the evolving regulatory landscape.

SUMMARY

[0008] The present invention relates to use of environmentally friendly refrigerants with low GWP, (GWP less than or equal to 100), preferably with low toxicity (class A or B per ANSI/ASHRAE standard 34 or ISO standard 817)), and also preferably low

flammability (class 2 or class 2L per ASHRAE 34 or ISO 817) with zero to low temperature glide for use in a hybrid, mild hybrid, plug-in hybrid, or full electric vehicles for complete vehicle thermal management (transferring heat from one part of the vehicle to another). The thermal management system may operate to provide cooling and/or heating of the power electronics, battery, motor and provide air conditioning (A/C) and/or heating to the passenger cabin. These refrigerants can also be used for mass transit mobile applications which benefit from a heat pump type system enabling both heating and cooling of batteries, motors and passenger compartment areas. Mass transit mobile applications are not limited to, but can include transport vehicles such as ambulances, buses, shuttles, and trains.

[0009] In one aspect of the invention the refrigerant for use in electric vehicles includes refrigerant comprising HFO-1252zc (1,1-difluoropropene, R-1252zc, $\text{CH}_3\text{-CH=CF}_2$).

[0010] The present inventors have discovered refrigerant comprising HFO-1252zc provides volumetric capacity more than 12% higher than HFO-1234yf alone under conditions defined by the SAE (Society of Automotive Engineers), COP significantly higher than the COP of HFO-1234yf alone, with zero to low average temperature glide, and that would be classified as class 3 flammability by ASHRAE (American Society of Heating, Refrigeration, and Air Conditioning Engineers). If blended with other lower flammability refrigerants, it may be possible to produce refrigerant blends comprising HFO-1252zc with class 2 or class 2L flammability.

[0011] In one embodiment, methods are provided for cooling and heating a passenger compartment of an electric or hybrid vehicle using a heat pump comprising providing a composition comprising HFO-1252zc as refrigerant to the heat pump.

[0012] According to any of the foregoing embodiments, also disclosed herein are systems for heating and cooling the passenger compartment of an electric or hybrid vehicle, comprising HFO-1252zc and optionally a lubricant. In another embodiment, the system comprises an evaporator, compressor, condenser and expansion device, each operably connected to perform a vapor compression cycle. In another embodiment, the system does not include a PTC heater. In another embodiment, system is a secondary loop system.

[0013] According to any of the foregoing embodiments, also disclosed herein are methods for replacing HFO-1234yf or HFC-134a in a heating and cooling system contained within an electric or hybrid vehicle, comprising providing a composition comprising HFO-1252zc as refrigerant. In another embodiment, the refrigerant produces volumetric capacity at least 10% higher, preferably, at least 12% higher than HFO-1234yf alone when operating under the same conditions. In another embodiment, the refrigerant produces COP at least 6% higher, preferably, at least 8% higher than the COP of HFO-1234yf alone when operating under the same conditions.

[0014] According to any of the foregoing embodiments, also disclosed herein is use of a composition comprising HFO-1252zc as refrigerant in heat pumps for thermal management in electric or hybrid vehicles. In another embodiment, thermal management comprises cooling and heating of the passenger compartment of the electric or hybrid vehicles.

[0015] According to any of the foregoing embodiments, also disclosed herein are methods wherein the composition further comprises at least one additional compound selected from HCFC-22, HFC-23, HCC-30, HCFC-31, HCC-40, HFC-41, methane, HFC-125, HFC-143, HFC-143a, HFC-152a, HFC-245cb, HCFC-253dc, HFC-254fb, HCC-260fb, HCFC-261fc, HCFC-262fc, HFC-263fb, HFC-272fb, propane, HFO-374, n-butane, allene, 2-butene, cyclobutene, 2-methyl propene, HCFO-1122, HFO-1132, HFO-1132a, HFO-1141, ethylene, HCFO-1233xf, HFO-1234yf, HCFO-1242zf, HFO-1243zf, HCFO-1251, HCO-1260zf, HFO-1261zf, propylene, HFO-1345, HFO-1252ze, HFO-1252yf, HFO-1252zf, HFO-1252ye, and E/Z-t-BuO-CF=CH-CH₃. In another embodiment, the total amount of additional compounds is greater than zero and less than 1 weight percent.

[0016] According to any of the foregoing embodiments, also disclosed herein are methods wherein the composition further comprises at least one additional compound selected from HFO-1234yf, HFO-1243zf, HFC-263fb, HFO-1252ze, HFO-1252yf, HFO-1252zf, and HFO-1252ye.

[0017] According to any of the foregoing embodiments, also disclosed herein are methods or systems wherein the compositions are determined to be class 3, for flammability as defined in ANSI/ASHRAE Standard 34.

[0018] According to any of the foregoing embodiments, also disclosed herein are methods or systems wherein the composition has an LFL of less than 10 volume percent when measured in accordance with ASTM-E681.

[0019] According to any of the foregoing embodiments, also disclosed herein are methods or systems wherein the composition further comprises a lubricant.

[0020] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein said lubricant is at least one selected from the group consisting of polyalkylene glycol, polyol ester, poly- α -olefin, and polyvinyl ether.

[0021] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein the lubricant is a polyol ester lubricant and is obtained by reacting a carboxylic acid with a polyol comprising a neopentyl backbone selected from the group consisting of neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and mixtures thereof. In another embodiment, the carboxylic acid has 2 to 18 carbon atoms.

[0022] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein said lubricant has at least one property selected from volume resistivity of greater than 10^{10} Ω -m at 20 °C; surface tension of from about 0.02 N/m to 0.04 N/m at 20 °C; kinematic viscosity of from about 20 cSt to about 500 cSt at 40 °C; a breakdown voltage of at least 25 kV; and a hydroxy value of at most 0.1 mg KOH/g.

[0023] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein said composition further comprises from 0.1 to 200 ppm by weight of water; from about 10 ppm by volume to about 0.35 volume percent oxygen; and/or from about 100 ppm by volume to about 1.5 volume percent air.

[0024] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein said composition further comprises a stabilizer.

[0025] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein said composition further comprises a stabilizer selected from the group consisting of nitromethane, ascorbic acid, terephthalic acid, azoles, phenolic compounds, cyclic monoterpenes, terpenes, phosphites, phosphates, phosphonates, thiols, and lactones.

[0026] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein said composition further comprises a stabilizer selected from tolutriazole, benzotriazole, tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-terbutyl-4-methylphenol, fluorinated epoxides, n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, d-limonene, α -terpinene, β -terpinene, α -pinene, β -pinene, or butylated hydroxytoluene.

[0027] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein said composition further comprises a stabilizer that is present in an amount from about 0.001 to 1.0 weight percent based on the weight of the refrigerant.

[0028] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein said composition further comprises at least one tracer.

[0029] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein said composition further comprises at least one tracer that is present in an amount from about 1.0 ppm by weight to about 1000 ppm by weight.

[0030] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein said composition further comprises at least one tracer that is selected from hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof.

[0031] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein said composition further comprises at least one tracer that is selected from HFC-23, HCFC-31, HFC-41, HFC-161, HFC-143a, HFC-134a, HFC-125, HFC-236fa, HFC-236ea, HFC-245cb, HFC-245fa, HFC-254eb, HFC-263fb, HFC-272ca, HFC-281ea, HFC-281fa, HFC-329p, HFC-329mmz, HFC338mf, HFC-338pcc, CFC-12, CFC-11, CFC-114, CFC-114a, HCFC-22, HCFC-123, HCFC-124, HCFC-124a, HCFC-141b, HCFC-142b, HCFC-151a, HCFC-244bb, HCC-40, HFO-1141, HCFO-1130, HCFO-1130a, HCFO-1131, HCFO-1122, HFO-1123, HFO-1234yf, HFO-1234ye, HFO-1243zf, HFO-1225ye, HFO-1225zc, PFC-116, PFC-

C216, PFC-218, PFC-C318, PFC-1216, PFC-31-10mc, PFC-31-10my, and combinations thereof.

[0032] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein the composition further comprises a UV dye.

[0033] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein the composition comprises a UV dye selected from the group consisting of naphthalimides, perylenes, coumarins, anthracenes, phenanthracenes xanthenes, thioxanthenes, naphthoxanthenes, fluoresceins, and derivatives or combinations thereof.

[0034] According to any of the foregoing embodiments, also disclosed herein are methods or systems, wherein the composition is free of or substantially free of Group A Fluorinated Substances, and wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] FIG. 1 illustrates a reversible cooling or heating loop system, according to an embodiment.

[0036] FIG. 2 illustrates a reversible cooling or heating loop system, according to an embodiment.

[0037] FIG. 3 illustrates a cooling or heating loop system, according to an embodiment.

[0038] FIG. 4 illustrates a reversible cooling or heating loop system, according to an embodiment.

[0039] FIG. 5 illustrates a reversible cooling or heating loop system, according to an embodiment.

[0040] FIG. 6 illustrates a cooling or heating system, according to an embodiment.

[0041] FIG. 7 illustrates a cooling or heating system, according to an embodiment.

[0042] FIG. 8 illustrates a cooling or heating system, according to an embodiment.

[0043] FIG. 9 illustrates a cooling or heating system, according to an embodiment.

[0044] FIG. 10 illustrates an embodiment of a secondary loop cooling and heating system for electric and hybrid vehicles.

DETAILED DESCRIPTION

Definitions

[0045] As used herein, electric and hybrid vehicles is meant to include hybrid electric vehicle (HEV) or plug-in hybrid electric vehicles (PHEV) or mild hybrid electric vehicles (MHEV), as well as vehicles, which are fully electric and have no internal combustion engine (ICE), such as full electric vehicles (EV), and including battery electric vehicles (BEV).

[0046] As used herein, the term heat transfer composition or heat transfer fluid means a composition used to carry heat from a heat source to a heat sink.

[0047] A heat source is defined as any space, location, object, or body from which it is desirable to add, transfer, move or remove heat. Example of a heat source in this embodiment is the vehicle passenger compartment requiring air conditioning.

[0048] A heat sink is defined as any space, location, object, or body capable of absorbing heat. Example of a heat sink in this embodiment is the vehicle passenger compartment requiring heating.

[0049] A heat transfer system is the system (or apparatus) used to produce a heating or cooling effect in a particular location. A heat transfer system in this invention implies the heating or cooling system which provides heating or cooling of the passenger compartment of an automobile. Sometimes this system is called a heat pump system and may be a reversible heating system or a reversible cooling system, or simply a heating and cooling system.

[0050] A heat transfer fluid comprises at least one refrigerant and at least one member selected from the group consisting of lubricants, stabilizers, tracers, UV dyes, and flame suppressants.

[0051] Volumetric capacity is the amount of heat absorbed or rejected divided by the theoretical compressor displacement. Heat removed or absorbed is the enthalpy difference across a heat exchanger multiplied by the refrigerant mass flowrate.

Theoretical compressor displacement is the refrigerant mass flowrate divided by the density of the gas entering the compressor (i.e., compressor suction density). More simply, volumetric capacity is the suction density multiplied by the heat exchanger enthalpy difference. Higher volumetric capacity allows the use of a smaller compressor for the same heat load. Herein, cooling capacity refers to the volumetric capacity in cooling mode and heating capacity refers to the volumetric capacity in heating mode.

[0052] Coefficient of performance (COP) is the amount of heat absorbed or rejected divided by the required energy input to operate the cycle (approximated by the compressor power). COP is specific to the mode of operation of a heat pump, thus COP for heating or COP for cooling. COP is directly related to the energy efficiency ratio (EER).

[0053] Subcooling refers to the reduction of the temperature of a liquid below that liquid's saturation point for a given pressure. The liquid saturation point is the temperature at which the vapor is completely condensed to a liquid. By cooling a liquid below the saturation temperature (or bubble point temperature), the net refrigeration effect can be increased. Subcooling thereby improves refrigeration capacity and energy efficiency of a system. The subcool amount is the amount of cooling below the saturation temperature (in degrees).

[0054] Superheating refers to the increase of the temperature of a vapor above that vapor's saturation point for a given pressure. The vapor saturation point is the temperature at which the liquid is completely evaporated to a vapor. Superheating continues to heat the vapor to a higher temperature vapor at the given pressure. By heating the vapor above the saturation temperature (or dew point temperature), the net refrigeration effect can be increased. Superheating thereby improves refrigeration capacity and energy efficiency of a system when it occurs in the evaporator. Suction line superheat does not add to the net refrigeration effect and can reduce efficiency and capacity. The superheat amount is the amount of heating above the saturation temperature (in degrees).

[0055] Temperature glide (sometimes referred to simply as "glide") is the absolute value of the difference between the starting and ending temperatures of a phase-change process by a refrigerant within a condenser of a refrigerant system, exclusive

of any subcooling or superheating. For an evaporator, the glide is the difference in temperature between the dew point and the evaporator inlet. Glide may be used to describe condensation or evaporation of a near azeotrope or non-azeotropic composition. When referring to the temperature glide of an air conditioning or heat pump system, it is common to provide the average temperature glide being the average of the temperature glide in the evaporator and the temperature glide in the condenser. Glide is applicable to blend refrigerants, i.e. refrigerants that are composed of at least 2 components. Single component refrigerants have zero temperature glide in evaporators and condensers.

[0056] 1,1-Difluoropropene (HFO-1252zc or R-1252zc) may be prepared by hydrogenation of 3,3,3-trifluoropropene (HFO-1243zf) over palladium on carbon catalyst to form 1,1,1-trifluoropropene (HFC-263fb) followed by dehydrofluorination of the HFC-263fb over chrome catalyst or by pyrolysis at high temperatures (see attorney docket number FL2084 (U.S. Provisional Patent Application No. 63/527,133), herein incorporated by reference).

[0057] As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a composition, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, process, method, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0058] The transitional phrase “consisting of” excludes any element, step, or ingredient not specified. If in the claim such would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase “consists of” appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

[0059] The transitional phrase "consisting essentially of" is used to define a composition, method that includes materials, steps, features, components, or elements, in addition to those literally disclosed provided that these additional included materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention, especially the mode of action to achieve the desired result of any of the processes of the present invention. The term 'consisting essentially of' occupies a middle ground between "comprising" and 'consisting of'.

[0060] Where applicants have defined an invention or a portion thereof with an open-ended term such as "comprising," it should be readily understood that (unless otherwise stated) the description should be interpreted to also include such an invention using the terms "consisting essentially of" or "consisting of" including, for example, a composition consisting essentially of or consisting of.

[0061] Also, use of "a" or "an" are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

Refrigerant Composition

[0062] Global warming potential (GWP) is an index for estimating relative global warming contribution due to atmospheric emission of a kilogram of a particular greenhouse gas compared to emission of a kilogram of carbon dioxide. GWP can be calculated for different time horizons showing the effect of atmospheric lifetime for a given gas. The GWP for the 100-year time horizon is commonly the value referenced. For mixtures, a weighted average can be calculated based on the individual GWPs for each component. The United Nations Intergovernmental Panel on Climate Change (IPCC) provides vetted values for refrigerant GWPs in official assessment reports (ARs.) The fourth assessment report is denoted as AR4 and the fifth assessment report is denoted as AR5. The GWP of HFO-1252zc is estimated at 1.

[0063] Ozone-depletion potential (ODP) is a number that refers to the amount of ozone depletion caused by a substance. The ODP is the ratio of the impact on ozone of a chemical compared to the impact of a similar mass of R-11 or trichlorofluoromethane. R-11 is a type of chlorofluorocarbon (CFC) and as such has chlorine in it which contributes to ozone depletion. Furthermore, the ODP of CFC-11 is defined to be 1.0. Other CFCs and hydrofluorochlorocarbons (HCFCs) have ODPs that range from 0.01 to 1.0. Hydrofluorocarbons (HFCs) and the hydrofluoroolefins (HFOs) described herein have zero ODP because they do not contain chlorine, bromine or iodine, species known to contribute to ozone breakdown and depletion. HFO-1252zc has zero ozone depletion potential.

[0064] The composition for use as refrigerant in thermal management of hybrid and electric vehicles and for use in the present inventive methods and systems comprises HFO-1252zc.

[0065] In one embodiment, the composition comprising, consisting of, or consisting essentially of HFO-1252zc provides capacity and COP higher than HFO-1234yf (2,3,3,3-tetrafluoropropene). In another embodiment, the composition comprising, consisting of, or consisting essentially of HFO-1252zc provides capacity and COP at least 10% higher than HFO-1234yf when the results are averages from the SAE 14 sets of conditions. In another embodiment, the composition comprising, consisting of, or consisting essentially of HFO-1252zc provides capacity and COP at least 20% higher than HFO-1234yf under these same conditions. In another embodiment, the composition comprising, consisting of, or consisting essentially of HFO-1252zc provides capacity and COP at least 30% higher than HFO-1234yf under these same conditions.

[0066] As a single compound, HFO-1252zc produces zero temperature glide in the heat exchangers (e.g., evaporators and condensers). Additionally, there is no fractionation or shifting of the composition during operation.

[0067] Flammability is a term used to mean the ability of a composition to ignite and/or propagate a flame. For refrigerants and other heat transfer compositions or working fluids, the lower flammability limit ("LFL") is the minimum concentration of the heat transfer composition in air that is capable of propagating a flame through a homogeneous mixture of the composition and air under test conditions specified in

ASTM (American Society of Testing and Materials) E681. The upper flammability limit ("UFL") is the maximum concentration of the heat transfer composition in air that is capable of propagating a flame through a homogeneous mixture of the composition and air under the same test conditions.

[0068] In order to be classified by ANSI/ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) Standard 34 or ISO 817 ISO 817:2014(en) Refrigerants — Designation and Safety Classification as non-flammable (class 1, no flame propagation), a refrigerant must not show flame propagation when tested in air at 140 Deg F (60 deg C) and 14.7 psia (101.3 kPa).

[0069] In order for a refrigerant to be classified by ANSI/ASHRAE as low flammability (class 2L), it must: 1) exhibit flame propagation when tested at 140°F (60°C) and 14.7 psia (101.3 kPa); 2) have an LFL >0.0062 lb/ft³ (0.10 kg/m³); 3) have a heat of combustion <8169 Btu/lb (19,000 kJ/kg); and 4) have a maximum burning velocity of ≤3.9 in./s (10 cm/s) when tested at 73.4°F (23.0°C) and 14.7 psia (101.3 kPa) in dry air.

[0070] In order for a refrigerant to be classified by ANSI/ASHRAE as flammable (class 2), it must: 1) exhibit flame propagation when tested at 140°F (60°C) and 14.7 psia (101.3 kPa); 2) have an LFL >0.0062 lb/ft³ (0.10 kg/m³); and 3) have a heat of combustion <8169 Btu/lb (19,000 kJ/kg).

[0071] ASHRAE Standard 34 provides a methodology to calculate the heat of combustion for refrigerant blends using a balanced stoichiometric equation based on the complete combustion of one mole of refrigerant with enough oxygen for a stoichiometric reaction.

[0072] HFO-1252zc is estimated as being class 3 flammability as defined by ANSI/ASHRAE standard 34 and ISO 817. Class 3 flammability can be managed in automotive heating/cooling systems.

[0073] As a class 3 flammability refrigerant HFO-1252zc may require use of a secondary loop heat pump.

[0074] In embodiments, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc may further comprise additional compounds. The

additional compounds are present in an amount of greater than about 0 and less than 1 wt. %.

[0075] The compositions comprising, consisting of, or consisting essentially of HFO-1252zc may further comprise at least one additional compound from the list in Table 1.

Table 1

Code	Name-ASHRAE Designation	Formula
R-22	Chlorodifluoromethane	CHF_2Cl
R-23	trifluoromethane (HFC-23)	CHF_3
R-30	dichloromethane (HCC-30)	CH_2Cl_2
R-31	chlorofluoromethane (HCFC-31)	CH_2FCl
R-40	methyl chloride (HCC-40)	CH_3Cl
R-41	fluoromethane (HFC-41)	CH_3F
R-50	Methane	CH_4
R-125	1,1,2,2,2-pentafluoroethane (HFC-125)	CF_2CF_3
R-143	1,1,2-trifluoroethane (HFC-143)	$\text{CF}_2\text{CH}_2\text{F}$
R-143a	1,1,1-trifluoroethane (HFC-143a)	CF_3CH_3
R-152a	1,1-difluoroethane (HFC-152a)	CHF_2CH_3
R-245cb	1,1,1,2,2-pentafluoropropane (HFC-245cb)	$\text{CF}_3\text{CF}_2\text{CH}_3$
R-253dc	2-chloro-1,1,1-trifluoropropane (HCFC-253dc)	$\text{CF}_3\text{CHClCH}_3$
R-254fb	1,1,1,3-tetrafluoropropane (HFC-254fb)	$\text{CF}_3\text{CH}_2\text{CH}_2\text{F}$
R-260fb	1,1,1-trichloropropane (HCC-260fb)	$\text{CCl}_3\text{CH}_2\text{CH}_3$
R-261fc	1,1-dichloro-1-fluoropropane (HCFC-261fc)	$\text{CCl}_2\text{FCH}_2\text{CH}_3$
R-262fc	1-chloro-1,1-difluoropropane (HCFC-262fc)	$\text{CClF}_2\text{CH}_2\text{CH}_3$
R-263fb	1,1,1-trifluoropropane (HFC-263fb)	$\text{CF}_3\text{CH}_2\text{CH}_3$
R-272fb	1,1-difluoropropane (HFC-272fb)	$\text{CHF}_2\text{CH}_2\text{CH}_3$
R-290	propane (HC-290)	$\text{CH}_3\text{CH}_2\text{CH}_3$
R-374	tetrafluorobutene (HFO-374)	$\text{C}_4\text{H}_6\text{F}_4$
R-600	butane (HC-600)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
	Allene	$\text{H}_2\text{C}=\text{C}=\text{CH}_2$
	2-butene	$\text{CC}_3\text{CH}=\text{CHCH}_3$
	Cyclobutene	C_4H_6
	2-methylpropene	$\text{CH}_3(\text{CH}_3)\text{C}=\text{CF}_3$
R-1122	1-chloro-2,2-difluoroethylene (HCFO-1122)	$\text{CHCl}=\text{CF}_2$
R-1132	1,2-difluoroethene (HFO-1132)	$\text{CHF}=\text{CHF}$
R-1132a	1,1-difluoroethene ((HFO-1132a)	$\text{CH}=\text{CF}_2$
R-1141	fluoroethene (HFO-1141)	$\text{CH}_2=\text{CHF}$
R-1150	ethylene (HO-1150)	$\text{CH}_2=\text{CH}_2$
R-1243zf	3,3,3-trifluoropropene	$\text{CF}_3\text{CH}=\text{CH}_2$
R-1233xf	2-chloro-3,3,3-trifluoropropene (HCFO-1233xf)	$\text{CF}_3\text{CCl}=\text{CH}_2$
R-1234yf	2,3,3,3-tetrafluoropropene(HFO-1234yf)	$\text{CF}_3\text{CH}=\text{CHF}$
R-1242zf	3-chloro-3,3-difluoropropene (HCFO-1242zf)	$\text{CClF}_2\text{CH}=\text{CH}_2$

Code	Name-ASHRAE Designation	Formula
R-1243zf	3,3,3-trifluoropropene (HFO-1243zf)	$\text{CF}_3\text{CH}=\text{CH}_2$
R-1251	HCFO-1251 isomer	$\text{C}_3\text{H}_4\text{FCl}$
R-1251	HCFO-1251 isomer	$\text{C}_3\text{H}_4\text{FCl}$
R-1252ze	1,3-difluoropropene (HFO-1252ze)	$\text{CH}_2\text{FCH}=\text{CHF}$
R-1252yf	2,3-difluoropropene (HFO-1252yf)	$\text{CH}_2\text{FCF}=\text{CH}_2$
R-1252zf	3,3-difluoropropene (HFO-1252zf)	$\text{CHF}_2\text{CH}=\text{CH}_2$
R-1252ye	1,2-difluoropropene (HFO-1252ye)	$\text{CH}_3\text{CF}=\text{CHF}$
R-1252zc	1,1-difluoropropene (HFO-1252zc)	$\text{CH}_3\text{CH}=\text{CF}_2$
R-1260zf	3-chloropropene (HCO-1260zf)	$\text{CH}_2\text{ClCH}=\text{CH}_2$
R-1261	3-fluoro-1-propene (HFO-1261)	$\text{CH}_2\text{FCH}=\text{CH}_2$
R-1270	propylene (HO-1270)	$\text{CH}_3\text{CH}=\text{CH}_2$
R-1345	pentafluorobutene (HFO-1345)	$\text{C}_4\text{H}_3\text{F}_5$
	E/Z- <i>t</i> -BuO-CF=CH-CH ₃	E/Z- <i>t</i> -BuO-CF=CH-CH ₃

[0076] In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc may further comprise at least one additional compound selected from HCFC-22, HCC-40, HFO-1234yf, HFO-1243zf, HFO-263fb, HFO-1252ze, HFO-1252yf, HFO-1252zf, and HFO-1252ye. In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc may further comprise at least one additional compound comprising HFO-1234yf. In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc may further comprise at least one additional compound comprising HFO-1243zf. In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc may further comprise at least one additional compound comprising HFO-263fb.

[0077] Some of the compounds present in the compositions of the present invention identified in Table 1 may exist as different configurational isomers or stereoisomers. The present invention is intended to include all single configurational isomers, single stereoisomers or any combination or mixture thereof. For instance, 1,2-difluoroethene (HFO-1132) is meant to represent the cis-isomer (Z), trans-isomer (E), or any combination or mixture of both isomers in any ratio. Single isomers or multiple isomers of the same compound may be used in any proportion.

[0078] The amount of additional compounds present in any of the foregoing refrigerant compositions can be greater than 0 ppm and less than 5,000 ppm and, in

particular, can range from greater than zero to about 1,000 ppm, about 5 to about 500 ppm and about 1 to about 100 ppm.

[0079] In one embodiment, the amount of additional compounds present in any of the foregoing refrigerant compositions can be greater than 0 and less than 1 wt% of the refrigerant composition, preferably less than 0.5 weight percent, or more preferably less than 0.1 weight percent.

[0080] Another embodiment of the invention relates to storing any of the foregoing compositions in gaseous and/or liquid phases within a sealed container. The water concentration within the gas and/or liquid phase in the sealed container ranges from about 0.1 to 200 ppm by weight. The oxygen concentration within the gas and/or liquid phase in the sealed container ranges from about 10 ppm by volume to about 0.35 volume percent at about 25 C. The air concentration within the gas and/or liquid phase in the sealed container ranges from about 100 ppm by volume to about 1.5 volume percent.

[0081] In one embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that (i) contains at least one fully fluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) carbon atom (without any H/Cl/Br/I attached to it); and (ii) meets the criterion for persistence in soil/sediment and water established in Annex XIII (Section 1.1.1) of the European Union's REACH Regulation (<https://reachonline.eu/reach/en/annex-xiii-1-1.1-1.1.1.html> as accessed on May 2, 2023) and referenced in the Annex XV Restriction Report dated March 22, 2023, the disclosure of which is hereby incorporated by reference (<https://echa.europa.eu/documents/10162/f605d4b5-7c17-7414-8823-b49b9fd43aea> as accessed on May 2, 2023). In one embodiment, Group A Fluorinated Substances include, but are not limited to, trifluoroacetic acid (TFA).

[0082] In another embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that has a Henry's Law constant $\leq 250 \text{ Pa}\cdot\text{m}^3/\text{mol}$ and contains at least one fully fluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) carbon atom (without any H/Cl/Br/I attached to it). In one embodiment, Group A Fluorinated Substances include, but are not limited to, TFA.

[0083] Thus, according to some embodiments, compositions of the present invention which comprise, consist of, or consist essentially of HFO-1252zc, and are

free of or substantially free of Group A Fluorinated Substances, such as TFA. In one embodiment, the phrase "free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by gas chromatography with a flame ionization detector, gas chromatography with a mass detector by analysis of a gas sample or liquid sample, and/or ion chromatography by analysis of a water sample after bubbling the thermal fluid through water. Such methodologies are well known to those skilled in the art. In one embodiment, the phrase "substantially free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is > 0 wt.% and ≤ 5 wt.%, or > 0 wt.% and ≤ 4 wt.%, or > 0 wt.% and ≤ 3 wt.%, or > 0 wt.% and ≤ 2 wt.%, or > 0 wt.% and ≤ 1 wt.%, and all values and ranges therebetween, when measured by gas chromatographic (GC) techniques, for example gas chromatography (GC) with a flame ionization or electron-capture detector, or GC coupled with a mass detector (gas chromatography/mass spectral (GC/MS) method), by ion chromatograph(IC) or ion chromatography mass spectrometry (IC-MS) techniques, or by high-performance liquid chromatography (HPLC) or high-performance liquid chromatography mass spectrometry (HPLC-MS) techniques. The TFA analytical standard may be used in either gas chromatography or ion chromatography and is available from, for example, Sigma Aldrich.

[0084] Further, in some embodiments, degradation products of such compositions of the present invention which comprise, consist of, or consist essentially of HFO-1252zc are free of or substantially free of Group A Fluorinated Substances, such as TFA. In one embodiment, the phrase "free of" as used herein with respect to the formation of Group A Fluorinated Substances by the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during tropospheric degradation of the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by GC techniques, for example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques. In one embodiment, the phrase "substantially free of" as

used herein with respect to the formation of Group A Fluorinated Substances by the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during tropospheric degradation of the compositions is $> 0\%$ and $\leq 5\%$, or $> 0\%$ and $\leq 4\%$, or $> 0\%$ and $\leq 3\%$, or $> 0\%$ and $\leq 2\%$, or $> 0\%$ and $\leq 1\%$, and all values and ranges therebetween, when measured by GC techniques, for example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques.

Refrigerant Additives

[0085] The compositions of the present invention comprising, consisting of, or consisting essentially of HFO-1252zc may further comprise a lubricant and be used as a heat transfer fluid. The composition of the present invention containing the refrigerant blend of the present invention and the lubricant may contain additives such as a stabilizer, a leakage detection material (e.g., UV dye), a tracer, and other beneficial additives.

[0086] The lubricant chosen for this composition preferably has sufficient solubility in the refrigerant blend to ensure that the lubricant can return to the compressor from the evaporator. Furthermore, the miscibility must not be so great as to reduce the effective viscosity of the lubricant for lubricating the compressor. In one preferred embodiment, the lubricant and refrigerant blend are miscible over a broad range of temperatures. For use in mobile air-conditioning and heating, miscibility over a temperature range from about -40°C to about $+40^{\circ}\text{C}$ is desirable.

[0087] Lubricants of the invention may include polyalkylene glycol lubricants (PAG), polyol ester lubricants (POE), polyvinyl ether lubricants (PVE), and even poly- α -olefins (PAO), alkylbenzenes, mineral oils, fluorinated polyethers, and even silicon lubricants.

[0088] Preferred lubricants may be one or more polyalkylene glycol type lubricants (PAG), one or more polyol ester type lubricants (POE), one or more poly- α -olefins (PAO), or one or more polyvinyl ether lubricants. Additionally, lubricants for combination with HFO-1252zc refrigerant may be mixtures of any of PAG, POE, and/or PVE lubricants.

[0089] Polyalkylene glycol (PAG) oils may be homopolymers or copolymers consisting of two or more oxypropylene groups. PAG oils can be un-capped, single-end capped, or double-end capped. Examples of commercial PAG oils include, but are not limited to ND-8, Castrol PAG 46, Castrol PAG 100, Castrol PAG 150, Daphne Hermetic PAG PL, and Daphne Hermetic PAG PR.

[0090] PAG lubricant properties that make them of use in the present invention include volume resistivity of greater than 10^{10} Ω -m at 20°C, surface tension of from about 0.02 N/m to 0.04 N/m at 20°C, kinematic viscosity of from about 20 cSt to about 500 cSt at 40°C, breakdown voltage of at least 25 kV, and hydroxy value of at most 0.1 mg KOH/g.

[0091] In one embodiment, the lubricant comprises PAG is stable when exposed to HFO-1252zc, has a Total Acid Number (TAN) mg KOH/g number of less than about 1; greater than 0 and less than 1; greater than 0 and less than about 0.75; and, in some cases, greater than 0 and less than about 0.4. In an aspect of this embodiment, the lubricant comprises PAG and the refrigerant comprises, consists of, or consists essentially of HFO-1252zc. And, in a further aspect, the refrigerant composition further comprises greater than about 0 and less than 1 wt.% of additional compounds.

[0092] Preferred lubricants may be one or more polyol ester type lubricants (POE) or one or more polyvinyl ether lubricants (PVE).

[0093] In one embodiment, the compositions comprise, consist of, or consist essentially of HFO-1252zc and POE lubricants. POE lubricants are typically formed by a chemical reaction (esterification) of a carboxylic acid, or a mixture of carboxylic acids, with an alcohol, or mixture of alcohols.

[0094] In one embodiment, the polyol esters as used herein include esters of a diol or a polyol having from about 3 to 20 hydroxyl groups and a carboxylic acid (or fatty acid) having from about 1 to 24 carbon atoms is preferably used as the polyol. An ester which can be used as the base oil is described in EUROPEAN Patent Application published in accordance with Art. 153(4) EP 2 727 980 A1, which is hereby incorporated by reference. Here, examples of the diol include ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,2-butanediol, 2-methyl-1,3-propanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 2-ethyl-2-methyl-1,3-propanediol,

1,7-heptanediol, 2-methyl-2-propyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol, and the like.

[0095] Examples of the above-described polyol include a polyhydric alcohol such as trimethylolethane, trimethylolpropane, trimethylolbutane, di(trimethylolpropane), tri(trimethylolpropane), pentaerythritol, di(pentaerythritol), tri(pentaerythritol), glycerin, polyglycerin (dimer to eicosamer of glycerin), 1,3,5-pentanetriol, sorbitol, sorbitan, a sorbitol-glycerin condensate, adonitol, arabitol, xylitol, mannitol, etc.; a saccharide such as xylose, arabinose, ribose, rhamnose, glucose, fructose, galactose, mannose, sorbose, cellobiose, maltose, isomaltose, trehalose, sucrose, raffinose, gentianose, melezitose, among others; partially etherified products and methyl glucosides thereof; and the like. Among these, a hindered alcohol such as neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolbutane, di(trimethylolpropane), tri(trimethylolpropane), pentaerythritol, di(pentaerythritol), tri(pentaerythritol), etc. is preferable as the polyol

[0096] Though the fatty acid is not particularly limited on its carbon number, in general, a fatty acid having from 1 to 24 carbon atoms is used. In the fatty acid having from 1 to 24 carbon atoms, a fatty acid having 3 or more carbon atoms is preferable, a fatty acid having 4 or more carbon atoms is more preferable, a fatty acid having 5 or more carbon atoms is still more preferable, and a fatty acid having 10 or more carbon atoms is the most preferable from the standpoint of lubricating properties. In addition, a fatty acid having not more than 18 carbon atoms is preferable, a fatty acid having not more than 12 carbon atoms is more preferable, and a fatty acid having not more than 9 carbon atoms is still more preferable from the standpoint of compatibility with the refrigerant. In one embodiment the carboxylic acid has 2 to 18 carbon atoms.

[0097] In addition, the fatty acid may be either of a linear fatty acid and a branched fatty acid, and the fatty acid is preferably a linear fatty acid from the standpoint of lubricating properties, whereas it is preferably a branched fatty acid from the standpoint of hydrolysis stability. Furthermore, the fatty acid may be either of a saturated fatty acid and an unsaturated fatty acid. Specifically, examples of the above-described fatty acid include a linear or branched fatty acid such as pentanoic

acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, icosanoic acid, oleic acid, etc.; a so-called neo acid in which a carboxylic group is attached to a quaternary carbon atom; and the like. More specifically, preferred examples thereof include valeric acid (n-pentanoic acid), caproic acid (n-hexanoic acid), enanthic acid (n-heptanoic acid), caprylic acid (n-octanoic acid), pelargonic acid (n-nonanoic acid), capric acid (n-decanoic acid), oleic acid (cis-9-octadecenoic acid), isopentanoic acid (3-methylbutanoic acid), 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, 3,5,5-trimethylhexanoic acid, and the like. Incidentally, the polyol ester maybe a partial ester in which the hydroxyl groups of the polyol remain without being fully esterified; a complete ester in which all of the hydroxyl groups are esterified; or a mixture of a partial ester and a complete ester, with a complete ester being preferable.

[0098] In the polyol ester, an ester of a hindered alcohol such as neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolbutane, di(trimethylolpropane), tri(trimethylolpropane), pentaerythritol, di(pentaerythritol), tri(pentaerythritol), etc. is more preferable, with an ester of neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolbutane, or pentaerythritol being still more preferable, from the standpoint of more excellent hydrolysis stability; and an ester of pentaerythritol is the most preferable from the standpoint of especially excellent compatibility with the refrigerant and hydrolysis stability.

[0099] Preferred specific examples of the polyol ester include a diester of neopentyl glycol with one kind or two or more kinds of fatty acids selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid; a triester of trimethylolethane with one kind or two or more kinds of fatty acids selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid; a triester of trimethylolpropane with one kind or two or more kinds of fatty acids selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-

methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3, 5, 5-trimethylhexanoic acid; a triester of trimethylolbutane with one kind or two or more kinds of fatty acids selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid; and a tetraester of pentaerythritol with one kind or two or more kinds of fatty acids selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid. Incidentally, the ester with two or more kinds of fatty acids may be a mixture of two or more kinds of esters of one kind of a fatty acid and a polyol, and an ester of a mixed fatty acid of two or more kinds thereof and a polyol, particularly an ester of a mixed fatty acid and a polyol is excellent in low-temperature properties and compatibility with the refrigerant.

[0100] The POE lubricant used for electrified automotive air-conditioning application may have a kinematic viscosity (measured at 40°C, according to ASTM D445) between 20-500 cSt, or 75-110 cSt, and ideally about 80 cSt-100 cSt and most specifically, between 85 cSt-95 cSt. However, not wanting to limit the invention, it should be noted that other lubricant viscosities may be included depending on the needs of the electrified vehicle heat pump compressor. Suitable characteristics of an automotive POE type lubricant for use with the inventive composition are listed in Table 2 below.

TABLE 2

Specification Item	Units	Method	POE Properties
Viscosity at 40°C	cSt	ASTM D445	80-90
Viscosity at 100°C	cSt	ASTM D445	9.0-9.3
Viscosity Index		ASTM D2270	>80
Color	Gardner	ASTM D1500	<1
Flash point (COC)	°C	ASTM 92	250 min
Pour point	°C	ASTM D97	-40 max
Specific Gravity (20°C)	Kg/m ³	ASTM D1298	0.950-1.10
Capping Efficiency	%	ASTM E326	80-90
Total Acid Number	mgKOH/g	ASTM D974	0.1 max
Water content	ppm	ASTM E284	50 max

[0101] In one embodiment, the lubricant comprises POE and the POE is stable when exposed to HFO-1252zc wherein the refrigeration composition has an F-ion of

less than about 500 ppm and in some cases an F-ion amount of greater than 0 and less than 500 ppm, greater than 0 and less than 100 ppm and, in some cases, greater than 0 and less than 50 ppm.

[0102] In one embodiment, the lubricant comprises POE is stable when exposed to the inventive composition wherein the refrigerant blend composition has a Total Acid Number (TAN), mg KOH/g number of less than about 1; greater than 0 and less than 1; greater than 0 and less than about 0.75; and, in some cases, greater than 0 and less than about 0.4. And, in a further aspect, the refrigerant composition further comprises greater than about zero and less than 1 wt.% of additional compounds.

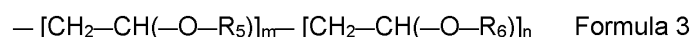
[0103] In one embodiment, the compositions comprise, consist of, or consist essentially of HFO-1252zc and PVE lubricants. Though not meant to limit the scope of the present invention in any way, in an embodiment of the present invention, the polyvinyl ether oil includes those taught in the literature such as described in U.S. Pat. Nos. 5,399,631 and 6,454,960. In another embodiment of the present invention, the polyvinyl ether oil is composed of structural units of the type shown by Formula 1:



where R_1 , R_2 , R_3 , and R_4 are independently selected from hydrogen and hydrocarbons, where the hydrocarbons may optionally contain one or more ether groups. In a preferred embodiment of the present invention, R_1 , R_2 , and R_3 are each hydrogen, as shown in Formula 2:



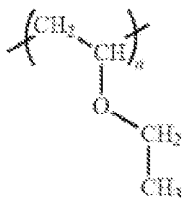
[0104] In another embodiment of the present invention, the polyvinyl ether oil is composed of structural units of the type shown by Formula 3:



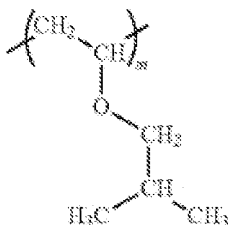
where R_5 and R_6 are independently selected from hydrogen and hydrocarbons and where m and n are integers.

[0105] In one embodiment, the polyvinyl ether oil comprises copolymers of the following 2 units:

Unit 1:



Unit 2:



[0106] The properties of the lubricant (viscosity, solubility of the refrigerant and miscibility with the refrigerant) may be adjusted by varying the m/n ratio and the sum of m+n. In another embodiment, the PVE lubricants are those that are 50-95 weight percent of unit 1.

[0107] In one embodiment, the lubricant comprises PVE is stable when exposed to the inventive composition wherein the refrigerant blend composition has a Total Acid Number (TAN), mg KOH/g number of less than about 1; greater than 0 and less than 1; greater than 0 and less than about 0.75; and, in some cases, greater than 0 and less than about 0.4. In an aspect of this embodiment, the lubricant comprises PVE. And, in a further aspect, the refrigerant composition further comprises greater than about zero and less than 1 wt. % of additional compounds.

[0108] Similar properties and characteristics may be required for use of PVE lubricants in the compositions described herein and, in particular, for use in automotive cooling and heating systems, as for POE lubricants.

[0109] In a preferred embodiment, the lubricant is soluble in the refrigerant at temperatures between about -40°C and about 80°C, and more preferably in the

range of about -30°C and about 40°C, and even more specifically between -25°C and 40°C. In another embodiment, attempting to maintain the lubricant in the compressor is not a priority and thus high temperature insolubility is not preferred.

[0110] The amount of lubricant can range from about 1 wt% to about 20 wt%, about 1 wt% to about 7 wt%, and, in some cases, about 1 wt% to about 3 wt%.

[0111] To suppress the hydrolysis of the lubricating oil, it is necessary to control the moisture concentration in the heating/cooling system for electric type vehicles. Therefore, the lubricant in this embodiment needs to have low moisture, typically less than 100 ppm by weight of water.

[0112] In a preferred embodiment, the lubricant comprises a POE lubricant that is soluble in the vehicle heat pump system refrigerant blend at temperatures between about -35°C and about 100°C, and more preferably in the range of about -35°C and about 50°C, and even more specifically between -30°C and 40°C. In another preferred embodiment, the POE lubricant is soluble at temperatures above about 70°C, more preferably at temperatures above about 80°C, and most preferably at temperatures between about 90 to about 95°C.

[0113] Of particular note are PAG, POE, PAO, and PVE lubricants having: volume resistivity of greater than 10^{10} Ω -m at 20°C; surface tension of from about 0.02 N/m to 0.04 N/m at 20°C; a kinematic viscosity of from about 20 cSt to about 500 cSt, or about 50 cSt to about 200 cSt, or about 75 cSt to about 100 cSt at 40°C; a breakdown voltage of at least 25 kV; and a hydroxy value of at most 0.1 mg KOH/g.

[0114] HFO type refrigerants, due to the presence of a double bond, may be subject to thermal instability and decompose under extreme use, handling or storage situations. Therefore, there may be advantages to adding stabilizers to HFO-1252zc. Stabilizers may notably include nitromethane, ascorbic acid, terephthalic acid, azoles such as tolutriazole or benzotriazole, phenolic compounds such as tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-tertbutyl-4-methylphenol, epoxides (possibly fluorinated or perfluorinated alkyl epoxides or alkenyl or aromatic epoxides) such as n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, cyclic monoterpenes, terpenes, such as d-limonene, α -terpinene, β -terpinene, γ -terpinene, α -pinene, or β -pinene, phosphites, phosphates,

phosphonates, thiols and lactones. Examples of suitable stabilizers are disclosed in WO2019213004, WO2020222864, and WO2020222865; the disclosures of which are hereby incorporated by reference.

[0115] If the refrigerant does include a stabilizer, it may include any amount from 0.001 wt% up to 1 wt%, preferably from about 0.01 to about 0.5 weight percent, more preferably, from about 0.01 to about 0.3 weight percent of any of the stabilizers listed above, and, in most case, preferably d-limonene.

[0116] In some embodiments, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc may contain a tracer compound or tracers. The tracer may comprise two or more tracer compounds. In some embodiments, the tracer is present in the compositions at a total concentration of about 50 parts per million by weight (ppm) to about 1000 ppm, based on the weight of the total composition. In other embodiments, the tracer is present at a total concentration of about 50 ppm to about 500 ppm. Alternatively, the tracer is present at a total concentration of about 100 ppm to about 300 ppm.

[0117] The tracer may be present in HFO-1252zc in predetermined quantities to allow detection of any dilution, contamination, or other alteration of the composition. The presence of certain compounds in the composition may indicate by what method or process one of the components has been produced. The tracer may also be added to the composition in a specified amount in order to identify the source of the composition. In this manner, detection of infringement on patent rights may be accomplished. The tracers may be refrigerant compounds but are present in the composition at levels that are unlikely to impact performance of the refrigerant component of the composition.

[0118] Tracer compounds may be hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof. Examples of tracer compounds include, but are not limited to HFC-23 (trifluoromethane), HCFC-31 (chlorofluoromethane), HFC-41 (fluoromethane), HFC-161 (fluoroethane), HFC-143a (1,1,1-trifluoroethane), HFC-134a (1,1,1,2-tetrafluoroethane), HFC-125 (pentafluoroethane), HFC-236fa

(1,1,1,3,3,3-hexafluoropropane), HFC-236ea (1,1,1,2,3,3-hexafluoropropane), HFC-245cb (1,1,1,2,2-pentafluoropropane), HFC-245fa (1,1,1,3,3-pentafluoropropane), HFC-254eb (1,1,1,2-tetrafluoropropane), HFC-263fb (1,1,1-trifluoropropane), HFC-272ca (2,2-difluoropropane), HFC-281ea (2-fluoropropane), HFC-281fa (1-fluoropropane), HFC-329p (1,1,1,2,2,3,3,4,4-nonafluorobutane), HFC-329mmz (1,1,1-trifluoro-2-methylpropane), HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane), HFC-338pcc (1,1,2,2,3,3,4,4-octafluorobutane), CFC-12 (dichlorodifluoromethane), CFC-11 (trichlorofluoromethane), CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane), CFC-114a (1,1-dichloro-1,2,2,2-tetrafluoroethane), HCFC-22 (chlorodifluoromethane), HCFC-123 (1,1-dichloro-2,2,2-trifluoroethane), HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane), HCFC-124a (1-chloro-1,1,2,2-tetrafluoroethane), HCFC-141b (1,1-dichloro-1-fluoroethane), HCFC-142b (1-chloro-1,1-difluoroethane), HCFC-151a (1-chloro-1-fluoroethane), HCFC-244bb (2-chloro-1,1,1,2-tetrafluoropropane), HCC-40 (chloromethane), HFO-1141 (fluoroethene), HCFO-1130 (1,2-dichloroethene), HCFO-1130a (1,1-dichloroethene), HCFO-1131 (1-chloro-2-fluoroethene), HCFO-1122 (2-chloro-1,1-difluoroethene), HFO-1123 (1,1,2-trifluoroethene), HFO-1234ye (1,2,3,3-tetrafluoropropene), HFO-1243zf (3,3,3-trifluoropropene), HFO-1225ye (1,2,3,3,3-pentafluoropropene), HFO-1225zc (1,1,3,3,3-pentafluoropropene), PFC-116 (hexafluoroethane), PFC-C216 (hexafluorocyclopropane), PFC-218 (octafluoropropane), PFC-C318 (octafluorocyclobutane), PFC-1216 (hexafluoroethane), PFC-31-10mc (1,1,1,2,2,3,3,4,4,4-decafluorobutane), PFC-31-10my (1,1,1,2,3,3,3-heptafluoro-2-trifluoromethylpropane), and combinations thereof.

[0119] In another embodiment, the compositions comprise, consist of, or consist essentially of HFO-1252zc and an ultra-violet dye (UV dye). The UV dye is a useful component for detecting leaks of the compositions by permitting one to observe the fluorescence of the dye in the composition at a leak point in the vicinity of heat pump apparatus.

[0120] By UV dye is meant a UV fluorescent composition that absorbs light in the ultra-violet or near-ultra-violet region of the electromagnetic spectrum. The fluorescence produced by the UV dye under illumination of a UV light that emits radiation with wavelength from about 10 nanometer to about 750 nanometer may be detected. Therefore, if a composition containing such a UV fluorescent dye is

leaking from a given point in a heat pump apparatus, the fluorescence can be detected at the leak point. Such UV dyes include, but are not limited to, naphthalimides, perylenes, coumarins, anthracene, phenanthracenes xanthenes, thioxanthenes, naphthoxanthenes, fluoresceins, and derivatives or combinations thereof.

[0121] The container for storing the foregoing compositions can be constructed of any suitable material and design that is capable of sealing the compositions therein while maintaining gaseous and liquids phases. Examples of suitable containers comprise pressure resistant containers such as a tank, a filling cylinder, and a secondary filling cylinder. The container can be constructed from any suitable material such as carbon steel, manganese steel, chromium-molybdenum steel, among other low-alloy steels, stainless steel and in some case an aluminum alloy.

[0122] The compositions of the present invention may be prepared by any convenient method to combine the desired amount of the individual components. A preferred method is to weigh the desired component amounts and thereafter combine the components in an appropriate vessel. Agitation may be used, if desired. In another embodiment, any of the foregoing refrigerant compositions can be prepared by blending HFO-1252zc with the optional non-refrigerant components, such as tracers, or UV dyes, and, in some cases, at least one of the additional compounds.

[0123] In a further embodiment, the compositions may be prepared from recycled or reclaimed refrigerant. One or more of the components may be recycled or reclaimed by means of removing contaminants, such as air, water, or residue, which may include lubricant or particulate residue from system components. The means of removing the contaminants may vary widely, but can include distillation, decantation, filtration, and/or drying by use of molecular sieves or other absorbents. Then the recycled or reclaimed component(s) may be combined with the other component(s) as describe above.

Systems and Methods

[0124] The compositions comprising, consisting of, or consisting essentially of HFO-1252zc are useful as refrigerants in electric and hybrid vehicles for thermal

management. This may be for cooling or heating the passenger compartment of an electric or hybrid vehicle or for cooling or heating other components for proper operation. For instance, the battery of an electric or hybrid vehicle may require cooling during operation. Additionally, certain components of the electric or hybrid vehicles may need heating, particularly in cold ambient conditions to allow efficient operation.

[0125] In one embodiment, a method for cooling and heating a passenger compartment of an electric or hybrid vehicle using a heat pump comprising providing a composition comprising HFO-1252zc as refrigerant to the heat pump.

[0126] In an embodiment, a system for heating and cooling the passenger compartment of an electric vehicle is provided the system comprising, consisting of, or consisting essentially of HFO-1252zc and optionally a lubricant. The system comprises an evaporator, compressor, condenser and expansion device, each operably connected to perform a vapor compression cycle, wherein the system contains a composition comprising, consisting of, or consisting essentially of HFO-1252zc and optionally a lubricant. Due to the excellent performance of the heat pump system in both cooling and heating of the passenger compartment of an electric vehicle, the system may no longer require a positive temperature coefficient (PTC) heater. However, it is contemplated that under extreme cold conditions, the system may still comprise a PCT heater.

[0127] In some embodiments, a secondary loop heat pump system may be used that contains the composition comprising, consisting of, or consisting essentially of HFO-1252zc. In this case, the cycle that provides cooling to the passenger compartment may contain a heat transfer fluid such as water or a glycol solution. Or the secondary loop may utilize a fluid that changes phases, such as a fluorocarbon or other heat transfer fluid.

[0128] The refrigerant may be used in a variety of heating and cooling systems. In some embodiments, a reversing valve is used and the same loop is used for cooling and heating. In other embodiments, air side bypass or refrigerant valving/system design changes can accomplish the same effect as a reversible cycle, without a reversing valve.

[0129] In the embodiment of FIG. 1, a refrigeration system 100 having a refrigeration loop 110 comprises a first heat exchanger 120, a pressure regulator 130, a second heat exchanger 140, a compressor 150 and a four-way valve 160. The first and second heat exchangers are of the air/refrigerant type. The first heat exchanger 120 has passing through it the refrigerant of the loop 110 and the stream of air created by a fan.

[0130] In cooling mode, the refrigerant set-in motion by the compressor 150 passes, via the valve 160, through the heat exchanger 120 which acts as a condenser, that is to say gives up thermal energy to the outside, then through the pressure regulator 130 then through the heat exchanger 140 that is acting as an evaporator thus cooling the stream of air intended to be blown into the motor vehicle cabin interior.

[0131] In heat pump mode, the direction of flow of the refrigerant is reversed using the valve 160. The heat exchanger 140 acts as a condenser while the heat exchanger 120 acts as an evaporator. The heat exchanger 140 can then be used to heat up the stream of air intended for the motor vehicle cabin.

[0132] Additional heat transfer loops may be connected to the heat pump system and absorb or reject heat at the heat exchangers 120 and/or 140 to allow transfer of heat away from the motor or battery, and therefore serve to provide thermal management of those components of the vehicle as well as cooling and heating for the passenger cabin.

[0133] In the embodiment of FIG. 2, a refrigeration system 300 having a refrigeration loop 310 comprises a first heat exchanger 320, a pressure regulator 330, a second heat exchanger 340, a compressor 350 and a four-way valve 360. The first and second heat exchangers 320 and 340 are of the air/refrigerant type. The way in which the heat exchangers 320 and 340 operate is the same as in the first embodiment depicted in FIG. 1. Two fluid/liquid heat exchangers 370 and 380 are installed both on the refrigeration loop circuit 310 and on the engine cooling circuit or on a secondary glycol-water circuit. Installing fluid/liquid heat exchangers without going through an intermediate gaseous fluid (e.g., air) contributes to improving heat exchange by comparison with air/fluid heat exchangers.

[0134] In one embodiment, the system for heating and cooling the passenger compartment of an electric vehicle, the system further comprises a reheater operably connected between the compressor and the condenser for reduction of humidity in the passenger compartment during cooling mode.

[0135] In the embodiment of FIG. 3, a refrigeration system 400 having a refrigeration loop 410 comprises a first heat exchanger (condenser) 420, a pressure regulator 430, a second heat exchanger (evaporator) 440, a compressor 450, a three-way valve 460, and a third heat exchanger (for reheat) 470. In cooling mode, at least a portion of the discharge flow exiting the compressor 450 is directed through the three-way valve 460 and into the third heat exchanger 470. The exit stream from the third heat exchanger 470 discharges into the inlet of the first heat exchanger 420. The refrigerant is condensed by the first heat exchanger 420 using an external fan 480 and ambient air as the heat sink. The existing saturated or subcooled liquid is expanded in the pressure regulator 430 and the resulting lower pressure saturated mixture of refrigerant liquid and vapor enters the second heat exchanger 440. The refrigerant evaporates in the second heat exchanger 440 through the use of a second fan 490 that is external to the refrigeration loop. The air passing across the second heat exchanger 440 is cooled to below the air dew point temperature. This causes the moisture in the air to partially condense, thereby lowering the absolute humidity of the air. The air then passes over the third heat exchanger 470, which transfers heat into the air, increasing the air temperature to above the dew point and lowering the relative humidity of the air, which is then supplied to the passenger compartment. This process of cooling to below the dew point temperature to remove moisture and subsequently reheating to above the dew point temperature allows for cooling and relative humidity control of the vehicle cabin. In heating mode, the three-way valve 460 is modulated to prohibit the flow of refrigerant to the first heat exchanger 420 and all vehicle cabin heating is accomplished using the third heat exchanger 470 in the heat pump configuration described in FIG. 1.

[0136] In the embodiment of FIG. 4, an air-conditioning (AC) and heat pump (HP) system 500, heating, cooling, or both can be accomplished in a vehicle cabin or for other vehicle loads. The system 500 includes an AC circuit 510 and a HP circuit 520. In air-conditioning only mode, the HP control valve 530 upstream of the heat

pump condenser 540 will be closed and the refrigerant will flow from the compressor 550 into the air-cooled AC condenser 560, through an AC expansion valve 570, and into the AC evaporator 580; providing cooling to the cabin. From the AC evaporator 580, the refrigerant will flow back to the compressor 550. In heat pump only mode, the AC control valve 535 upstream of the AC condenser 560 will be closed and the refrigerant will flow from the compressor 550 into the HP condenser 540 to provide heating to the cabin. From the HP condenser 540 the refrigerant will flow through the HP expansion valve 575 to the HP evaporator 585. A separate humidity control mode could be accomplished by sending a portion of the compressor discharge gas into the AC circuit 510 and the remaining portion into the HP circuit 520.

[0137] In the embodiment of FIG. 5, a system 600 for heating, cooling, or both can be accomplished for a vehicle cabin or for other vehicle loads. The system 600 includes an AC circuit 610 and a water-cooled/HP circuit 620. In AC only mode, the water loop control valve 630 upstream of the water-cooled condenser 640 will be closed and the refrigerant will flow from the compressor 650 into the AC condenser 660, through an AC expansion valve 670, and into the AC evaporator 680; providing cooling to the cabin. In HP only mode, the AC control valve 635 upstream of the AC condenser 660 will be closed and the refrigerant will flow from the compressor 650 into the water-cooled condenser 640. A heat transfer fluid (e.g., water or other heat transfer fluid) will take the heat generated in the water-cooled condenser 640 and transfer it to the cabin heater core 690; providing heat to the cabin. The heat transfer fluid may return from the cabin heater core 690 to the water-cooled condenser 640. The refrigerant will flow from the water-cooled condenser 640 through an HP expansion valve 675 into the HP evaporator 685 that cools a heat transfer fluid, which may be used to cool other components of the automobile and then back to the compressor 650. In some embodiments, there is one or more water/heat transfer fluid loop that may be used to heat and/or cool various other components of the vehicle. A separate humidity control mode could be accomplished by sending a portion of the compressor discharge gas into the AC circuit 610 and the remaining portion into the water cooled/HP circuit 620.

[0138] In the embodiments of FIG. 6 through FIG. 9, the same components exist in the system, but depending on the mode of operation, only some of those components are utilized.

[0139] In one embodiment, in heating mode wherein specific conditions exist where both the vehicle cabin and other vehicle components require heat, the refrigerant circuit 700 operates as shown in FIG. 6. Starting at the compressor 750, discharge refrigerant vapor will take two paths. One path is through the cabin condenser 740. The cabin condenser 740 is a refrigerant-to-air heat exchanger typically of the fin-tube or microchannel type and can be single or multiple pass. A first fan 745 in the vehicle ventilation ductwork will induce a flow of either 100% outside air or a mixture of outside air and return air from the vehicle cabin across this cabin condenser 740 and the refrigerant as it condenses will heat the air. In this mode, a physical bypass 735 within the vehicle ventilation ductwork will prevent any air from flowing over the cabin evaporator 730. The second path of refrigerant out of the compressor is through valve 770 and into a liquid/heat transfer fluid heat exchanger 720, which allows heat to be transferred from the warm refrigerant to the vehicle's heat transfer fluid loop (not shown). This vehicle heat transfer loop can then be used to manage other vehicle heat loads. The heat transfer fluid of the heat transfer fluid loop may be water or a water/glycol solution. The condensed refrigerant out of exchanger 720 then combines with the condenser 740 liquid refrigerant outlet and the combined stream flows through an expansion device 775, which will drop the pressure of the liquid refrigerant and generate a liquid-vapor mixture. This liquid-vapor mixture then flows through the outdoor heat exchanger 780 (i.e., evaporator in this setup). The outdoor heat exchanger 780 will be a refrigerant-to-air heat exchanger typically of the fin-tube or microchannel type and can be single or multiple pass. A second fan 785 will induce airflow across the outdoor heat exchanger 780 and allow the liquid-vapor refrigerant mixture to pick up heat from the ambient air and vaporize completely before it flows back to the compressor 750.

[0140] In another embodiment, in heating mode when specific conditions exist where only cabin heating is required, the refrigerant circuit 800 operates as shown in FIG. 7. Starting at the compressor 850, discharge vapor will first flow through the cabin condenser 840. A first fan 845 in the vehicle ventilation ductwork will induce a flow of either 100% outside air or a mixture of outside air and return air from the vehicle cabin across this cabin condenser 840 and the refrigerant will exchange heat between the condenser 840 and the air. In this mode, a physical bypass 835 within

the vehicle ventilation ductwork will prevent any air from flowing over the cabin evaporator 830. The refrigerant will condense in the cabin condenser 840 and flow to an expansion device 875 which will drop the pressure of the liquid refrigerant and generate a liquid-vapor mixture. This liquid-vapor mixture flows through the outdoor heat exchanger 880 (i.e., evaporator in this setup). A second fan 885 will induce airflow across the outdoor heat exchanger 880 and allow the liquid-vapor refrigerant mixture to pick up heat from the ambient air and vaporize completely before it travels back to the compressor 850.

[0141] In another embodiment, in cooling mode when specific conditions exist where both the vehicle cabin and the vehicle components require cooling, the refrigerant circuit 900 operates as shown in FIG. 8. Starting at the compressor 950, discharge refrigerant vapor will first flow through the cabin condenser 940, wherein there will be no heat transfer as in this mode, a physical bypass 945 within the vehicle ventilation ductwork will prevent any air from flowing over the cabin condenser 940. Vapor refrigerant will pass through the cabin condenser 940 and flow through valve 975 and into the outdoor heat exchanger 980. In this mode, the outdoor heat exchanger 980 acts as a condenser as a first fan 985 induces flow across the heat exchanger and the hot refrigerant vapor exchanges heat and condenses to a liquid. A portion of this liquid refrigerant will leave the outdoor heat exchanger 980 and enter the internal heat exchanger 990. Liquid refrigerant will be subcooled in the internal heat exchanger 990 and then flow to an expansion device 910 and into the cabin evaporator 930. This air-to-refrigerant cabin evaporator 930 will be of the fin-tube or microchannel type of heat exchanger and can be single or multiple pass. A second fan (or cabin blower fan) 935 will induce a flow of either 100% outside air or a mixture of outside air and return air from the cabin across the coil of the cabin evaporator 930 where heat will be exchanged between the air and refrigerant. The refrigerant will vaporize and travel back to the internal heat exchanger 990 where it will be further superheated until it finally re-enters the compressor 950. The remaining portion of refrigerant exiting the condenser 980 will flow through expansion valve 915 and into the liquid/heat transfer fluid heat exchanger 920 wherein vehicle component heat is transferred via a heat transfer fluid loop (not shown) into the refrigerant. This vehicle heat transfer loop can then be used to manage other vehicle heat loads. The refrigerant vaporizes in heat

exchanger 920 and joins the refrigerant exiting internal heat exchanger 990 at the suction of the compressor 950.

[0142] In another embodiment, in cooling mode when specific conditions exist where only vehicle cabin cooling is required, the refrigerant circuit 1000 operates as shown in FIG. 9. Starting at the compressor 1050, discharge refrigerant vapor will first flow through the cabin condenser 1040, wherein there will be no heat transfer, as in this mode, a physical bypass 1045 within the vehicle ventilation ductwork will prevent any air from flowing over the cabin condenser 1040. Vapor refrigerant will pass through the cabin condenser 1040 and flow through a valve 1075 to the outdoor heat exchanger 1080. In this mode, the outdoor heat exchanger 1080 acts as a condenser as a first fan 1085 induces flow across the heat exchanger 1080 and the hot refrigerant vapor exchanges heat and condenses to a liquid. This liquid refrigerant will leave the outdoor heat exchanger 1080 and enter the internal heat exchanger 1090. Liquid refrigerant will be subcooled in the internal heat exchanger 1090 and then flow to an expansion device 1010 and into the cabin evaporator 1030. A second fan (or cabin blower fan) 1035 will induce a flow of either 100% outside air or a mixture of outside air and return air from the cabin across the cabin evaporator 1030 where heat will be exchanged between the air and refrigerant. The refrigerant will vaporize and flow back to the internal heat exchanger 1090 where it will be further superheated until it finally returns to the compressor 1050.

[0143] With reference to FIG. 10, it illustrates an electric vehicle heat pump with secondary loops. The purpose of the secondary loops are to separate the refrigerant from the “users” or various vehicle heat exchangers used to cool/heat the cabin air, the power electronics, and the battery to enable the use of refrigerants with a higher flammability than historic refrigerants used for vehicles. The heat pump itself consists of a compressor (1), a condenser (2), an expansion valve (3), and an evaporator (4). The concept here is that the refrigerant loop is close coupled, contained within the “engine compartment,” and does not require reversing capability. Two separate heat transfer fluid (i.e. water, or a glycol solution, oils, refrigerants) loops are in communication with the refrigerant loop via the condenser (2) and evaporator (4). The first heat transfer fluid loop is contained within the “engine compartment” and utilizes an air-to-liquid heat exchanger (5) and circulation pump (6) to discharge heat from the condenser (2) in air-conditioning mode or

provide heat to the evaporator (4) in heat pump mode or a combination of both. Air flows over the heat exchanger (5) via an external fan. The second heat transfer fluid loop consists of a pump (7) and heat exchanger (8). For simplicity, one heat exchanger is shown, when in reality, several heat exchangers could be employed providing heating/cooling to the cabin air, the power electronics, and the battery. Control valves (9), (10), (11), and (12) are used to depict the flexibility of such a system to provide heating, cooling, or both to any given heat exchanger via communication with the heat pump condenser (2) and evaporator (4).

[0144] The compositions containing HFO-1252zc have low GWP for use in a hybrid, mild hybrid, plug-in hybrid, or full electric vehicles for thermal management (transferring heat from one part of the vehicle to the other) of the passenger compartment providing air conditioning (A/C) or heating to the passenger cabin. Additionally, the refrigerant provides improved performance under the same conditions as compared to HFO-1234yf, in particular, the capacity is higher than HFO-1234yf alone, even 12% higher or more than HFO-1234yf alone when operating under the same conditions, and COP higher than HFO-1234yf alone. The COP is preferably at least 6% higher than HFO-1234yf alone, or more preferably at least 8% higher than HFO-1234yf alone when operating under the same conditions.

[0145] In another embodiment, also disclosed herein is a method for replacing HFO-1234yf or HFC-134a in a heating and cooling system contained within an electric vehicle, comprising providing a composition comprising HFO-1252zc to said heating and cooling system as a heat transfer fluid. According to any of the foregoing embodiments, the refrigerant produces volumetric capacity at least 8% higher, or 10% higher, or 12% higher than HFO-1234yf alone when operating under the same conditions. Additionally, in the method for replacing HFO-1234yf or HFC-134a, the refrigerant comprising HFO-1252zc produces COP at least 6% higher, or 8% higher than HFO-1234yf alone when operating under the same conditions.

[0146] In one embodiment is provided a use of any of the foregoing compositions comprising a refrigerant comprising, consisting of, or consisting essentially of HFO-1252zc as a heat transfer fluid in a system for heating and cooling the passenger compartment of an electric or hybrid vehicle. This use of the present inventive

refrigerants has been described in detail in the foregoing description and will be demonstrated in the forthcoming examples.

[0147] In other embodiments, including compositions intended to replace conventional high GWP refrigerant in refrigeration, air-conditioning, and heat pump applications, it is desirable that the refrigerant composition exhibit a low GWP as well as similar or improved refrigerant properties compared to conventional refrigerants.

[0148] The following Examples are provided to illustrate certain aspects of the invention and shall not limit the scope of the appended claims.

EXAMPLE

Example 1

[0149] A thermodynamic modeling program was used to calculate the expected performance of the refrigerant comprising HFO-1252zc compared to HFO-1234yf alone. Fourteen different sets of conditions were modeled, the conditions being specified by the Society of Automotive Engineers (SAE) for characterization of refrigerant performance in an automobile heat pump system. Physical properties for the components were taken from NIST REFPROP Version 10.

[0150] The conditions used are as described herein below and in Table 3:

Evaporator super heat = 10 K
Suction line super heat = 0 K
Subcooling = 5 K
Compressor isentropic efficiency = 70%
Compressor volumetric efficiency = 95 %

Table 3

Point #	Speed	Ambient	Outlet Air	Inlet Air	Vehicle Cabin Load	Battery Load	Electric Motor and Power Electronics Load	PTC Heater Load	Mode	Evap Avg Temp	Cond Avg Temp
-	[kph]	[°C]	[°C]	[°C]	[kW]	[kW]	[kW]	[kW]	-	[°C]	[°C]
1	0	-40	55	-5	5.5	1.5	0	0	Heating	-15	65

Point #	Speed	Ambient	Outlet Air	Inlet Air	Vehicle Cabin Load	Battery Load	Electric Motor and Power Electronics Load	PTC Heater Load	Mode	Evap Avg Temp	Cond Avg Temp
-	[kph]	[°C]	[°C]	[°C]	[kW]	[kW]	[kW]	[kW]	-	[°C]	[°C]
2	0	-20	55	-20	7	1	0	0	Heating	-30	65
3	0	35	8	35	7	0.1	0	0	Cooling	-2	55
4	0	45	3	28	2.5	5	0	0	Cooling	-7	48
5	50	-20	55	-20	3	4	0	0	Heating	-30	65
6	50	-20	55	-20	7	0	0	0	Heating	-30	65
7	50	0	55	0	5	1	1	0	Heating	-10	65
8 (PTC*)	50	15	3	15	1	1.5	0	1.5	Cooling	-2	35
8a (PTC*)	50	25	3	25	3.5	2	1	2.5	Cooling	-2	45
9	100	-20	55	-20	7	0.5	1	0	Heating	-30	65
10	100	-20	55	-20	7	0	0	0	Heating	-30	65
11	100	0	55	0	5	0	2	0	Heating	-10	65
12	100	35	8	35	7	1	2	0	Cooling	-2	55
13	100	45	3	28	5	2	5	0	Cooling	-7	48

*PTC= positive coefficient heater

[0151] Thermodynamic Modeling Comparison for the Heat Pump Systems: HFO-1252zc relative to HFO-1234yf. The results displayed in Table 4 are the average for volumetric capacity (relative to 1234yf), and the average for COP (relative to 1234yf) for the SAE points 1-13 (see Table 3 above). Capacity (Cap) and COP are the percent above the corresponding value for the HFO-1252zc vs. HFO-1234yf alone.

Table 4

Refrigerant	GWP (AR5)	NBP (°F)	Avg Capacity (kJ/m ³)	Avg Cap rel to 1234yf (% above)	Avg COP	Avg COP rel to 1234yf (% above)
134a	1300	-26.1	1339.4	6.2	2.2	6.7
1234yf	<1	-29.4	1260.8	na	2.06	na
1252zc	1*	-29.3	1416.8	12.4	2.23	8.5

*the GWP for 1252zc is estimated

[0152] The above data demonstrate that HFO-1252zc surprisingly provides performance with volumetric capacity over 12% higher than that for HFO-1234yf, many being and COP that is over 8% higher than that for HFO-1234yf alone. HFO-1252zc performance is even an improvement over HFC-134a with higher average capacity and higher average COP. The improved performance shows that the new fluid can easily be used to provide more than adequate cooling and heating to a passenger cabin of an electric or hybrid vehicle.

[0153] While the invention has been described with reference to a preferred embodiment, it will be understood by those skilled in the art that various changes may be made, and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

CLAIMS

What is claimed is:

1. A method for cooling and heating a passenger compartment of an electric or hybrid vehicle using a heat pump, the method comprising providing a composition comprising HFO-1252zc as refrigerant to the heat pump.
2. The method of claim 1, wherein the composition further comprises at least one additional compound selected from the group consisting of HCFC-22, HFC-23, HCC-30, HCFC-31, HCC-40, HFC-41, methane, HFC-125, HFC-143, HFC-143a, HFC-152a, HFC-245cb, HCFC-253dc, HFC-254fb, HCC-260fb, HCFC-261fc, HCFC-262fc, HFC-263fb, HFC-272fb, propane, HFO-374, n-butane, allene, 2-butene, cyclobutene, 2-methyl propene, HCFO-1122, HFO-1132, HFO-1132a, HFO-1141, ethylene, HCFO-1233xf, HFO-1234yf, HCFO-1242zf, HFO-1243zf, HCFO-1251, HCO-1260zf, HFO-1261zf, propylene, HFO-1345, HFO-1252ze, HFO-1252yf, HFO-1252zf, HFO-1252ye, and E/Z-t-BuO-CF=CH-CH₃.
3. The method of any of claims 1 or 2, wherein the composition further comprises at least one additional compound and wherein the total amount of additional compounds comprises greater than zero and less than 1 weight percent.
4. The method of any of claims 1 to 3, wherein the additional compounds comprise HFO-1234yf, HFO-1243zf, HFC-263fb, HFO-1252ze, HFO-1252yf, HFO-1252zf, and HFO-1252ye.
5. The method of any of claims 1 to 4, wherein the composition is determined to be class 3 for flammability as defined in ANSI/ASHRAE Standard 34.
6. The method of any of claims 1 to 5, wherein the composition has an LFL of less than 10 volume percent when measured in accordance with ASTM-E681.
7. The method of any of claims 1 to 6, wherein the composition further comprises a lubricant.
8. The method of claim 7, wherein said lubricant is at least one selected from the group consisting of polyalkylene glycol, polyol ester, poly- α -olefin, and polyvinyl ether.

9. The method of claim 7 or 8, wherein the lubricant is a polyol ester lubricant and is obtained by reacting a carboxylic acid with a polyol comprising a neopentyl backbone selected from the group consisting of neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and mixtures thereof.
10. The method of claim 9, wherein the carboxylic acid has 2 to 18 carbon atoms.
11. The method of any of claims 7 to 10, wherein said lubricant has at least one property selected from the group consisting of volume resistivity of greater than 10^{10} Ω -m at 20°C; surface tension of from about 0.02 N/m to 0.04 N/m at 20°C; kinematic viscosity of from about 20 cSt to about 500 cSt at 40°C; a breakdown voltage of at least 25 kV; and a hydroxy value of at most 0.1 mg KOH/g.
12. The method of any of claims 1 to 11, wherein said composition further comprises from 0.1 to 200 ppm by weight of water; from about 10 ppm by volume to about 0.35 volume percent oxygen; and/or from about 100 ppm by volume to about 1.5 volume percent air.
13. The method of any of claims 1 to 12, wherein said composition comprises a stabilizer.
14. The method of claim 13, wherein the stabilizer is selected from the group consisting of nitromethane, ascorbic acid, terephthalic acid, azoles, phenolic compounds, cyclic monoterpenes, terpenes, phosphites, phosphates, phosphonates, thiols, and lactones.
15. The method of any of claims 13 or 14, wherein the stabilizer is selected from the group consisting of tolutriazole, benzotriazole, tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-terbutyl-4-methylphenol, fluorinated epoxides, n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, d-limonene, α -terpinene, β -terpinene, α -pinene, β -pinene, or butylated hydroxytoluene.
16. The method of any of claims 13 to 15, wherein the stabilizer is present in an amount from about 0.001 to 1.0 weight percent based on the weight of the refrigerant.

17. The method of any of claims 1 to 16, wherein the composition comprises at least one tracer.
18. The method of claim 17, wherein said at least one tracer is present in an amount from about 1.0 ppm by weight to about 1000 ppm by weight.
19. The method of any of claims 17 or 18, wherein said at least one tracer is selected from the group consisting of hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof.
20. The method of any of claims 17 to 19, wherein said at least one tracer is selected from the group consisting of HFC-23, HCFC-31, HFC-41, HFC-161, HFC-143a, HFC-134a, HFC-125, HFC-236fa, HFC-236ea, HFC-245cb, HFC-245fa, HFC-254eb, HFC-263fb, HFC-272ca, HFC-281ea, HFC-281fa, HFC-329p, HFC-329mmz, HFC338mf, HFC-338pcc, CFC-12, CFC-11, CFC-114, CFC-114a, HCFC-22, HCFC-123, HCFC-124, HCFC-124a, HCFC-141b, HCFC-142b, HCFC-151a, HCFC-244bb, HCC-40, HFO-1141, HCFO-1130, HCFO-1130a, HCFO-1131, HCFO-1122, HFO-1123, HFO-1234yf, HFO-1234ye, HFO-1243zf, HFO-1225ye, HFO-1225zc, PFC-116, PFC-C216, PFC-218, PFC-C318, PFC-1216, PFC-31-10mc, PFC-31-10my, and combinations thereof.
21. The method of any of claims 1 to 20, wherein the composition comprises a UV dye.
22. The method of any of claims 1 to 21, wherein the composition comprises a UV dye selected from the group consisting of naphthalimides, perylenes, coumarins, anthracenes, phenanthracenes xanthenes, thioxanthenes, naphthoxanthenes, fluoresceins, and derivatives or combinations thereof.
23. A system for heating and cooling the passenger compartment of an electric or hybrid vehicle, the system comprising HFO-1252zc and optionally a lubricant.

24. The system of claim 23 comprising an evaporator, compressor, condenser and expansion device, each operably connected to perform a vapor compression cycle.
25. The system of any of claims 23 or 24, wherein the system does not include a PTC heater.
26. The system of any of claims 23 to 25, wherein said system is a secondary loop system.
27. The system of any of claims 23 to 26, wherein said system uses a heat transfer fluid to transport cooling or heating to the passenger compartment, wherein said heat transfer fluid comprises water, glycol solution, oils, or refrigerants.
28. A method for replacing HFO-1234yf or HFC-134a in a heating and cooling system contained within an electric or hybrid vehicle, comprising providing a composition comprising HFO-1252zc as refrigerant.
29. The method of claim 28, wherein the refrigerant produces volumetric capacity at least 10% higher, preferably, at least 12% higher than HFO-1234yf alone when operating under the same conditions.
30. The method of any of claims 28 to 29, wherein the refrigerant produces COP at least 6% higher, preferably, at least 8% higher than the COP of HFO-1234yf alone when operating under the same conditions.
31. Use of a composition comprising HFO-1252zc as refrigerant in heat pumps for thermal management in electric or hybrid vehicles.
32. The use of claim 31, wherein thermal management comprises cooling and heating of the passenger compartment of the electric or hybrid vehicles.
33. The use of claim 31 or 32, wherein the composition further comprises at least one additional compound selected from the group consisting of HCFC-22, HFC-23, HCC-30, HCFC-31, HCC-40, HFC-41, methane, HFC-125, HFC-143, HFC-143a, HFC-152a, HFC-245cb, HCFC-253dc, HFC-254fb, HCC-260fb, HCFC-261fc, HCFC-262fc, HFC-263fb, HFC-272fb, propane, HFO-374, n-butane, allene, 2-butene, cyclobutene, 2-methyl propene, HCFO-1122, HFO-

1132, HFO-1132a, HFO-1141, ethylene, HCFO-1233xf, HFO-1234yf, HCFO-1242zf, HFO-1243zf, HCFO-1251, HCO-1260zf, HFO-1261zf, propylene, HFO-1345, HFO-1252ze, HFO-1252yf, HFO-1252zf, HFO-1252ye, and E/Z-t-BuO-CF=CH-CH₃.

34. The use of any of claims 31 to 33, wherein the composition further comprises at least one additional compound and wherein the total amount of additional compounds comprises greater than zero and less than 1 weight percent.
35. The use of any of claims 31 to 34, wherein the additional compounds comprise HFO-1234yf, HFO-1243zf, HFC-263fb, HFO-1252ze, HFO-1252yf, HFO-1252zf, and HFO-1252ye.
36. The use of any of claims 31 to 35, wherein the composition is determined to be class 3 for flammability as defined in ANSI/ASHRAE Standard 34.
37. The use of any of claims 31 to 36, wherein the composition further comprises a lubricant.
38. The use of claim 37, wherein said lubricant is at least one selected from the group consisting of polyalkylene glycol, polyol ester, poly- α -olefin, and polyvinyl ether.
39. The use of claim 37 or 38, wherein the lubricant is a polyol ester lubricant and is obtained by reacting a carboxylic acid with a polyol comprising a neopentyl backbone selected from the group consisting of neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and mixtures thereof.
40. The use of claim 39, wherein the carboxylic acid has 2 to 18 carbon atoms.
41. The use of any of claims 37 to 40, wherein said lubricant has at least one property selected from the group consisting of volume resistivity of greater than 10^{10} Ω -m at 20 °C; surface tension of from about 0.02 N/m to 0.04 N/m at 20 °C; kinematic viscosity of from about 20 cSt to about 500 cSt at 40 °C; a breakdown voltage of at least 25 kV; and a hydroxy value of at most 0.1 mg KOH/g.
42. The use of any of claims 31 to 41, wherein said composition further comprises from 0.1 to 200 ppm by weight of water; from about 10 ppm by volume to about

0.35 volume percent oxygen; and/or from about 100 ppm by volume to about 1.5 volume percent air.

43. The use of any of claims 31 to 42, wherein said composition comprises a stabilizer.
44. The use of claim 43, wherein the stabilizer is selected from the group consisting of nitromethane, ascorbic acid, terephthalic acid, azoles, phenolic compounds, cyclic monoterpenes, terpenes, phosphites, phosphates, phosphonates, thiols, and lactones.
45. The use of any of claims 43 or 44, wherein the stabilizer is selected from the group consisting of tolutriazole, benzotriazole, tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-terbutyl-4-methylphenol, fluorinated epoxides, n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, d-limonene, α -terpinene, β -terpinene, α -pinene, β -pinene, or butylated hydroxytoluene.
46. The use of any of claims 43 to 45, wherein the stabilizer is present in an amount from about 0.001 to 1.0 weight percent based on the weight of the refrigerant.
47. The use of any of claims 32 to 46, wherein the composition comprises at least one tracer.
48. The use of claim 47, wherein said at least one tracer is present in an amount from about 1.0 ppm by weight to about 1000 ppm by weight.
49. The use of any of claims 47 or 48, wherein said at least one tracer is selected from the group consisting of hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof.
50. The use of any of claims 47 to 49, wherein said at least one tracer is selected from the group consisting of HFC-23, HCFC-31, HFC-41, HFC-161, HFC-143a, HFC-134a, HFC-125, HFC-236fa, HFC-236ea, HFC-245cb, HFC-245fa,

HFC-254eb, HFC-263fb, HFC-272ca, HFC-281ea, HFC-281fa, HFC-329p, HFC-329mmz, HFC338mf, HFC-338pcc, CFC-12, CFC-11, CFC-114, CFC-114a, HCFC-22, HCFC-123, HCFC-124, HCFC-124a, HCFC-141b, HCFC-142b, HCFC-151a, HCFC-244bb, HCC-40, HFO-1141, HCFO-1130, HCFO-1130a, HCFO-1131, HCFO-1122, HFO-1123, HFO-1234yf, HFO-1234ye, HFO-1243zf, HFO-1225ye, HFO-1225zc, PFC-116, PFC-C216, PFC-218, PFC-C318, PFC-1216, PFC-31-10mc, PFC-31-10my, and combinations thereof.

51. The use of any of claims 31 to 50, wherein the composition comprises a UV dye.
52. The use of any of claims 31 to 51, wherein the composition comprises a UV dye selected from the group consisting of naphthalimides, perylenes, coumarins, anthracenes, phenanthracenes xanthenes, thioxanthenes, naphthoxanthenes, fluoresceins, and derivatives or combinations thereof.
53. The method of any of claims 1 to 22 or 28 to 30, wherein the composition is free of or substantially free of Group A Fluorinated Substances, and wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.
54. The system of any of claims 23 to 27 or the use of any of claims 31 to 52, wherein the composition is free of or substantially free of Group A Fluorinated Substances, and wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.
55. The use of any of claims 31 to 52, wherein the composition is free of or substantially free of Group A Fluorinated Substances, and wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.