

TITLE

A PROCESS OF COPRODUCING E/Z-1,2-DIFLUOROETHYLENE
AND COMPOSITIONS THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application 63/541,445 filed September 29, 2023, the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention is directed to processes for producing 1,2-difluoroethylene, compositions and uses thereof.

BACKGROUND OF THE INVENTION

[0003] Hydrofluoroolefins (HFOs) having low ozone depletion potential (ODP) and low global warming potential (GWP) have been replacing saturated CFCs (chlorofluorocarbons) and HCFCs (hydrochlorofluorocarbons) in a variety of applications for several years as hydrofluorocarbons tend to have high GWP values. For example, HFC-32, HFC-125, and HFC-134a have GWPs of 675, 3500 and 1430, respectively. As a result, low ODP and GWP materials continue to be of interest for use as refrigerants, solvents, foam expansion agents, cleaning agents, aerosol propellants, dielectrics, fire extinguishants, and power cycle working fluids.

[0004] This regulatory landscape is continuously evolving, taking into consideration properties beyond just ODP and GWP. More particularly, there is a need for refrigerant compositions that not only meet low ODP standards and have low GWP, but that also exhibit low or no flammability, provide superior performance in a variety of applications and which meet the standards of evolving regulations.

[0005] There is a need in this art for new refrigerants that meet evolving regulations as well as provide heat transfer and refrigerant characteristics that meet or exceed the effectiveness of conventional refrigerants.

[0006] Some fluoroolefins, such as E/Z-1,2-difluoroethylene (E/Z-HFO-1132), are such potential new refrigerants. There continues to be need for effective and efficient processes for preparing E/Z-HFO-1132 and intermediates and compositions thereof.

SUMMARY OF THE INVENTION

[0007] The present invention relates to process for coproducing the E- and Z- isomers of 1,2-difluoroethylene (HFO-1132), compositions thereof and methods of using.

[0008] In certain embodiments disclosed herein, 1,2-dichloro-1,2-difluoroethylene (CFO-1112) is converted to the E- and Z- isomers of HFO-1132 with H₂ in the vapor phase.

[0009] In certain embodiments disclosed herein, CFO-1112 is converted to the E- and Z- isomers of HFO-1132 with H₂ in the vapor phase in the presence of a hydrogenation catalyst.

[0010] In certain embodiments disclosed herein, CFO-1112 is converted to the E- and Z- isomers of HFO-1132 with H₂ in the vapor phase in the presence of a hydrogenation catalyst at a pressure of between about 10 psig to 250 psig, or between about 20 psig to 200 psig, or about 30 psig to 150 psig.

[0011] In one embodiment of the invention disclosed herein, CFO-1112 contacts hydrogen at temperature ranging from between about 175°C to about 300°C, or between about 200°C to about 275°C, or between about 225°C to about 275°C, including but not limited to between at least about 180°C, at least about 190°C, at least 200°C, at least about 210°C, at least about 230°C, at least about 240°C and less than about 300°C, or less than about 275°C.

[0012] In another embodiment of the invention disclosed herein, CFO-1112 contacts hydrogen in the presence of a support or unsupported hydrogenation catalyst.

[0013] In certain embodiments disclosed herein, the catalyst comprises, consists essentially of, or consists of one of copper, nickel, palladium, or combination of them on a support which is selected from carbon, Al₂O₃ and SiC.

[0014] In certain embodiments disclosed herein, the catalyst comprises, consists essentially if, or consists of copper combined with palladium and supported on carbon.

[0015] In certain embodiments the Cu-Pd catalyst comprises, consists essentially of, or consists of 0.1 to 1.0 weight percent palladium and 0.1 to 20 weight percent copper, or between 0.1 to 0.75 weight percent palladium and between 1 to about 5.0 weight percent copper, and all values and ranges therebetween.

[0016] In another embodiment of the invention disclosed herein, CFO-1112 contacts hydrogen in the presence of a support or unsupported hydrogenation catalyst, at temperature ranging from between about 175°C to about 300°C, or between about 200°C to about 275°C, or between about 225°C to about 275°C, including but not limited to between at least about 180°C, at least about 190°C, at least 200°C, at least about 210°C, at least about 230°C, at least about 240°C and less than about 300°C, or less than about 275°C.

[0017] In another embodiment of the invention disclosed herein, CFO-1112 is hydrogenated in the presence of hydrogen at subatmospheric, atmospheric or super atmospheric pressure.

[0018] Another embodiment disclosed herein relates to a composition comprising, consisting essentially of, or consisting of E-HFO-1132 and/or Z-HFO-1132, and one or more additional compounds selected from methane, ethane, fluoromethane (HFC-41), 1,2-dichloro-1,2-difluoroethane (HFC-132), 1,2-dichloroethane (HCC-150), 1-chloro-2-fluoroethane (HCFC-151), 1,2-difluoroethane (HFC-152), fluoroethane (HFC-161), 1,2-dichloro-1,2-difluoroethylene (CFO-1112), E-1-chloro-1,2-difluoroethylene (E-HCFO-1122a), (Z)-1-chloro-1,2-difluoroethylene (Z-HCFO-1122a), 1-chloro-2-fluoroethylene (HCFO-1131) and fluoroethylene (HFO-1141).

[0019] Another embodiment disclosed herein relates to a composition comprising, consisting essentially of, or consisting of E-HFO-1132 and/or Z-HFO-1132, and two or more additional compounds selected from methane, ethane, HFC-41, HCFC-132, HCC-150, HCFC-151, HFC-152, HFC-161, CFO-1112, E- HCFO-1122a, Z-HCFO-1122a, HCFO-1131 and HFO-1141.

[0020] Another embodiment disclosed herein relates to a composition comprising, consisting essentially of, or consisting of E-HFO-1132 and/or Z-HFO-1132, and three or more additional compounds selected from methane, ethane, HFC-41, HCFC-132, HCC-150, HCFC-151, HFC-152, HFC-161, CFO-1112, E- HCFO-1122a, Z-HCFO-1122a, HCFO-1131 and HFO-1141.

[0021] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, suitable methods and materials are described below. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] Fig. 1 illustrates one embodiment of the invention.

[0023] Fig. 2 illustrates another embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The present invention relates to processes for co-producing E-HFO-1132 and Z-HFO-1132 by the hydrogenation of CFO-1112, compositions including E-HFO-1132, Z-HFO-1132 or mixtures thereof, and methods of using the same.

[0025] Before addressing details of embodiments described herein, some terms are defined or clarified as follows.

[0026] The term “compound” as used herein is meant to include all stereoisomers, geometric isomers, tautomers, and isotopes of the structures or chemical described. Compounds herein identified by name or structure as one particular tautomeric form are intended to include other tautomeric forms unless otherwise specified.

[0027] The term “hydrohaloalkane,” as used herein means a molecule containing hydrogen, carbon, fluorine and/or chlorine and/or bromine and/or iodine, with no

carbon-carbon double bond (halo = fluoro, chloro, bromo, iodo). Examples are described throughout the instant specification.

[0028] The term “hydrohaloalkene” is intended to mean a chemical compound selected from the classes of hydrofluoroolefms (HFOs) and hydrochlorofluoroolefins (HCFOs) which include a double bond between adjacent carbon atoms and can contain 1 to 8 carbon atoms.

[0029] In addition to the reactors disclosed herein, heat exchangers, effluent lines, units associated with mass transfer, contacting vessels (pre-mixers), distillation columns, and feed and material transfer lines associated with reactors, heat exchangers, vessels, columns, and units that are used in the processes of embodiments disclosed herein should be constructed of materials resistant to corrosion. Preferably, the reactors and components are made of an acid resistant alloy, e.g., Hastelloy®, such as nickel-based alloys, Special Metals Corp. Nickel commercially available under the trade name of Inconel® (hereafter “Inconel®”) Chromium alloy or includes containers with nickel-copper alloy or fluoropolymer linings marketed under the trade name Monel®. In addition to the reactors disclosed herein, preheaters and vaporizers, heat exchangers, feed and effluent lines, units associated with mass transfer, contacting vessels (pre-mixers), distillation columns, and valving associated with reactors, heat exchangers, vessels, columns, and units that are used in the processes of various embodiments disclosed herein should be constructed of materials resistant to corrosion.

[0030] 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 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 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 is true (or present).

[0031] 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.

[0032] 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.’

[0033] 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.”

[0034] 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.

[0035] Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range. Moreover, all ranges set forth herein are intended to include not only the particular ranges specifically described, but also any combination of values therein, including the minimum and maximum values recited.

[0036] When an amount, concentration, or other value or parameter is given as either a range, preferred range, or a list of upper preferable values and/or lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range

limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

[0037] As used herein GC/FID peak area correlates to the amount of a compound present as a proportion of the total area of all detected peaks. FID area% can be converted to mol% using a response factor either calculated or measured

[0038] Unless specified otherwise, as used herein, the term “substantially free” means that less than about 0.0001 percent by weight is present (1 ppm).

[0039] As used herein the term “about” in certain embodiments can be quantified to mean $\pm 1\%$, $\pm 2\%$, $\pm 3\%$ up to and including $\pm 10\%$ of the stated value, and all whole numbers and fractions therebetween.

[0040] By way of example, mention is made of the following compounds:

HC-50:	methane, CH ₄
HC-70:	ethane, C ₂ H ₆
HFC-41:	fluoromethane, CH ₃ F
HCFC-132:	1,2-dichloro-1,2-difluoroethane, CHClFCHClF
HCC-150:	1,2-dichloroethane, CH ₂ ClCH ₂ Cl
HCFC-151:	1-chloro-2-fluoroethane, CH ₂ ClCH ₂ F
HFC-152:	1,2-Difluoroethane, CH ₂ FCH ₂ F
HFC-161:	fluoroethane, CH ₃ CH ₂ F
CFO-1112:	1,2-dichloro-1,2-difluoroethylene, CClF=CClF
HCFO-1121:	1,2-dichloro-1-fluoroethene, CClF=CHCl
HCFO-1122a:	(E/Z)-1-Chloro-1,2-difluoroethylene, CClF=CHF
HFO-1123:	1,1,2-trifluoroethylene, CF ₂ =CHF
HCFO-1131:	1-chloro-2-fluoroethylene, CHCl=CHF
HFO-1132:	(E/Z)-1,2-difluoroethylene, CHF=CHF
HFO-1141:	fluoroethylene, CHF=CH ₂

[0041] Some of the compounds present in the compositions of the present invention identified herein 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-difluoroethylene (HFO-1132) is meant to represent the cis-isomer (Z), trans-isomer (E), or any combination or mixture of both isomers in any ratio. Similarly, 1-chloro-1,2-difluoroethylene and 1-chloro-1,2-difluoroethylene exist as 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.

[0042] In certain embodiments disclosed herein, CFO-1112 is converted by hydrogenation to form a product mixture comprising, consisting essentially of, or consisting of the E- and Z- isomers of HFO-1132.

[0043] In certain embodiments disclosed herein, CFO-1112 is converted by hydrogenation a product mixture comprising, consisting essentially of, or consisting of the E- and Z- isomers of HFO-1132 in the vapor in a reactor or reaction zone at temperatures ranging from between about 175°C to about 300°C, or between about 200°C to about 275°C, or between about 225°C to about 275°C, including but not limited to between at least about 180°C, at least about 190°C, at least 200°C, at least about 210°C, at least about 230°C, at least about 240°C and less than about 300°C, or less than about 275°C.

[0044] In certain embodiments disclosed herein, CFO-1112 is converted by hydrogenation a product mixture comprising, consisting essentially of, or consisting of the E- and Z- isomers of HFO-1132 in the vapor in a reactor or reaction zone at temperatures ranging from between about 200°C to about 275°C, or between about 225°C to about 275°C, including, but not limited to 225°C, 230°C, 235°C, 240°C, 245°, 250°C, 255°C, 260°C, 265°, 270°C, or 275°C and all values and ranges therebetween.

[0045] In certain embodiments disclosed herein, CFO-1112 is converted to the E- and Z- isomers of HFO-1132 in the vapor phase, in a reaction zone or reactor at elevated temperature in the presence of a hydrogenation catalyst at subatmospheric, atmospheric or super atmospheric, including between about 10 psig to 90 psig, or

between about 20 psig to 80 psig, or about 30 psig to 70 psig. In some embodiments, the reactor or reaction zone is heated to a temperature ranging from between about 175°C to about 300°C, between about 200°C to about 275°C, or between about 225°C to about 275°C, including but not limited to between at least about 180°C, at least about 190°C, at least 200°C, at least about 210°C, at least about 230°C, at least about 240°C and less than about 300°C, or less than about 275°C. In some embodiments, the reactor or reaction zone is heated to a temperature ranging from between about 200°C to about 275°C, or between about 225°C to about 275°C, including, but not limited to 225°C, 230°C, 235°C, 240°C, 245°, 250°C, 255°C, 260°C, 265°, 270°C, or 275°C and all values and ranges therebetween.

[0046] In certain embodiments disclosed herein, CFO-1112 is converted to the E- and Z- isomers of HFO-1132 in the vapor phase, in a reaction zone or reactor at elevated temperature in the presence of a hydrogenation catalyst at subatmospheric, atmospheric or super atmospheric, including between about 10 psig to 250 psig, or between about 20 psig to 200 psig, or about 30 psig to 150 psig. The reactor or reaction zone is heated to a temperature ranging from between about 200°C to about 275°C, or between about 225°C to about 275°C, including, but not limited to 225°C, 230°C, 235°C, 240°C, 245°, 250°C, 255°C, 260°C, 265°, 270°C, or 275°C and all values and ranges therebetween, wherein the catalyst comprises, consists essentially of one of copper, nickel, palladium, combination of them on a support which is selected from carbon, Al₂O₃ and SiC.

[0047] In catalytic hydrogenation embodiments disclosed herein, the catalyst comprises, consists essentially of, or consists of copper combined with palladium and supported on carbon.

[0048] In catalytic hydrogenation embodiments disclosed herein, the catalyst comprises, consists essentially of, or consists of 0.1 to 1.0 weight percent palladium and 0.1 to 20 weight percent copper, or between 0.1 to 0.75% palladium and between 1 to about 5.0 weight percent copper, and all values and ranges therebetween.

[0049] In certain embodiments disclosed herein, CFO-1112 is converted to the E- and Z- isomers of HFO-1132 in the vapor phase, in a reaction zone or reactor at

elevated temperature in the presence of a hydrogenation catalyst at subatmospheric, atmospheric or super atmospheric, including between about 10 psig to 250 psig, or between about 20 psig to 200 psig, or about 30 psig to 150 psig. The reactor or reaction zone is heated to a temperature ranging from between about 200°C to about 275°C, or between about 225°C to about 275°C, including, but not limited to 225°C, 230°C, 235°C, 240°C, 245°, 250°C, 255°C, 260°C, 265°, 270°C, or 275°C and all values and ranges therebetween, wherein the catalyst comprises a Cu-Pd catalyst comprising, consisting essentially of, or consisting of 0.1 to 1.0 weight percent palladium and 0.1 to 20 weight percent copper, or between 0.1 to 0.75% palladium and between 1 to about 5.0 weight percent copper, and all values and ranges therebetween.

[0050] In another embodiment of the invention disclosed herein, CFO-1112 contacts hydrogen in the presence of a support or unsupported hydrogenation catalyst, at temperatures ranging from between about 175°C to about 300°C, between about 200°C to about 275°C, or between about 225°C to about 275°C, including but not limited to between at least about 180°C, at least about 190°C, at least 200°C, at least about 210°C, at least about 230°C, at least about 240°C and less than about 300°C, or less than about 275°C.

[0051] In another embodiment of the invention disclosed herein, CFO-1112 is hydrogenated in the presence of hydrogen at subatmospheric, atmospheric or super atmospheric pressure.

[0052] Certain embodiments disclosed herein relate a process comprising, consisting essentially of, or consisting of one or more of the following steps:

- a. providing a feed of CFO-1112,
- b. providing a feed of hydrogen,
- c. providing a heated reaction zone,
- d. providing a hydrogenation catalyst
- e. loading a hydrogenation catalyst into the reaction zone,
- f. activating the hydrogenation catalyst,
- g. contacting CFO-1112 and hydrogen in the heated reaction zone to produce a product mixture comprising at least E-HFO-1132 and Z-HFO-1132, and one

or more additional compounds comprising, consisting essentially, or consisting of methane, ethane, HFC-41, HCFC-132, HCC-150, HCFC-151, HFC-152, HFC-161, CFO-1112, E-HCFO-1122a, Z-HCFO-1122a, HCFO-1131 and HFO-1141, and

- h. recovering at least one of E-HFO-1132 and Z-HFO-1132.

[0053] Certain embodiments disclosed herein relate to a process comprising, consisting essentially or, or consisting of at least:

- a. contacting CFO-1112 and hydrogen in the heated reaction zone to produce a product mixture comprising at least E-HFO-1132 and/or Z-HFO-1132, and one or more additional compounds comprising, consisting essentially or consisting of methane, ethane, HFC-41, HCFC-132, HCC-150, HCFC-151, HFC-152, HFC-161, CFO-1112, E- HCFO-1122a, Z- HCFO-1122a, HCFO-1131 and HFO-1141, and
- b. optionally including at least one or more of the following steps:
- providing a feed of CFO-1112,
 - providing a feed of hydrogen,
 - providing a heated reaction zone,
 - providing a hydrogenation catalyst,
 - loading a hydrogenation catalyst into the reaction zone,
 - activating the hydrogenation catalyst, and
 - recovering E-HFO-1132 and/or Z-HFO-1132 from the product mixture.

[0054] Certain embodiments disclosed herein relate to a process comprising, consisting essentially of, or consisting of contacting CFO-1112 and hydrogen,

- in a heated reaction zone,
- in the presence of a hydrogenation catalyst, and
- at subatmospheric, atmospheric or super atmospheric.

[0055] Certain embodiments disclosed herein relate a process comprising, consisting essentially or, or consisting of contacting CFO-1112 and hydrogen,

- in the heated reaction zone at temperature ranging from between about 175°C to about 300°C, between about 200°C to about 275°C, or between about 225°C to about 275°C, including but not limited to between at least

about 180°C, at least about 190°C, at least 200°C, at least about 210°C, at least about 230°C, at least about 240°C and less than about 300°C, or less than about 275°C, preferably at a temperature ranging from between about 200°C to about 275°C, or between about 225°C to about 275°C, including, but not limited to 225°C, 230°C, 235°C, 240°C, 245°, 250°C, 255°C, 260°C, 265°C, 270°C, or 275°C and all values and ranges therebetween,

- b. in the presence of a hydrogenation catalyst wherein the catalyst comprises, consists essentially if, or consists of one of copper, nickel, palladium, combination of them on a support which is selected from carbon, Al₂O₃ and SiC, and,
- c. at subatmospheric, atmospheric or super atmospheric preferably at one of between about 10 psig to 250 psig, or between about 20 psig to 200 psig, or about 30 psig to 150 psig.

[0056] Certain embodiments disclosed herein relate to compositions comprising at least one of E-HFO-1132 and Z-HFO-1132.

[0057] Certain embodiments disclosed herein relate to compositions comprising at least one of E-HFO-1132 and Z-HFO-1132 produced by any and all method embodiments disclosed herein.

[0058] Certain embodiments disclosed herein relate to compositions comprising at least one of E-HFO-1132 and Z-HFO-1132, and one or more additional compounds selected from methane, ethane, HFC-41, HCFC-132, HCC-150, HCFC-151, HFC-152, HFC-161, CFO-1112, E- HCFO-1122a, Z- HCFO-1122a, HCFO-1131 and HFO-1141, or two or more additional compounds or three or more additional compounds.

[0059] In certain embodiments of the invention disclosed herein, any of the foregoing compositions are free of or substantially free of Group A Fluorinated Substances. In one embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that (i) contains at least one fully fluorinated methyl (–CF₃) or methylene (–CF₂–) 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).

[0060] 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).

[0061] In embodiments, Group A Fluorinated Substances include, but are not limited to, TFA.

[0062] 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. 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 $> 0 \text{ wt.}\%$ and $\leq 5 \text{ wt.}\%$, or $> 0 \text{ wt.}\%$ and $\leq 4 \text{ wt.}\%$, or $> 0 \text{ wt.}\%$ and $\leq 3 \text{ wt.}\%$, or $> 0 \text{ wt.}\%$ and $\leq 2 \text{ wt.}\%$, or $> 0 \text{ wt.}\%$ and $\leq 1 \text{ wt.}\%$, 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.

[0063] In a preferred embodiment, degradation products of compositions according to the present invention are free of or substantially free of Group A Fluorinated

Substances. The phrase "free of" as used herein with respect to the formation of Group A Fluorinated Substances as degradation products of 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. 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.

[0064] In certain embodiments of the invention disclosed herein, any of the foregoing compositions include one or more additional members selected from hydrofluorocarbons (HFCs), hydrochlorocarbons (HCC's), hydrofluorochlorocarbons (HCFCs), hydrofluoroolefins (HFOs), hydrofluorochloroolefins (HFCOs), C₂-C₄ alkanes, C₂-C₄ alkenes and t-butoxypropenes. In some embodiments, such compositions are free of or substantially free of Group A Fluorinated Substances and/or degradation products of such compositions are free of or substantially free of Group A Fluorinated Substances, as defined herein.

[0065] In certain embodiments disclosed herein, at least one of E-HFO-1132 and Z-HFO-1132 are recovered from the product mixture produced by reaction of CFO-1112 and hydrogen.

[0066] In certain embodiments disclosed herein, the recovered E-HFO-1132 and/or Z-HFO-1132 are blended with other refrigerants.

[0067] Certain embodiments disclosed herein relate to a process of recovering E-HFO-1132 and Z-HFO-1132 and forming refrigerant blends.

[0068] One embodiment of the invention relates to a composition comprising: at least one fluoroethylene selected from (E)-1,2-difluoroethylene ((E)-HFO-1132), (Z)-1,2-difluoroethylene ((Z)-HFO-1132), tetrafluoroethylene (FO-1114), 1-chloro-1,2-difluoroethylene (HCFO-1122a), trifluoroethylene (HFO-1123), 1-chloro-2-fluoroethylene (HCFO-1131), and combinations thereof.

[0069] One embodiment of the invention relates a system and method for heating or cooling using a refrigerant composition comprising at least E-HFO-1132 and/or Z-HFO-1132.

[0070] One embodiment of the invention relates to using E-HFO-1132 and/or Z-HFO-1132 hydrofluoroolefin compositions in heat transfer systems, including but not limited to refrigeration systems, refrigerators, air conditioning systems, heat pumps, chillers, and mobile air conditioning systems, as for example illustrated in **Fig. 2**. **Fig. 2** illustrates a system **200** where a source of refrigerant **210** (a refrigerant composition comprising at least E-HFO-1132 and/or Z-HFO-1132) can be connected to a refrigerant circuit **250** of a refrigerant system which includes, generally in series, charging valve **212**, expansion device **214**, heat exchanger **220**, compressor **230**, heat exchanger **240** and flow lines **213**, **215**, **222**, **231** and **241**. The refrigerant **210** is charged via line **211** which is in fluid communication with charging valve **212**, which when opened and charges refrigerant circuit **250**.

[0071] One embodiment of the invention relates to using E-HFO-1132 and/or Z-HFO-1132 as a component for making refrigerant blends for use in stationary heat transfer systems with a refrigerant composition comprising at least one of E-HFO-1132 and Z-HFO-1132.

[0072] One embodiment of the invention relates to a method for heating or cooling comprising: condensing a refrigerant composition comprising at least one of E-HFO-1132 and Z-HFO-1132, and 2,3,3,3-tetrafluoropropene (HFO-1234yf).

[0073] **Fig. 1** illustrates one embodiment for the conversion of CFO-1112 using system **100**. The CFO-1112 feed flows from line **101** and is conveyed by pump **104** to and through optional vaporizer **110** and discharged through line **114** to be combined with hydrogen feed **112** in mixer **116** (or instead of mixer **116** the feed can be connected through valving directly to the reactor **120**). The combined CFO-1112/H₂ feed is fed into reactor **120** and through bed **122** where CFO-1112 is

converted to E/Z-HFO-1132. Reactor **120** is heated using any system suitable for heating, controlling, and regulating temperatures ranging from between about 175°C and 300°C. The product mixture from reactor **120** is discharged and transferred through line **124** into and through a purification system **130**, e.g., scrubbers (via scrubbing fluid **132**, distillation columns (not shown), etc. to purify and recover HFO-1132 in line **134**.

EXAMPLE 1

[0074] Into an Inconel (0.5-inch OD) tube reactor, e.g., reactor **120**, was added 10 cc of 0.6%Pd-1.5%Cu/C catalyst. The catalyst was activated by H₂ treated at 250°C for 2 hours. CFO-1112 was fed by a pump and H₂ was fed through a mass flow controller into the reactor. The reaction test conditions are listed in Table 1 below. The pressure was approximately 50 psi. The reaction mixture flowed through the reactor containing the catalyst bed. Part of the reactor effluent was passed through a GC sample loop and analyzed by GC-MS-FID. The results of GC analysis are listed in Table 1 below.

TABLE 1

Temp C	1112 cc/hr	H2 sccm	FID Area%					
			Ethane	1141	E-1132	161	Z-1132	1131
215	0.29	7.64	1.72	0.13	2.25	0.00	5.66	0.00
230	0.29	7.64	2.008	0.17	2.12	1.00	4.99	0.00
230	0.29	7.64	2.233	0.19	2.40	1.03	5.72	0.00
245	0.29	7.64	4.181	0.34	3.69	1.61	7.48	0.08
245	0.29	7.64	4.657	0.35	4.40	1.67	9.01	0.12
260	0.29	7.64	8.751	0.63	6.35	2.50	11.25	0.00
260	0.29	7.64	9.135	0.60	7.37	2.43	13.21	0.00
200	0.30	11.92	2.080	0.13	2.36	0.00	1.79	0.25
200	0.30	11.92	1.307	0.09	1.48	0.00	0.97	0.23
200	0.30	11.92	1.160	0.09	1.35	0.00	0.81	0.23
200	0.30	11.92	0.000	0.08	1.21	0.69	0.00	0.00
215	0.30	11.92	1.698	0.12	1.85	0.00	1.03	0.00
215	0.30	11.92	1.993	0.14	2.31	0.00	1.22	0.00
230	0.30	11.92	3.493	0.22	3.65	1.93	6.99	0.16
230	0.30	11.92	4.003	0.24	4.50	2.16	8.48	0.19
245	0.30	11.92	6.606	0.35	6.44	2.95	9.92	0.08
245	0.30	11.92	7.215	0.36	7.78	3.04	12.05	0.15

TABLE 1 (CONTINUED)

Temp C	1112 cc/hr	H2 sccm	FID Area%					
			152	E-1122a	Z-1122a	1112	132	others
215	0.29	7.64	0.00	20.82	10.26	53.12	0.01	6.03
230	0.29	7.64	0.10	17.89	8.83	58.80	0.00	4.20
230	0.29	7.64	0.13	20.72	10.41	52.78	0.13	4.26
245	0.29	7.64	6.50	22.22	10.54	41.78	0.19	1.38
245	0.29	7.64	0.00	25.00	11.97	33.20	0.23	9.40
260	0.29	7.64	11.79	22.82	10.82	21.25	0.28	3.56
260	0.29	7.64	11.85	24.58	11.60	14.77	0.18	4.28
200	0.30	11.92	4.43	17.95	10.09	54.33	0.03	6.56
200	0.30	11.92	1.47	12.83	7.78	69.15	0.08	4.61
200	0.30	11.92	1.14	12.60	7.70	71.43	0.00	4.16
200	0.30	11.92	0.93	12.21	7.47	73.03	0.00	5.04
215	0.30	11.92	2.26	14.08	8.08	65.84	0.00	5.15
215	0.30	11.92	2.93	16.71	9.47	58.89	0.00	6.41
230	0.30	11.92	7.27	18.61	9.70	46.93	0.15	0.90
230	0.30	11.92	8.69	20.96	10.72	38.21	0.16	1.67
245	0.30	11.92	14.03	20.40	10.06	26.67	0.17	2.32
245	0.30	11.92	15.72	21.35	10.19	19.27	0.10	2.78

Example 2

[0075] An Inconel (0.5-inch OD) tube reactor was loaded with 10 cc of 0.6%Pd-1.5%Cu/C catalyst. The catalyst was activated by treatment with H₂ at 250°C for 2 hours. CFO-1112 was fed by a pump and H₂ was fed through a mass flow controller into the reactor under the conditioned specified in Table 2 below. The reaction mixture flowed through the reactor containing the catalyst bed. Part of the reactor effluent was passed through a GC sample loop and analyzed by GC-MS-FID. The results of GC analysis are listed in Table 2 below.

TABLE 2

Conditions:**Feed Rate:** H₂:12 sccm; CFO-1112: 3 ml/hr**Temperature:** 245°C **Pressure:** 50 psig

Peak #	FID area%	Comp
1	0.57%	methane
2	0.02%	41
3	6.11%	ethane
4	0.32%	1141
5	5.95%	E-1132
6	2.73%	161
7	9.16%	Z-1132
8	0.08%	1131
9	12.99%	152
10	19.94%	E-1122a
11	13.34%	Z-1122a
12	1.68%	150
13	1.91%	151
14	24.95%	1112
15	0.25%	132

Example 3

[0076] An Inconel (0.5-inch OD) tube reactor was loaded with 10 cc of 0.6%Pd-1.5%Cu/C catalyst. The catalyst was activated by treatment with H₂ at 250°C for 2 hours. CFO-1112 was fed by a pump and H₂ was fed through a mass flow controller into the reactor under the conditions specified in Table 3 below. The reaction mixture flowed through the reactor containing the catalyst bed. Part of the reactor effluent was passed through a GC sample loop and analyzed by GC-MS-FID. The results of GC analysis are listed in Table 3 below.

TABLE 3

Conditions:**Feed Rate:** H₃: 8.3 sccm; CFO-1112: 3ml/hr**Temperature:** 250°C **Pressure:** 30 psig

Peak #	FID area%	Comp
1	0.6556%	methane
2	0.0182%	41
3	7.9078%	ethane
4	0.5687%	1141
5	5.7398%	E-1132
6	2.2659%	161
7	10.1556%	Z-1132
8	10.6874%	152
9	22.5661%	E-1122a
10	15.8799%	Z-1122a
11	1.4039%	150
12	2.5214%	151
13	19.3144%	1112
14	0.3152%	132

Other Embodiments

[0077] In another embodiment disclosed herein, the composition E-HFO-1132 and/or Z-HFO-1132, and further comprises at least one additional compound selected from E-HCFO-1122a, Z-HCFO-1122a, HFC-161, HCC-150, HCFC-151, HFC-152, CFO-1112, HCFO-1131, FO-1141, HFC-41, methane and ethane.

[0078] In another embodiment disclosed herein, the composition comprises E-HFO-1132 and/or Z-HFO-1132, between 10 and 40 mole percent E/Z-HCFO-1122a based on the total amount of the composition, and further comprises HFC-152, HFC-161, CFO-1112, fluoroethylene HFC-1141, HC-50 (methane) and HC-70 (ethane).

[0079] In another embodiment disclosed herein, the composition comprises E-HFO-1132 and/or Z-HFO-1132, between 30 and 50 mole percent E/Z-HCFO-1122a

based on the total amount of the composition, and further comprises HFC-152, HFC-161, CFO-1112, fluoroethylene HFC-1141, HC-50 (methane) and HC-70 (ethane).

[0080] In another embodiment disclosed herein, the composition comprises E-HCFO-1122a, Z-HCFO-1122a, HFC-161, HCC-150, CFC-151, HFC-152, CFO-1112, E-HFO-1132, Z-HFO-1132, HCFO-1131, HFO-1141, HFC-41, methane and ethane, and less than 30 mole percent CFO-1112 based on the total amount of the composition, or less than 25 mole percent CFO-1112 based on the total amount of the composition.

[0081] Process A1: A process comprising contacting CFO-1112 and hydrogen in the heated reaction zone, in the presence of a catalyst, and producing a mixture comprising at least E-HFO-1132 and Z-HFO-1132.

[0082] Process A2: The process of claim 1, wherein the CFO-1112 contacts hydrogen in the vapor phase.

[0083] Process A3: The process of Process A1 or A2, wherein the CFO-1112 contacts hydrogen in a reaction zone at temperatures ranging from between about 175°C to about 300°C.

[0084] Process A4: The process of any of Process A1-A3, wherein the CFO-1112 contacts hydrogen in a reactor zone at temperatures ranging from one of between about 200°C to about 275°C, or between about 225°C to about 275°C.

[0085] Process 5: The process of any of Process A1-A4, wherein the CFO-1112 contacts hydrogen in a reaction zone at temperatures selected from one of between at least about 180°C, at least about 190°C, at least 200°C, at least about 210°C, at least about 230°C, at least about 240°C and less than about 300°C, and less than about 275°C.

[0086] Process A6: The process of any of Process A1-A5, wherein the CFO-1112 contacts hydrogen in a reaction zone at temperatures selected from one of between at least about 180°C, at least about 190°C, at least 200°C, at least about 210°C, at least about 230°C, at least about 240°C and less than about 300°C, and less than about 275°C.

[0087] Process A7: The process of any of Process A1-A6, wherein the CFO-1112 contacts hydrogen in a reaction zone at temperatures selected from between one of 225°C, 230°C, 235°C, 240°C, 245°, 250°C, 255°C, 260°C, 265°, 270°C, or to about 275°C.

[0088] Process A8: The process of any of Process A1-A7, wherein the CFO-1112 contacts hydrogen in a reaction zone at one of subatmospheric, atmospheric or super atmospheric pressure.

[0089] Process A9: The process of any of Process A1-A8, wherein the CFO-1112 contacts hydrogen in a reaction zone at a pressure selected from one of between about 10 psig to 250 psig, or between about 20 psig to 200 psig, or about 30 psig to 150 psig.

[0090] Process A10: The process of any of Process A1-A9, wherein the reaction zone is heated to a temperature selected from one of between about 200°C to about 275°C, or between about 225°C to about 275°C, and a pressure selected from one of between about including between about 10 psig to 250 psig, or between about 20 psig to 200 psig, or about 30 psig to 150 psig.

[0091] Process A11: The process of any of Process A1-A10, wherein the CFO-1112 contacts hydrogen at pressure selected from one of between about including between about 10 psig to 250 psig, or between about 20 psig to 200 psig, or about 30 psig to 150 psig, a temperature ranging from between about 200°C to about 275°C, and the catalyst comprises a copper-palladium (Cu-Pd)/carbon catalyst.

[0092] Process A12: The process of Process A12, wherein the catalyst is selected from one of 0.1 to 1.0 weight percent palladium and 0.1 to 20 weight percent copper and between 0.1 to 0.75% palladium and between 1 to about 5.0 weight percent copper.

[0093] Process A13: The process of any of Process A1-A13, further comprising activating the catalyst prior to contacting CFO-1112 and hydrogen.

[0094] Process A14: The process of any of Process A1-A14, further comprising recovering at least one of E-HFO-1132 and Z-HFO-1132.

[0095] Process A15: The process of any of Process A1-A14, further comprising blending the recovered E-HFO-1132 and/or Z-HFO-1132 with another refrigerant compound.

[0096] A composition comprising at least one of E-HFO-1132 and Z-HFO-1132, and one or more compounds selected from methane, ethane, HFC-41, HCFC-132, HCC-150, HCFC-151, HFC-152, HFC-161, CFO-1112, Z-HCFO-1122a, E-HCFO-1122a, HCFO-1131 and HFO-1141.

[0097] A composition comprising at least one of E-HFO-1132 and Z-HFO-1132, and two or more compounds selected from methane, ethane, HFC-41, HCFC-132, HCC-150, HCFC-151, HFC-152, HFC-161, CFO-1112, E-HCFO-1122a, Z-HCFO-1122a, HCFO-1131 and HFO-1141.

[0098] A composition comprising at least one of E-HFO-1132 and Z-HFO-1132, and three or more compounds selected from methane, ethane, HFC-41, HCFC-132, HCC-150, HCFC-151, HFC-152, HFC-161, CFO-1112, E- HCFO-1122a, Z- HCFO-1122a, HCFO-1131 and HFO-1141.

[0099] A composition comprising: at least one fluoroethylene selected from (E)-1,2-difluoroethylene ((E)-HFO-1132), (Z)-1,2-difluoroethylene ((Z)-HFO-1132), tetrafluoroethylene (FO-1114), 1-chloro-2,2-difluoroethylene (HCFO-1122a), 1-chloro-1,2-difluoroethylene (HFO-1122a), trifluoroethylene (HFO-1123), 1-chloro-2-fluoroethylene (HCFO-1131), and combinations thereof.

[0100] A composition formed by any process embodiment described herein.

[0101] In some embodiments, any of the foregoing compositions are free of or substantially free of Group A Fluorinated Substances.

[0102] In some embodiments, degradation products of any of the foregoing compositions are free of or substantially free of Group A Fluorinated Substances.

[0103] A process comprising heating or cooling using a refrigerant in a heat transfer systems selected from one of refrigeration systems, refrigerators, air conditioning systems, heat pumps, chillers, and mobile air conditioning systems.

[0104] A process comprising blending tri, tetra- and penta- C₂-C₃ fluoro(chloro)olefins with at least one of E-HFO-1132 and Z-HFO-1132, optionally

containing one of HCFO-1131 and HFO-1123, to form a blend, and charging a stationary heat transfer system with the blend.

[0105] A system comprising a contained source of refrigerant, a refrigerant circuit comprising an evaporator, a compressor, a condenser, a charging valve, and a charging line for temporarily connecting said contained source and said charging valve, wherein said contained source comprises a refrigerant including at least one of E-HFO-1132 and Z-HFO-1132.

[0106] A system comprising a contained source of refrigerant, a refrigerant circuit comprising an evaporator, a compressor, a condenser, a charging valve and a charging line for temporarily connecting said contained source and said charging valve, wherein said contained source comprises a refrigerant including at least one of E-HFO-1132 and Z-HFO-1132, wherein the system is part of a heat transfer system selected from one of refrigeration systems, refrigerators, air conditioning systems, heat pumps, chillers, and mobile air conditioning systems.

[0107] Although certain aspects, embodiments and principals have been described above, it is understood that this description is made only way of example and not as limitation of the scope of the invention or appended claims. The foregoing various aspects, embodiments and principals can be used alone and in combinations with each other.

CLAIMS

What is claimed is:

1. A process comprising contacting 1,2-dichloro-1,2-difluoroethylene (CFO-1112) and hydrogen in a heated reaction zone, in the presence of a catalyst, to produce a mixture comprising at least E-1,2-difluoroethylene and Z-1,2-difluoroethylene.
2. The process of claim 1, wherein the CFO-1112 contacts hydrogen in the vapor phase.
3. The process of claim 1 or 2, wherein the catalyst comprises a metal selected from the group consisting of copper, nickel, palladium, and combinations thereof, on a support which is selected from the group consisting of carbon, Al₂O₃ and SiC.
4. The process of claim 3, wherein the catalyst comprises a copper-palladium (Cu-Pd)/carbon catalyst.
5. The process of claim 4, wherein the catalyst is selected from one of (i) about 0.1 to about 1.0 weight percent palladium and about 0.1 to about 20 weight percent copper and, (ii) about 0.1 to about 0.75 weight percent palladium and about 1 to about 5.0 weight percent copper.
6. The process of any of claims 1 to 5, the process further comprising activating the catalyst prior to contacting the CFO-1112 and hydrogen.
7. The process of any of claims 1 to 6, wherein the CFO-1112 contacts hydrogen in a reaction zone at temperatures ranging from between about 175°C to about 300°C.
8. The process of any of claims 1 to 7, wherein the CFO-1112 contacts hydrogen in a reactor zone at temperatures ranging from about 200°C to about 275°C, or from about 225°C to about 275°C.
9. The process of any of claims 1 to 7, wherein the CFO-1112 contacts hydrogen in a reaction zone at temperatures selected from one of (i) at least about 180°C, at least about 190°C, at least 200°C, at least about 210°C, at least about

230°C, or at least about 240°C, and (ii) less than about 300°C or less than about 275°C.

10. The process of any of claims 1 to 7, wherein the CFO-1112 contacts hydrogen in a reaction zone at temperatures selected from between one of (i) 225°C, 230°C, 235°C, 240°C, 245°, 250°C, 255°C, 260°C, 265°C or 270°C, and (ii) about 275°C.
11. The process any of claims 1 to 10, wherein the CFO-1112 contacts hydrogen in a reaction zone at one of subatmospheric, atmospheric or super atmospheric pressure.
12. The process of any of claims 1 to 11, wherein the CFO-1112 contacts hydrogen in a reaction zone at a pressure selected from one of (i) between about 10 psig and 250 psig, (ii) between about 20 psig and 200 psig, or (iii) between about 30 psig and 150 psig.
13. The process of any of claims 1 to 12, wherein the reaction zone is heated to a temperature selected from one of between about 200°C to about 275°C, or between about 225°C to about 275°C, and a pressure selected from one of between about 10 psig to 250 psig, between about 20 psig to 200 psig, or between about 30 psig to 150 psig.
14. The process of any of claims 1 to 13, further comprising recovering at least one of the E-HFO-1132 and the Z-HFO-1132.
15. The process of claim 14, further comprising blending the recovered E-HFO-1132 and/or the Z-HFO-1132 with at least one of a difluoropropene, a trifluoropropene, a tetrafluoropropene, and a pentafluoropropene, and optionally with at least one of HCFO-1131 and HFO-1123.
16. A composition formed by the process of any of claims 1 to 15.
17. A process comprising providing heating or cooling by a heat transfer system selected from the group consisting of refrigeration systems, refrigerators, air conditioning systems, heat pumps, chillers, and mobile air conditioning systems, the process comprising circulating and/or charging a composition

formed according to the process of any of claims 1 to 15 in or to the heat transfer system.

18. A process comprising providing heating or cooling by a heat transfer system selected from the group consisting of refrigeration systems, refrigerators, air conditioning systems, heat pumps, chillers, and mobile air conditioning systems, the process comprising circulating and/or charging a composition in or to the heat transfer system, the composition comprising at least one of E-HFO-1132 and Z-HFO-1132, preferably the composition comprising at least one of E-HFO-1132 and Z-HFO-1132 and further comprising one or more additional compounds selected from the group consisting of methane, ethane, HFC-41, HCFC-132, HCC-150, HCFC-151, HFC-152, HFC-161, CFO-1112, E-HCFO-1122a, Z-HCFO-1122a, HCFO-1131 and HFO-1141.
19. A composition comprising at least one of E-HFO-1132 and Z-HFO-1132, and further comprising one or more additional compounds selected from the group consisting of methane, ethane, HFC-41, HCFC-132, HCC-150, HCFC-151, HFC-152, HFC-161, CFO-1112, E-HCFO-1122a, Z-HCFO-1122a, HCFO-1131 and HFO-1141.
20. The composition of claim 19, the composition comprising two or more additional compounds, preferably three or more additional compounds.
21. A composition comprising: at least one fluoroethylene selected from the group consisting of (E)-1,2-difluoroethylene ((E)-HFO- 1132), (Z)-1,2-difluoroethylene ((Z)-HFO- 1132), tetrafluoroethylene (FO-1114), 1-chloro-1,2-difluoroethylene (HCFO-1122a), trifluoroethylene (HFO-1123), 1-chloro-2-fluoroethylene (HCFO-1131), and combinations thereof.
22. The composition of any of claims 16 or 19 to 21, wherein the composition is free of or substantially free of Group A Fluorinated Substances.
23. The composition of any of claims 16 or 19 to 21, wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.
24. A process comprising blending at least one fluoropropene selected from the group consisting of a difluoropropene, a trifluoropropene, a tetrafluoropropene,

and a pentafluoropropene, with at least one of (E)-1,2-difluoroethylene ((E)-HFO-1132) and (Z)-1,2-difluoroethylene ((Z)-HFO-1132), and optionally with at least one of HCFO-1131 and HFO-1123, to form a composition, and charging a stationary heat transfer system with the composition.

25. A system comprising a contained source of refrigerant, a refrigerant circuit comprising an evaporator, a compressor, a condenser, a charging valve and a charging line for temporarily connecting said contained source and said charging valve, wherein said contained source comprises a refrigerant including at least one of (E)-1,2-difluoroethylene ((E)-HFO-1132) and (Z)-1,2-difluoroethylene ((Z)-HFO-1132).