

COMPOSITIONS COMPRISING 1,3,3,3-TETRAFLUOROPROPENE, METHODS
OF MAKING SAME, AND USES THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application 63/546,485 filed October 30, 2023, U.S. Provisional Application 63/574,940 filed April 5, 2024, U.S. Provisional Application 63/662,915 filed June 21, 2024, and U.S. Provisional Application 63/678,572 filed August 2, 2024, the disclosure of each of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention is directed to fluoropropene compositions, methods of producing the same, and methods and systems using the same.

BACKGROUND OF THE INVENTION

[0003] The fluorocarbon industry has been working for the past few decades to find replacement refrigerants for the ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) being phased out as a result of the Montreal Protocol. The solution for many applications has been the commercialization of hydrofluorocarbon (HFC) compounds for use as refrigerants, solvents, fire extinguishing agents, blowing agents and propellants. These new compounds, such as HFC refrigerants, HFC-134a and HFC-125 being the most widely used at this time, have zero ozone depletion potential (ODP) and thus are not affected by the current regulatory phase-out as a result of the Montreal Protocol. In addition to ozone depleting concerns, global warming is another environmental concern in many of these applications. HFC refrigerants such as HFC-134a and HFC-125 respectively have global warming potentials (GWP) of 1,300 and 3,170 according to the UN's IPCC Fifth Assessment Report (AR5).

[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 global warming potentials, 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 refrigerant compositions that meet evolving regulations as well as provide heat transfer and refrigerant characteristics that meet or exceed the effectiveness of conventional refrigerants and refrigerant blends.

[0006] 1,3,3,3-tetrafluoropropene (HFO-1234ze) ($\text{CF}_3\text{CH}=\text{CHF}$), like HFO-1234yf, has zero ozone depletion and very low global warming potential, and has thus been identified as a potential useful refrigerant. For example, U.S. Patent No 7,862,742 discloses compositions comprising HFO-1234ze and HFO-1234yf. U.S. Patent No. 9,302,962 discloses methods for making HFO-1234ze. The disclosures of U.S. Patent No. 7,862,742 and U.S. Patent No. 9,302,962 are hereby incorporated by reference in their entireties.

[0007] 1,3,3,3-tetrafluoropropene (HFO-1234ze) exists as both a Z-isomer and an E-isomer. The Z-isomer, in particular, i.e., HFO-1234ze(Z), which has zero ozone depletion and very low global warming potential and with a boiling point of 10.6°C, possesses physical properties that make it an attractive option for heat pump and air conditioning applications or for use as a blowing agent, either as a single fluid or in blends.

[0008] The instant invention provides economical manufacturing processes to make HFO-1234ze(Z) and provide HFO-1234ze(Z)-based compositions which meet the evolving regulatory landscape.

SUMMARY OF THE INVENTION

[0009] The foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as defined in the appended claims. The various embodiments of the invention can be used alone or in combinations with each other. Other features and advantages of the present invention will be apparent from the following more detailed description of the preferred embodiment, taken in conjunction with the accompanying drawings, which illustrate, by way of example, the principles of the invention.

[0010] Embodiment 1. A process of preparing a mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene, the process comprising: (i) reacting vinyl chloride ($\text{CH}_2=\text{CHCl}$) and carbon tetrachloride (CCl_4) in the presence of catalyst system comprising a metal-containing compound and a phosphorus-containing compound to make a product comprising 1,1,1,3,3-pentachloropropane ($\text{CCl}_3\text{CH}_2\text{CHCl}_2$, HCC-240fa); (ii) fluorinating the HCC-240fa with a fluorination agent in the presence of a fluorination catalyst to produce a product comprising 1,1,1,3,3-pentafluoropropane ($\text{CF}_3\text{CH}_2\text{CHF}_2$, HFC-245fa); and (iii) contacting HFC-245fa in the gas phase with a catalyst, in the presence of an oxygen containing gas, to form a reaction mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene.

[0011] Embodiment 2. A process of preparing a mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene, the process comprising: (i) reacting vinyl chloride ($\text{CH}_2=\text{CHCl}$) and carbon tetrachloride (CCl_4) in the presence of catalyst system comprising a metal-containing compound and a phosphorus-containing compound to make a product comprising 1,1,1,3,3-pentachloropropane ($\text{CCl}_3\text{CH}_2\text{CHCl}_2$, HCC-240fa); (ii) fluorinating the HCC-240fa with a fluorination agent to produce a product comprising 1,1,1,3,3-pentachloropropene ($\text{CF}_3\text{CH}=\text{CHCl}$, E/Z-HFO-1233zd); and (iii) fluorinating the E/Z-HFO-1233zd with a fluorination agent in the presence of a fluorination catalyst to form a reaction mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene.

[0012] Embodiment 3. A process of preparing a mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene, the process comprising: (i) reacting vinyl chloride ($\text{CH}_2=\text{CHCl}$) and carbon tetrachloride (CCl_4) in the presence of catalyst system comprising a metal-containing compound and a phosphorus-containing compound to make a product comprising 1,1,1,3,3-pentachloropropane ($\text{CCl}_3\text{CH}_2\text{CHCl}_2$, HCC-240fa); and (ii) fluorinating the HCC-240fa with a fluorination agent in the presence of a fluorination catalyst to form a reaction mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene.

[0013] Embodiment 4. The process of any one of Embodiments 1, 2 or 3, wherein a feed composition comprising the carbon tetrachloride further comprises one or more additional compounds selected from the group consisting of trichloroethylene

(CClH=CCl₂), tetrachloroethylene (CCl₂=CCl₂), hexachloroethane (CCl₃CCl₃), bromotrichloromethane (CCl₃Br), chloroform (CCl₃H), 1,1,1-trichloroethane (CCl₃CH₃), 1,1,2-trichloroethane (CHCl₂CH₂Cl), trans-1,2-dichloroethylene (E-CHCl=CHCl), cis-1,2-dichloroethylene (Z-CHCl=CHCl) and 1,1-dichloroethylene (CH₂=CCl₂).

[0014] Embodiment 5. The process of any one of Embodiments 1, 2 or 3, wherein the product comprising HCC-240fa further comprises one or more additional compounds selected from the group consisting of 1-chlorobutane; 1,2,3-trichloropropene (CHCl=CCl-CH₂Cl, HCO-1240xd); HCO-1230xd (CHCl=CCl-CHCl₂, 1,2,3,3-tetrachloropropene); 1,1,1,3-tetrachloropropane (CCl₃-CH₂-CH₃, HCC-250fb); 1,4 dichlorobutane; 1,2-dichloro-cyclobutane, 1,1,4,4-tetrachlorobutadiene; 1,1,3,4 tetrachlorobutadiene; 1,1,1,2,3-pentachloropropane (HCC-240db); C₅H₇Cl₃ isomer(s) and C₄H₇Cl₃ isomer(s).

[0015] Embodiment 6. The process of Embodiment 5, wherein a total amount of the additional compounds is greater than 0 wt.% and less than or equal to about 5 wt.%, preferably less than or equal to about 1 wt.%, based on the total weight of the composition.

[0016] Embodiment 7. The process of any one of Embodiments 1, 2 or 3, wherein the metal-containing compound of the catalyst system of step (i) comprises an iron-containing compound.

[0017] Embodiment 8. The process of any one of Embodiments 1, 2 or 3, wherein the phosphorous-containing compound of the catalyst system comprises a phosphine, preferably triphenyl phosphine or tributyl phosphine, or a phosphate, preferably tributyl phosphate.

[0018] Embodiment 9. The process of Embodiment 1, wherein the fluorination catalyst is a Lewis acid catalyst, preferably selected from the group consisting of SbCl₅, SbCl₃, SbF₅, SnCl₄, TiCl₄, NiF₅, FeCl₃, and combinations of two or more thereof.

[0019] Embodiment 10. The process of Embodiment 1, wherein the product comprising HFC-245fa further comprises two or more additional compounds selected from the group consisting of: (i) HFC-143a, HFC-1225zc, HFC-236fa, HFO-E/Z-

1234ze, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa; or (ii) HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234ze(Z), HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

[0020] Embodiment 11. The process of Embodiment 10, wherein a total amount of the additional compounds is greater than 0 wt.% and less than or equal to about 5 wt.%, preferably less than or equal to about 1 wt.%, based on the total weight of the composition.

[0021] Embodiment 12. The process of Embodiment 1, wherein the catalyst of step (iii) comprises chromium.

[0022] Embodiment 13. The process of any of Embodiments 1, 2 or 3, wherein an E:Z ratio of the reaction mixture is from about 10:1 to about 3:1.

[0023] Embodiment 14. The process of any of Embodiments 1, 2 or 3, the process further comprising separating HFO-1234ze(E) and HFO-1234ze(Z) from the reaction mixture.

[0024] Embodiment 15. The process of Embodiment 1, the process further comprising separating HFO-1234ze(E), HFO-1234ze(Z) and HFC-245fa from the reaction mixture.

[0025] Embodiment 16. The process of Embodiment 2, the process further comprising separating HFO-1233zd(E), HFO-1234ze(Z) and HFC-245fa from the reaction mixture.

[0026] Embodiment 17. The process of Embodiment 2, the process further comprising separating HFO-1233zd(E) and HFO-1234ze(Z) from the reaction mixture.

[0027] Embodiment 18. The process of Embodiment 2, the process further comprising separating HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E) from the reaction mixture.

[0028] Embodiment 19. The process of Embodiment 2, the process further comprising separating HFO-1233zd(E), HFO-1234ze(Z), HFO-1234ze(E) and HFC-245fa from the reaction mixture.

[0029] Embodiment 20. The process of Embodiment 3, the process further comprising separating HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E) from the reaction mixture.

[0030] Embodiment 21. The process of any of Embodiments 14-15, 18, 19 or 20, the process further comprising separating the HFO-1234ze(Z) from the HFO-1234ze(E).

[0031] Embodiment 22. The process of Embodiment 21, the process further comprising isomerizing the HFO-1234ze(E) to HFO-1234ze(Z).

[0032] Embodiment 23. A high purity etching gas composition comprising HFO-1234ze(Z), the composition having a purity of greater than 99.5 wt. % and being free of or substantially free of chlorinated compounds.

[0033] Embodiment 24. A composition comprising HFO-1234ze(E) and HFO-1234ze(Z), the composition being produced by the process of any of Embodiments 1, 2 or 3.

[0034] Embodiment 25. The composition of Embodiment 24, the composition further comprising one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

[0035] Embodiment 26. A composition comprising (a) HFO-1234ze(E), HFO-1234ze(Z) and HFC-245fa; (b) HFO-1234ze(Z), HFO-1234ze(E), HFO-1233zd(E) and HFC-245fa; or (c) HFO-1234ze(Z) and HFC-245fa.

[0036] Embodiment 27. The composition of Embodiment 26, wherein the composition is produced by the process of Embodiment 1.

[0037] Embodiment 28. The composition of Embodiments 26-27, wherein the composition (a) further comprises (i) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HCFC-124, CFC-114, trifluoropropylene, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); (ii) one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; and (iii) one or more additional compounds selected from the group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFC-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130; wherein the composition (b) further comprises (i) one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; (ii) one or more additional compounds selected from the group consisting of Z-HFO-1234ze, E-HFO-1234ze and HFC-245fa; (iii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HCFC-124, CFC-114, trifluoropropylene, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb and HFO-1243zf; and (iv) one or more

additional compounds selected from the group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130; or wherein the composition (c) further comprises (i) one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; and (ii) one or more additional compounds selected from the group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HFO-1234ze(E), HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

[0038] Embodiment 29. A composition comprising HFO-1233zd(E), HFO-1234ze(Z) and HFC-245fa.

[0039] Embodiment 30. The composition of Embodiment 29, wherein the composition is produced by the process of Embodiment 2.

[0040] Embodiment 31. The composition of Embodiments 29-30, the composition further comprising (i) one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a,

HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; (ii) an additional compound of E-HFO-1234ze; and (iii) one or more additional compounds selected from the group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HFO-1234ze(E), HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFC-338mf, HFC-356mff, HFO-1234ze(Z), HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

[0041] Embodiment 32. A blowing agent composition comprising HFO-1233zd(E) and HFO-1234ze(Z).

[0042] Embodiment 33. The blowing agent composition of Embodiment 32, wherein the composition is produced by the process of Embodiment 2.

[0043] Embodiment 34. The blowing agent composition of Embodiments 32-33, the composition further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; and one or more additional compounds selected from the group consisting of E-HFO-1234ze and HFC-245fa.

[0044] Embodiment 35. A composition comprising HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E).

[0045] Embodiment 36. The composition of Embodiment 25, wherein the composition is produced by the process of Embodiment 2 or Embodiment 3.

[0046] Embodiment 37. The composition of Embodiments 35-36, the composition further comprising (i) one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; (ii) an

additional compound of HFC-245fa; and (iii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb and HFO-1243zf.

[0047] Embodiment 38. A composition comprising HFO-1233zd(E), HFO-1234ze(Z), HFO-1234ze(E) and HFC-245fa.

[0048] Embodiment 39. The composition of Embodiment 38, wherein the composition is produced by the process of Embodiment 2.

[0049] Embodiment 40. The composition of Embodiments 38-39, the composition further comprising (i) one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; (ii) one or more additional compounds selected from the group consisting of Z-HFO-1234ze, E-HFO-1234ze and HFC-245fa; (iii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb and HFO-1243zf; and (iv) one or more additional compounds selected from the group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

[0050] Embodiment 41. A composition comprising HFO-1234ze(Z) and at least one compound selected from the group consisting of HFO-1234ze(E), HFO-

1233zd(E), HFC-245fa, HFO-1336mzz(E), HFO-1336mzz(Z), HFC-227ea, HFC-134a and HFC-134.

[0051] Embodiment 42. The composition of Embodiment 41, wherein the HFO-1234ze(Z) is produced by any of the preceding process Embodiments 1-22.

[0052] Embodiment 43. The composition of Embodiments 41-42, the composition further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

[0053] Embodiment 44. A composition comprising HFO-1234ze(Z) and at least one compound selected from the group consisting of HFO-1234ze(E), HFO-1233zd(E) and HFC-245fa.

[0054] Embodiment 45. The composition of Embodiment 44, wherein the composition is produced by any of the preceding process Embodiments 1-22.

[0055] Embodiment 46. The composition of Embodiments 44-45, the composition further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

[0056] Embodiment 47. A blowing agent composition comprising (i) HFO-1234ze(Z), or (ii) HFO-1234ze(Z) and at least one compound selected from the group consisting of HFO-1336mzz(E), HFO-1336mzz(Z), HCFO-1224yd(Z) and HFO-1233zd(E).

[0057] Embodiment 47a. A blowing agent composition comprising HFO-1234ze(Z) and one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0058] Embodiment 48. A blowing agent composition comprising HFO-1234ze(Z) and HFO-1336mzz(E), and further comprising one or more additional compounds selected from the group consisting of HCFO-1233xf, HFO-1336ft, HCFC-133a, CO-1140, HCFO-1233zd(E), HFC-245fa, HFO-1327mz, HFC-347mef, HFO-1243zf, and further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0059] Embodiment 49. A blowing agent composition comprising HFO-1234ze(Z) and HFO-1336mzz(Z), and further comprising one or more additional compounds selected from the group consisting of HFO-1336mzz(E), HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb, and further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0060] Embodiment 50. A blowing agent composition comprising HFO-1234ze(Z) and HFO-1233zd(E), and further comprising one or more additional compounds selected from the group consisting of Z-HFO-1234ze, E-HFO-1234ze and HFC-245fa, and further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0061] Embodiment 51. A blowing agent composition comprising HFO-1234ze(Z) and HCFO-1224yd(Z), and further comprising one or more additional compounds selected from HFO-1234yf, HFO-1234ze(E) + HFO-1243zf, HFC-263fb, HFC-254eb, CFC-1215yb, HCFC-244bb, HFO-1224 isomer(s) other than 1224yd(Z), HCFO-1224yd(E), CFC-1112a, HCFC-225ca, HCFC-225cb and HCFC-234bb, and further comprising one or more additional compounds selected from the group consisting of

HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0062] Embodiment 52. The blowing agent composition of any of Embodiments 47-51, wherein the HFO-1234ze(Z) is produced by any of the process Embodiments 1-22.

[0063] Embodiment 53. A composition comprising HFO-1234ze(Z), HFO-1234ze(E) and HFC-227ea, and further comprising (i) one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; (ii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, HFO-1234ze(Z), CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and (iii) one or more additional compounds selected from the group consisting of FC-1216 and HCFC-124.

[0064] Embodiment 54. A composition comprising HFO-1234ze(Z), HFO-1234ze(E), and HFC-134a, and further comprising (i) one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, (ii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, HFO-1234ze(Z), CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E), and (iii) one or more additional compounds selected from the group consisting of HFC-134, HCFC-124, HCFO-1122, HFC-143a, HCFC-31, HFC-32, HFC-125, CFC-114 and CFC-114a.

[0065] Embodiment 55. The composition of Embodiment 53 or Embodiment 54, wherein the HFO-1234ze(Z) is produced from any of the process Embodiments 1-22.

[0066] Embodiment 56. The composition of Embodiment 53 or Embodiment 54, wherein a mixture of the HFO-1234ze(Z) and the HFO-1234ze(E) is produced from any of the process Embodiments 1-22.

[0067] Embodiment 57. The composition of any of Embodiments 23-56, wherein the composition has a GWP of 300 or less, preferably 150 or less.

[0068] Embodiment 58. The composition of any of Embodiments 23-57, wherein the composition has a flammability classification of 1, 2L or 2 as determined by ASHRAE Standard 34 and ASTM E681-09.

[0069] Embodiment 59. The composition of any of Embodiments 23-58, the composition further comprising at least one lubricant.

[0070] Embodiment 60. The composition of Embodiment 59, wherein the lubricant is selected from the group consisting of polyalkylene glycols, polyol esters, polyvinyl ethers, poly-alpha-olefins, and combinations thereof.

[0071] Embodiment 61. A system for cooling or heating comprising an evaporator, compressor, condenser, and expansion device, said system containing the composition of any of Embodiments 23-60.

[0072] Embodiment 62. A method for producing heating in a high temperature heat pump, the method comprising condensing the composition of any of Embodiments 23-60 in a condenser, wherein the high temperature heat pump uses condenser operating temperatures greater than about 55°C, preferably from about 55°C to about 150°C.

[0073] Embodiment 63. A high temperature heat pump comprising a condenser and the composition of any of Embodiments 23-60, wherein an operating temperature of the condenser is greater than about 55°C, preferably from about 55°C to about 150°C, more preferably greater than about 150°C.

[0074] Embodiment 64. The composition of any of Embodiments 23-60, 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.

[0075] Embodiment 65. The process of Embodiment 1, wherein a feed composition for (iii) comprises HFC-245fa, and one or more additional compounds selected from the group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HFO-E/Z-1234ze, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234ze(Z), HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130, and wherein the feed composition has a moisture content of less than about 50 ppm, preferably less than about 20 ppm, more preferably less than about 10 ppm, and a non-absorbable gases (NAG) content of greater than zero and less than about 10%, preferably less than about 5%, more preferably less than about 3%, most preferably less than about 1.5%.

[0076] Embodiment 66. The process of any one of Embodiments 1, 2 or 3, the process further comprising a step of adding one or more compounds to the reaction mixture.

[0077] Embodiment 67. A process comprising using a composition as a dielectric gas, wherein the composition is a composition comprising Z-HFO-1234ze produced by the process of any one of Embodiments 1-22, preferably wherein the Z-HFO-1234ze has a purity of greater than 99.5%.

[0078] Embodiment 68. A process comprising using a composition as an etching gas, wherein the composition is a composition of Embodiment 23.

[0079] Embodiment 69. A process comprising using a composition as a propellant in a sprayable composition of a medical product, wherein the composition is a composition comprising Z-HFO-1234ze produced by the process of any one of Embodiments 1-22, the Z-HFO-1234ze having a purity of 99.9% or greater.

[0080] Embodiment 70. The process of Embodiment 2, wherein the (ii) fluorination of the HCC-240fa with a fluorination agent is conducted in the vapor phase in the presence of a fluorination catalyst.

[0081] Embodiment 71. The process of Embodiment 2, wherein the (ii) fluorination of the HCC-240fa with a fluorination agent is conducted in the liquid phase in the presence or absence of a fluorination catalyst.

[0082] Embodiment 72. The process of Embodiment 22, wherein isomerization of the HFO-1234ze(E) to HFO-1234ze(Z) is carried out in the presence of an oxygen containing gas.

[0083] Embodiment 73. The process of Embodiment 22 or claim 72, wherein the isomerization of the HFO-1234ze(E) to HFO-1234ze(Z) is carried out in the presence of an isomerization catalyst.

[0084] Embodiment 74. The process of Embodiment 73, wherein the isomerization catalyst comprises a metal compound selected from the group consisting of chromium, aluminum, zinc, magnesium, and combinations thereof, preferably wherein the isomerization catalyst is selected from the group consisting of Cr₂O₃, Al₂O₃, and combinations thereof.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0085] The following detailed description of preferred embodiments of the present invention will be better understood when read in conjunction with the appended drawing. For the purposes of illustrating the invention, there is shown in the drawing an embodiment which is presently preferred. It is understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown. In the drawings:

[0086] Fig. 1 depicts a distillation step of an integrated process according to a first embodiment of the present invention;

[0087] Figs. 2A-2B depict the integrated process according to embodiments of the present invention;

[0088] Fig. 3 depicts a distillation step of an integrated process according to a second embodiment of the present invention;

[0089] Fig. 4 depicts a distillation process to separate HFO-1234ze(Z) from HFO-1234ze(E);

[0090] Fig. 5 depicts the integrated process according to the first embodiment of the present invention;

[0091] Fig. 6 depicts the integrated process according to the first embodiment of the present invention, including a step of isomerizing HFO-1234ze(E) to HFO-1234ze(Z);

[0092] Figs. 7A-7B depict the integrated process according to the second embodiment of the present invention;

[0093] Fig. 8 depicts the integrated process according to the second embodiment of the present invention, including a step of isomerizing HFO-1234ze(E) to HFO-1234ze(Z);

[0094] Figs. 9A-9B depict the integrated process according to the third embodiment of the present invention;

[0095] Fig. 10 depicts the integrated process according to the third embodiment of the present invention, including a step of isomerizing HFO-1234ze(E) to HFO-1234ze(Z); and

[0096] Figs. 11-12 show combination with other compounds and/or adjust of component ratios as needed for desired blend composition.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0097] A refrigerant is defined as a heat transfer fluid that undergoes a phase change from liquid to gas and back again during a cycle used to transfer of heat.

[0098] A heat transfer system is the system (or apparatus) used to produce a heating or cooling effect in a particular space. A heat transfer system may be a mobile system or a stationary system.

[0099] Examples of heat transfer systems are any type of refrigeration systems and air conditioning systems including, but are not limited to, stationary heat transfer

systems, air conditioners, freezers, refrigerators, heat pumps, flooded evaporator heat pumps, direct expansion chillers heat pumps, chillers, flooded evaporator chillers, direct expansion chillers, walk-in coolers, mobile refrigerators, mobile heat transfer systems, mobile heat pumps, mobile air conditioning units, dehumidifiers, and combinations thereof.

[0100] Refrigeration capacity (also referred to as cooling capacity) is a term which defines the change in enthalpy of a refrigerant in an evaporator per pound of refrigerant circulated, or the heat removed by the refrigerant in the evaporator per unit volume of refrigerant vapor exiting the evaporator (volumetric capacity). The refrigeration capacity is a measure of the ability of a refrigerant or heat transfer composition to produce cooling. Therefore, the higher the capacity, the greater the cooling that is produced. Cooling rate refers to the heat removed by the refrigerant in the evaporator per unit time.

[0101] Coefficient of performance (COP) is the amount of heat removed divided by the required energy input to operate the cycle. The higher the COP, the higher is the energy efficiency. COP is directly related to the energy efficiency ratio (EER) that is the efficiency rating for refrigeration or air conditioning equipment at a specific set of internal and external temperatures.

[0102] As used herein, a working fluid is a composition comprising a compound or mixture of compounds that primarily function to transfer heat from one location at a lower temperature (e.g., an evaporator) to another location at a higher temperature (e.g., a condenser) in a cycle wherein the working fluid undergoes a phase change from a liquid to a vapor, is compressed and is returned back to liquid through cooling of the compressed vapor in a repeating cycle. The cooling of a vapor compressed above its critical point can return the working fluid to a liquid state without condensation. The repeating cycle may take place in systems such as heat pumps, refrigeration systems, refrigerators, freezers, air conditioning systems, air conditioners, chillers, and the like. Working fluids may be a portion of formulations used within the systems. The formulations may also contain other chemical components (e.g., additives) such as those described below.

[0103] The term “subcooling” refers to the reduction of the temperature of a liquid below that liquid's saturation point for a given pressure. The saturation point is the

temperature at which the vapor is completely condensed to a liquid, but subcooling continues to cool the liquid to a lower temperature liquid at the given pressure. By cooling a liquid below the saturation temperature (or bubble point temperature), the net refrigeration capacity can be increased. Subcooling thereby improves refrigeration capacity and energy efficiency of a system. Subcool amount is the amount of cooling below the saturation temperature (in temperature units).

[0104] Superheat is a term that defines how far above its saturation vapor temperature (the temperature at which, if the composition is cooled, the first drop of liquid is formed, also referred to as the “dew point”) a vapor composition is heated. By heating a vapor above the saturation point, the likelihood of condensation upon compression is minimized, and thus superheating minimizes the risk of liquid entering the compressor. The superheat can also contribute to the cycle's cooling and heating capacity.

[0105] 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 component of a refrigerant system, exclusive of any subcooling or superheating. This term may be used to describe condensation or evaporation of a zeotropic composition. When referring to the temperature glide of a refrigeration, 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.

[0106] The net refrigeration effect is the quantity of heat that each kilogram of refrigerant absorbs in the evaporator to produce useful cooling.

[0107] The mass flow rate is the quantity of refrigerant in kilograms circulating through the refrigeration, heat pump or air conditioning system over a given period of time.

[0108] As used herein, the term “lubricant” means any material added to a composition or a compressor (and in contact with any heat transfer composition in use within any heat transfer system) that provides hydrodynamic lubrication to the compressor to aid in preventing parts from seizing.

[0109] 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, 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. Determination of whether a refrigerant compound or mixture able to propagate a flame or not is also done by testing under the conditions of ASTM E-681.

[0110] During a refrigerant leak, the more volatile components of a mixture may leak preferentially. Thus, the composition in the system as well as the vapor leaking can vary over the time period of the leak. Thus, a non-flammable mixture may become able to propagate a flame under leakage scenarios. In order to be classified as non-flammable by ASHRAE (American Society of Heating, Refrigeration and Air-conditioning Engineers), a refrigerant or heat transfer composition must be non-flammable as formulated, but also under leakage conditions.

[0111] 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.

[0112] 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 CFC-11 (fluorotrichloromethane). Thus, the ODP of CFC-11 is defined to be 1.0. Other CFCs and HCFCs have ODPs that range from 0.01 to 1.0. HFCs and HFOs have zero ODP because they do not contain chlorine or other ozone depleting halogens.

[0113] An azeotropic composition may refer to a constant-boiling mixture of two or more substances that behave as a single substance. One way to characterize an azeotropic composition is that the vapor produced by partial evaporation or distillation of the liquid has the same composition as the liquid from which it is evaporated or distilled. For example, the mixture distills/refluxes without compositional change. Constant-boiling compositions are characterized as azeotropic because they exhibit either a maximum or minimum boiling point, as compared with that of the non-azeotropic mixture of the same compounds. An azeotropic composition will not fractionate within a refrigeration or air conditioning system during operation. Additionally, an azeotropic composition will not fractionate upon leakage from a refrigeration or air conditioning system.

[0114] By "azeotrope-like" or "azeotropic-like" composition (sometimes referred to as "near-azeotrope") is meant essentially constant boiling, or substantially constant boiling, liquid admixture of two or more substances that behaves as a single substance. One way to characterize an azeotrope-like composition is that the vapor produced by partial evaporation or distillation of the liquid has substantially the same composition as the liquid from which it was evaporated or distilled, that is, the admixture distills/refluxes without substantial composition change. Another way to characterize an azeotrope-like composition is that the bubble point vapor pressure and the dew point vapor pressure of the composition at a particular temperature are substantially the same, for example within 3 percent. Another way to characterize an azeotrope-like composition is that the difference between the bubble point pressure ("BP") and dew point pressure ("DP") of the composition at a particular temperature is less than or equal to 5 percent based upon the bubble point pressure, i.e., $[(BP-VP)/BP] \times 100 \leq 5$.

[0115] Another manner to characterize a near-azeotropic composition is that the bubble point vapor pressure and the dew point pressure of the composition at a particular temperature are substantially the same. Herein, a composition of the invention is near-azeotropic if, after 50 weight percent (50 wt.%) of the composition is removed, such as by evaporation or boiling off, the difference in vapor pressure, between the original composition and the composition remaining after 50 weight percent of the original composition has been removed, is less than about 10 percent (10%).

[0116] An azeotrope-like composition can also be characterized by the area that is adjacent to the maximum or minimum bubble-point pressure in a plot of composition vapor pressure at a given temperature as a function of mole fraction of components in the composition.

[0117] 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.

[0118] 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.

[0119] The transitional phrase “consisting essentially of” is used to define a composition, method or apparatus 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. The term “consisting essentially of” occupies a middle ground between “comprising” and “consisting of”. Typically, components of the refrigerant mixtures and the refrigerant mixtures themselves can contain minor amounts (e.g., less than about 0.5 weight percent total) of impurities and/or byproducts (e.g., from the manufacture of the refrigerant components or reclamation of the refrigerant components from other systems) which do not materially affect the novel and basic characteristics of the refrigerant mixture.

[0120] 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 describe such an invention using the terms “consisting essentially of” or “consisting of.”

[0121] 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.

[0122] 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. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the disclosed compositions, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety, unless a particular passage is cited. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

Processes of Making

[0123] In one embodiment, the present invention relates to methods of producing 1,3,3,3-tetrafluoropropene ($\text{CF}_3\text{CH}=\text{CHF}$, HFO-1234ze) by way of integrated sequences of reactions. In one embodiment, the present invention relates to methods of producing E-1,3,3,3-tetrafluoropropene (E-HFO-1234ze) and Z-1,3,3,3-tetrafluoropropene (Z-HFO-1234ze) by way of integrated sequences of reactions, with the Z isomer being the primary or main product of the integrated processes. In one embodiment, the present invention relates to methods of producing a mixture of E-HFO-1234ze and Z-HFO-1234ze by way of integrated sequences of reactions, separation, and purification.

[0124] In one embodiment, the integrated sequences of reactions of the present invention are carried out in a reactor comprising a series of reaction zones in fluid communication with each other. In another embodiment, the integrated sequences of reactions of the present invention are carried out in a series of reactors, each of which comprises a reaction zone, in fluid communication with each other. In certain embodiments, each reactor is a cylindrical tube or pipe, which may be straight or

coiled. The reactors are depicted as boxed labeled with a step number in the accompanying figures.

[0125] In addition to the reactors disclosed herein, heaters, effluent lines, units associated with mass transfer, contacting vessels (pre-mixers), distillation columns, and feed and material transfer lines associated with reactors, heaters, vessels, columns, and units that are used in the processes of embodiments disclosed herein should be constructed of materials resistant to corrosion, such as those recited herein with respect to the reactors.

[0126] In some embodiments, the present invention provides an integrated process for producing a mixture comprising both HFO-1234ze(Z) and HFO-1234ze(E).

[0127] In one embodiment, the integrated process (i.e., Integrated Process A) comprises reaction of carbon tetrachloride (CCl_4) with vinyl chloride ($\text{CH}_2=\text{CHCl}$) to produce 1,1,1,3,3-pentachloropropane ($\text{CCl}_3\text{CH}_2\text{CHCl}_2$, HCC-240fa) (Step 1A), followed by fluorination of the HCC-240fa either in the vapor phase or the liquid phase and preferably in the presence of a fluorination catalyst to produce 1,1,1,3,3-pentafluoropropane ($\text{CF}_3\text{CH}_2\text{CHF}_2$, HFC-245fa) (Step 2A), and dehydrofluorination of the HFC-245fa in the presence of an oxygen containing gas to produce a mixture comprising HFO-1234ze(Z) and HFO-1234ze(E) (Step 3A).

[0128] In some embodiments, Integrated Process A further comprises separation of HFO-1234ze(Z) and HFO-1234ze(E) from the mixture produced by Step 3A, and thus the product of Integrated Process A is a composition comprising HFO-1234ze(Z) and HFO-1234ze(E).

[0129] In some embodiments, Integrated Process A further comprises separation of HFO-1234ze(Z), HFO-1234ze(E) and HFC-245fa from the mixture produced by Step 3A, and thus the product of Integrated Process A is a composition comprising HFO-1234ze(Z), HFO-1234ze(E) and HFC-245fa.

[0130] In some embodiments, Integrated Process A further comprises separation of HFO-1234ze(Z), HFO-1234ze(E), HFO-1233zd(E) and HFC-245fa from the mixture produced by Step 3A, and thus the product of Integrated Process A is a composition comprising HFO-1234ze(Z), HFO-1234ze(E), HFO-1233zd(E) and HFC-

245fa. The amount of HFO-1233zd(E) present in the composition produced by Integrated Process A is preferably less than about 1 wt.% based on the total weight of the composition.

[0131] In some embodiments, Integrated Process A further comprises separation of HFO-1234ze(Z) and HFC-245fa from the reaction mixture, and thus the product of Integrated Process A is a composition comprising HFO-1234ze(Z) and HFC-245fa, which is particularly beneficial for use as a foam blowing agent composition. The amount of HFC-245fa present in the composition produced by Integrated Process A is less than about 30 wt.%, preferably less than about 10 wt.%, more preferably less than about 5 wt.%, based on the total weight of the composition.

[0132] In one embodiment, the integrated process (i.e., Integrated Process B) comprises reaction of CCl₄ with vinyl chloride to produce HCC-240fa) (Step 1B), followed by catalytic fluorination of the HCC-240fa to produce HFO-1233zd (Step 2B), and catalytic fluorination of the HFO-1233zd to produce a mixture comprising HFO-1234ze(Z) and HFO-1234ze(E) (Step 3B).

[0133] In some embodiments, Integrated Process B further comprises separation of HFO-1234ze(Z) and HFO-1234ze(E) from the mixture produced by Step 3B, and thus the product of Integrated Process B is a composition comprising HFO-1234ze(Z) and HFO-1234ze(E).

[0134] In some embodiments, Integrated Process B further comprises separation (e.g., removal and recovery) of HFO-1234ze(E) from the mixture produced by Step 3B, and separation of HFO-1233zd, HFC-245fa and HFO-1234ze(Z) from the mixture produced by Step 3B, and thus the product of Integrated Process B is a composition comprising HFO-1234ze(Z), HFO-1233zd and HFC-245fa.

[0135] More particularly, in some embodiments, Integrated Process B comprises separation (e.g., removal and recovery) of HFO-1234ze(E) from the mixture produced by Step 3B, and separation of HFO-1233zd(E), HFC-245fa and HFO-1234ze(Z) from the mixture produced by Step 3B, and thus the product of Integrated Process B is a composition comprising HFO-1234ze(Z), HFO-1233zd(E) and HFC-245fa.

[0136] In some embodiments, Integrated Process B further comprises separation of HFO-1234ze(Z) and HFO-1233zd(E) from the reaction mixture, and thus the product of Integrated Process B is a composition comprising HFO-1234ze(Z) and HFO-1233zd(E), which is particularly beneficial for use as a foam blowing agent composition.

[0137] In some embodiments, Integrated Process B further comprises separation of HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E) from the reaction mixture, such that the product of Integrated Process B is a composition comprising HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E).

[0138] In some embodiments, Integrated Process B further comprises separation of HFO-1233zd(E), HFO-1234ze(Z), HFO-1234ze(E) and HFC-245fa from the reaction mixture, such that the product of Integrated Process B is a composition comprising HFO-1233zd(E), HFO-1234ze(Z), HFO-1234ze(E) and HFC-245fa.

[0139] In one embodiment, the integrated process (i.e., Integrated Process C) comprises reaction of CCl_4 with vinyl chloride to produce HCC-240fa (Step 1C), followed by catalytic fluorination of the HCC-240fa to produce a mixture comprising HFO-1233zd, HFO-1234ze(E) and HFO-1234ze(Z) (Step 2C). More particularly, in some embodiments, catalytic fluorination of the HCC-240fa produces a mixture comprising HFO-1233zd(E), HFO-1234ze(E) and HFO-1234ze(Z) (Step 2C).

[0140] In some embodiments, Integrated Process C further comprises separation of HFO-1234ze(Z) and HFO-1234ze(E) from the mixture produced by Step 2C, and thus the product of Integrated Process C is a composition comprising HFO-1234ze(Z) and HFO-1234ze(E).

[0141] In some embodiments, Integrated Process C further comprises separation of HFO-1234ze(Z) and HFO-1233zd(E) from the reaction mixture, and thus the product of Integrated Process C is a composition comprising HFO-1234ze(Z) and HFO-1233zd(E), which is particularly beneficial for use as a foam blowing agent composition.

[0142] In some embodiments, for each of the integrated processes disclosed herein, where the Z isomer is the primary desired product, the integrated process may further comprise an optional step to separate HFO-1234ze(Z) from the mixture

produced by Step 3A, 3B or 2C, and thus the product of the integrated process is a composition comprising HFO-1234ze(Z).

[0143] In some embodiments, for each of the integrated processes disclosed herein, where the Z isomer is the primary desired product, the integrated process may further comprise an optional step to isomerize any HFO-1234ze(E) which is present in the product mixture to the Z isomer. Thus, in some embodiments, each of the integrated processes disclosed herein produces HFO-1234ze(Z) as a final reaction product.

[0144] These integrated processes are reflected in the reaction sequences shown below:

Integrated Process A

Step 1A: $\text{CCl}_4 + \text{CH}_2=\text{CHCl} \rightarrow \text{CCl}_3\text{CH}_2\text{CHCl}_2$ (HCC-240fa)

Step 2A: $\text{CCl}_3\text{CH}_2\text{CHCl}_2$ (HCC-240fa) + HF $\rightarrow$ $\text{CF}_3\text{CH}_2\text{CHF}_2$ (HFC-245fa)

Step 3A: $\text{CF}_3\text{CH}_2\text{CHF}_2$ (HFC-245fa) $\rightarrow$ $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(Z)) +
 $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(E)) + HF

Step 4A: $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(E)) $\rightarrow$ $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(Z))
 (Optional)

Integrated Process B

Step 1B: $\text{CCl}_4 + \text{CH}_2=\text{CHCl} \rightarrow \text{CCl}_3\text{CH}_2\text{CHCl}_2$ (HCC-240fa)

Step 2B: $\text{CCl}_3\text{CH}_2\text{CHCl}_2$ (HCC-240fa) + HF $\rightarrow$ $\text{CF}_3\text{CH}=\text{CHCl}$ (E/Z-HFO-1233zd)

Step 3B: $\text{CF}_3\text{CH}=\text{CHCl}$ (HFO-1233zd) + HF $\rightarrow$ $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(Z)) +
 $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(E))

Step 4B: $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(E)) $\rightarrow$ $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(Z))
 (Optional)

Integrated Process C

Step 1C: $\text{CCl}_4 + \text{CH}_2=\text{CHCl} \rightarrow \text{CCl}_3\text{CH}_2\text{CHCl}_2$ (HCC-240fa)

Step 2C: $\text{CCl}_3\text{CH}_2\text{CHCl}_2$ (HCC-240fa) + HF $\rightarrow$ $\text{CF}_3\text{CH}=\text{CHCl}$ (E/Z-HFO-1233zd) + $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(Z)) + $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(E))

Step 3C: $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(E)) $\rightarrow$ $\text{CF}_3\text{CH}=\text{CHF}$ (HFO-1234ze(Z))
(Optional)

[0145] According to embodiments of the present invention, in each of the integrated processes disclosed herein, the first reaction in the sequence of reactions comprises reaction of carbon tetrachloride (CCl_4) with vinyl chloride to produce 1,1,1,3,3-pentachloropropane ($\text{CCl}_3\text{CH}_2\text{CHCl}_2$, HCC-240fa), for example as disclosed in U.S. Patent No. 11,731,925 or U.S. Patent No. 6,313,360, the disclosure of each of which is incorporated herein by reference in its entirety.

[0146] More particularly, in one embodiment, HCC-240fa may be produced by a metal catalyzed olefin insertion process that includes the use of a metal and a ligand by insertion of an olefin (e.g., vinyl chloride) into a haloalkane reactant (e.g., carbon tetrachloride). In particular, in one embodiment, the olefin insertion process comprises contacting carbon tetrachloride with vinyl chloride in the presence of a catalyst system that consists of metallic iron and a phosphine as set forth in U.S. Patent No. 11,731,925 or a catalyst system comprising an organophosphate solvent, iron metal and ferric chloride as set forth in U.S. Patent No. 6,313,360, to produce HCC-240fa under predetermined reaction parameters.

[0147] In one embodiment, the carbon tetrachloride feed comprises carbon tetrachloride and at least one or two additional compounds selected from trichloroethylene ($\text{CClH}=\text{CCl}_2$), tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$), hexachloroethane (CCl_3CCl_3), bromotrichloromethane (CCl_3Br), chloroform (CCl_3H), 1,1,1-trichloroethane (CCl_3CH_3), 1,1,2-trichloroethane ($\text{CHCl}_2\text{CH}_2\text{Cl}$), trans-1,2-dichloroethylene ($\text{E-CHCl}=\text{CHCl}$), cis-1,2-dichloroethylene ($\text{Z-CHCl}=\text{CHCl}$) and 1,1-dichloroethylene ($\text{CH}_2=\text{CCl}_2$). In one embodiment, the total amount of the additional compounds is less than 5 wt.%, or less than 4 wt.%, or less than 3 wt.%, or less than

2 wt%, preferably less than 1 wt.%. In one embodiment, the carbon tetrachloride feed comprises at least about 95% by weight, at least about 96% by weight, at least about 97% by weight, at least about 98% by weight, at least about 99% by weight, at least 99.5% by weight, at least 99.6% by weight, at least 99.7% by weight, at least 99.8% by weight, or about 99.9% by weight of carbon tetrachloride and one or more of the additional compounds.

[0148] In certain embodiments, the metallic iron component of the catalyst may be from any source (including a combination of sources) of an iron component, may be any iron containing species such as FeCl_2 and FeCl_3 , and may be iron powder, iron wire, iron screen or iron turnings. In other embodiments, copper or copper halides may be used in combination with an organic nitrile compound, such as but not limited to acetonitrile propionitrile.

[0149] In some embodiments, the catalyst may comprise a phosphorous containing compound, such as a phosphine ligand which may be an alkylphosphine or arylphosphine, including but not limited to triphenyl phosphine, tributyl phosphine and the like.

[0150] In other embodiments, the catalyst may comprise a phosphorous containing compound, such as a phosphate, such as but not limited to, trimethyl phosphate, triethyl phosphate, tripropyl phosphate, tributyl phosphate, diethyl phosphate, dibutyl phosphate, monophenyl phosphate, monobutyl phosphate, dimethylphenyl phosphate, diethylphenyl phosphate, dimethylethyl phosphate and phenyl ethyl methyl phosphate.

[0151] The reaction product produced by the reaction of CCl_4 with vinyl chloride preferably comprises HCC-240fa and at least one or two additional compounds. In one embodiment, the at least one additional compound comprises 1-chlorobutane; 1,2,3-trichloropropene ($\text{CHCl}=\text{CCl}-\text{CH}_2\text{Cl}$, HCO-1240xd); HCO-1230xd ($\text{CHCl}=\text{CCl}-\text{CHCl}_2$, 1,2,3,3-tetrachloropropene); 1,1,1,3-tetrachloropropane ($\text{CCl}_3-\text{CH}_2-\text{CH}_3$, HCC-250fb); 1,4 dichlorobutane; 1,2-dichloro-cyclobutane, 1,1,4,4-tetrachlorobutadiene; 1,1,3,4 tetrachlorobutadiene; 1,1,1,2,3-pentachloropropane (HCC-240db); $\text{C}_5\text{H}_7\text{Cl}_3$ isomer(s) and $\text{C}_4\text{H}_7\text{Cl}_3$ isomer(s). The HCC-240fa is utilized as a feed material for subsequent reactions in each of the integrated processes disclosed herein.

[0152] In one embodiment, the total amount of the one or more additional compounds is less than 5 wt.%, or less than 4 wt.%, or less than 3 wt.%, or less than 2 wt%, preferably less than 1 wt.%. In one embodiment, the HCC-240fa reaction product/feed composition comprises at least about 95% by weight, at least about 96% by weight, at least about 97% by weight, at least about 98% by weight, at least about 99% by weight, at least 99.5% by weight, at least 99.6% by weight, at least 99.7% by weight, at least 99.8% by weight, or about 99.9% by weight of HCC-240fa and one or more of the additional compounds selected from 1-chlorobutane; 1,2,3-trichloropropene ($\text{CHCl}=\text{CCl}-\text{CH}_2\text{Cl}$, HCO-1240xd); HCO-1230xd ($\text{CHCl}=\text{CCl}-\text{CHCl}_2$, 1,2,3,3-tetrachloropropene); 1,1,1,3-tetrachloropropane ($\text{CCl}_3-\text{CH}_2-\text{CH}_3$, HCC-250fb); 1,4 dichlorobutane; 1,2-dichloro-cyclobutane, 1,1,4,4-tetrachlorobutadiene; 1,1,3,4 tetrachlorobutadiene; 1,1,1,2,3-pentachloropropane (HCC-240db); $\text{C}_5\text{H}_7\text{Cl}_3$ isomer(s) and $\text{C}_4\text{H}_7\text{Cl}_3$ isomer(s).

Integrated Process A

[0153] In one embodiment, as shown in Fig. 2, Integrated Process A comprises a step of reacting the HCC-240fa with hydrogen fluoride (HF), either in the vapor phase or the liquid phase, preferably in the presence of a fluorination catalyst, to form a reaction product comprising HFC-245fa (Step 2A), as disclosed in U.S. Patent No. 6,023,004, the entire disclosure of which is incorporated herein by reference. The HFC-245fa may be separated from any other compounds present by conventional techniques such as distillation. Azeotropic compositions of HFC-245fa and HF can be produced in this manner, as is known in the art.

[0154] In some embodiments, the catalyst for the fluorination of the HCC-240fa is a Lewis acid catalyst, such as a metal halide catalyst, including but not limited to antimony halides, tin halides, thallium halides, iron halides and combinations of two or more. In certain embodiments, metal chlorides and metal fluorides are employed, including but not limited to SbCl_5 , SbCl_3 , SbF_5 , SnCl_4 , TiCl_4 , NiF_5 , FeCl_3 , and combinations of two or more of these.

[0155] In some embodiments, examples of liquid phase fluorination catalysts include but are not limited to antimony halide, tin halide, tantalum halide, titanium halide, niobium halide, molybdenum halide, iron halide, fluorinated chrome halide, fluorinated chrome oxide or combinations thereof. In some embodiments, examples

of liquid phase fluorination catalysts include but are not limited to SbCl_5 , SbCl_3 , SbF_5 , SnCl_4 , TaCl_5 , TiCl_4 , NbCl_5 , MoCl_6 , FeCl_3 , fluorinated species of SbCl_5 , fluorinated species of SbCl_3 , fluorinated species of SnCl_4 , fluorinated species of TaCl_5 , fluorinated species of TiCl_4 , fluorinated species of NbCl_5 , fluorinated species of MoCl_6 , fluorinated species of FeCl_3 , or combinations thereof. These catalysts can be readily regenerated by any means known in the art if they become deactivated.

[0156] In one embodiment, the liquid phase fluorination catalyst is selected from SbF_5 , SnCl_4 , TaCl_5 , TiCl_4 , NbCl_5 , and fluorinated species thereof. In another embodiment, the liquid phase fluorination catalyst is selected from SbF_5 , SnCl_4 , TaCl_5 , TiCl_4 and/or fluorinated species thereof. In another embodiment the liquid phase fluorination catalyst is SbF_5 or SbCl_5 .

[0157] In one embodiment, the reaction mixture produced by the fluorination of HCC-240fa comprises HFC-245fa and one or more additional compounds selected from Table 1 and/or Table 2, or at least two additional compounds or at least three additional compounds or more.

Table 1

Name	Structure	Chemical Name
HFC-143a	$\text{CF}_3\text{-CH}_3$	1,1,1-trifluoroethane
HCFO-1225zc	$\text{CF}_2=\text{CH-CCl}_2\text{F}$	3,3-dichloro-1,1,3-trifluoropropene
HFC-236fa	$\text{CF}_3\text{-CH}_2\text{-CF}_3$	1,1,1,3,3,3-Hexafluoropropane
HFO-E/Z-1234ze	$\text{CHF}=\text{CH-CH}_2\text{F}$	1,3,3,3-tetrafluoropropene
HCFC-22	CHClF_2	Chlorodifluoromethane
CFC-12	CCl_2F_2	Dichlorodifluoromethane
HCFC-142b	$\text{CClF}_2\text{-CH}_3$	1-Chloro-1,1-difluoroethane
HCFC-133a	$\text{CH}_2\text{Cl-CH}_2\text{-CF}_3$	1-Chloro-2,2,2-Trifluoroethane
HCFO-1224	C_3HClF_4	N/A
HCFC-235fa	$\text{CClF}_2\text{-CH}_2\text{-CF}_3$	1-Chloro-1,1,3,3,3-pentafluoropropane
HCFO-1233	$\text{C}_3\text{H}_2\text{ClF}_3$	N/A
HCFC-235da	$\text{CF}_3\text{-CHCl-CHF}_2$	2-Chloro-1,1,1,3,3-pentafluoropropane
HCFC-123	$\text{CHCl}_2\text{-CF}_3$	1,1-Dichloro-2,2,2-trifluoroethane
HCFC-141b	$\text{CCl}_2\text{F-CH}_3$	1,1-Dichloro-1-fluoroethane
HCFC-234fb	$\text{CCl}_2\text{F-CH}_2\text{-CF}_3$	1,1-Dichloro-1,3,3,3-tetrafluoropropane
HCFO-1223xd	$\text{CHCl=CCl-CH}_2\text{F}$	1,2-dichloro-3,3,3-trifluoropropene
HCC-20	CHCl_3	trichloromethane (chloroform)
HCFC-224aa	$\text{CHClF-CCl}_2\text{-CF}_3$	1,2,2-trichloro-1,3,3,3-tetrafluoropropane
CFO-1213xa	$\text{CCl}_2=\text{CCl-CH}_2\text{F}$	1,1,2-trichloro-3,3,3-trifluoropropene
HCFC-233da	$\text{CHCl}_2\text{-CHCl-CH}_2\text{F}$	1,1,2-Trichloro-3,3,3-trifluoropropane
HCFC-223aa	$\text{CHClF-CCl}_2\text{-CHF}_2$	1,2,2-trichloro-1,3,3-trifluoropropane

Table 2

Name	Structure	Chemical Name
HFO-1234ze(E)	CHF=CH-CF ₃	1,3,3,3-tetrafluoropropene
HFC-338mf	CF ₃ -CH ₂ -CF ₂ -CF ₃	1,1,1,2,2,4,4,4-octofluorobutane
HFC-356mff	CF ₃ -CH ₂ -CH ₂ -CF ₃	1,1,1,4,4,4-hexafluorobutane
HFO-1234ze(Z)	CHF=CH-CF ₃	1,3,3,3-tetrafluoropropene
HFO-1234zc	CF ₂ =CH-CHF ₂	1,1,3,3-tetrafluoropropene
HFC-347 isomer	C ₄ F ₇ H ₃	heptafluorobutane isomer
HCFC-133a	CH ₂ Cl-CF ₃	1-Chloro-2,2,2-Trifluoroethane
HCFC-244bb	CF ₃ -CClF-CH ₃	2-Chloro-1,1,1,2-tetrafluoropropane
HCFC-235fa	CClF ₂ -CH ₂ -CF ₃	1-Chloro-1,1,3,3,3-pentafluoropropane
HCFO-1326mxz(Z)	CF ₃ -CCl=CH-CF ₃	Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene
HCFO-1224yd	CHCl=CF-CF ₃	1-Chloro-2,3,3,3-tetrafluoropropene
HCFO-1233zd(E)	CHCl=CH-CF ₃	E-1-chloro-3,3,3-trifluoropropene
HCFO-1224zc	CF ₂ =CH-CClF ₂	3-Chloro-1,1,3,3-tetrafluoropropene
HCC-160	CH ₂ Cl-CH ₃	Chloroethane (ethyl chloride)
HCFC-244	C ₃ H ₃ ClF ₄	N/A
HCFO-1335	C ₄ H ₂ ClF ₅	N/A
HCFC-123	CHCl ₂ -CF ₃	1,1-Dichloro-2,2,2-trifluoroethane
HCFC-123a	CClF ₂ -CHClF	1,2-Dichloro-1,1,2-trifluoroethane
HCFO-1233zd(Z)	CHCl=CH-CF ₃	Z-1-chloro-3,3,3-trifluoropropene
1233zd (Br)	CF ₃ CH=CHBr	1-Bromo-3,3,3-trifluoropropene
CFO-1214ya	CCl ₂ =CF-CF ₃	1,1-dichloro-2,3,3,3-tetrafluoropropene
HCC-30	CH ₂ Cl ₂	Dichloromethane (Methylene chloride)
CFC-113	CCl ₂ F-CClF ₂	1,1,2-Trichloro-1,2,2-trifluoroethane
HCFO-1223xd	CHCl=CCl-CF ₃	1,2-dichloro-3,3,3-trifluoropropene
HCO-1130a	CCl ₂ =CH ₂	1,1-dichloroethylene
HCO-1130	CHCl=CHCl	1,2-dichloroethylene

[0158] In one embodiment, the total amount of the additional compounds is greater than 0 and less than about 5 weight percent, about 4 weight percent, about 3 weight percent, about 2 weight percent, about 1 weight percent, about 0.5 weight percent, about 0.1 weight percent.

[0159] In one embodiment, the compositions of the present invention comprise HFC-245fa and one additional compound, or two additional compounds, or three or more additional compounds selected from Table 1 and/or Table 2.

[0160] The additional compounds listed in Tables 1 and 2 are available commercially or can be made by processes known in the art. For example, such compounds can be purchased from a specialty fluorochemical supplier, such as SynQuest Laboratories, Inc. (Alachua, Florida, USA).

[0161] In one embodiment, the compositions of the present invention comprise at least about 95% by weight, at least 98% by weight, at least about 99% by weight, at least 99.5% by weight, at least 99.6% by weight, at least 99.7% by weight, at least 99.8% by weight, or about 99.9% by weight of HFC-245fa and one or more additional compounds selected from Table 1 and/or Table 2, and mixtures thereof.

[0162] In one embodiment, for any of the foregoing compositions, the total amount of additional compound(s) in the composition comprising HFC-245fa ranges from greater than 0 wt.% to less than or equal to about 5 wt.%, about 4 wt.%, about 3 wt.%, about 2 wt.%, about 1 wt.%, about 0.9 wt.%, about 0.8 wt.%, about 0.7 wt.%, about 0.6 wt.%, about 0.5 wt.%, about 0.4 wt.%, about 0.3 wt.%, about 0.2 wt.%, about 0.1 wt.%, based on the total weight of the composition. In another embodiment, the total amount of additional compound(s) ranges from 0.01 ppm (weight) to about 1 wt.%, and all values therebetween up to 1 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.1 ppm (weight) to about 1 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to about 1 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to about 0.5 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to 0.4 wt.% or less, based on the total weight of the composition. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to 0.1 wt.% or less, based on the total weight of the composition. In one embodiment, the total amount of additional compound(s) is about 0.1 wt.% based on the total weight of the composition.

[0163] In one embodiment, the compositions comprise at least about 99% by weight, in some cases at least about 99.5% by weight, of HFC-245fa and one or more additional compounds selected from Table 1 and/or Table 2, and mixtures thereof, wherein the total amount of the additional compound(s) is about 1% by weight or less, or about 0.5% by weight or less, or about 0.4% by weight or less, or about 0.3% by weight or less, or about 0.2% by weight or less, or about 0.1% by weight or less, based on the total weight of the composition.

[0164] In one embodiment, the reaction mixture preferably comprises the exemplary composition shown in Table 3.

Table 3

Compound Name	ppm (wt.)
HFC-143a	8
HCFO-1225zc	129
HFC-236fa	38
E/Z-HFO-1234ze	87
HCFC-22	394
CFC-12	--
HCFC-142b	31
HCFC-133a	14
HCFO-1224	27
HCFC-235fa	3861
HCFO-1233	43
HCFC-235da	9
Unknown (HCFC)	2634
Acetone/HCFC-123	--
HCFC-141b	804
HCFC-234fb	15
HCFC-1223xd	110
Unknown (HCFC)	230
HCC-20	6
HCFC-224aa	--
CFC-1213xa	4
HCFC-233da	--
Toluene	2
HCFC-223aa	--
Others	48
HFC-245fa	99.1506 %

[0165] In one embodiment, the reaction mixture preferably comprises the exemplary composition shown in Table 4.

Table 4

Compound Name	Percent (mol%)
HFO-1234ze(E)	8.96453E-05
HFC-338mf	5.15947E-05
HFC-245fa	99.79409
HFC-356mff	0.01362
HFO-1234ze(Z) + HFO-1234zc+ HFC-347 isomer	0.00158
HCFC-133a	0.00029
HCFC-244bb	0.00037
HCFC-235fa	0.00340
HCFO-1326mxz(Z)	0.02643
HCFO-1224yd	0.01540

Compound Name	Percent (mol%)
HCFO-123zd(E)	0.06520
HCFO-1224zc	0.02305
HCC-160	0.00028
HCFC-244	0.00449
HCFO-1335	0.00014
HCFC-123	0.00319
HCFC-123a	0.00083
HCFO-123zd(Z)	0.00023
1233zd (Br)	3.53341E-05
CFO-1214ya	0.00012
HCC-30	0.01262
CFC-113	0.04428
HCFO-1223xd	6.29217E-05
HCO-Z-1130	9.13973E-05

[0166] In one embodiment, the compositions comprise, consist of or consist essentially of (i) HFC-245fa, (ii) 3,3-dichloro-1,1,1-trifluoropropane ($\text{CF}_3\text{CH}_2\text{CHCl}_2$ or HFC-243fa), (iii) 3-chloro-1,1,1,3-tetrafluoropropane ($\text{CF}_3\text{CH}_2\text{CHFCl}$ or HCFC-244fa), (iv) one or more additional compounds selected from 233da, (E)-2,4,5-trichloro-1,1,1,6,6,6-hexafluorohex-2-ene, (Z)-2,4,5-trichloro-1,1,1,6,6,6-hexafluorohex-2-ene, (E)-2-chloro-4-(dichloromethyl)-1,1,1,5,5,5-hexafluoropent-2-ene, (Z)-2-chloro-4-(dichloromethyl)-1,1,1,5,5,5-hexafluoropent-2-ene, (E)-4,5,5-trichloro-1,1,1,6,6,6-hexafluorohex-2-ene, (E)-4-chloro-2-(dichloromethyl)-1,1,1,5,5,5-hexafluoropent-2-ene, (Z)-4-chloro-2-(dichloromethyl)-1,1,1,5,5,5-hexafluoropent-2-ene, (2Z,4E)-2,5-dichloro-1,1,1,6,6,6-hexafluorohexa-2,4-diene, (E)-1,3-dichloro-5,5,5-trifluoro-2-(trifluoromethyl)pent-1-ene, (Z)-1,3-dichloro-5,5,5-trifluoro-2-(trifluoromethyl)pent-1-ene, (E)-4,5-dichloro-1,1,1,6,6,6-hexafluorohex-2-ene, and (E)-4,5,6-trichloro-1,1,1,6,6-pentafluorohex-2-ene, and (v) optionally one or more additional compounds selected from any of Table 1, Table 2, Table 3, Table 4, and combinations thereof, wherein the total amount of the additional compound(s) is about 1% by weight or less, or about 0.5% by weight or less, or about 0.4% by weight or less, or about 0.3% by weight or less, or about 0.2% by weight or less, or about 0.1% by weight or less, based on the total weight of the composition.

[0167] In one embodiment, Integrated Process A comprises a step of dehydrofluorination of the HFC-245fa produced by Step 2A to form a reaction mixture comprising HFO-1234ze(Z) and HFO-1234ze(E) and HF (Step 3A).

[0168] In one embodiment, the HFC-245fa feed composition for Step 3A has a moisture content of less than about 50 ppm, preferably less than about 20 ppm, more preferably less than about 10 ppm, and comprises HFC-245fa and one or more additional compounds selected from Table 1 and/or Table 2. In one embodiment, the non-absorbable gases (NAGs or NCGs) in the HFC-245fa feed composition may be greater than 0% and may include, for example but not limited to, air and a mixture of air and nitrogen.

[0169] In one embodiment, the dehydrofluorination of the HFC-245fa of Step 3A is carried out in the presence of an oxygen containing gas, such as air. In another embodiment, no additional oxygen containing gas is added to the reactor, and the oxygen content of the HFC-245fa feed composition is sufficient to facilitate the dehydrofluorination reaction.

[0170] Dehydrofluorination of the HFC-245fa may be carried out by any method known in the art. For example, in one embodiment, Integrated Process A comprises a step of dehydrofluorination of the HFC-245fa using a strong base in aqueous or alcoholic solution or by means of chromium-containing catalyst in the presence of oxygen at elevated temperature, to form HFO-1234ze(Z) (Step 3A), as disclosed in U.S. Patent No. Application Publication No. 2008/0051611, the disclosure of which is incorporated herein by reference in its entirety. In one embodiment, the dehydrofluorination reaction may take place in the vapor phase in the presence or absence of catalyst, or in the liquid phase by reaction with a caustic composition, such as NaOH or KOH. These reactions are described in more detail in U.S. Patent Publication Nos. 2008/0051611 and 2006/0106263, the entire disclosure of each of which is incorporated herein by reference.

[0171] According to this process embodiment, the instant invention relates to feeding an amount of HFC-245fa to a dehydrofluorination reactor containing a catalyst in the absence or presence of an oxygen containing gas, such as air, at a predetermined rate and a predetermined temperature. In one embodiment, the oxygen containing gas is present in an amount from greater than 0 ppm to less than

10 mol% of the total feed. In one embodiment, the reactor is preferably a fixed bed reactor.

[0172] According to this process, both E-HFO-1234ze and Z-HFO-1234ze, among other compounds, are produced from the HFC-245a. The conversion is between about 10% to about 100%. The E/Z ratio is about 3:1 and can be adjusted in the range of 10 to 1 by varying reaction conditions, such as temperature, pressure and contact time.

[0173] Hydrogen fluoride may be removed by scrubbing, by passing the reactor effluent through a solution of aqueous caustic such as but not limited to a NaOH, KOH, Na₂CO₃, NaHCO₃, K₂CO₃, or KHCO₃ solution or by passing the reactor effluent through another type of scrubbing solution such as but not limited to water or concentrated sulfuric acid, by an adsorbent, by distillation, or by any combination of one or more of such methods. In one embodiment, the composition formed from the process of the present disclosure includes both HFO-1234ze(E) and HFO-1234ze(Z), which are not separated.

[0174] In some embodiments, Integrated Process A further comprises separating HFO-1234ze(E) and HFO-1234ze(Z) from the reaction mixture produced by Step 3A, such that the composition produced by the process comprises HFO-1234ze(E) and HFO-1234ze(Z). The process may also comprise optionally purifying the HFO-1234ze(E) and HFO-1234ze(Z), such as by distillation, fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional purification method known in the art, or a combination of any such purification methods.

[0175] For example, as shown in Figs. 1-2A, in some embodiments, Integrated Process A comprises distilling the reaction mixture F1 of Step 3A, which comprises HFC-245fa, HFO-1234ze(Z) and HFO-1234ze(E), via a first distillation column, producing a bottoms stream B1 comprising HFC-245fa and HFO-1234ze(Z), and recovering an overhead stream O1 comprising a mixture of HFO-1234ze(E) and HFO-1234ze(Z).

[0176] In some embodiments, Integrated Process A further comprises separating HFO-1234ze(E), HFO-1234ze(Z) and HFC-245fa from the reaction mixture produced by Step 3A, such that the composition produced by the process comprises HFO-1234ze(E), HFO-1234ze(Z) and HFC-245fa. The process may also comprise optionally purifying the HFO-1234ze(E), HFO-1234ze(Z) and HFC-245fa, such as by distillation,

fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional purification method known in the art, or a combination of any such purification methods.

[0177] For example, as shown in Fig. 3, in some embodiments, Integrated Process A comprises distilling the reaction mixture F1 of Step 3A, which comprises HFC-245fa, HFO-1234ze(Z) and HFO-1234ze(E), via a first distillation column, producing a bottoms stream B1 comprising HFC-245fa and HFO-1234ze(Z), and recovering an overhead stream O1 comprising a mixture of HFO-1234ze(E), HFO-1234ze(Z) and HFC-245fa.

[0178] The concentrations of the components of the overhead stream O1 and bottoms stream B1 may be adjusted as desired by varying the operating conditions of the distillation column. Exemplary feed compositions, overhead streams and bottom streams are shown in Table 5.

Table 5

Mixture of 1234ze-E + 1234ze-Z with 10 ppm 245fa			
	Concentration by weight		
Stream	245fa	1234ze-E	1234ze-Z
F1	60.0%	30.0%	10.0%
O1	10 ppm	99.0%	1.0%
B1	86.1%	0.0%	12.9%
Mixture of 1234ze-E + 1234ze-Z with 0.5 weight% 245fa			
	Concentration by weight		
Stream	245fa	1234ze-E	1234ze-Z
F1	60.0%	30.0%	10.0%
O1	0.5%	74.7%	24.8%
B1	100.0%	0.0%	0.0%
Mixture of 1234ze-E + 1234ze-Z with 10 weight% 245fa			
	Concentration by weight		
Stream	245fa	1234ze-E	1234ze-Z
F1	60.0%	30.0%	10.0%
O1	10.0%	67.5%	22.5%
B1	100.0%	0.0%	0.0%
Mixture of 1234ze-E + 1234ze-Z with 10 ppm 245fa			
	Concentration by weight		
Stream	245fa	1234ze-E	1234ze-Z
F1	7.2%	73.0%	19.8%
O1	10 ppm	84.1%	15.9%
B1	54.4%	0.0%	45.6%

Mixture of 1234ze-E + 1234ze-Z with 0.5 weight% 245fa			
	Concentration by weight		
Stream	245fa	1234ze-E	1234ze-Z
F1	7.2%	73.0%	19.8%
O1	0.5%	78.3%	21.2%
B1	100.0%	0.0%	0.0%

[0179] In some embodiments, Integrated Process A further comprises separating HFO-1234ze(E), HFO-1234ze(Z), HFO-1233zd(E) and HFC-245fa from the reaction mixture produced by Step 3A, such that the composition produced by the process comprises HFO-1234ze(E), HFO-1234ze(Z), HFO-1233zd(E) and HFC-245fa. The process may also comprise optionally purifying the HFO-1234ze(E), HFO-1234ze(Z), HFO-1233zd(E) and HFC-245fa, such as by distillation, fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional purification method known in the art, or a combination of any such purification methods. The amount of HFO-1233zd(E) present in the composition produced by Integrated Process A is preferably less than about 1 wt. % based on the total weight of the composition.

[0180] In some embodiments, Integrated Process A further comprises separating HFO-1234ze(Z) and HFC-245fa from the reaction mixture produced by Step 3A, such that the composition produced by the process comprises HFO-1234ze(E), HFO-1234ze(Z) and HFC-245fa, which is particularly suitable for use as a blowing agent. The process may also comprise optionally purifying the HFO-1234ze(Z) and HFC-245fa, such as by distillation, fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional purification method known in the art, or a combination of any such purification methods. The amount of HFC-245fa present in the composition produced by Integrated Process A is less than about 30 wt. %, preferably less than about 10 wt. %, more preferably less than about 5 wt. %, based on the total weight of the composition.

[0181] In some embodiments, as shown in Fig. 2B, the reaction mixture of Step 3A comprises HFC-245fa, HFO-1234ze(E), HFO-1234ze(Z) and HFO-1233zd(E), and Integrated Process A comprises distilling the reaction mixture via a first distillation column producing a bottoms stream comprising HFC-245fa, HFO-1233zd(E) and HFO-1234ze(Z), and an overhead stream comprising a mixture of HFO-1234ze(E) and HFO-1234ze(Z).

The mixture of HFO-1234ze(E) and HFO-1234ze(Z) may then be further purified to separate HFO-1234ze(E) from HFO-1234ze(Z).

[0182] In some embodiments, Integrated Process A further comprises further distillation or purification of the bottoms stream (HFC-245fa, HFO-1233zd(E) and HFO-1234ze(Z)) to produce a mixture of HFO-1234ze(Z) and HFC-245fa (second overhead stream), which may optionally be recycled to the dehydrofluorination reaction, and a mixture of HFO-1234zd(E) and HFC-245fa (second bottoms stream). The dehydrofluorination reaction is free of isomerization or substantially free of isomerization from HFO-1234ze(Z) to HFO-1234ze(E). By “free of isomerization” it is meant that the process to make HFO-1234ze(E) is independent of HFO-1234ze(Z) to HFO-1234ze(E) isomerization, and that the HFO-1234ze(Z) content in the reactor feed, if present, is purposely selected based on the reaction equilibrium at a given pressure and temperature to render it as functionally inert and not a net contributor to the production of HFO-1234ze(E) by isomerization. By “substantially free of isomerization” it is meant that the process for making HFO-1234ze(E) does not employ a separate step for converting, isomerizing or otherwise using the Z isomer to obtain the E isomer, wherein the amount of Z converted to E is less than about 5 mol percent, less than about 2 mol percent and typically about 0 mol percent.

[0183] The HFO-1234zd(E)/HFC-245fa mixture may either be purged (not shown) or, as shown in Fig. 2B, may be optionally recycled to the HCC-240fa fluorination reaction (Step 2A). For further utilization, in some embodiments, the HCFO-1233zd can be converted to HFC-245fa instead of being purged as waste. Similarly, the HFC-245fa may be recycled to the HCC-240fa fluorination reactor and undergo purification to be used as feed, instead of being purged as waste.

[0184] The feed composition for the dehydrofluorination reaction of Step 3A comprises HFC-245fa, HFO-1233zd(E) as an additional compound, one or more additional compounds selected from Tables 1 and/or 2, and one or more additional compounds selected from HFO-1234ze(Z), HFO-1234ze(E) and HCFO-1233zd(Z).

[0185] HFO-1233zd(E) may be present in the feed as an additional compound of the HFC-245fa composition, or it can be generated during the HFC-245fa dehydrofluorination reaction through various chemical transformations of one or more of the chlorinated compounds of the HFC-245fa feed composition.

[0186] In one embodiment, where HFO-1234ze(Z) is the desired product, the process further comprises separating Z-HFO-1234ze from the reaction mixture produced by Step 3A, and further optionally purifying the HFO-1234ze(Z), such as by distillation, fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional purification method known in the art, or a combination of any such purification methods.

[0187] For example, as shown in Figs. 4-5, in some embodiments, Integrated Process A comprises distilling the reaction mixture F1 of Step 3A via a first distillation column, producing a bottoms stream B2 comprising a first mixture of HFC-245fa and HFO-1234ze(Z), recovering an overhead stream O2 comprising a second mixture of HFO-1234ze(E) and HFO-1234ze(Z) and optionally HFC-245fa, distilling the second mixture O2 in a second distillation column to produce a bottoms stream B3 comprising HFO-1234ze(Z) and an overhead stream O3 comprising HFO-1234ze(E).

[0188] The concentrations of the components of the overhead streams O2, O3 and bottoms streams B2, B3 may be adjusted as desired by varying the operating conditions of the distillation columns. Exemplary feed compositions, overhead streams and bottom streams are shown in Table 6.

Table 6

Stream	Concentration by weight		
	245fa	1234ze-E	1234ze-Z
F1	60.0%	30.0%	10.0%
O2	10 ppm	99.0%	1.0%
B2	86.1%	0.0%	12.9%
O3	0.0%	100.0%	0.0%
B3	0.1%	0.0%	99.9%
F1	7.2%	73.0%	19.8%
O2	0.0%	84.1%	15.9%
B2	54.4%	0.0%	45.6%
O3	0%	100%	0%
B3	0%	0%	100%

[0189] In some embodiments all or a portion of the bottoms stream (i.e., HFC-245a and Z-HFO-1234ze) may be recycled back to the feed of the reactor. In other embodiments, all or a portion of the bottoms stream (i.e., HFC-245a and Z-HFO-

1234ze) may be utilized for another end use or application, such as components to make up a blended or reclaimed composition.

[0190] Optionally, in one embodiment, as shown in Fig. 6, the process further also comprises isomerizing the E-HFO-1234ze of the overhead stream O3 to Z-HFO-1234ze (Optional Step 4A). The E-HFO-1234ze may be optionally purified before and/or after the isomerization reaction.

[0191] Referring to Figs. 11-12, in one embodiment, parameters such as contact time, temperature and pressure of one or more of the reactions of Integrated Process A and subsequent distillation, separation and/or purification processes may be adjusted in order to achieve a desired ratio of components in the distillation fraction (e.g., E-HFO-1234ze:Z-HFO-1234ze or E-HFO-1234ze:Z-HFO-1234ze:HFC-245fa or E-HFO-1234ze:Z-HFO-1234ze:E-HFO-1233zd:HFC-245fa). Accordingly, the processes of the present invention simplify manufacturing and reduce costs, since the desired mixture is directly prepared by the manufacturing process and the components are very pure.

[0192] Further, referring to Figs. 11-12, in some embodiments, Integrated Process A further comprises a step of adjusting the composition of the final product (distillation fraction) to achieve a desired blend, if needed after analysis of the composition. For example, as part of each integrated process, an additional amount of E-HFO-1234ze, Z-HFO-1234ze, E-HFO-1233zd and/or HFC-245fa may be added to adjust the ratios of the compounds to achieve a desired blend composition, and/or one or more other compounds such as but not limited to one or more HFOs (e.g., one or more of, for example but not limited to, HFO-1336mzz(E), HFO-1336mzz(Z), HCFO-1224yd(Z), HFO-1132(Z) and HFO-1132(E)), HFCs (e.g., one or more of, for example but not limited to, HFC-32, HFC-134a, HFC-134, HFC-227ea and HFC-152a), hydrofluoroethers (HFE), hydrocarbons, ethers, aldehydes, ketones, and the like may be added to the final product to obtain a desired blend composition.

[0193] In one embodiment, the dehydrofluorination reaction may be carried out at a temperature of between about 200°C to about 400°C, or between about 250°C to about 375°C, or about 250°C to about 350°C, and in some cases at a temperature of about 370°C.

[0194] In one embodiment, the contact time is typically from about 10 to about 80 seconds, and more preferably from about 30 to about 60 seconds, and most preferably from about 45 to about 50 seconds.

[0195] The reaction pressure can be subatmospheric, atmospheric, or superatmospheric. In one embodiment, the reaction is conducted at a pressure of from 14 psig to about 100 psig. In another embodiment, the reaction is conducted at a pressure of from 14 psig to about 60 psig. In yet another embodiment, the reaction is conducted at a pressure of from 40 psig to about 85 psig. In yet another embodiment, the reaction is conducted at a pressure of from 50 psig to 75 psig. In general, increasing the pressure in the reactor above atmospheric pressure will act to increase the contact time of the reactants in the process. Longer contact times will necessarily increase the degree of conversion in a process, without having to increase temperature.

[0196] Depending on the temperature of the reactor and the contact time, the product mixture from the reactor will contain varying amounts of unreacted HFC-245fa and other constituents. More particularly, depending on the temperature of the reactor and the contact time, the reactor effluent of this process embodiment using HFC-245fa as the feed may include one or more of HFO-1141, HFC-143a, HFC-152a, trifluoropropyne, HFO-1234yf, E-HFO-1234ze, Z-HFO-1234ze, HFC-245fa, E-HCFO-1233zd and Z-HCFO-1233zd.

[0197] In one embodiment, the reactor feed is preheated in a vaporizer to a temperature of from about 30°C to about 100°C. In another embodiment, the reactor feed is preheated in a vaporizer to a temperature of from about 30°C to about 80°C.

[0198] The catalyst can be readily regenerated by any means known in the art if they become deactivated. For example, an oxygen containing gas may be supplied for regeneration of the catalyst.

[0199] Also disclosed herein, in one embodiment, is a composition comprising the compound Z-HFO-1234ze produced by the dehydrofluorination reaction of this first process embodiment, and more particularly by Integrated Process A in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises HFO-1234ze(Z) and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-

1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; or at least two additional compounds or at least three additional compounds or more.

[0200] Also disclosed herein, in one embodiment, is a composition comprising a mixture of E-HFO-1234ze and Z-HFO-1234ze produced from the dehydrofluorination reaction of this first process embodiment, and more particularly by Integrated Process A in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises HFO-1234ze(E) and HFO-1234ze(Z); one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

[0201] Also disclosed herein, in one embodiment, is a composition comprising a mixture of E-HFO-1234ze, Z-HFO-1234ze and HFC-245fa produced by the dehydrofluorination reaction of this first process embodiment, and more particularly by Integrated Process A in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises (i) HFO-1234ze(E), (ii) HFO-1234ze(Z), (iii) HFC-245fa, (iv) one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E), (v) one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, and (vi) one or more additional compounds selected from HFC-143a, HFC-1225zc, HFC-236fa, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, acetone, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-

1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, toluene and HCFC-223aa, or one or more additional compounds selected from HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

[0202] Also disclosed herein, in one embodiment, is a composition comprising a mixture of E-HFO-1234ze, Z-HFO-1234ze, HFO-1233zd(E) and HFC-245fa produced by the dehydrofluorination reaction of this first process embodiment, and more particularly by Integrated Process A in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises (i) HFO-1234ze(E), (ii) HFO-1234ze(Z), (iii) HFO-1233zd(E), (iv) HFC-245fa, (v) one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E), (vi) one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, (vii) an additional compound such as HFC-245fa, and (viii) one or more additional compounds selected from HFC-143a, HFC-1225zc, HFC-236fa, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, acetone, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, toluene and HCFC-223aa, or one or more additional compounds selected from HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130. The amount of HFO-1233zd(E) present in the composition produced by Integrated Process A is preferably less than about 1 wt.% based on the total weight of the composition.

[0203] Also disclosed herein, in one embodiment, is a composition, preferably a blowing agent composition, comprising a mixture of Z-HFO-1234ze and HFC-245fa

produced by the dehydrofluorination reaction of this first process embodiment, and more particularly by Integrated Process A in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises (i) HFO-1234ze(Z), (ii) HFC-245fa, (iii) one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, and (iv) one or more additional compounds selected from HFC-143a, HFC-1225zc, HFC-236fa, HFO-1234ze(E), HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130. The amount of HFC-245fa present in the composition produced by Integrated Process A is less than about 30 wt.%, preferably less than about 10 wt.%, more preferably less than about 5 wt.%, based on the total weight of the composition.

Integrated Process B

[0204] In one embodiment, as shown in Figs. 7A-8, Integrated Process B comprises a step of reacting the HCC-240fa with HF, in the vapor phase, preferably in the presence of a fluorination catalyst, as disclosed in U.S. Patent No. 6,018,084, the entire disclosure of which is incorporated herein in its entirety, or in the liquid phase, in the presence or absence of a fluorination catalyst, as disclosed in U.S. Patent No. 6,844,475 and U.S. Patent Application Publication No. 2012/0059199, the entire disclosure of each of which is incorporated herein in its entirety, to form a reaction product comprising HFO-1233zd (both the E and Z isomers) (Step 2B). The HFO-1233zd(E) and HFO-1233zd(Z) may be separated from any other compounds present by conventional techniques, such as by distillation, fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional

purification method known in the art, or a combination of any such purification methods.

[0205] In some embodiments, examples of vapor phase catalysts for the fluorination of HCC-240fa include but are not limited to chromium containing catalysts, with or without support, such as Cr_2O_3 or CrCl_3 , or fluorinated Al_2O_3 , all which may be optionally doped with one of Zn, Na, K, Mg, and the like.

[0206] In some embodiments, examples of liquid phase fluorination catalysts include but are not limited to antimony halide, tin halide, tantalum halide, titanium halide, niobium halide, molybdenum halide, iron halide, fluorinated chrome halide, fluorinated chrome oxide or combinations thereof. In some embodiments, examples of liquid phase fluorination catalysts include but are not limited to SbCl_5 , SbCl_3 , SbF_5 , SnCl_4 , TaCl_5 , TiCl_4 , NiF_5 , NbCl_5 , MoCl_6 , FeCl_3 , fluorinated species of SbCl_5 , fluorinated species of SbCl_3 , fluorinated species of SnCl_4 , fluorinated species of TaCl_5 , fluorinated species of TiCl_4 , fluorinated species of NbCl_5 , fluorinated species of MoCl_6 , fluorinated species of FeCl_3 , or combinations thereof. These catalysts can be readily regenerated by any means known in the art if they become deactivated.

[0207] In one embodiment, the liquid phase fluorination catalyst is selected from SbF_5 , SnCl_4 , TaCl_5 , TiCl_4 , NbCl_5 , and fluorinated species thereof. In another embodiment, the liquid phase fluorination catalyst is selected from SbF_5 , SnCl_4 , TaCl_5 , TiCl_4 and/or fluorinated species thereof. In another embodiment the liquid phase fluorination catalyst is SbF_5 or SbCl_5 .

[0208] In one embodiment, the reaction mixture produced by the fluorination of HCC-240fa comprises HCFO-1233zd(E) and HCFO-1233zd(Z), and one or more additional compounds selected from HFO-1234ze(Z), HFO-1234ze(E) and HFC-245fa, or at least two additional compounds or at least three additional compounds or more.

[0209] In one embodiment, the reaction mixture produced by the fluorination of HCC-240fa comprises HCFO-1233zd(E) and one or more additional compounds selected from HFO-1234ze(Z), HFO-1234ze(E), HCFO-1233zd(Z), and HFC-245fa, or at least two additional compounds or at least three additional compounds or more.

[0210] In one embodiment, the compositions of the present invention comprise at least about 95% by weight, at least 96% by weight, at least 97% by weight, at least 98% by weight, at least about 99% by weight, at least 99.5% by weight, at least 99.6% by weight, at least 99.7% by weight, at least 99.8% by weight, or about 99.9% by weight of HCFO-1233zd and one or more additional compounds and mixtures thereof.

[0211] In one embodiment, for any of the foregoing compositions, the total amount of additional compound(s) in the composition comprising HCFO-1233zd ranges from greater than 0 wt.% to less than or equal to about 5 wt.%, about 4 wt.%, about 3 wt.%, about 2 wt.%, about 1 wt.%, about 0.9 wt.%, about 0.8 wt.%, about 0.7 wt.%, about 0.6 wt.%, about 0.5 wt.%, about 0.4 wt.%, about 0.3 wt.%, about 0.2 wt.%, about 0.1 wt.%, based on the total weight of the composition. In another embodiment, the total amount of additional compound(s) ranges from 0.01 ppm (weight) to about 5 wt.%, and all values therebetween. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to about 5 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to about 1 wt.%, or about 0.5 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to 0.4 wt.% or less, based on the total weight of the composition. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to 0.1 wt.% or less, based on the total weight of the composition. In one embodiment, the total amount of additional compound(s) is about 0.1 wt.% based on the total weight of the composition.

[0212] In one embodiment, Integrated Process B comprises a step of fluorination of the HCFO-1233zd(E) and/or HCFO-1233zd(Z) produced by Step 2B to form a reaction mixture comprising HFO-1234ze(Z) and HFO-1234ze(E) (Step 3B).

[0213] More particularly, Step 3B comprises fluorination of HCFO-1233zd by reaction with a fluorinating agent, such as HF, in a reactor, preferably in the vapor phase, in the presence of a fluorinated catalyst, to make a reaction mixture comprising a reaction mixture comprising E-HFO-1234ze and Z-HFO-1234ze, as shown in Fig. 7A.

[0214] According to this process, both E-HFO-1234ze and Z-HFO-1234ze, among other compounds, are produced from the HCFO-1233zd. The conversion is between about 10% to about 100%.

[0215] In some embodiments, Integrated Process B further comprises separating (e.g., by distillation) HFO-1234ze(E) and HFO-1234ze(Z) from the reaction mixture produced by Step 3B, such that the composition produced by the process comprises HFO-1234ze(E) and HFO-1234ze(Z), as shown in Fig. 7B. The process may also comprise optionally purifying the HFO-1234ze(E) and HFO-1234ze(Z) mixture, such as by distillation, fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional purification method known in the art, or a combination of any such purification methods.

[0216] In some embodiments, Integrated Process B further comprises separating, e.g., via one or more distillation columns, HFO-1233zd, HFO-1234ze(Z) and HFC-245fa from the reaction mixture produced by Step 3B, such that the composition produced by the process comprises HFO-1233zd, HFO-1234ze(Z) and HFC-245fa.

[0217] In some embodiments, Integrated Process B further comprises separating, e.g., via one or more distillation columns, HFO-1233zd(E), HFO-1234ze(Z) and HFC-245fa from the reaction mixture produced by Step 3B, such that the composition produced by the process comprises HFO-1233zd(E), HFO-1234ze(Z) and HFC-245fa.

[0218] In some embodiments, Integrated Process B further comprises separating, e.g., via one or more distillation columns, HFO-1233zd(E) and HFO-1234ze(Z) from the reaction mixture produced by Step 3B, such that the composition produced by the process comprises HFO-1233zd(E) and HFO-1234ze(Z), which is particularly beneficial for use as a foam blowing agent composition.

[0219] In some embodiments, Integrated Process B further comprises separating, e.g., via one or more distillation columns, HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E) from the reaction mixture produced by Step 3B, such that the composition produced by the process comprises HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E).

[0220] In some embodiments, Integrated Process B further comprises separating, e.g., via one or more distillation columns, HFO-1233zd(E), HFO-1234ze(Z), HFO-1234ze(E) and HFC-245fa from the reaction mixture produced by Step 3B, such that the

composition produced by the process comprises HFO-1233zd(E), HFO-1234ze(Z), HFO-1234ze(E) and HFC-245fa.

[0221] The process may also comprise optionally purifying any of the separated mixtures, such as by distillation, fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional purification method known in the art, or a combination of any such purification methods.

[0222] In one embodiment, where HFO-1234ze(Z) is the desired product, the process further comprises separating Z-HFO-1234ze from the reaction mixture produced by Step 3B, and further optionally purifying the HFO-1234ze(Z), such as by distillation, fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional purification method known in the art, or a combination of any such purification methods. Optionally, in one embodiment, the process further also comprises separating E-HFO-1234ze from the reaction mixture and isomerizing it to make Z-HFO-1234ze (Optional Step 4B), as shown in Fig. 8. The E-HFO-1234ze may be optionally purified before and/or after the isomerization reaction.

[0223] Referring to Figs. 11-12, in one embodiment, parameters such as contact time, temperature and pressure of one or more of the reactions of Integrated Process B and subsequent distillation, separation and/or purification processes may be adjusted in order to achieve a desired ratio of components of the distillation fraction (e.g., E-HFO-1234ze:Z-HFO-1234ze or HFO-1233zd(E):Z-HFO-1234ze:HFC-245fa or HFO-1233zd(E):Z-HFO-1234ze or E-HFO-1234ze:Z-HFO-1234ze:E-HFO-1233zd:HFC-245fa).

[0224] Further, referring to Figs. 11-12, in some embodiments, Integrated Process B further comprises a step of adjusting the composition of the final product (distillation fraction) to achieve a desired blend, if needed after analysis of the composition. For example, as part of each integrated process, an additional amount of E-HFO-1234ze, Z-HFO-1234ze, E-HFO-1233zd and/or HFC-245fa may be added to adjust the ratios of the compounds to achieve a desired blend composition, and/or one or more other compounds such as but not limited to one or more HFOs (e.g., one or more of, for example but not limited to, HFO-1336mzz(E), HFO-1336mzz(Z), HCFO-1224yd(Z), HFO-1132(Z) and HFO-1132(E)), HFCs (e.g., one or more of, for example but not limited to, HFC-32, HFC-134a, HFC-134, HFC-227ea and HFC-

152a), HFEs, hydrocarbons, ethers, aldehydes, ketones, and the like may be added to the final product to obtain a desired blend composition.

[0225] The fluorination agent is preferably anhydrous or substantially anhydrous. By "substantially anhydrous," we mean that the fluorination agent contains less than about 0.05 wt.% water, and preferably contains less than about 0.02 wt.% water.

[0226] In some embodiments, the fluorinating agent is selected from hydrogen fluoride, antimony trifluoride, antimony tetrafluoride, antimony pentafluoride, antimony trichloride/hydrogen fluoride, antimony tetrachloride/hydrogen fluoride, or any mixture thereof. In some embodiments, the fluorinating agent is hydrogen fluoride (HF). In some embodiments, the HF is preferably anhydrous or substantially anhydrous. By "substantially anhydrous," we mean that the HF contains less than about 0.05 wt.% water, and preferably contains less than about 0.02 wt.% water.

[0227] The fluorinated catalyst can be readily regenerated by any means known in the art if they become deactivated. One suitable method of regenerating the catalyst involves, for example, supply oxygen containing gas to the catalyst system.

[0228] In one embodiment, the fluorination reaction may be performed by introducing the HCFO-1233zd starting material and the fluorinating agent into a reaction vessel or zone, and then heating the mixture with agitation.

[0229] The reactor is preferably preheated to a fluorination reaction temperature while anhydrous or substantially anhydrous HF is fed to the reactor. The HCFO-1233zd and HF may be fed to the reactor at any convenient temperature and pressure. In a one embodiment, either or both of the HCFO-1233zd and HF are pre-vaporized or preheated to a temperature of from about 30°C to about 150°C, preferably about 80°C, prior to entering the reactor. In another embodiment, the HCFO-1233zd and HF are vaporized in the reactor.

[0230] In some embodiments, the HF and HCFO-1233zd feeds may be adjusted to the desired mole ratio. The HF to HCFO-1233zd mole ratio preferably ranges from about 3:1 to about 100:1; more preferably from about 4:1 to about 50:1 and most preferably from about 5:1 to about 20:1. In a preferred embodiment, the HF to HCFO-1233zd mole ratio is 20:1.

[0231] In other embodiments, the reactor is a fixed bed reactor.

[0232] In one embodiment, the contact time for the fluorination reaction may be from about 1 to about 90 seconds, preferably about 3 to about 60 seconds, and more preferably from about 5 to about 30 seconds.

[0233] After introduction of the feed reactants, the temperature of the reactor is increased. The fluorination reaction is conducted at a temperature ranging from about 80°C to about 400°C, more preferably from about 100°C to about 375°C, and most preferably from about 300°C to about 350°C.

[0234] The reaction pressure can be subatmospheric, atmospheric, or superatmospheric. In one embodiment, the reaction is conducted at a pressure of from 14 psig to about 100 psig. In another embodiment, the reaction is conducted at a pressure of from 14 psig to about 60 psig. In yet another embodiment, the reaction is conducted at a pressure of from 40 psig to about 85 psig. In yet another embodiment, the reaction is conducted at a pressure of from 50 psig to 75 psig. In general, increasing the pressure in the reactor above atmospheric pressure will act to increase the contact time of the reactants in the process. Longer contact times will necessarily increase the degree of conversion in a process, without having to increase temperature.

[0235] The HCFO-1233zd converted by the reaction produces Z-HFO-1234ze, HCFO-1233zd (E and Z isomers) and E-HFO-1234ze, among other compounds. The conversion to Z-HFO-1234ze and E-HFO-1234ze is preferably from about 10% to about 100%. Depending on the temperature of the reactor and the contact time, the product mixture from the reactor will contain varying amounts of unreacted E- and Z-HCFO-1233zd, as well as other constituents. More particularly, depending on the temperature of the reactor and the contact time, the reactor effluent may include one or more of E-HFO-1234ze, Z-HFO-1234ze, E-HCFO-1233zd, Z-HCFO-1233zd, HFO-1234yf, HFC-236fa, HFC-245fa, HFO-1233xf and HFC-243fa. The process thus further comprises separating the desired Z-HFO-1234ze from the reaction product.

[0236] In some embodiments, unreacted HCFO-1233zd may optionally be recycled back to the feed of the reactor, optionally with a small amount of Z-HFO-1234ze and/or E-HFO-1234ze. In other embodiments, the byproduct mixture may be used for another end use or applications, such as making up a new or reclaimed blend composition.

[0237] Also disclosed herein, in one embodiment, is a composition comprising the compound Z-HFO-1234ze produced from the fluorination reaction of this second process embodiment, and more particularly by Integrated Process B in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises HFO-1234ze(Z) and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; or at least two additional compounds or at least three additional compounds or more.

[0238] Also disclosed herein, in one embodiment, is a composition comprising a mixture of E-HFO-1234ze and Z-HFO-1234ze produced from the fluorination reaction of this second process embodiment, and more particularly by Integrated Process B in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises HFO-1234ze(E) and HFO-1234ze(Z); one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

[0239] Also disclosed herein, in one embodiment, is a composition comprising a mixture of HFO-1233zd(E), Z-HFO-1234ze and HFC-245fa produced from the fluorination reaction of this second process embodiment, and more particularly by Integrated Process B in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises (i) HFO-1233zd(E), (ii) Z-HFO-1234ze, (iii) HFC-245fa, (iv) one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, (v) an additional compound such as E-HFO-1234ze, and (vi) one or more additional

compounds selected from HFC-143a, HFC-1225zc, HFC-236fa, HFO-1234ze(E), HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, acetone, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, toluene and HCFC-223aa, or one or more additional compounds selected from HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234ze(Z), HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

[0240] Also disclosed herein, in one embodiment, is a composition comprising a mixture of HFO-1233zd(E) and Z-HFO-1234ze produced from the fluorination reaction of this second process embodiment, and more particularly by Integrated Process B in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises (i) HFO-1233zd(E), (ii) Z-HFO-1234ze, (iii) one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, and (iv) one or more additional compounds selected from E-HFO-1234ze and HFC-245fa.

[0241] Also disclosed herein, in one embodiment, is a composition comprising a mixture of HFO-1233zd(E), Z-HFO-1234ze and E-HFO-1234ze produced from the fluorination reaction of this second process embodiment, and more particularly by Integrated Process B in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises (i) HFO-1233zd(E), (ii) Z-HFO-1234ze, (iii) E-HFO-1234ze, (iv) one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, (v) an additional compound such as HFC-245fa, and (vi) one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb and HFO-1243zf.

[0242] Also disclosed herein, in one embodiment, is a composition comprising a mixture of HFO-1233zd(E), Z-HFO-1234ze, E-HFO-1234ze, and HFC-245fa produced from the fluorination reaction of this second process embodiment, and more particularly by Integrated Process B in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises (i) HFO-1233zd(E), (ii) Z-HFO-1234ze, (iii) E-HFO-1234ze, (iv) HFC-245fa, (v) one or more additional compounds selected from HFC-263fb, HFO-1234zc, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, (v) one or more additional compounds selected from Z-HFO-1234ze, E-HFO-1234ze and HFC-245fa, (vi) one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb and HFO-1243zf, and (vii) one or more additional compounds selected from HFC-143a, HFC-1225zc, HFC-236fa, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, acetone, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, toluene and HCFC-223aa, or one or more additional compounds selected from HFC-338mf, HFC-356mff, HFO-1234ze(Z), HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

Integrated Process C

[0243] In one embodiment, as shown in Figs. 9A-10, Integrated Process C comprises a step of fluorination of HCC-240fa by reaction with a fluorinating agent, such as hydrogen fluoride, in a reactor, preferably in the vapor phase, in the presence of a fluorinated catalyst, to form a reaction mixture comprising HFO-1234ze(Z) and HFO-1234ze(E) (Step 2C).

[0244] More particularly, in one embodiment, fluorination of the HCC-240fa according to Step 2C of Integrated Process C produces a reaction mixture comprising HFO-1233zd, HFO-1234ze(Z) and HFO-1234ze(E).

[0245] According to this process, both E-HFO-1234ze and Z-HFO-1234ze, among other compounds, are produced from the HCC-240fa. The conversion of HCC-240fa to HFO-1234(E)/(Z) is between about 10% to about 100%.

[0246] In some embodiments, Integrated Process C further comprises separating HFO-1234ze(E) and HFO-1234ze(Z) from the reaction mixture produced by Step 2C. The process may also comprise optionally purifying the HFO-1234ze(E) and HFO-1234ze(Z), such as by distillation, fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional purification method known in the art, or a combination of any such purification methods.

[0247] In some embodiments, Integrated Process C further comprises separating HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E) from the reaction mixture produced by Step 2C. The process may also comprise optionally purifying the HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E), such as by distillation, fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional purification method known in the art, or a combination of any such purification methods, as shown in Fig. 9A.

[0248] In one embodiment, as shown in Fig. 9B, where HFO-1234ze(Z) is the desired product, the process further comprises separating Z-HFO-1234ze from the reaction mixture produced by Step 2C, and further optionally purifying the HFO-1234ze(Z), such as by distillation, fractionation, azeotropic distillation, extractive distillation, adsorption, absorption, or another conventional purification method known in the art, or a combination of any such purification methods.

[0249] Optionally, in one embodiment, as shown in Fig. 10, the process further also comprises separating E-HFO-1234ze from the reaction mixture and isomerizing it to make Z-HFO-1234ze (Optional Step 3C). The E-HFO-1234ze may be optionally purified before and/or after the isomerization reaction.

[0250] Referring to Figs. 11-12, in one embodiment, parameters such as contact time, temperature and pressure of one or more of the reactions of Integrated Process C and subsequent distillation, separation and/or purification processes may be adjusted in order to achieve a desired ratio of components of the distillation fraction (e.g., E-HFO-1234ze:Z-HFO-1234ze or HFO-1233zd(E):Z-HFO-1234ze:E-HFO-1234ze).

[0251] Further, referring to Figs. 11-12, in some embodiments, Integrated Process C further comprises a step of adjusting the composition of the final product (distillation fraction) to achieve a desired blend, if needed after analysis of the composition. For example, as part of each integrated process, an additional amount of E-HFO-1234ze, Z-HFO-1234ze, E-HFO-1233zd and/or HFC-245fa may be added to adjust the ratios of the compounds to achieve a desired blend composition, and/or one or more other compounds such as but not limited to one or more HFOs (e.g., one or more of, for example but not limited to, HFO-1336mzz(E), HFO-1336mzz(Z), HCFO-1224yd(Z), HFO-1132(Z) and HFO-1132(E)), HFCs (e.g., one or more of, for example but not limited to, HFC-32, HFC-134a, HFC-134, HFC-227ea and HFC-152a), HFEs, hydrocarbons, ethers, aldehydes, ketones, and the like may be added to the final product to obtain a desired blend composition.

[0252] The fluorination agent is preferably anhydrous or substantially anhydrous. By "substantially anhydrous," we mean that the fluorination agent contains less than about 0.05 wt.% water, and preferably contains less than about 0.02 wt.% water.

[0253] In some embodiments, the fluorinating agent is selected from hydrogen fluoride, antimony trifluoride, antimony tetrafluoride, antimony pentafluoride, antimony trichloride/hydrogen fluoride, antimony tetrachloride/hydrogen fluoride, or any mixture thereof. In some embodiments, the fluorinating agent is hydrogen fluoride (HF). In some embodiments, the HF is preferably anhydrous or substantially anhydrous. By "substantially anhydrous," we mean that the HF contains less than about 0.05 wt.% water, and preferably contains less than about 0.02 wt.% water.

[0254] The fluorinated catalyst can be readily regenerated by any means known in the art if they become deactivated. For example, an oxygen containing gas may be supplied for regeneration of the catalyst.

[0255] In one embodiment, the fluorination reaction may be performed by introducing the HCC-240a starting material and the fluorinating agent into a reaction vessel or zone, and then heating the mixture with agitation.

[0256] The reactor is preferably preheated to a fluorination reaction temperature while anhydrous or substantially anhydrous HF is fed to the reactor. The HCC-240fa and HF may be fed to the reactor at any convenient temperature and pressure. In a one embodiment, either or both of the HCC-240fa and HF are pre-vaporized or

preheated to a temperature of from about 30°C to about 300°C, preferably about 150°C, prior to entering the reactor. In another embodiment, the HCC-240fa and HF are vaporized in the reactor.

[0257] In some embodiments, the HF and HCC-240fa feeds may be adjusted to the desired mole ratio. The HF to HCC-240fa mole ratio preferably ranges from about 3:1 to about 100:1; more preferably from about 4:1 to about 50:1 and most preferably from about 5:1 to about 20:1. In a preferred embodiment, the HF to HCC-240fa mole ratio is 20:1.

[0258] In other embodiments, the reactor is a fixed bed reactor.

[0259] In one embodiment, the contact time for the fluorination reaction may be from about 1 to about 90 seconds, preferably about 3 to about 60 seconds, and more preferably from about 5 to about 30 seconds.

[0260] After introduction of the feed reactants, the temperature of the reactor is increased. The fluorination reaction is conducted at a temperature ranging from about 80°C to about 400°C, more preferably from about 100°C to about 375°C, and most preferably from about 200°C to about 350°C.

[0261] The reaction pressure can be subatmospheric, atmospheric, or superatmospheric. In one embodiment, the reaction is conducted at a pressure of from 14 psig to about 100 psig. In another embodiment, the reaction is conducted at a pressure of from 14 psig to about 60 psig. In yet another embodiment, the reaction is conducted at a pressure of from 40 psig to about 85 psig. In yet another embodiment, the reaction is conducted at a pressure of from 50 psig to 75 psig. In general, increasing the pressure in the reactor above atmospheric pressure will act to increase the contact time of the reactants in the process. Longer contact times will necessarily increase the degree of conversion in a process, without having to increase temperature.

[0262] The HFC-240fa converted by the reaction produces Z-HFO-1234ze, E-HFO-1234ze, HCFO-1233zd(E) and HCFO-1233zd(Z), among other compounds. The conversion to E-HFO-1234ze and Z-HFO-1234ze is between about 10% to about 100%. Depending on the temperature of the reactor and the contact time, the product mixture from the reactor will contain varying amounts of unreacted HFC-

240fa and other constituents. More particularly, depending on the temperature of the reactor and the contact time, the reactor effluent may include one or more of E-HFO-1234ze, Z-HFO-1234ze, HFC-245fa, HFO-1233xf, E-HCFO-1233zd and Z-HCFO-1233zd, HCFC-244fa, HFC-243fa and HFC-243fb. The process thus further comprises separating the desired Z-HFO-1234ze or both Z-HFO-1234ze and E-HFO-1234ze from the reaction product.

[0263] In some embodiments, unreacted HFC-240fa, along with R-1233zd, R-244fa and/or R-243fa may optionally be recycled back to the feed of the reactor, optionally with a small amount of Z-HFO-1234ze and/or E-HFO-1234ze.

[0264] Also disclosed herein, in one embodiment, is a composition comprising the compound Z-HFO-1234ze produced from the fluorination reaction of this third process embodiment, and more particularly by Integrated Process C in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises HFO-1234ze(Z) and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; or at least two additional compounds or at least three additional compounds or more.

[0265] Also disclosed herein, in one embodiment, is a composition comprising a mixture of E-HFO-1234ze and Z-HFO-1234ze produced from the fluorination reaction of this third process embodiment and more particularly by Integrated Process C in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises HFO-1234ze(E) and HFO-1234ze(Z); one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

[0266] Also disclosed herein, in one embodiment, is a composition comprising HFO-1233zd(E), E-HFO-1234ze and Z-HFO-1234ze produced from the fluorination reaction of this third process embodiment, and more particularly by Integrated Process C in accordance with any of the embodiments discussed above. In certain embodiments, the composition comprises (i) HFO-1233zd(E), (ii) HFO-1234ze(E), (iii) HFO-1234ze(Z); (iv) an additional compound such as HFC-245fa, (v) one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb and HFO-1243zf, and (vi) one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

[0267] In one embodiment, the Z-HFO-1234ze produced from any of the embodiments of Integrated Process A, Integrated Process B or Integrated Process C disclosed herein is of a high purity and is free of or substantially free of chlorinated compounds, making it suitable for etching gas applications. By “high purity” is meant a purity greater than 99.5 wt. %, or greater than 99.6 wt. %, or greater than 99.7 wt. %, or greater than 99.8 wt. %, preferably 99.9 wt. % or greater. By “substantially free of” with respect to chlorinated compounds is meant that the amount of chlorinated compounds present in the composition is less than about 100 ppm, preferably less than about 50 ppm, more preferably less than about 10 ppm, and most preferably less than about 1 ppm.

[0268] In one embodiment, the Z-HFO-1234ze produced from any of the embodiments of Integrated Process A, Integrated Process B or Integrated Process C disclosed herein has a purity of greater than about 99.9% and is free of or substantially free of chlorinated compounds.

[0269] In one embodiment, the highly pure composition comprises Z-HFO-1234ze and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134a, HFC-134 and HFC-245cb. In one embodiment, the highly pure Z-HFO-1234ze is free of or substantially free of E-HFO-1234ze, with “substantially free of”

meaning that the total amount of E-HFO-1234ze present in the composition is less than about 10 ppm, preferably less than about 1 ppm.

[0270] In one embodiment, the following is an exemplary (prophetic) composition of Z-HFO-1234ze having high purity and being free of or substantially free of chlorinated compounds, and thus being particularly suited for etching gas applications.

Compound	Weight (ppm)
HFC-227ca	3
HFC-263fb	10
HFO-1234zc	5
HFC-245fa	50

[0271] In one embodiment, the Z-HFO-1234ze produced from any of the embodiments of Integrated Process A, Integrated Process B or Integrated Process C disclosed herein is of a high purity such that it is suitable for use in a pharmaceutical grade application. For example, the Z-HFO-1234ze may be used as a propellant in a sprayable composition of a medical product such as a metered dose inhaler. For pharmaceutical grade applications, the Z-HFO-1234ze preferably has a purity of at least 99.9%.

[0272] In some embodiments, any of the process embodiments disclosed herein may further comprise passing the reaction mixture through a drying media or desiccant, such as activated alumina, silica gel, molecular sieve, zeolite, and the like for moisture removal. In some embodiments, optionally, the reaction mixture of any of the process embodiments disclosed herein may further be contacted with an absorbent, such as an aluminium-containing absorbent, activated carbon, or a mixture thereof, for removing trace amounts of HF. In some embodiments, the absorbent material may generate CaF₂ upon reaction with the HF removed from the reaction mixture.

[0273] In some embodiments, for any of the processes described herein, an inert diluent gas is used as a carrier gas for one or more of the reactants. In one embodiment, the carrier gas is selected from nitrogen, argon, helium, or carbon dioxide.

[0274] The reactor or vessel, distillation columns, feed lines, effluent lines and any other associated units utilized in carrying out any of the process embodiments

disclosed herein should be constructed from materials which are resistant to the corrosive effects of hydrogen fluoride, such as nickel and its alloys, including Hastelloy, Monel, and Inconel, or vessels lined with fluoropolymers. These may be a single tube, or multiple tubes packed with an appropriate catalyst depending on the reaction to be carried out.

[0275] Useful catalysts for the processes of any of the process embodiments disclosed herein include chromium-based catalysts such as fluorinated chromium oxide, and aluminum-based catalysts such as fluorinated alumina oxide. The catalyst may either be unsupported, or supported on a support such as activated carbon, graphite, fluoride graphite, or alumina fluoride. The catalyst may either be used alone, or in the presence of a co-catalyst selected from nickel, cobalt, manganese, or zinc salt. In one embodiment, a chromium catalyst is high surface area chromium oxide, or chromium/nickel on alumina fluoride (Cr/Ni/AlF_3), the preparation of which is reported in European Patent EP486,333. In another embodiment, the catalyst is fluorinated Guignet's green catalyst. Additional suitable catalysts include, but are not limited to, JM 62-2 (chrome catalyst available from Johnson Matthey), LV (chrome catalyst available from Chemours), JM-62-3 (chrome catalyst available from Johnson Matthey), and Newport Chrome (chrome catalyst available from Chemours). The chromium catalysts are preferably activated before use, typically by a procedure whereby the catalyst is heated to from 350°C to 400°C under a flow of nitrogen for a period of time, after which the catalyst is heated under a flow of HF and nitrogen or air for an additional period of time.

[0276] In one embodiment, the Guignet's Green of the fluoride-activated Guignet's Green catalyst used in the present invention is made by reacting (fusing) boric acid with alkali metal dichromate at 500°C to 800°C, followed by hydrolysis of the reaction product, whereby said Guignet's Green contains boron, alkali metal, and water of hydration. The usual alkali metal dichromates are the Na and/or K dichromates. The reaction is typically followed by the steps of cooling the reaction product in air, crushing this solid to produce a powder, followed by hydrolysis, filtering, drying, milling, and screening. The Guignet's Green is bluish green, but is known primarily as a green pigment, whereby the pigment is commonly referred to as Guignet's Green. When used as a catalyst, it is also referred to as Guignet's Green as disclosed in U.S. Pat. No. 3,413,363. In U.S. Pat. No. 6,034,289, Cr_2O_3 catalysts are

disclosed as preferably being in the alpha form, and Guignet's Green is also disclosed as a commercially available green pigment having the composition: Cr_2O_3 79–83 %, H_2O 16–18 %, B_2O_5 1.5 to 2.7 % (sentence bridging cols. 2 and 3) that can be converted to the alpha form (col. 3, l. 3). U.S. Pat. No. 7,985,884 acknowledges the presence of alkali metal in the Guignet's Green in the composition of Guignet's Green disclosed in Example 1: 54.5% Cr, 1.43% B, 3,400 ppm Na, and 120 ppm K.

[0277] The physical shape of the catalyst is not critical and may, for example, include pellets, extrudates, powders, or granules. The fluoride activation of the catalyst is preferably carried out on the final shape of the catalyst.

[0278] For any of the process embodiments disclosed herein, the desired Z-HFO-1234ze or Z-HFO-1234ze/E-HFO-1234ze mixture may be purified by a conventional method for purifying reaction products and separated from the reaction mixture by methods known in the art (e.g., distillation).

[0279] Any unreacted feed materials may be recycled back to the reactor with additional material for further production of the reaction mixture. Further, any excessive amount of hydrogen fluoride present may be removed by scrubbing, distillation, and the like.

[0280] In some embodiments, where the primary desired product is Z-HFO-1234ze, the E-HFO-1234ze may also be separated and recovered from the reaction mixture by known methods and further treated for isomerization to Z-HFO-1234ze. The isomerization step or method comprises reacting the E-HFO-1234ze, preferably in the vapor phase, with at least one fluorinated catalyst, optionally in the presence of an oxygen containing gas. The E-HFO-1234ze may optionally be purified before isomerization.

[0281] In one embodiment, the contacting for the isomerization reaction occurs at a reaction temperature from about 50°C to about 450°C, preferably from about 50°C to about 400°C, and more preferably 50°C to about 375°C, to isomerize at least a portion the E-HFO-1234ze into Z-HFO-1234ze. The contact time is typically from about 2 to about 90 seconds, or from about 10 to about 70 seconds.

[0282] In some embodiments, a catalyst suitable for use in the isomerization reaction scheme includes a vapor phase chromium oxide (Cr_2O_3), aluminum oxide

(Al₂O₃) catalyst or combinations thereof. In one embodiment, the isomerization catalyst includes chromium oxide supported on aluminum oxide. In one embodiment, the isomerization catalyst includes zinc doped chromium oxide. Suitable isomerization catalysts comprise metal compounds, such as chromium, aluminum, zinc, magnesium, or combinations thereof. Suitable isomerization catalysts include, but are not limited to, chromium oxide, fluorinated chromium oxide, oxyfluorides of chrome, chromium halide, alumina, aluminum fluoride, fluorided alumina, metal compounds on aluminum fluoride, metal compounds on fluorided alumina; oxides, fluorides, and oxyfluorides of magnesium, zinc and mixtures of magnesium and zinc and/or aluminum; lanthanum oxide and fluorided lanthanum oxide; carbon, acid-washed carbon, activated carbon, three dimensional matrix carbonaceous materials; and metal compounds supported on carbon. The metal compounds are oxides, fluorides, and oxyfluorides of at least one metal selected from the group consisting of sodium, potassium, rubidium, cesium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, chromium, iron, cobalt, rhodium, nickel, copper, zinc, and mixtures thereof. The catalyst is contacted for a time sufficient to affect the desired isomerization.

[0283] The reaction pressure used in the isomerization reaction can be sub-atmospheric, atmospheric, or super-atmospheric. In one embodiment, the reaction pressure for the isomerization reaction is about 10 to about 150 psig.

[0284] In some embodiments, the overall conversion of E-HFO-1234ze into Z-HFO-1234ze may be about 2% to about 70%.

[0285] For each of the integrated processes disclosed herein, parameters such as contact time, temperature and pressure of the last reaction and subsequent distillation, separation and/or purification processes may be adjusted in order to achieve a desired ratio of E-HFO-1234ze to Z-HFO-1234ze.

[0286] For each of the integrated processes disclosed herein, the heat of reaction generated in any step of the process can be recovered and utilized. The heat of reaction for each step of each integrated process disclosed herein is provided in Table A below, the heats of reaction having been calculated with GaussView 5.0.

Table A

Process Step	Reaction	Delta Ho (Kcal/mole)
1A, 1B, 1C	$\text{CCl}_4 + \text{VCM} \rightarrow 240\text{fa}$	-31.9
2C	$240\text{fa} + 3.2\text{HF} \rightarrow 0.8\ 1233\text{zd}(\text{E}) + 0.2\ 1234\text{ze}(\text{E}) + 4.2\text{HCl}$	-9.9
2B	$240\text{fa} + 3\text{HF} \rightarrow 1233\text{zd}(\text{E}) + 4\text{HCl}$	-10.7
3B	$1233\text{zd}(\text{E}) + \text{HF} \rightarrow 1234\text{ze}(\text{E}) + \text{HCl}$	4
2A	$240\text{fa} + 5\text{HF} \rightarrow 245\text{fa} + 5\text{HCl}$	-29.1
3A	$245\text{fa} \rightarrow 1234\text{ze}(\text{E}) + \text{HF}$	22.4
4A, 4B, 3C	$1234\text{ze}(\text{E}) \rightarrow 1234\text{ze}(\text{Z})$	-2.2

[0287] In some embodiments, the heat of reaction generated in any step of an integrated process can be utilized in the same process where energy such as heating is required and/or applied to other operations where heat is needed. For example, in some embodiments, the heat of the reaction generated by the exothermic reactions of Step 1A and/or 2A can be utilized as heat for the endothermic reaction of Step 3A; and/or the heat of the reaction generated by the exothermic reactions of Step 1B and/or 2B can be utilized as heat for the endothermic reaction of Step 3B. As further examples, in some embodiments, the heat of reaction generated in any step of each integrated process disclosed herein can be used as heat for reactions or steps of the integrated process, such as distillation, separation, and/or material vaporization (e.g., vaporization of a starting or intermediate material such as HCC-240fa). Alternatively or additionally, in some embodiments, the heat of reaction generated in any step of each integrated process disclosed herein can be applied to other (different) processes or chemical reactions being carried out at the same site or at an adjacent site, such as a thermoconverter for waste treatment or other chemical production, or facility heating such as for heating of a building. It will be understood by those skilled in the art that utilization of the heat of reaction can be carried out with proper engineering design processes and protocols in place.

[0288] Additionally, the compositions of the present invention 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), if needed, as described above.

COMPOSITIONS

[0289] In one embodiment, the present disclosure provides a composition comprising HFO-1234ze(Z) produced by any one of Integrated Processes A, B or C. In one embodiment, the compositions according to the present invention comprise HFO-1234ze(Z) and at least one additional compound selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; or at least two additional compounds or at least three additional compounds or more.

[0290] In one embodiment, the present disclosure provides a composition comprising a mixture of E-HFO-1234ze and Z-HFO-1234ze produced by any one of Integrated Processes A, B or C. In one embodiment, the compositions according to the present invention comprise HFO-1234ze(E) and HFO-1234ze(Z); one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

[0291] In one embodiment, the present disclosure provides a composition comprising HFO-1234ze(Z) and at least one additional compound selected from HFO-1234ze(E), HFC-1233xf, HCFC-243fa, HCFC-243fb, and HCFC-244fa, and the total amount of the additional members is greater than 0 and less than about 2 weight percent, greater than 0 and less than about 1 weight percent, greater than 0 and less than about 0.5 weight percent, greater than 0 and less than or equal to

about 0.1 weight percent, or at least two additional members or at least three additional members or more.

[0292] In some embodiments, certain precursor compounds to HFO-1234ze(Z) or HFO-1234ze(E) contain compounds that then appear as additional compounds in the HFO-1234ze(Z) or HFO-1234(Z)/ HFO-1234ze(E) compositions. In other embodiments, these precursor compounds may themselves react during the HFO-1234ze(Z) or HFO-1234ze(E) formation to produce additional compounds that then appear in the HFO-1234ze(Z) or HFO-1234ze(Z)/ HFO-1234ze(E) compositions. In other embodiments, the reaction conditions under which the HFO-1234ze(Z) and/or HFO-1234ze(E) is produced also produce by-products, by which is meant adventitious reaction pathways may occur simultaneously to produce compounds other than HFO-1234ze(Z) and/or HFO-1234ze(E) and the quantity and identity of these additional compounds will depend upon the particular conditions under which the HFO-1234ze(Z) and/or HFO-1234ze(E) is produced.

[0293] Some of the additional compounds making up the compositions according to the present invention are defined in Table 7.

Table 7

Name	Formula	Chemical Name
HFO-1234ze	CHF=CH-CF ₃	1,3,3,3-tetrafluoropropene
HFC-263fb	CF ₃ -CH ₂ -CH ₃	1,1,1-trifluoropropane
HFO-1234zc	CF ₂ =CH-CHF ₂	1,1,3,3-tetrafluoropropene
HFC-245fa	CF ₃ -CH ₂ -CHF ₂	1,1,1,3,3-Pentafluoropropane
HCFO-1233zd(E)	CHCl=CH-CF ₃	1-chloro-3,3,3-trifluoropropene
HCFO-1233zd(Z)	CHCl=CH-CF ₃	1-chloro-3,3,3-trifluoropropene
HCFO-1233xf	CH ₂ =CCl-CF ₃	2-chloro-3,3,3-trifluoropropene
HCFC-124	CHClF-CF ₃	1-Chloro-1,2,2,2-tetrafluoroethane
HCC-40	CH ₃ Cl	Chloromethane
CFC-114	CClF ₂ -CClF ₂	1,2-Dichlorotetrafluoroethane
HCFO-1131(E)	CHCl=CHF	1-chloro-2-fluoroethylene
CFC-114a	CCl ₂ F-CF ₃	1,1-Dichlorotetrafluoroethane
HCFC-124a	CClF ₂ -CHF ₂	1-Chloro-1,1,2,2-tetrafluoroethane
HFC-227ca	CF ₃ -CF ₂ -CHF ₂	1,1,2,2,3,3,3-Heptafluoropropane
HFO-1234yf	CH ₂ =CF-CF ₃	2,3,3,3-tetrafluoropropene
HFC-152a	CHF ₂ -CH ₃	1,1-Difluoroethane
HFO-1243zf	CH ₂ -CH-CF ₃	3,3,3-trifluoropropene
HFC-245cb	CF ₃ -CF ₂ -CH ₃	1,1,1,2,2-Pentafluoropropane

Name	Formula	Chemical Name
HFC-125	CF ₃ -CHF ₂	Pentafluoroethane
HFC-143a	CF ₃ -CH ₃	1,1,1-trifluoropropane
N/A	CH::C-CF ₃	3,3,3-trifluoropropyne
HFC-134a	CHF ₂ -CHF ₂	1,1,1,2-Tetrafluoroethane
HFO-1225zc	CF ₂ =CH-CF ₃	1,1,3,3,3-pentafluoropropene
HFO-1225ye(E)	CHF=CF-CF ₃	1,2,3,3,3-pentafluoropropene
HFO-1225ye(Z)	CHF=CF-CF ₃	1,2,3,3,3-pentafluoropropene
HFO-1225ye	CHF=CF-CF ₃	1,2,3,3,3-pentafluoropropene
HFC-236fa	CF ₃ -CH ₂ -CF ₃	1,1,1,3,3,3-Hexafluoropropane
HFC- 236ea	CF ₃ -CHF-CHF ₂	1,1,1,2,3,3-Hexafluoropropane

[0294] The additional compounds listed in Table 7 are available commercially or can be made by processes known in the art. For example, such compounds can be purchased from a specialty fluorochemical supplier, such as SynQuest Laboratories, Inc. (Alachua, Florida, USA).

[0295] In one embodiment, compositions of the present invention comprise at least about 98% by weight, at least about 99% by weight, at least 99.5% by weight, at least 99.6% by weight, at least 99.7% by weight, at least 99.8% by weight, or about 99.9% by weight of HFO-1234ze(Z) and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb and mixtures thereof.

[0296] In one embodiment, compositions of the present invention comprise at least about 98% by weight, at least about 99% by weight, at least 99.5% by weight, at least 99.6% by weight, at least 99.7% by weight, at least 99.8% by weight, or about 99.9% by weight of HFO-1234ze(E) and HFO-1234ze(Z); one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-

114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

[0297] In some embodiments, the sum total of the amounts of R-143a, R-152a, trifluoropropyne, R-1233xf, R-1233zd(E), and R-1233zd(Z) in compositions comprising a mixture of HFO-1234ze(E) and HFO-1234ze(Z) is between 0.00001 mole percent and 2 mole percent, based on the total fluoropropene composition. In one embodiment, the fluoropropene composition includes R-1233zd(E) in an amount of 0.7 mole percent to 1.15 mole percent, based on the total heat transfer media. In one embodiment, the fluoropropene composition includes R-1233zd(Z) in an amount of 0.05 mole percent to 0.25 mole percent, based on the total heat transfer media. In one embodiment, the fluoropropene composition includes R-143a in an amount of 0.05 mole percent to 0.25 mole percent, based on the total fluoropropene composition.

[0298] In other embodiments, compositions according to the present invention comprise HFO-1234ze(E) and HFO-1234ze(Z), and optionally further comprise one or more of 1224yd, 1224zc, 1326mxz, 113, 32, 23, trifluoropropyne, 356mff, 1326mxz, HFC-245fa and HFC-245cb in a total amount ranging from about 0.001 to about 1 mole%, about 0.001 to about 0.9 and, in some cases, about 0.001 to about 0.7 mole%. In one particular embodiment, the sum total of the amounts 1224yd, 1224zc, 1326mxz, 113, 32, 23, trifluoropropyne, 356mff, 1326mxz, HFC-245fa and HFC-245cb is between 0.001 mole percent and 2 mole percent, about 0.001 to about 0.1 mole%, about 0.001 to about 0.09 and, in some cases, or about 0.001 to about 0.07 mole%, based on the total fluoropropene composition.

[0299] In one embodiment, for any of the foregoing compositions, the total amount of additional compound(s) in the composition ranges from greater than 0 wt.% to less than or equal to about 2 wt.%, about 1 wt.%, about 0.9 wt.%, about 0.8 wt.%, about 0.7 wt.%, about 0.6 wt.%, about 0.5 wt.%, about 0.4 wt.%, about 0.3 wt.%, about 0.2 wt.%, about 0.1 wt.%, based on the total weight of the composition. In another embodiment, the total amount of additional compound(s) ranges from 0.01 ppm (weight) to about 1 wt.%, and all values therebetween up to 1 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.1 ppm (weight) to about 1 wt.%. In another embodiment, the total amount of additional

compound(s) ranges from 0.001 wt.% to about 1 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to about 0.5 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to 0.4 wt.% or less, based on the total weight of the composition. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to 0.1 wt.% or less, based on the total weight of the composition. In one embodiment, the total amount of additional compound(s) is about 0.1 wt.% based on the total weight of the composition.

[0300] In one embodiment, the compositions comprise at least about 99% by weight, in some cases at least about 99.5% by weight, of HFO-1234ze(Z) and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb and mixtures thereof, wherein the total amount of the additional compound(s) is about 1% by weight or less, or about 0.5% by weight or less, or about 0.4% by weight or less, or about 0.3% by weight or less, or about 0.2% by weight or less, or about 0.1% by weight or less, based on the total weight of the composition. In one embodiment, the amount of the additional compound HFO-1234ze(E) can range from about 1 ppm to about 500 ppm by weight, about 100 to about 375 ppm, and preferably about 150 ppm to about 250 ppm.

[0301] In one embodiment, the compositions comprise at least about 99% by weight, in some cases at least about 99.5% by weight, of HFO-1234ze(E) and HFO-1234ze(Z); one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropylene, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; and mixtures thereof, wherein the total amount of the additional compound(s) is about 1% by weight or less, or about 0.5% by weight or less, or about 0.4% by weight or less, or about 0.3% by weight or less, or about

0.2% by weight or less, or about 0.1% by weight or less, based on the total weight of the composition.

[0302] In one embodiment, for any of the compositions disclosed herein, the amount of the additional compound HCFO-1233zd (E isomer) can range from about 1 ppm to about 3,750 ppm by weight, about 750 ppm to about 2,800 ppm, and preferably about 1,125 ppm to about 1,875 ppm.

[0303] In one embodiment, for any of the compositions disclosed herein, the amount of the additional compound HFC-245fa can range from about 1 ppm to about 2,500 ppm by weight, about 500 ppm to about 1,875 ppm, and preferably about 750 to about 1,250 ppm.

[0304] In one embodiment, for any of the compositions disclosed herein, the amount of the additional compound HCFO-1233xf can range from about 1 ppm to about 1,250 ppm by weight, about 250 to about 950 ppm, and preferably about 375 to about 625 ppm.

[0305] In one embodiment, for any of the compositions disclosed herein, the amount of the additional compound HCFC-124a can range from about 1 ppm to about 500 ppm by weight, about 100 to about 375 ppm, and preferably about 150 to about 250 ppm.

[0306] In one embodiment, for any of the compositions disclosed herein, the amount of the additional compound HCFO-1233zd (Z isomer) can range from about 1 to about 500 ppm by weight, about 100 to about 375 ppm, and preferably about 150 to about 250 ppm.

[0307] In one embodiment, for any of the foregoing compositions, the amount of the additional compound HCFC-124 can range from about 1 ppm to about 250 ppm by weight, about 50 to about 200 ppm, and preferably about 75 to about 125 ppm.

[0308] In one embodiment, for any of the compositions disclosed herein, the amount of the additional compound CFC-114a can range from about 1 ppm to about 250 ppm by weight, about 50 to about 200 ppm, and preferably about 75 to about 125 ppm.

[0309] In one embodiment, for any of the compositions disclosed herein, the amount of the additional compound HFC-263fb can range from about 0.5 to about 100 ppm by weight, about 3 to about 50 ppm, and preferably about 4 to about 8 ppm.

[0310] In one embodiment, for any of the compositions disclosed herein, the amount of the additional compound HFO-1234zc can range from about 0.5 ppm to about 160 ppm by weight, about 30 ppm to about 120 ppm, and preferably about 45 ppm to about 80 ppm.

[0311] In one embodiment, for any of the compositions disclosed herein, the amount of the additional compound HCC-40 can range from about 1 ppm to about 50 ppm by weight, about 1 ppm to about 4 ppm, and preferably about 1.5 to about 2.5 ppm.

[0312] In one embodiment, for any of the compositions disclosed herein, the amount of CFC-114 can range from about 1 ppm to about 125 ppm by weight, about 25 to about 100 ppm, and preferably about 35 to about 65 ppm.

[0313] In one embodiment, for any of the compositions disclosed herein, the amount of the additional compound HCFC-1131 (E isomer) can range from about 1 ppm to about 50 ppm by weight, about 1 ppm to about 4 ppm, and preferably about 1.5 to about 2.5 ppm.

[0314] In one embodiment, for any of the compositions disclosed herein, the total amount of one or more additional compounds selected from HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb can range from about 10 ppm to about 500 ppm, about 20 ppm to about 90 ppm, and preferably about 50 ppm to about 85 ppm.

[0315] In one embodiment, for any of the compositions disclosed herein, the total amount of one or more additional compounds selected from HFO-1234yf and HFC-245cb is preferably about 3000 ppm or less.

[0316] It will be readily understood by those skilled in the art that the additional compounds present in the compositions and respective amounts of each additional compound which is present will depend upon the method of manufacture and/or parameters thereof.

[0317] In one embodiment, the Z-HFO-1234ze produced from any of the processes disclosed herein is of a high purity and is free of or substantially free of chlorinated compounds, making it suitable for etching gas applications. By “high purity” is meant a purity greater than 99.5 wt.%, or greater than 99.6 wt.%, or greater than 99.7 wt.%, or greater than 99.8 wt.%, preferably 99.9 wt.% or greater. By “substantially free of” with respect to chlorinated compounds is meant that the amount of chlorinated compounds present in the composition is less than about 100 ppm, preferably less than about 50 ppm, more preferably less than about 10 ppm, and most preferably less than about 1 ppm.

[0318] For the sake of example only, one embodiment of the compositions according to the present invention comprises “neat” HFO-1234ze(Z) and a plurality of additional compounds in the amounts shown in Table 8 totaling less than about 0.4 % by weight. It will be understood that the total amount of the additional compounds may be less than about 0.5 % by weight, less than about 0.4 % by weight, less than about 0.3 % by weight, less than about 0.2 % by weight or less than about 0.1 % by weight.

Table 8
Exemplary Composition of One Embodiment

Column	ppm
1234ze-E	200.00
263fb	6.36
1234zc	63.65
245fa	1000.00
1233zd-E	1500.00
1234ze-Z	996000.00
1233zd-Z	200.00
1233xf	500.00
124	100.00
40	2.00
114	50.00
1131-E	2.00
114a	100.00
124a	200.00
Others*	75.98

**“Others” represents a combined total amount of HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.*

[0319] In one embodiment, the Z-HFO-1234ze produced from any of the processes disclosed herein is particularly suitable for use as a blowing agent.

Blend Compositions

[0320] In another embodiment, compositions of the present invention comprise HFO-1234ze(Z) and at least one compound selected from HFO-1234yf, HFO-1234ze(E), HFO-1132(E), HFO-1132(Z), HFO-1252zc, HFC-1225ye(E), HFC-1225ye(Z), HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1336yf, HFO-1336ze(E), HFO-1336ze(Z), HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1224yd(Z), HCFO-1224yd(E), CFO-1112(E), CFO-1112(Z), HFC-245fa, HFC-236fa, HFC-227ea, trans-1,2-dichloroethylene, HFO-1132(E), HFO-1132(Z), HFC-152a, HFC-134a, HFC-134, HFC-32, HFC-125, 1243zf, 1243yc, carbon dioxide, isobutene, propane, butane, isobutane, pentane and isopentane.

[0321] In another embodiment, compositions of the present invention comprise HFO-1234ze(Z) and at least one compound selected from HFO-1234yf, HFO-1234ze(E), HFO-1132(E), HFO-1132(Z), HFO-1252zc, HFC-1225ye(E), HFC-1225ye(Z), HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1336yf, HFO-1336ze(E), HFO-1336ze(Z), HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1224yd(Z), HCFO-1224yd(E), CFO-1112(E), CFO-1112(Z), HFC-245fa, HFC-236fa, HFC-227ea, trans-1,2-dichloroethylene, HFO-1132(E), HFO-1132(Z), HFC-152a, HFC-134a, HFC-134, HFC-32, HFC-125, carbon dioxide, isobutene, propane, butane, isobutane, pentane and isopentane, and further comprise one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

[0322] In another embodiment, blend compositions of the present invention comprise HFO-1234ze(Z) and at least one compound selected from HFO-1234ze(E), HFO-1233zd(E), HFC-245fa, HFO-1336mzz(E), HFO-1336mzz(Z), HFC-227ea, HFC-134a and HFC-134.

[0323] In another embodiment, blend compositions of the present invention comprise HFO-1234ze(Z) and at least one compound selected from HFO-1234ze(E), HFO-1233zd(E), HFC-245fa, HFO-1336mzz(E), HFO-1336mzz(Z), HFC-227ea, HFC-134a and HFC-134, and further comprise one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-

1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

[0324] In one embodiment, compositions of the present invention comprise HFO-1234ze(Z) and at least one compound selected from HFO-1234ze(E), HFC-245fa and HFO-1233zd(E), and mixtures thereof.

[0325] For any of the compositions disclosed herein, the HFO-1234ze(Z) is preferably produced by one of the integrated processes disclosed herein.

[0326] In another embodiment, blend compositions of the present invention comprise HFO-1234ze(Z) and HFO-1234ze(E), the mixture preferably being produced directly from any of the integrated processes (i.e., Integrated Process A, B or C) disclosed herein. In one embodiment, after purification and/or separation, no blending or mixing steps are required to achieve the desired blend composition (i.e., the E:Z ratio in the mixture after purification/separation meets the desired blend composition). In another embodiment, after purification and/or separation, the E:Z ratio may be adjusted by blending with additional amounts of Z-HFO-1234ze and/or E-HFO-1234ze. See Figs. 11-12.

[0327] As noted above, such compositions produced by Integrated Process A, B or C comprise HFO-1234ze(E) and HFO-1234ze(Z); one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; and mixtures thereof.

[0328] In some embodiments, compositions of the present invention comprise HFO-1234ze(E) in an amount of about 0.0001 wt% to about 99.99 wt% and HFO-1234ze(Z) in an amount of about 0.0001 wt% to about 99.99 wt%, or HFO-1234ze(E) in an amount of about 0.001 wt% to about 99.99 wt% and HFO-1234ze(Z) in an

amount of about 0.001 wt% to about 99.99 wt%, or HFO-1234ze(E) in an amount of about 0.01 wt% to about 99.99 wt% and HFO-1234ze(Z) in an amount of about 0.01 wt% to about 99.99 wt%, or HFO-1234ze(E) in an amount of about 0.1 wt% to about 99.9 wt% and HFO-1234ze(Z) in an amount of about 0.1 wt% to about 99.9 wt%, or HFO-1234ze(E) in an amount of about 0.2 wt% to about 99.8 wt% and HFO-1234ze(Z) in an amount of about 0.2 wt% to about 99.8 wt%, or HFO-1234ze(E) in an amount of about 0.3 wt% to about 99.7 wt% and HFO-1234ze(Z) in an amount of about 0.3 wt% to about 99.7 wt%, or HFO-1234ze(E) in an amount of about 0.4 wt% to about 99.6 wt% and HFO-1234ze(Z) in an amount of about 0.4 wt% to about 99.6 wt%, or HFO-1234ze(E) in an amount of about 0.5 wt% to about 99.5 wt% and HFO-1234ze(Z) in an amount of about 0.5 wt% to about 99.5 wt%, or HFO-1234ze(E) in an amount of about 1 wt% to about 99 wt% and HFO-1234ze(Z) in an amount of about 1 wt% to about 99 wt%, or HFO-1234ze(E) in an amount of about 2 wt% to about 98 wt% and HFO-1234ze(Z) in an amount of about 2 wt% to about 98 wt%, or HFO-1234ze(E) in an amount of about 4 wt% to about 96 wt% and HFO-1234ze(Z) in an amount of about 4 wt% to about 96 wt%, or HFO-1234ze(E) in an amount of about 5 wt% to about 95 wt% and HFO-1234ze(Z) in an amount of about 5 wt% to about 95 wt%, or HFO-1234ze(E) in an amount of about 10 wt% to about 90 wt% and HFO-1234ze(Z) in an amount of about 10 wt% to about 90 wt%, or HFO-1234ze(E) in an amount of about 20 wt% to about 80 wt% and HFO-1234ze(Z) in an amount of about 20 wt% to about 80 wt%, or HFO-1234ze(E) in an amount of about 30 wt% to about 70 wt% and HFO-1234ze(Z) in an amount of about 30 wt% to about 70 wt%, or HFO-1234ze(E) in an amount of about 40 wt% to about 60 wt% and HFO-1234ze(Z) in an amount of about 40 wt% to about 60 wt%, or in one particular embodiment HFO-1234ze(Z) in an amount of about 84 wt% and HFO-1234ze(E) in an amount of about 16 wt%, based on the total composition, with up to about 0.5 wt% containing one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, and one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, HFO-1234ze(Z),

CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E).

[0329] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) and at least one compound selected from HFO-1336mzz(E), HFO-1336mzz(Z), HCFO-1224yd(Z) and HFO-1233zd(E).

[0330] In some embodiments, a composition of the present invention comprises HFO-1234ze(Z) and HFO-1336mzz(E).

[0331] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) and HFO-1336mzz(E), and further comprise one or more additional compounds selected from HCFO-1233xf, HFO-1336ft, HCFC-133a, CO-1140, HCFO-1233zd(E), HFC-245fa, HFO-1327mz, HFC-347mef, HFO-1243zf, and further comprise one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0332] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) in an amount of about 0.5 wt% to about 99.5 wt% and HFO-1336mzz(E) in an amount of about 0.5 wt% to about 99.5 wt%, based on the total composition, with up to about 2 wt%, or up to about 1.5 wt%, or up to about 1 wt%, or up to about 0.5 wt% containing one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, and one or more additional compounds selected from HCFO-1233xf, HFO-1336ft, HCFC-133a, CO-1140, HCFO-1233zd(E), HFC-245fa, HFO-1327mz, HFC-347mef, HFO-1243zf.

[0333] In one embodiment, compositions of the present invention comprising HFO-1234ze(Z) and HFO-1336mzz(E) are suitable for use as blowing agents or as heat transfer fluids in a heat pump, preferably a high temperature heat pump.

[0334] In one embodiment, compositions for heat pumps, preferably high temperature heat pumps, comprise HFO-1234ze(Z) in an amount of about 29 wt% to

about 66 wt%, and HFO-1336mzz(E) in an amount of about 34 wt% to about 71 wt%, based on the total composition, with up to about 0.5 wt%, or up to about 0.4 wt%, or up to about 0.3 wt%, or up to about 0.2 or 0.1 wt% containing one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, and one or more additional compounds selected from HCFO-1233xf, HFO-1336ft, HCFC-133a, CO-1140, HCFO-1233zd(E), HFC-245fa, HFO-1327mz, HFC-347mef, HFO-1243zf.

[0335] In one embodiment, blowing agent compositions comprise HFO-1234ze(Z) in an amount of about 10 wt% to about 90 wt%, and HFO-1336mzz(E) in an amount of about 10 wt% to about 90 wt%, or HFO-1234ze(Z) in an amount of about 30 wt% to about 70 wt%, and HFO-1336mzz(E) in an amount of about 30 wt% to about 30 wt%, based on the total composition, with up to about 2 wt%, or up to about 1.5 wt%, or up to about 1 wt%, or up to about 0.5 wt% containing one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, and one or more additional compounds selected from HCFO-1233xf, HFO-1336ft, HCFC-133a, CO-1140, HCFO-1233zd(E), HFC-245fa, HFO-1327mz, HFC-347mef, HFO-1243zf.

[0336] In some embodiments, a composition of the present invention comprises HFO-1234ze(Z) and HFO-1336mzz(Z).

[0337] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) and HFO-1336mzz(Z), and further comprise one or more additional compounds selected from HFO-1336mzz(E), HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb, and further comprise one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0338] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) in an amount of about 0.5 wt% to about 99.5 wt% and HFO-1336mzz(Z) in an amount of about 0.5 wt% to about 99.5 wt%, based on the total composition, with up to about 2 wt%, or up to about 1.5 wt%, or up to about 1 wt%, or up to about 0.5 wt% containing one or more additional compounds selected from HFO-1336mzz(E), HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb, and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0339] In one embodiment, compositions of the present invention comprising HFO-1234ze(Z) and HFO-1336mzz(Z) are suitable for use as blowing agents or as heat transfer fluids in a heat pump, preferably a high temperature heat pump.

[0340] In some embodiments, compositions for heat pumps, preferably high temperature heat pumps, comprise HFO-1234ze(Z) in an amount of about 72 wt% to about 99.5 wt%, and HFO-1336mzz(Z) in an amount of about 0.5 wt% to about 28 wt%, based on the total composition, or HFO-1234ze(Z) in an amount of about 75 wt%, and HFO-1336mzz(Z) in an amount of about 25 wt%, based on the total composition, with up to about 0.5 wt%, or up to about 0.4 wt%, or up to about 0.3 wt%, or up to about 0.2 or 0.1 wt% containing one or more additional compounds selected from HFO-1336mzz(E), HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb, and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0341] In one embodiment, blowing agent compositions of the present invention comprise HFO-1234ze(Z) in an amount of about 10 wt% to about 90 wt%, and HFO-1336mzz(E) in an amount of about 10 wt% to about 90 wt%, or HFO-1234ze(Z) in an amount of about 30 wt% to about 70 wt%, and HFO-1336mzz(E) in an amount of about 30 wt% to about 30 wt%, based on the total composition, with up to about 2

wt%, or up to about 1.5 wt%, or up to about 1 wt%, or up to about 0.5 wt% containing one or more additional compounds selected from HFO-1336mzz(E), HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb, and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0342] In some embodiments, a composition of the present invention comprises HFO-1234ze(Z), HFO-1336mzz(Z) and HFO-1336mzz(E).

[0343] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z), HFO-1336mzz(Z) and HFO-1336mzz(E), and further comprise one or more additional compounds selected from HCFO-1233xf, HFO-1336ft, HCFC-133a, CO-1140, HCFO-1233zd(E), HFC-245fa, HFO-1327mz, HFC-347mef, HFO-1243zf, and further comprise one or more additional compounds selected from HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb, and further comprise one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0344] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) in an amount of about 0.5 wt% to about 99.5 wt%, HFO-1336mzz(Z) in an amount of about 0.5 wt% to about 99.5 wt%, and HFO-1336mzz(E) in an amount of about 0.5 wt% to about 99.5 wt%, based on the total composition, with up to about 2 wt%, or up to about 1.5 wt%, or up to about 1 wt%, or up to about 0.5 wt% containing one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, and one or more additional compounds selected from HCFO-1233xf, HFO-1336ft, HCFC-133a, CO-1140, HCFO-1233zd(E), HFC-245fa, HFO-1327mz, HFC-347mef, HFO-1243zf, and

one or more additional compounds selected from HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb.

[0345] In one embodiment, compositions of the present invention comprising HFO-1234ze(Z), HFO-1336mzz(Z) and HFO-1336mzz(E) are suitable for use as blowing agents or as heat transfer fluids in a heat pump, preferably a high temperature heat pump.

[0346] In one embodiment, compositions for heat pumps, preferably high temperature heat pumps, comprise HFO-1234ze(Z) in an amount of about 40 wt% to about 90 wt%, HFO-1336mzz(Z) in an amount of about 5 wt% to about 30 wt%, and HFO-1336mzz(E) in an amount of about 5 wt% to about 30 wt%, based on the total composition, with up to about 0.5 wt%, or up to about 0.4 wt%, or up to about 0.3 wt%, or up to about 0.2 or 0.1 wt% containing one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, and one or more additional compounds selected from HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb, and one or more additional compounds selected from HCFO-1233xf, HFO-1336ft, HCFC-133a, CO-1140, HCFO-1233zd(E), HFC-245fa, HFO-1327mz, HFC-347mef, HFO-1243zf.

[0347] In one embodiment, blowing agent compositions comprise HFO-1234ze(Z) in an amount of about 30 wt% to about 80 wt%, HFO-1336mzz(Z) in an amount of about 30 wt% to about 80 wt%, and HFO-1336mzz(E) in an amount of about 30 wt% to about 80 wt%, based on the total composition, with up to about 2 wt%, or up to about 1.5 wt%, or up to about 1 wt%, or up to about 0.5 wt% containing one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, and one or more additional compounds selected from HCFO-1233xf, HFO-1336ft, HCFC-133a, CO-1140, HCFO-1233zd(E), HFC-245fa, HFO-1327mz, HFC-347mef, HFO-1243zf, and one or more additional

compounds selected from HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb.

[0348] In some embodiments, a composition of the present invention comprises HFO-1234ze(Z) and HFO-1233zd(E).

[0349] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) and HFO-1233zd(E), and further comprise one or more additional compounds selected from E-HFO-1234ze and HFC-245fa, and further comprise one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0350] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) in an amount of about 0.5 wt% to about 99.5 wt% and HFO-1233zd(E) in an amount of about 0.5 wt% to about 99.5 wt%, based on the total composition, with up to about 2 wt%, or up to about 1.5 wt%, or up to about 1 wt%, or up to about 0.5 wt% containing one or more additional compounds selected from E-HFO-1234ze and HFC-245fa, and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0351] In one embodiment, compositions of the present invention comprising HFO-1234ze(Z) and HFO-1233zd(E) are suitable for use as blowing agents or as heat transfer fluids in a heat pump, preferably a high temperature heat pump.

[0352] In one embodiment, compositions for heat pumps, preferably high temperature heat pumps, comprise HFO-1234ze(Z) in an amount of about 20 wt% to about 80 wt% and HFO-1233zd(E) in an amount of about 20 wt% to about 80 wt%, based on the total composition, with up to about 0.5 wt%, or up to about 0.4 wt%, or up to about 0.3 wt%, or up to about 0.2 or 0.1 wt% containing one or more additional compounds selected from E-HFO-1234ze and HFC-245fa, and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114,

HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0353] In one embodiment, blowing agent compositions comprise HFO-1234ze(Z) in an amount of about 30 wt% to about 70 wt% and HFO-1233zd(E) in an amount of about 30 wt% to about 70 wt%, based on the total composition, with up to about 2 wt%, or up to about 1.5 wt%, or up to about 1 wt%, or up to about 0.5 wt% containing one or more additional compounds selected from E-HFO-1234ze and HFC-245fa, and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0354] In some embodiments, a composition of the present invention comprises HFO-1234ze(Z) and HFC-245fa.

[0355] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) and HFC-245fa, and further comprise one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb; and further comprise one or more additional compounds selected from (i) HFC-143a, HFC-1225zc, HFC-236fa, HFO-1234ze(E), HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or (ii) HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFC-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

[0356] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) in an amount of about 0.5 wt% to about 99.5 wt% and HFC-245fa in an amount of about 0.0001 wt% to about 99.5 wt%, based on the total composition, with up to about 2 wt%, or up to about 1.5 wt%, or up to about 1 wt%, or up to about 0.5 wt% containing one or more additional compounds selected from HFO-

1234ze(E), HFC-263fb, HFO-1234zc, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb; and further comprise one or more additional compounds selected from (i) HFC-143a, HFC-1225zc, HFC-236fa, HFO-1234ze(E), HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or (ii) HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

[0357] In one embodiment, compositions of the present invention comprising HFO-1234ze(Z) and HFC-245fa are suitable for use as blowing agents or as heat transfer fluids in a heat pump, preferably a high temperature heat pump.

[0358] In one embodiment, compositions for heat pumps, preferably high temperature heat pumps, comprise HFO-1234ze(Z) in an amount of about 70 wt% to about 99 wt% and HFC-245fa in an amount of about 0.0001 wt% to about 30 wt%, based on the total composition, with up to about 0.5 wt%, or up to about 0.4 wt%, or up to about 0.3 wt%, or up to about 0.2 or 0.1 wt% containing one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb; and one or more additional compounds selected from (i) HFC-143a, HFC-1225zc, HFC-236fa, HFO-1234ze(E), HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or (ii) HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

[0359] In one embodiment, blowing agent compositions comprise HFO-1234ze(Z) in an amount of about 70 wt% to about 99 wt% and HFC-245fa in an amount of about 0.0001 wt% to about 30 wt%, based on the total composition, with up to about 2 wt%, or up to about 1.5 wt%, or up to about 1 wt%, or up to about 0.5 wt% containing one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb; and one or more additional compounds selected from (i) HFC-143a, HFC-1225zc, HFC-236fa, HFO-1234ze(E), HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or (ii) HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

[0360] In some embodiments, a blowing agent composition of the present invention comprises HFO-1234ze(Z) and HCFO-1224yd(Z).

[0361] In some embodiments, blowing agent compositions of the present invention comprise HFO-1234ze(Z) and HCFO-1224yd(Z), and further comprise one or more additional compounds selected from HFO-1234yf, HFO-1234ze(E) + HFO-1243zf, HFC-263fb, HFC-254eb, CFC-1215yb, HCFC-244bb, HFO-1224 isomer(s) other than 1224yd(Z), HCFO-1224yd(E), CFC-1112a, HCFC-225ca, HCFC-225cb and HCFC-234bb, and further comprise one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0362] In some embodiments, blowing agent compositions of the present invention comprise HFO-1234ze(Z) in an amount of about 0.5 wt% to about 99.5 wt% and HCFO-1224yd(Z) in an amount of about 0.5 wt% to about 99.5 wt%, based on the total composition, with up to about 2 wt%, or up to about 1.5 wt%, or up to about 1

wt%, or up to about 0.5 wt% containing one or more additional compounds selected from HFO-1234yf, HFO-1234ze(E) + HFO-1243zf, HFC-263fb, HFC-254eb, CFC-1215yb, HCFC-244bb, HFO-1224 isomer(s) other than 1224yd(Z), HCFO-1224yd(E), CFC-1112a, HCFC-225ca, HCFC-225cb and HCFC-234bb, and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

[0363] In some embodiments, compositions of the present invention comprise any one of the following mixtures, the mixtures having been produced directly from one or more of the integrated processes disclosed herein, and the mixtures having a compositional makeup including one or more additional compounds, as discussed in greater detail above: (i) E-HFO-1234ze and Z-HFO-1234ze; (ii) E-HFO-1234ze, Z-HFO-1234ze and HFC-245fa; (iii) E-HFO-1234ze, Z-HFO-1234ze and E-HFO-1233zd; (iv) E-HFO-1234ze, Z-HFO-1234ze, HFC-245fa and E-HFO-1233zd; 1234ze(Z)/1233zd(E); and (v) Z-HFO-1234ze, HFC-245fa and E-HFO-1233zd.

[0364] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) and HFO-1234ze(E), the mixture of which may optionally have been produced directly from any of the integrated processes disclosed herein, and further comprise one or more compounds selected from HFC-134a and HFC-227ea.

[0365] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z), HFO-1234ze(E) and HFC-227ea.

[0366] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z), HFO-1234ze(E) and HFC-227ea, and further comprise one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, and further comprise one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-

263fb, HFO-1243zf and HCFO-1233zd(E), and further comprise one or more additional compounds selected from FC-1216 and HCFC-124.

[0367] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) in an amount of about 1 wt% to about 99 wt%, HFO-1234ze(E) in an amount of about 1 wt% to about 99 wt%, and HFC-227ea in an amount of about 0.1 wt% to about 30 wt%, based on the total composition, with up to about 0.5 wt% containing one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropylene, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and/or one or more additional compounds selected from FC-1216 and HCFC-124.

[0368] In one embodiment, compositions of the present invention comprise HFO-1234ze(Z) in an amount of about 10 wt% to about 80 wt%, HFO-1234ze(E) in an amount of about 10 wt% to about 80 wt%, and HFC-227ea in an amount of about 0.1 wt% to about 30 wt%, based on the total composition, with up to about 0.5 wt% containing one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropylene, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and/or one or more additional compounds selected from FC-1216 and HCFC-124.

[0369] In another embodiment, compositions of the present invention comprise HFO-1234ze(Z) in an amount of about 30 wt% to about 68 wt%, HFO-1234ze(E) in an amount of about 24 wt% to about 70 wt%, and HFC-227ea in an amount of about 0.1 wt% to about 8 wt%, based on the total composition, with up to about 0.5 wt%

containing one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and/or one or more additional compounds selected from FC-1216 and HCFC-124.

[0370] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z), HFO-1234ze(E) and HFC-134a.

[0371] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z), HFO-1234ze(E), and HFC-134a, and further comprise (i) one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, (ii) one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E), and/or (iii) one or more additional compounds selected from HFC-134, HCFC-124, HCFO-1122, HFC-143a, HCFC-31, HFC-32, HFC-125, CFC-114 and CFC-114a.

[0372] In some embodiments, compositions of the present invention comprise HFO-1234ze(Z) in an amount of about 0.1 wt% to about 40 wt%, HFO-1234ze(E) in an amount of about 0.1 wt% to about 80 wt%, and HFC-134a in an amount of about 0.1 wt% to about 50 wt%, based on the total composition, with up to about 0.5 wt% containing one or more of the above-listed additional compounds.

[0373] The total amount of additional compounds in any of the blend compositions disclosed herein ranges from greater than 0 wt.% to less than or equal to about 2 wt.%, about 1 wt.%, about 0.9 wt.%, about 0.8 wt.%, about 0.7 wt.%, about 0.6 wt.%, about 0.5 wt.%, about 0.4 wt.%, about 0.3 wt.%, about 0.2 wt.%, about 0.1 wt.%,

based on the total weight of the composition. In another embodiment, the total amount of additional compound(s) ranges from 0.01 ppm (weight) to about 1 wt.%, and all values therebetween up to 1 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.1 ppm (weight) to about 1 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to about 1 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to about 0.5 wt.%. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to 0.4 wt.% or less, based on the total weight of the composition. In another embodiment, the total amount of additional compound(s) ranges from 0.001 wt.% to 0.1 wt.% or less, based on the total weight of the composition. In one embodiment, the total amount of additional compound(s) is about 0.1 wt.% based on the total weight of the composition.

[0374] Some of the compounds making up the blend compositions of the present invention are defined in Table 9.

Table 9

Name	Structure	Chemical name
HFO-1234ze	E(trans)-CF ₃ CH=CHF	E-1,3,3,3-tetrafluoropropene
HFO-1234yf	CF ₃ CF=CH ₂	2,3,3,3-tetrafluoro-1-propene
HFC-1225ye	CHF ₂ CF=CHF	1,2,3,3-tetrafluoro-1-propene
HFO-1336mzz	E- and/or Z-CF ₃ CH=CF ₃ CH	1,1,1,4,4,4-hexafluoro-2-butene
HFO-1336yf	CF ₃ CF ₂ CF=CH ₂	2,3,3,4,4,4-hexafluoro-1-butene
HFC-1336ze	CHF=CHCF ₂ CF ₃	1,3,3,4,4,4-hexafluoro-1-butene
HCFO-1233zd	E- and/or Z-CF ₃ CH=CHCl	1-chloro-3,3,3-trifluoropropene
HCFO-1224yd	E- and/or Z-CF ₃ CF=CHCl	1-chloro 2,3,3,3-tetrafluoropropene
HFO-1132	E- and/or Z-CHF=CHF	1,2-Difluoroethylene
CFO-1112	E- and/or Z-CClF=CClF	1,2-dichloro-1,2-difluoroethylene
HFC-245fa	CF ₃ CH ₂ CHF ₂	1,1,1,3,3-pentafluoropropane
HFC-236a	CF ₃ CH ₂ CF ₃	1,1,1,2,3,3-Hexafluoropropane
HFC-227ea	CF ₃ CF ₂ CHF ₂	1,1,1,2,2,3,3,3-heptafluoropropane
Trans-1,2-DCE	ClCH=CHCl	trans-1,2-Dichloroethylene
HFC-152a	CF ₂ HCH ₃	1,1-Difluoroethane
HFC-134a	CF ₂ HCFH ₂	1,1,1,2-tetrafluoroethane
HFC-32	CF ₂ H ₂	Difluoromethane
HFC-125	CF ₃ CF ₂ H	Pentafluoroethane
Isobutene	(CH ₃) ₂ C=CH ₂	2-methylpropene
Propane	CH ₃ CH ₂ CH ₃	-
Butane	CH ₃ CH ₂ CH ₂ CH ₃	-
Isobutane	CH(CH ₃) ₃	-
Pentane	CH ₃ (CH ₂) ₃ CH ₃	-
Isopentane	CH(CH ₃) ₂ (CH ₂ CH ₃)	-
HFO-1327mz	E- and/or Z-C ₄ HF ₇	1,1,1,2,4,4,4-heptafluoro-1-butene
HFO-1326mxz	E- and/or Z-CF ₃ CH=CClCF ₃	2-chloro-1,1,1,4,4,4-hexafluoro-2-butene
HFC-356mff	CF ₃ CH ₂ CH ₂ CF ₃	1,1,1,4,4,4-hexafluorobutane
CHFC-346mdf	CF ₃ CHClCH ₂ CF ₃	2-chloro-1,1,1,4,4,4-hexafluorobutane

Name	Structure	Chemical name
HFC-263fb	$\text{CF}_3\text{CH}_2\text{CH}_3$	1,1,1-trifluoropropane
HCFO-1233xf	$\text{CF}_3\text{CCl}=\text{CH}_2$	1,1,1-trifluoro-2-chloropropene
HFO-1336ft	$\text{CH}_2=\text{C}(\text{CF}_3)_2$	3,3,3-trifluoro-2-(trifluoromethyl)-1-propene
HCFC-133a	$\text{C}_2\text{H}_2\text{F}_3\text{Cl}$	1-chloro-2,2,2-trifluoroethane
HCO-1140	$\text{C}_2\text{H}_3\text{Cl}$	Chloroethylene (vinyl chloride)
HFC-347mef	$\text{CF}_3\text{CHFCH}_2\text{CF}_3$	1,1,1,2,4,4,4-heptafluorobutane
HFO-1243zf	$\text{CF}_3\text{CH}=\text{CH}_2$	3,3,3-trifluoro-1-propene

[0375] Certain of the compounds of Tables 7-9 exist as different configurational isomers or stereoisomers. When the specific isomer is not designated, the present invention is intended to include all single configurational isomers, single stereoisomers, single geometric or any combination thereof. For instance, HCFO-1233zd is meant to represent the *E*-isomer, *Z*-isomer, or any combination or mixture of both isomers in any ratio. As another example, HFO-1224zb is meant to represent the *E*-isomer, *Z*-isomer, or any combination or mixture of both isomers in any ratio.

[0376] In accordance with one embodiment of the present invention, the blend compositions may be azeotropic or azeotropic-like. In some embodiments, the blend compositions achieve a glide of less than about 10K, or less than about 5K, or less than about 1K.

[0377] In some embodiments, the HFO-1234ze(*Z*) compositions, HFO-1234ze(*E*)/HFO-1234ze(*Z*) compositions, and blends comprising HFO-1234ze(*E*) and/or HFO-1234ze(*Z*) (collectively referred to herein as the “HFO-1234ze composition” or “HFO-1234ze compositions”) have a flammability classification of 1, 2L or 2 as determined by ASHRAE Standard 34 and ASTM E681-09. Preferably, the HFO-1234ze compositions have a flammability rating of 1 or 2L, as determined by ASHRAE Standard 34 and ASTM E681-09.

[0378] In some embodiments, the HFO-1234ze compositions have a GWP of less than 700, preferably less than 300, more preferably less than 150, or less than 75, or less than 10 GWP, and all values and ranges therebetween. Since HFO-1234ze(*Z*) has a GWP of less than 1, it is possible that some compositions according to the present invention have a GWP of less than 1.

[0379] In some embodiments, the HFO-1234ze compositions according to the present invention and the degradation products thereof are preferably free of or substantially free of Group A Fluorinated Substances.

[0380] 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).

[0381] 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.

[0382] Thus, according to some embodiments, compositions of the present invention comprise HFO-1234ze(Z) and/or HFO-1234ze(E), as a single fluid or blend, 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 ≤ 15 wt.%, or > 0 wt.% and ≤ 10 wt.%, or > 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.

[0383] Further, in some embodiments, degradation products of such HFO-1234ze compositions of the present invention 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.

[0384] In some embodiments, compositions of the present invention comprise, consist of or consist essentially of HFO-1234ze(Z) and further comprise one or more

additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, and are free of or substantially free of Group A Fluorinated Substances. Further, in some embodiments, degradation products of these compositions are free of or substantially free of Group A Fluorinated Substances.

[0385] According to some embodiments, compositions of the present invention comprise HFO-1234ze(Z); one or more compounds selected from HFO-1234ze(E), HFO-1233zd(E), HFC-245fa, HFO-1336mzz(E), HFO-1336mzz(Z), HFC-227ea, HFC-134a and HFC-134; and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, and are free of or substantially free of Group A Fluorinated Substances. Further, degradation products of some of these compositions are free of or substantially free of Group A Fluorinated Substances.

[0386] In some embodiments, any of the neat or blend compositions disclosed herein are free of or substantially free of Group A Fluorinated Substances, such as TFA. Further, degradation products of these compositions are free of or substantially free of Group A Fluorinated Substances, such as TFA. Examples of such compositions, which are discussed in greater detail herein including disclosure of the full compositional makeup thereof, are as follows:

- HFO-1234ze(Z);
- HFO-1234ze(Z)/HFO-1234ze(E);
- HFO-1234ze(Z)/HFO-1336mzz(E);
- HFO-1234ze(Z)/HFO-1336mzz(Z);
- HFO-1234ze(Z)/HFO-1233zd(E);
- E-HFO-1234ze/Z-HFO-1234ze/HFC-245fa;
- E-HFO-1234ze/Z-HFO-1234ze/E-HFO-1233zd;
- E-HFO-1234ze/Z-HFO-1234ze/HFC-245fa/E-HFO-1233zd;

- Z-HFO-1234ze/HFC-245fa/E-HFO-1233zd;
- HFO-1234ze(Z)/HFO-1234ze(E)/HFC-134a; and
- HFO-1234ze(Z)/HFO-1234ze(E)/HFC-227ea.

[0387] 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, mix, or blend the components in an appropriate vessel. Agitation may be used, if desired.

[0388] In another embodiment, the compositions disclosed herein may be prepared by a method comprising (i) reclaiming a volume of one or more components of the refrigerant compositions disclosed herein from at least one refrigerant container, (ii) removing impurities sufficiently to enable reuse of said one or more of the reclaimed components, (iii) and optionally, combining all or part of said reclaimed volume of components with at least one additional refrigerant composition or component in order to produce a composition described in the various embodiments herein.

[0389] In another embodiment, a composition comprising, consisting of or consisting essentially of a mixture of HFO-1234ze(Z) and HFO-1234ze(E) may be formed directly from one of the integrated processes (i.e., Integrated Process A, B or C) disclosed herein.

[0390] A refrigerant container may be any container in which is stored a composition according to the present invention that has been used in a refrigeration apparatus, air-conditioning apparatus, or heat pump apparatus. Said container may be the refrigeration apparatus, air-conditioning apparatus, or heat pump apparatus in which the refrigerant composition was used. Additionally, the container may be a storage container for collecting reclaimed refrigerant components, including but not limited to pressurized gas cylinders.

[0391] Residual refrigerant means any amount of refrigerant or refrigerant blend component that may be moved out of the refrigerant container by any method known for transferring refrigerant blends or refrigerant blend components.

[0392] Impurities may be any component that is in the refrigerant or refrigerant blend component due to its use in a refrigeration apparatus, air-conditioning apparatus or heat pump apparatus. Such impurities include but are not limited to refrigeration lubricants, being those described earlier herein, particulates including but not limited to metal, metal salt or elastomer particles, that may have come out of the refrigeration apparatus, air-conditioning apparatus or heat pump apparatus, and any other contaminants that may adversely affect the performance of the refrigerant composition.

[0393] Such impurities may be removed sufficiently to allow reuse of the refrigerant or refrigerant blend component without adversely affecting the performance or equipment within which the refrigerant or refrigerant blend component will be used.

[0394] It may be necessary to provide additional refrigerant or refrigerant blend component to the residual refrigerant or refrigerant blend component in order to produce a composition that meets the specifications required for a given product. For instance, if a refrigerant blend has 3 components in a particular weight percentage range, it may be necessary to add one or more of the components in a given amount in order to restore the composition to within the specification limits.

FURTHER COMPOSITIONS

[0395] In one embodiment, compositions of the present invention may further comprise at least one non-refrigerant component. That is, in one embodiment, the present invention relates to compositions comprising a refrigerant composition, such as any of the compositions comprising HFO-1234ze(Z) disclosed herein, and one or more non-refrigerant components.

[0396] The optional non-refrigerant components (also referred to herein as “additives”) in the compositions disclosed herein may include one or more of the following components: lubricants, dyes (including UV dyes), solubilizing agents, compatibilizers, stabilizers, tracers, perfluoropolyethers, anti-wear agents, extreme pressure agents, corrosion and oxidation inhibitors, polymerization inhibitors, metal surface energy reducers, metal surface deactivators, acid scavengers, foam control agents, viscosity index improvers, pour point depressants, detergents, viscosity

adjusters, performance enhancers, flame suppressants and mixtures thereof. Indeed, many of these optional non-refrigerant components fit into one or more of these categories and may have qualities that lend themselves to achieve one or more performance characteristics.

[0397] The additive component(s) and amounts thereof selected for the disclosed compositions are elected on the basis of utility, individual equipment components, and/or the system requirements.

[0398] Lubricants which may be included in compositions of the present invention comprise those suitable for use with refrigeration or air-conditioning apparatus. Among these lubricants are those conventionally used in compression refrigeration apparatus utilizing chlorofluorocarbon refrigerants. Such lubricants and their properties are discussed in the 1990 ASHRAE Handbook, Refrigeration Systems and Applications, chapter 8, titled "Lubricants in Refrigeration Systems", pages 8.1 through 8.21, herein incorporated by reference. Lubricants of the present invention may comprise those commonly known as "mineral oils" in the field of compression refrigeration lubrication. Mineral oils comprise paraffins (i.e., straight-chain and branched-carbon-chain, saturated hydrocarbons), naphthenes (i.e., cyclic or ring structure saturated hydrocarbons, which may be paraffins) and aromatics (i.e., unsaturated, cyclic hydrocarbons containing one or more rings characterized by alternating double bonds). Lubricants of the present invention further comprise those commonly known as "synthetic oils" in the field of compression refrigeration lubrication. Synthetic oils comprise alkylaryls (i.e., linear and branched alkyl alkylbenzenes), synthetic paraffins and naphthenes, silicones, and polyalphaolefins. Representative conventional lubricants of the present invention are the commercially available BVM 100 N (paraffinic mineral oil sold by BVA Oils), naphthenic mineral oil commercially available under the trademark from Suniso® 3GS and Suniso® 5GS by Crompton Co., naphthenic mineral oil commercially available from Pennzoil under the trademark Sontex® 372LT, naphthenic mineral oil commercially available from Calumet Lubricants under the trademark Calumet® RO-30, linear alkylbenzenes commercially available from Shrieve Chemicals under the trademarks Zerol® 75, Zerol® 150 and Zerol® 500 and branched alkylbenzene, sold by Nippon Oil as HAB 22.

[0399] Lubricants of the present invention further comprise those which have been designed for use with hydrofluorocarbon refrigerants and are miscible with refrigerants of the present invention under compression refrigeration and air-conditioning apparatus' operating conditions. Such lubricants and their properties are discussed in "Synthetic Lubricants and High-Performance Fluids", R. L. Shubkin, editor, Marcel Dekker, 1993. Such lubricants include, but are not limited to, polyol esters (POEs) such as Castrol® 100 (Castrol, United Kingdom), polyalkylene glycols (PAGs) such as RL-488A from Dow (Dow Chemical, Midland, Mich.), and polyvinyl ethers (PVEs) such as PVE-FVC68D.

[0400] In one particular embodiment, the foregoing refrigerant compositions are combined with a PAG lubricant or a POE lubricant for usage in an automotive A/C system having an internal combustion engine or an electric or hybrid electric drive train.

[0401] In the compositions of the present invention including a lubricant, the lubricant may be present in an amount of less than 80 weight percent of the total composition. The lubricant may further be present in an amount of less than 60 weight percent of the total composition. In other embodiments, the amount of lubricant may be between about 0.1 and 50 weight percent of the total composition. The lubricant may also be between about 0.1 and 20 weight percent of the total composition. The lubricant may also be between about 0.1 and 5 weight percent of the total composition.

[0402] In one aspect of the invention, the inventive refrigerant composition is used to introduce lubricant into the A/C system as well as or alternatively other additives, such as a) acid scavengers, b) performance enhancers, and c) flame suppressants. In one preferred embodiment, the present compositions comprise an acid scavenger.

[0403] Examples of the acid scavengers that may be included in the present compositions include, but are not limited, the stabilizers and/or the epoxide component of the stabilizers disclosed in U.S. Patent No. 8,535,555 and the acid scavengers disclosed in International Application Publication No. WO 2020/222864, the disclosure of each of which is incorporated herein by reference in its entirety.

[0404] In some embodiments, an acid scavenger may comprise one or more epoxides, one or more amines and/or one or more hindered amines, such as, for example but not limited to, epoxybutane.

[0405] In some embodiments, an acid scavenger may comprise a siloxane, an activated aromatic compound, or a combination of both. Serrano et al (paragraph 38 of US 2011/0272624 A1), which is hereby incorporated by reference, discloses that the siloxane may be any molecule having a siloxyfunctionality. The siloxane may include an alkyl siloxane, an aryl siloxane, or a siloxane containing mixtures of aryl and alkyl substituents. For example, the siloxane may be an alkyl siloxane, including a dialkylsiloxane or a polydialkylsiloxane. Preferred siloxanes include an oxygen atom bonded to two silicon atoms, i.e., a group having the structure: SiOSi. For example, the siloxane may be a siloxane of Formula IV:

$R_1[Si(R_2R_3)_4O]_nSi(R_2R_3)R_4$, where n is 1 or more. Siloxanes of Formula IV have n that is preferably 2 or more, more preferably 3 or more, (e.g., about 4 or more).

Siloxanes of formula IV have n that is preferably about 30 or less, more preferably about 12 or less, and most preferably about 7 or less. Preferably the R₄ group is an aryl group or an alkyl group. Preferably the R₂ groups are aryl groups or alkyl groups or mixtures thereof. Preferably the R₃ groups are aryl groups or alkyl groups or mixtures thereof. Preferably the R₄ group is an aryl group or an alkyl group.

Preferably R₁, R₂, R₃, R₄, or any combination thereof are not hydrogen. The R₂ groups in a molecule may be the same or different. Preferably the R₂ groups in a molecule are the same. The R₂ groups in a molecule may be the same or different from the R₃ groups. Preferably, the R₂ groups and R₃ groups in a molecule are the same. Preferred siloxanes include siloxanes of Formula IV, wherein R₁, R₂, R₃, R₄, R₅, or any combination thereof is a methyl, ethyl, propyl, or butyl group, or any combination thereof. Exemplary siloxanes that may be used include hexamethyldisiloxane, polydimethylsiloxane, polymethylphenylsiloxane, dodecamethylpentasiloxane, decamethylcyclo-pentasiloxane, decamethyltetrasiloxane, octamethyltrisiloxane, or any combination thereof.

[0406] Incorporated by previous reference from Serrano et al paragraph notes that in one aspect of the invention, the siloxane is an alkylsiloxane containing from about 1 to about 12 carbon atoms, such as hexamethyldisiloxane. The siloxane may also be a polymer such as polydialkylsiloxane, Where the alkyl group is a methyl, ethyl,

propyl, butyl, or any combination thereof. Suitable polydialkylsiloxanes have a molecular weight from about 100 to about 10,000. Highly preferred siloxanes include hexamethyldisiloxane, polydimethylsiloxane, and combinations thereof. The siloxane may consist essentially of polydimethylsiloxane, hexamethyldisiloxane, or a combination thereof.

[0407] The activated aromatic compound may be any aromatic molecule activated towards a Friedel-Crafts addition reaction, or mixtures thereof. An aromatic molecule activated towards a Friedel-Crafts addition reaction is defined to be any aromatic molecule capable of an addition reaction with mineral acids. Especially aromatic molecules capable of addition reactions with mineral acids either in the application environment (AC system) or during the ASHRAE 97: 2007 "Sealed Glass Tube Method to Test the Chemical Stability of Materials for Use within Refrigerant Systems" thermal stability test. Such molecules or compounds are typically activated by substitution of a hydrogen atoms of the aromatic ring with one of the following groups: NH₂, NHR, NR₂, ADH, AD, NHCOCH₃, NHCOR, 4OCH₃, OR, CH₃, 4C₂H₅, R, or C₆H₅, where R is a hydrocarbon (preferably a hydrocarbon containing from about 1 to about 100 carbon atoms). The activated aromatic molecule may be an alcohol, or an ether, where the oxygen atom (i.e., the oxygen atom of the alcohol or ether group) is bonded directly to an aromatic group. The activated aromatic molecule may be an amine Where the nitrogen atom (i.e., the nitrogen atom of the amine group) is bonded directly to an aromatic group. By way of example, the activated aromatic molecule may have the formula ArXR_n, Where X is O (i.e., oxygen) or N (i.e., nitrogen); n:1 When X:O; n:2 When x:N; Ar is an aromatic group (i.e., group, C₆H₅); R may be H or a carbon containing group; and When n:2, the R groups may be the same or different. For example, R may be H (i.e., hydrogen), Ar, an alkyl group, or any combination thereof, Exemplary activated aromatic molecules that may be employed in a refrigerant composition according to the teachings herein include diphenyl oxide (i.e., diphenyl ether), methyl phenyl ether (e.g., anisole), ethyl phenyl ether, butyl phenyl ether or any combination thereof. One highly preferred aromatic molecule activated to Wards a Friedel-Crafts addition reaction is diphenyl oxide.

[0408] Incorporated by previous reference from Serrano et al. The acid scavenger (e.g., the activated aromatic compound, the siloxane, or both) may be present in any

concentration that results in a relatively low total acid number, a relatively low total halides concentration, a relatively low total organic acid concentration, or any combination thereof.

[0409] Preferably the acid scavenger is present at a concentration greater than about 0.0050 wt%, more preferably greater than about 0.05 wt% and even more preferably greater than about 0.1 wt% (e.g. greater than about 0.5 wt%) based on the total weight of the refrigerant composition. The acid scavenger preferably is present in a concentration less than about 5 wt%, less than about 4 wt%, less than about 3 wt%, more preferably less than about 2.5 wt% and most preferably greater than about 2 wt% (e. g., less than about 1.8 wt%) based on the total weight of the refrigerant composition.

[0410] Additional examples of acid scavengers which may be included in the refrigerant composition and preferably are excluded from the refrigerant composition include those described by Kaneko (U.S. patent application Ser. No. 11/575,256, published as U.S. Patent Publication 2007/0290164, paragraph 42, expressly incorporated herein by reference), such as one or more of: phenyl glycidyl ethers, alkyl glycidyl ethers, alkylene glycol glycidylethers, cyclohexeneoxides, oxetanes, or epoxy compounds such as epoxidized soybean oil, and those described by Singh et al. (U.S. patent application Ser. No. 11/250,219, published as 20060116310, paragraphs 34-42, expressly incorporated herein by reference).

[0411] Preferred additives include those described in U.S. Pat. Nos. 5,152,926; 4,755,316, which are hereby incorporated by reference. In particular, the preferred extreme pressure additives include mixtures of (A) tolyltriazole or substituted derivatives thereof, (B) an amine (e.g. Jeffamine M-600) and (C) a third component which is (i) an ethoxylated phosphate ester (e.g. Antara LP-700 type), or (ii) a phosphate alcohol (e.g. ZELEC 3337 type), or (iii) a Zinc dialkyldithiophosphate (e.g. Lubrizol 5139, 5604, 5178, or 5186 type), or (iv) a mercaptobenzothiazole, or (v) a 2,5-dimercapto-1,3,4-triazole derivative (e. g. Curvan 826) or a mixture thereof. Additional examples of additives which may be used are given in U.S. Pat. No. 5,976,399 (Schnur, 5:12-6:51, hereby incorporated by reference).

[0412] Acid number is measured according to ASTM D664-01 in units of mg KOH/g. The total halides concentration, the fluorine ion concentration, and the total

organic acid concentration is measured by ion chromatography. Chemical stability of the refrigerant system is measured according to ASHRAE 97: 2007 (RA 2017) "Sealed Glass Tube Method to Test the Chemical Stability of Materials for Use within Refrigerant Systems". The viscosity of the lubricant is tested at 40°C according to ASTM D-7042.

[0413] Mouli et al. (WO 2008/027595 and WO 2009/042847) teach the use of alkyl silanes as a stabilizer in refrigerant compositions containing fluoroolefins. Phosphates, phosphites, epoxides, and phenolic additives also have been employed in certain refrigerant compositions. These are described for example by Kaneko (U.S. patent application Ser. No. 11/575,256, published as U.S. Publication 2007/0290164) and Singh et al. (U.S. patent application Ser. No. 11/250,219, published as U.S. Publication 2006/0116310). All of these aforementioned applications are expressly incorporated herein by reference.

[0414] Preferred flame suppressants include the flame retardants described in patent application "Refrigerant compositions containing fluorine substituted olefins CA 2557873 A1" and incorporated by reference, as well as fluorinated products such as HFC-125 and/or Krytox® lubricants, also incorporated by reference and described in patent application "Refrigerant compositions comprising fluoroolefins and uses thereof WO2009018117A1."

[0415] In one embodiment, compositions of the present invention include a composition comprising HFO-1234ze(Z) and at least one acid scavenger. In particular, in some embodiments, any of the HFO-1234ze(Z) compositions disclosed herein may include at least one acid scavenger.

[0416] Additionally, the present compositions may further comprise at least one tracer compound or mixture of tracer compounds. Tracers may be used to identify the process by which a refrigerant, or refrigerant mixture is produced. The tracer compounds may be specific to the manner of production or may be added as a single tracer or mixture of tracers in particular amounts in order to detect dilution, adulteration, contamination, or other unauthorized practices.

[0417] The tracer may be a single compound or two or more tracer compounds from the same class of compounds or from different classes of compounds. In some embodiments, the tracer is present in the compositions at a total concentration of

about 1 part per million by weight (ppm) to about 5000 ppm, based on the weight of the total composition. In other embodiments, the tracer is present at a total concentration of about 1 ppm to about 1000 ppm. In other embodiments, the tracer is present at a total concentration of about 2 ppm to about 500 ppm. Alternatively, the tracer is present at a total concentration of about 10 ppm to about 300 ppm.

[0418] The tracer compound or compounds in amounts up to 100 ppm, 200 ppm, 300, ppm, 400 ppm, 500 ppm, 600 ppm, 700 ppm, 800 ppm and 900 ppm may be selected from hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof. In particular, the tracers may include, but are not limited to compounds selected from HFC-23 (trifluoromethane), HCFC-31 (chlorofluoromethane), HFC-41 (fluoromethane), HFC-161 (fluoroethane), HFC-152a (1,1-difluoromethane), HFC-143a (1,1,1-trifluoroethane), HFC-227ca (1,1,1,2,2,3,3-heptafluoropropane), HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane), HFC-236fa (1,1,1,3,3,3-hexafluoropropane), HFC-236cb (1,1,1,2,2,3,3-hexafluoropropane), HFC-236ea (1,1,1,2,3,3,3-hexafluoropropane), HFC-245cb (1,1,1,2,2-pentafluoropropane), HFC-245fa (1,1,1,3,3-pentafluoropropane), HFC-245eb (1,1,1,2,3-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 (2-trifluoromethyl-1,1,1,3,3,3-hexafluoropropane), 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 (2,2-dichloro-1,1,1,2-tetrafluoroethane), CFC-115 (chloropentafluoroethane), HCFC-22 (chlorodifluoromethane), HCFC-123 (2,2-dichloro-1,1,1-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 (fluoroethylene), HCO-1130 (1,2-dichloroethylene, E- and/or Z-isomer), HCO-1130a (1,1-dichloroethylene), HCFO-1131 (1-chloro-2-

fluoroethylene, E- and/or Z-isomer), HCFO-1131a (1-chloro-1-fluoroethylene), HCFO-1122 (2-chloro-1,1-difluoroethylene), HFO-1123 (trifluoroethylene), HFO-1234ye (1,2,3,3-tetrafluoropropene), HFO-1243zf (3,3,3-trifluoropropene), HFO-1225yeZ (1,2,3,3,3-pentafluoropropene), HFO-1225zc (1,1,3,3,3-pentafluoropropene), PFC-116 (hexafluoroethane), PFC-C216 (hexafluorocyclopropane), PFC-218 (octafluoropropene), PFC-C318 (octafluorocyclobutane), PFC-1216 (hexafluoropropene), PFC-31-10mc (decafluorobutane), PFC-31-10my (2-trifluoromethyl-1,1,1,2,3,3,3-heptafluoropropene), 2-chloro-1,1,2-trifluoroethylene (CFO-1113), 1,1,1,3,3-pentafluorobutane (HFC-365mfc), 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-43-10mee), 1,1,1,2,2,3,4,5,5,6,6,7,7,7-tetradecafluoroheptane, hexafluorobutadiene, 3,3,3-trifluoropropyne, deuterated hydrocarbons, deuterated hydrofluorocarbons, perfluorocarbons, fluoroethers, and mixtures thereof.

[0419] In some embodiments, the tracer is a blend containing two or more hydrofluorocarbons, or one hydrofluorocarbon in combination with one or more perfluorocarbons. In other embodiments, the tracer is a blend of at least one CFC and at least one HCFC, HFC, or PFC. In one embodiment, compositions of the present invention may comprise HFO-1234ze(Z), HFO-1336mzz(Z), HFO-1336mzz(E), HCFO-1224yd(E), HCFO-1224yd(Z), HFO-1327mz(Z), HFO-1327mz(E), one or more hydrofluoroethers, and one or more hydrofluorocarbons.

Utility and Systems

[0420] The compositions comprising HFO-1234ze(Z) or HFO-1234ze(Z) and HFO-1234ze(E), discussed relative to the following utilities, systems and methods, include the single component composition disclosed herein and any of the blend compositions disclosed herein. For the sake of brevity, these compositions are collectively referred to in this discussion as the “HFO-1234ze composition” or “HFO-1234ze compositions”.

[0421] The HFO-1234ze compositions disclosed herein are useful as low global warming potential (GWP) heat transfer compositions, working fluids, aerosol propellants, foaming agents, blowing agents, solvents, cleaning agents, carrier fluids, displacement drying agents, buffing abrasion agents, polymerization media, expansion agents for polyolefins and polyurethane, gaseous dielectrics,

extinguishing agents, and fire suppression agents in liquid or gaseous form. The disclosed compositions can act as a working fluid for heat transfer and refrigeration applications, particularly to carry heat from a heat source to a heat sink. Such heat transfer compositions may also be useful as a refrigerant in a cycle wherein the fluid undergoes a phase change; that is, from a liquid to a gas and back or vice versa.

[0422] In one embodiment, the HFO-1234ze compositions are useful in heat transfer systems. Examples of heat transfer systems include but are not limited to air conditioners, freezers, refrigerators, heat pumps, flooded evaporator heat pumps, direct expansion heat pumps, water chillers, flooded evaporator chillers, direct expansion chillers, walk-in coolers, mobile refrigerators, mobile air conditioning units and combinations thereof.

[0423] In one embodiment, the HFO-1234ze compositions are useful in mobile heat transfer systems, including refrigeration, air conditioning, or heat pump systems or apparatus. In another embodiment, the compositions are useful in stationary heat transfer systems, including refrigeration, air conditioning, chillers, or heat pump systems or apparatus.

[0424] As used herein, mobile refrigeration apparatus, mobile air conditioning or mobile heating apparatus refers to any refrigeration, air conditioner, or heating apparatus incorporated into a transportation unit for the road, rail, sea or air. In addition, mobile refrigeration or air conditioner units, include those apparatus that are independent of any moving carrier and are known as “intermodal” systems. Such intermodal systems include “containers” (combined sea/land transport) as well as “swap bodies” (combined road/rail transport).

[0425] As used herein, stationary heat transfer systems are systems that are fixed in place during operation. A stationary heat transfer system may be associated within or attached to buildings of any variety or may be stand-alone devices located out of doors, such as a soft drink vending machine. These stationary applications may be stationary air conditioning and heat pumps (including but not limited to chillers, high temperature heat pumps, including trans-critical heat pumps with condenser or supercritical heat rejection heat exchanger temperatures above 50°C, 70°C, 80°C, 100°C, 120°C, 140 °C, 160°C, 180°C, or 200°C), residential, commercial or industrial air conditioning systems, and including window, ductless, ducted,

packaged terminal, chillers, and those exterior but connected to the building such as rooftop systems). In stationary refrigeration applications, the disclosed compositions may be useful in high temperature, medium temperature and/or low temperature refrigeration equipment including commercial, industrial or residential refrigerators and freezers, ice machines, self-contained coolers and freezers, flooded evaporator chillers, direct expansion chillers, walk-in and reach-in coolers and freezers, and combination systems. In some embodiments, the disclosed compositions may be used in supermarket refrigerator systems.

[0426] More particularly, high temperature refrigeration systems include those specifically for the supermarket produce section. Medium temperature refrigeration systems includes supermarket and convenience store refrigerated cases, such as cases for beverages, dairy, fresh food, and other refrigerated items. Medium temperature refrigeration systems may also include fresh food transport systems. Low temperature refrigeration systems include supermarket and convenience store freezer cabinets and displays, ice machines, and frozen food transport systems. Other specific uses may be in commercial, industrial, and/or residential refrigerators and freezers, ice machines, self-contained coolers and freezers, supermarket rack and distributed systems, walk-in and reach-in coolers and freezers, and combination systems.

[0427] Therefore, in accordance with the present invention, the HFO-1234ze compositions as disclosed herein may be useful in methods for producing cooling, producing heating, and transferring heat.

[0428] The HFO-1234ze compositions disclosed herein may be useful as low global warming potential (GWP) replacements for currently used refrigerants, including but not limited to HCFO-123zd(E), HFO-1336mzz(E) and HFO-1336mzz(Z), among others.

[0429] In many applications, some embodiments of the HFO-1234ze compositions are useful as refrigerants and provide at least comparable cooling performance (meaning cooling capacity and energy efficiency) as the refrigerant for which a replacement is being sought.

[0430] In another embodiment is provided a method for recharging a heat transfer system that contains a refrigerant to be replaced and a lubricant. The method

comprises removing the refrigerant to be replaced from the heat transfer system while retaining a substantial portion of the lubricant in said system and introducing one of the HFO-1234ze compositions to the heat transfer system.

[0431] In one embodiment, a method for replacing a first refrigerant composition with a second refrigerant composition in a cooling or heating system is provided. The method comprises removing the first refrigerant composition from the cooling or heating system and charging second refrigerant composition to the cooling or heating system. In one embodiment, the first refrigerant is selected from any of R-1233zdE, R-1336mzzE and R-1336mzzZ, and the second refrigerant composition comprises any of the HFO-1234ze compositions disclosed herein (e.g., HFO-1234ze(Z); HFO-1234ze(Z)/HFO-1234ze(E); HFO-1234ze(Z)/HFO-1336mzz(E); HFO-1234ze(Z)/HFO-1336mzz(Z); HFO-1234ze(Z)/HFO-1233zd(E); E-HFO-1234ze/Z-HFO-1234ze/HFC-245fa; E-HFO-1234ze/Z-HFO-1234ze/E-HFO-1233zd; E-HFO-1234ze/Z-HFO-1234ze/HFC-245fa/E-HFO-1233zd; Z-HFO-1234ze/HFC-245fa/E-HFO-1233zd; HFO-1234ze(Z)/HFO-1234ze(E)/HFC-134a; and HFO-1234ze(Z)/HFO-1234ze(E)/HFC-227ea).

[0432] In another embodiment, a heat exchange system containing any of the HFO-1234ze(Z) compositions is provided, wherein said system is selected from the group consisting of air conditioners, freezers, refrigerators, heat pumps, water chillers, walk-in coolers, heat pumps, mobile refrigerators, mobile air conditioning units, and systems having combinations thereof. Additionally, the HFO-1234ze(Z) compositions may be useful in secondary loop systems wherein these compositions serve as the primary refrigerant thus providing cooling to a secondary heat transfer fluid that thereby cools a remote location.

[0433] Vapor-compression refrigeration, air-conditioning, or heat pump systems include an evaporator, a compressor, a condenser, and an expansion device. A vapor-compression cycle re-uses refrigerant in multiple steps producing a cooling effect in one step and a heating effect in a different step. The cycle can be described simply as follows. Liquid refrigerant enters an evaporator through an expansion device, and the liquid refrigerant boils in the evaporator, by withdrawing heat from the environment, at a low temperature to form a gas and produce cooling. The low-pressure gas enters a compressor where the gas is compressed to raise its pressure

and temperature. The higher-pressure (compressed) gaseous refrigerant then enters the condenser in which the refrigerant condenses and discharges its heat to the environment. The refrigerant returns to the expansion device through which the liquid expands from the higher-pressure level in the condenser to the low-pressure level in the evaporator, thus repeating the cycle.

[0434] In one embodiment, there is provided a heat transfer system containing any of the HFO-1234ze compositions. In another embodiment is disclosed a refrigeration, air-conditioning or heat pump apparatus containing any of the HFO-1234ze compositions. In another embodiment, is disclosed a stationary refrigeration or air-conditioning apparatus containing any of the HFO-1234ze compositions. In yet another embodiment is disclosed a mobile refrigeration or air conditioning apparatus containing a composition as disclosed herein.

[0435] In one embodiment, a method is provided for producing cooling comprising expanding any of the HFO-1234ze compositions in the vicinity of a body to be cooled, and thereafter compressing the composition.

[0436] In another embodiment, a method is provided for producing heating comprising compressing any of the HFO-1234ze compositions in the vicinity of a body to be heated, and thereafter expanding the composition.

[0437] The method for producing heating may further comprise passing a heat transfer medium through the condenser, whereby said condensation of working fluid heats the heat transfer medium and passing the heated heat transfer medium from the condenser to a body to be heated.

[0438] A body to be heated or cooled may be any space, object or fluid that may be heated such as water or air for space heating. In one embodiment, a body to be heated or cooled may be a room, building, or the passenger compartment of an automobile. Alternatively, in another embodiment, a body to be heated or cooled may be a second or the medium or heat transfer fluid, such as a chemical process stream.

[0439] In another embodiment, disclosed is a method of using the HFO-1234ze compositions as a heat transfer fluid composition. The method comprises transporting the working fluid from a heat source to a heat sink.

[0440] In another embodiment, the HFO-1234ze compositions of the present invention may be used to top-off a refrigerant charge in a heat transfer system. For instance, if a heat transfer system has diminished performance due to leakage of refrigerant, the compositions as disclosed herein may be added to bring performance back up to specification.

[0441] In accordance with this invention, a method is provided for converting heat from a heat source to mechanical energy. This method comprises heating a working fluid using heat supplied from the heat source; and expanding the heated working fluid to lower the pressure of the working fluid and generate mechanical energy as the pressure of the working fluid is lowered. The method is characterized by using a working fluid comprising a HFO-1234ze composition disclosed herein. The method for converting heat from a heat source to mechanical energy is a power cycle and may be an organic Rankine cycle (ORC).

[0442] The method is provided for converting heat from a heat source to mechanical energy may be a may be a sub-critical power cycle in which the organic working fluid used in the cycle receives heat at a pressure lower than the critical pressure of the organic working fluid and the working fluid remains below its critical pressure throughout the entire cycle.

[0443] The method is provided for converting heat from a heat source to mechanical energy may be a trans-critical power cycle, in which the organic working fluid used in the cycle receives heat at a pressure higher than the critical pressure of the organic working fluid. In a trans-critical cycle, the working fluid is compressed to a pressure above its critical pressure prior to being heated, and then during expansion the working fluid pressure is reduced to below its critical pressure.

[0444] The method is provided for converting heat from a heat source to mechanical energy may be a super-critical power cycle. In a super critical cycle, the working fluid remains above its critical pressure for the complete cycle (e.g., compression, heating, expansion and cooling).

[0445] In one preferred embodiment of the present invention is provided a heat pump apparatus containing a working fluid comprising any of the HFO-1234ze(Z) compositions, either as a single component working fluid or as a working fluid blend. In one embodiment, the present invention relates to a method for producing heating

and/or cooling in a heat pump utilizing any of the HFO-1234ze(Z) compositions of the present invention as the working fluid.

[0446] A heat pump is a type of apparatus for producing heating and/or cooling. A heat pump includes an evaporator, a compressor, a condenser or supercritical working fluid cooler, and an expansion device. A working fluid circulates through these components in a repeating cycle. Heating is produced at the condenser where energy (in the form of heat) is extracted from the vapor working fluid as it is condensed to form liquid working fluid. Cooling is produced at the evaporator where energy is absorbed to evaporate the working fluid to form vapor working fluid.

[0447] In one embodiment, the high temperature heat pump apparatus of the present invention comprises (a) an evaporator through which a working fluid flows and is evaporated; (b) a compressor in fluid communication with the evaporator that compresses the evaporated working fluid to a higher pressure; (c) a condenser in fluid communication with the compressor through which the high pressure working fluid vapor flows and is condensed; and (d) a pressure reduction device in fluid communication with the condenser wherein the pressure of the condensed working fluid is reduced and said pressure reduction device further being in fluid communication with the evaporator such that the working fluid then repeats flow through components (a), (b), (c) and (d) in a repeating cycle.

[0448] A heat pump may be a residential heat pump for heating air. Residential heat pumps are used to produce heated air to warm a residence or home (including single family or multi-unit attached homes) and produce maximum condenser operating temperatures from about 30°C to about 50°C. In another embodiment, a heat pump may be a high temperature heat pump, by which is meant a heat pump with condenser temperatures above 55°C, or with condenser temperatures above 80°C, or even with condenser temperatures above 100°C.

[0449] In one embodiment, the present invention relates to a method for producing heating in a high temperature heat pump comprising condensing a vapor working fluid comprising the HFO-1234ze(Z) composition, in a condenser, thereby producing a liquid working fluid. The high temperature heat pump may operate at a condenser temperature of at least about 100°C. The high temperature heat pump may comprise a centrifugal compressor or positive displacement compressor.

[0450] In some embodiments, a method and system are provided for producing heating in a high temperature heat pump having a condenser wherein a vapor working fluid is condensed to heat a heat transfer medium and the heated heat transfer medium is transported out of the condenser to a body to be heated. The method comprises condensing a vapor working fluid in a condenser, thereby producing a liquid working fluid wherein said vapor and liquid working fluid comprises any of the present compositions comprising HFO-1234ze(Z).

[0451] In one embodiment is provided a method for producing heating in a high temperature heat pump comprising extracting heat from a working fluid, thereby producing a cooled working fluid wherein said working fluid comprises any of the present compositions comprising HFO-1234ze(Z).

[0452] Heat pumps may include flooded evaporators or direct expansion evaporators.

[0453] One or more of the HFO-1234ze(Z) compositions disclosed herein are useful as heat transfer compositions, aerosol propellants, foaming agents, blowing agents, carrier fluids, displacement drying agents, buffing abrasion agents, polymerization media, expansion agents for polyolefins and polyurethane, and gaseous dielectrics.

[0454] In some embodiments, Z-HFO-1234ze is used as a dielectric in an electrical apparatus. In some embodiments, Z-HFO-1234ze is used alone. In some embodiments, Z-HFO-1234ze is used in admixture with one or more of the compounds disclosed herein. In an electrical apparatus for medium- or high-voltages, the functions of electrical insulation and electric arc extinction are typically performed by an insulating gas that is confined inside the apparatus. In the generally accepted sense of the term, "medium-voltage" denotes a voltage that is greater than 1,000 volts AC and strictly greater than 1,500 volts DC, but that does not exceed 52,000 volts AC or exceed 75,000 volts DC, whereas the term "high-voltage" denotes a voltage that is strictly greater than 52,000 volts AC and greater than 75,000 DC. In some embodiments, the insulating gas used inside these apparatuses contains Z-HFO-1234ze. In some embodiments, the insulating gas used inside these apparatuses is a blend comprising Z-HFO-1234ze.

[0455] Etching gases used in the semiconductor industry are used to etch deposits from a surface. Chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PECVD) chambers need to be regularly cleaned to remove deposits from the chamber walls and platens. This cleaning process reduces the productive capacity of the chamber since the chamber is out of active service during a cleaning cycle. The cleaning process may include, for example, the evacuation of reactant gases and their replacement with a cleaning gas, activation of that gas, followed by a flushing step to remove the cleaning gas from the chamber using an inert carrier gas. The cleaning gases typically work by etching the contaminant build-up from the interior surfaces, thus the etching rate of the cleaning gas is an important parameter in the utility and commercial use of the gases, and some cleaning gases can also be used as etching gases. These gases can generate relatively high amounts of toxic waste gases, which may pose additional GWP or Environmental, Health, and Safety (EHS) issues apart from the GWP of the cleaning or etch gas itself.

[0456] Thus, there is a need to reduce the harm of global warming caused by the cleaning and operation of CVD reactors with an effective and inexpensive cleaning/etching gas that has a high etch rate and a lower GWP and ESH impact than incumbent gases. In some embodiments, provided is a clean gas mixture that has low EHS and GWP, so that even if unreacted gases are released, they have reduced environmental impact. In some embodiments, provided are methods of using these gases, comprising activating the gas, either in a remote chamber or in situ in the process chamber, wherein the gas mixture comprises an oxygen source and a hydrofluoroolefin, and contacting the activated gas with the surface deposits for a time sufficient to remove said deposits. In some embodiments, the gas mixture is activated by a radio frequency (RF) source using sufficient power for a sufficient time such that the gas mixture reaches a neutral temperature of about 1000-3,000 K to form an activated gas mixture. In some embodiments, a glow discharge is used to activate the gas. In some embodiments, the activated gas mixture is contacted with the surface deposits and thereby removing at least some of the surface deposits.

[0457] In some embodiments, the gas mixtures comprise Z-HFO-1234ze. In some embodiments, the gas mixture comprises Z-HFO-1234ze alone. In some embodiments, the gas mixture comprises Z-HFO-1234ze in an admixture with one or

more compounds. The Z-HFO-1234ze of these gas mixtures preferably has a purity greater than 99.5 wt.%, or greater than 99.6 wt.%, or greater than 99.7 wt.%, or greater than 99.8 wt.%, preferably 99.9 wt.% or greater, and preferably has a chlorinated compounds content of less than about 100 ppm, preferably less than about 50 ppm, more preferably less than about 10 ppm, and most preferably less than about 1 ppm.

[0458] In another embodiment, the present invention relates to blowing agent compositions comprising the HFO-1234ze compositions of the present invention.

[0459] In another embodiment, the present invention relates to foam expansion agent compositions comprising HFO-1234ze for use in preparing foams. In other embodiments the invention provides foamable compositions, and preferably thermoset (like polyurethane, polyisocyanurate, or phenolic) foam compositions, and thermoplastic (like polystyrene, polyethylene, or polypropylene) foam compositions and method of preparing foams. In such foam embodiments, one or more of the HFO-1234ze compositions are included as a foam expansion agent in foamable compositions, which composition preferably includes one or more additional components capable of reacting and/or mixing and foaming under the proper conditions to form a foam or cellular structure.

[0460] In one embodiment, the present invention further relates to a method of forming a foam comprising: (a) adding to a foamable composition a HFO-1234ze composition of the present invention; and (b) processing the foamable composition under conditions effective to form a foam.

[0461] Another embodiment of the present invention relates to the use of the HFO-1234ze compositions of the present invention as propellants in sprayable compositions. Additionally, the present invention relates to a sprayable composition comprising HFO-1234ze. The active ingredient to be sprayed together with inert ingredients, solvents and other materials may also be present in a sprayable composition. In one embodiment, a sprayable composition is an aerosol. The present compositions can be used to formulate a variety of industrial aerosols or other sprayable compositions such as contact cleaners, dusters, lubricant sprays, mold release sprays, insecticides, and the like, and consumer aerosols such as personal care products (such as, e.g., hair sprays, deodorants, and perfumes),

household products (such as, e.g., waxes, polishes, pan sprays, room fresheners, and household insecticides), and automotive products (such as, e.g., cleaners and polishes), as well as medicinal materials such as anti-asthma and anti-halitosis medications. Examples of this includes metered dose inhalers (MDIs) for the treatment of asthma and other chronic obstructive pulmonary diseases and for delivery of medicaments to accessible mucous membranes or intra-nasally.

[0462] The present invention further relates to a process for producing aerosol products comprising the step of adding a composition of the present invention comprising HFO-1234ze to a formulation, including active, ingredients in an aerosol container, wherein said composition functions as a propellant. Additionally, the present invention further relates to a process for producing aerosol products comprising the step of adding a composition of the present invention comprising HFO-1234ze to a barrier type aerosol package (like a bag-in-a-can or piston can) wherein said composition is kept separated from other formulation ingredients in an aerosol container, and wherein said composition functions as a propellant. Additionally, the present invention further relates to a process for producing aerosol products comprising the step of adding only a composition of the present invention comprising HFO-1234ze to an aerosol package, wherein said composition functions as the active ingredient (e.g., a duster, or a cooling or freezing spray). In one embodiment, the Z-HFO-1234ze is of sufficiently high purity to be suitable for use as a pharmaceutical grade propellant. For pharmaceutical grade applications, the Z-HFO-1234ze preferably has a purity of at least 99.9%.

[0463] Also provided is a method for detecting a leak from a container comprising sampling the air in the vicinity of the container and detecting at least one fluorinated compound with means for detecting the leak, wherein the composition of the present invention comprising HFO-1234ze is contained inside the container.

[0464] A container may be any known container or system or apparatus that is filled with a HFO-1234ze composition of the present invention. A container may include but is not limited to a storage container, a transport container, an aerosol can, a fire extinguishing system, a chiller apparatus, a heat pump apparatus, heat transfer container, and a power cycle apparatus (e.g., an organic Rankine cycle system).

[0465] Means for detecting a leak may be any known sensor designed to detect leaks. In particular, means for detecting the leak includes, but is not limited to, electrochemical, corona discharge and mass spectroscopic leak detectors.

[0466] By “in the vicinity of” the container is meant within 12 inches of the outside surface of the container. Alternatively, in the vicinity may be within 6 inches, within 3 inches or within one inch of the outside surface of the container.

[0467] In some embodiments, the HFO-1234ze compositions of the present invention may be used in a refrigeration system. One embodiment of a refrigeration system includes an evaporator, a condenser, a compressor, an expansion device, and a heat transfer media. The heat transfer media includes the HFO-1234ze compositions of the present invention.

[0468] In another embodiment, the HFO-1234ze compositions of the present invention may be used in a process to transfer heat. The process may include providing an article and contacting the article with a heat transfer media including the HFO-1234ze compositions of the present invention. In some embodiments, the article may include electrical equipment (e.g., circuit board, computer, display, semiconductor chip, or transformer), a heat transfer surface (e.g., heat sink), or article of clothing (e.g., a body suit).

[0469] In some embodiments, the HFO-1234ze compositions disclosed herein may be useful as heat transfer fluids for direct-to-chip cooling, for example, for cooling of data center servers. In some embodiments, the composition comprising HFO-1234ze(Z) and optionally one or more of the additional compounds, the composition comprising HFO-1234ze(Z), HFC-245fa, HFO-1233zd(E) and optionally one or more of the additional compounds, the composition comprising HFO-1234ze(Z), HFO-1233zd(E) and optionally one or more of the additional compounds, the composition comprising HFO-1234ze(Z), HFO-1336mzz(Z) and optionally one or more of the additional compounds, the composition comprising HFO-1234ze(Z), HFO-1336mzz(E) and optionally one or more of the additional compounds, are particularly suited for data center cooling, and more particularly as a heat transfer fluid, particularly coolant, for a direct to chip cooling loop. Any of these compositions can be used as a liquid coolant, in place of water, for cooling of data center servers, particularly by direct to chip cooling. In such an application, the HFO-1234ze(Z)

containing composition circulates through a cold-plate heat exchanger located directly on the chip. The heat which dissipates from the computer chip is absorbed into the coolant loop, and the heated fluid is then circulated through a piping network until it reaches a lower-temperature heat exchanger, to reject the heat to, for example, a cooled water loop, and/or to the server room's air conditioning system, and/or to outside ambient air.

[0470] In some embodiments, the HFO-1234ze compositions disclosed herein may be useful as chiller fluids for cooling of data center servers, particularly for use with a cooling medium such as air, water or an ethylene glycol/water composition. In some embodiments, the composition comprising HFO-1234ze(Z) and optionally one or more of the additional compounds is particularly suited for use as chiller fluids for data center cooling, and more particularly as a heat transfer fluid, particularly coolant, for use with a cooling medium, such as air, water or ethylene glycol/water, for cooling of data center servers.

[0471] In another embodiment, provided herein is a storage container for refrigerant containing the HFO-1234ze compositions of the present invention, wherein the refrigerant comprises gaseous and liquid phases.

[0472] Another embodiment of the invention relates to storing the foregoing HFO-1234ze compositions in gaseous and/or liquid phases within a sealed container. The container will be properly prepared for loading with the present compositions by evacuation and heating such that there are limits on the amount of water and/or oxygen to prevent reaction or degradation of the refrigerant portion of the compositions within the container. In one embodiment, the water is limited to 0.1 to 200 ppm by weight, or 0.1 to 100 ppm by weight, or 0.1 to 50 ppm by weight or 0.1 to 10 ppm by weight. In another embodiment, the oxygen is limited to 0.6 volume percent or less of the vapor phase. In another embodiment, the oxygen is present from about 0.01 to 0.35 volume percent. In yet another embodiment, the oxygen is limited to 0.01 to 0.25 volume percent. And in yet another embodiment, the oxygen is limited to 0.01 to 0.15 volume percent.

[0473] The container for storing the HFO-1234ze compositions of the present invention 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 cases an aluminum alloy. The container can include a pierce top or valves suitable for dispensing flammable substances.

[0474] While any suitable method can be employed for stabilizing the HFO-1234ze compositions of the present invention, examples of such methods including blending the foregoing inhibitors with the HFO-1234ze compositions of the present invention, purging lines and containers with a material comprising the inhibitor (e.g., an inhibitor with a nitrogen carrier, or the inventive stabilized composition); among other suitable methods.

[0475] Another embodiment of the invention includes a refrigerant charging kit comprising the HFO-1234ze compositions of the present invention (which may be in the stabilized form) in a sealed cannister, and optionally carbon dioxide, and a tube for connecting a discharge end of the refrigerant cannister to a valve of a refrigerant circuit. In certain embodiments, any of the above-mentioned additives can be included in the stabilized refrigerant blend. Thus, the refrigerant charging kit can include any of the disclosed refrigerant blends which have been stabilized, but without a lubricant.

[0476] In another embodiment, the present invention relates to processes for the reclamation of any of the foregoing compositions, such integrated processes being described in U.S. Provisional Application No. 63/402,727, titled "Liquid Reclamation and Solid Foam Recycling/Reclamation: Compositions and Methods", filed on August 31, 2022, and U.S. Provisional Application No. 63/422,656, titled "Integrated System and Process for Producing Reclaimed, Stabilized and Traceable Refrigerant Compositions", filed on November 4, 2022, the entire contents of both of which are incorporated herein in their entireties.

[0477] For example, in one embodiment, provided herein is a process comprising the following steps: a) providing an unreclaimed refrigerant comprising at least HFO-1234ze(Z) or at least HFO-1234ze(Z) and HFO-1234ze(E); testing the unreclaimed refrigerant composition comprising at least HFO-1234ze(Z) or at least HFO-

1234ze(Z) and HFO-1234ze(E) and which may further comprise contaminants, non-condensable gases (NCG), and physical properties; checking and comparing the purity of the unreclaimed refrigerant composition relative to AHRI 700 standards; and if the unreclaimed refrigerant composition does not meet AHRI 700 standards, treating and purifying the unreclaimed refrigerant composition and providing at least one first treated product; and optionally repeating the procedure on the first treated product if needed to meet AHRI 700 standards; and optionally adding additional refrigerant components to the first treated product to form a first target refrigerant or refrigerant blend if the first treated product meets or exceeds AHRI 700 standards, or (2) further purifying the first treated product if it does not meet AHRI 700 standards to produce a second treated product and repeating the procedure as needed to obtain a second treated product which meets or exceeds AHRI 700 standards.

[0478] In another embodiment, a system for heating and/or cooling is provided. The system comprises an evaporator, compressor, condenser, and expansion device. The system contains any of the compositions disclosed herein.

[0479] Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The following specific embodiments are, therefore, to be construed as merely illustrative, and do not constrain the remainder of the disclosure in any way whatsoever.

[0480] The invention will be described in greater detail below by way of specific examples. The following examples are offered for illustrative purposes and are not intended to limit the invention in any manner. Those of skill in the art will readily recognize a variety of non-critical parameters which can be changed or modified to yield essentially the same results.

EXAMPLES

Materials

[0481] The materials used to prepare the Examples are commercially available or may be prepared by known methods.

[0482] Purification methods to obtain final products in each of the following Examples comprised one or more, preferably at least two or more, of the following

techniques/equipment/instrumentation: distillation columns, sulfuric acid drier, molecular sieves and/or alumina drier, water scrubber, caustic scrubber, and the like.

Example 1: Preparation of HCC-240fa

[0483] Vinyl chloride (7.4 g, 0.118 mol) is added to a mixture of CCl_4 (3700 g, 0.24 mol) (including less than 5 wt.% tetrachloroethylene, trichloroethylene, hexachloroethane, bromotrichloromethane, chloroform, 1,1,1-trichloroethane, 1,1,2-trichloroethane, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene and 1,1-dichloroethylene), Fe powder (0.62 g, 0.011 mol), and tributyl phosphate (0.72 g, 0.0027 mol) in a 210 mL Hastelloy® reactor. The reactor is heated up to 100°C for two hours. The conversion is 100% with 98% selectivity to produce HCC-240fa. A reaction product comprising HCC-240fa and less than 5 wt.% of one or more of 1-chlorobutane, HCO-1240xd, HCO-1230xd, 1,1,1,3-tetrachloropropane, 1,4 dichlorobutane, 1,2-dichloro-cyclobutane, 1,1,4,4-tetrachlorobutadiene, 1,1,3,4 tetrachlorobutadiene, 1,1,1,2,3-pentachloropropane (HCC-240db), $\text{C}_5\text{H}_7\text{Cl}_3$ isomer(s) and $\text{C}_4\text{H}_7\text{Cl}_3$ isomer(s) is obtained by distillation.

Example 2: Preparation of HFC-245fa

[0484] A 240 mL Hastelloy® C shaker tube is charged with SbCl_5 (11 g, 0.037 mol) and cooled to 20°C with dry ice/acetone. HF (48 g, 2.4 mol) is added to the shaker tube and the shaker tube is cooled and evacuated 3 times. The mixture is heated to 100°C for an hour. After venting off HF, the reaction product of Example 1 (i.e., HCC-240fa and less than 5 wt.% of one or more of 1-chlorobutane, HCO-1240xd, HCO-1230xd, 1,1,1,3-tetrachloropropane, 1,4 dichlorobutane, 1,2-dichloro-cyclobutane, 1,1,4,4-tetrachlorobutadiene, 1,1,3,4 tetrachlorobutadiene, 1,1,1,2,3-pentachloropropane (HCC-240db), $\text{C}_5\text{H}_7\text{Cl}_3$ isomer(s) and $\text{C}_4\text{H}_7\text{Cl}_3$ isomer(s)) (26 g, 0.12 mol) is added to the shaker tube, and the shaker tube is then heated to 90°C for 8 hours. Conversion of the reaction is 100% with 95% selectivity of HFC-245fa. The reaction product is purified by distillation and comprises HFC-245fa and one or more of the additional compounds of Tables 1 or 2 above.

Example 3: Preparation of HFO-1234ze(Z)/(E) from HFC-245fa

[0485] An inconel tube (1/2 inch {13 mm} OD) was filled with 5 cc of fluorinated Cr_2O_3 catalyst (Louisville Cr). A flow of air (3.6 vol% O_2) and $\text{CF}_3\text{CH}_2\text{CHF}_2$ (HFC-245fa) (including two or more of the additional compounds of Tables 1 or 2 above) (e.g., as produced in Example 2) were fed at 0.7 ml/hr over the catalyst bed at 370°C . Contact time in the reactor was 47 seconds. The $\text{CF}_3\text{CH}_2\text{CHF}_2$ was vaporized at 80°C . Part of the reactor effluent was passed through a series of valves and analyzed by Agilent® 6890 GC/5975C MS and a Restek® PC2618 5% Krytox® CBK-D/60/80 6-meter x 2mm ID 1/8" OD packed column purged with helium at 30 sccm. Samples were taken in hourly intervals. The data is shown in Table 10, with the amounts of components being expressed as mole percent.

Table 10: Example 3

Inj	Unknowns	1141	143a	152a	Trifluoropropyne	1234yf
1	1.12%	0.03%	0.52%	0.00%	0.51%	0.93%
2	0.16%	0.04%	0.37%	0.00%	0.57%	0.68%
3	0.15%	0.04%	0.35%	0.00%	0.58%	0.64%
4	0.15%	0.04%	0.33%	0.00%	0.58%	0.56%
5	0.14%	0.04%	0.31%	0.00%	0.58%	0.53%
6	0.13%	0.03%	0.28%	0.00%	0.59%	0.46%
7	0.11%	0.03%	0.27%	0.00%	0.60%	0.39%
8	0.12%	0.03%	0.28%	0.00%	0.59%	0.46%
9	0.10%	0.03%	0.35%	0.00%	0.61%	0.32%
10	0.05%	0.03%	0.24%	0.00%	0.59%	0.33%
11	0.05%	0.03%	0.25%	0.00%	0.60%	0.36%
12	0.12%	0.04%	0.30%	0.00%	0.61%	0.45%
13	0.20%	0.06%	0.35%	0.00%	0.63%	0.56%
14	0.20%	0.06%	0.35%	0.00%	0.63%	0.55%

Inj	E-1234ze	Z-1234ze	245fa	E-1233zd	Z-1233zd
1	70.84%	18.47%	6.78%	0.66%	0.13%
2	71.12%	19.22%	7.05%	0.66%	0.14%
3	71.12%	19.25%	7.06%	0.66%	0.14%
4	71.29%	19.19%	7.06%	0.65%	0.15%
5	71.32%	19.23%	7.04%	0.66%	0.15%
6	71.36%	19.28%	7.07%	0.65%	0.14%
7	71.41%	19.39%	7.00%	0.66%	0.14%
8	71.38%	19.31%	7.03%	0.65%	0.14%
9	71.60%	19.34%	6.94%	0.67%	0.14%
10	71.66%	19.28%	7.09%	0.60%	0.13%
11	71.61%	19.41%	7.07%	0.51%	0.11%
12	71.66%	19.26%	6.91%	0.54%	0.12%
13	71.52%	19.30%	6.68%	0.57%	0.13%
14	71.60%	19.25%	6.67%	0.56%	0.13%

[0486] The analysis showed 93% conversion of HFC-245fa and a selectivity to E/Z-1234ze of greater than 97%. The E/Z ratio was 3.7:1.

[0487] The final reaction product, after purification, had a purity of greater than 99.5%. That is, the composition comprised about 99.5% by weight of HFO-1234ze(E) and HFO-1234ze(Z), and one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, HFO-1234ze(Z), CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

Example 4: Liquid Phase Preparation of Z/E-HFO-1233zd from HCC-240fa

[0488] A 240 mL Hastelloy® C shaker tube is charged with SbCl₅ (11 g, 0.037 mol) and cooled to 20°C with dry ice/acetone. HF (48 g, 2.4 mol) is added to the shaker tube and the shaker tube is cooled and evacuated 3 times. The mixture is heated to 100°C for an hour. After venting off HF, the reaction product of Example 1 (i.e., HCC-240fa and less than 5 wt.% of one or more of 1-chlorobutane, HCO-1240xd, HCO-1230xd, 1,1,1,3-tetrachloropropane, 1,4 dichlorobutane, 1,2-dichlorocyclobutane, 1,1,4,4-tetrachlorobutadiene, 1,1,3,4 tetrachlorobutadiene, 1,1,1,2,3-pentachloropropane (HCC-240db), C₅H₇Cl₃ isomer(s) and C₄H₇Cl₃ isomer(s)) (26 g, 0.12 mol) is added to the shaker tube, and the shaker tube is then heated to 70°C for 8 hours. Conversion of the reaction is 100% with 95% selectivity of E/Z-HFO-1233zd. The final reaction product, after purification, has a purity of greater than 99.5%. That is, the composition comprises about 99.5% by weight of HCFO-1233zd(E) and HCFO-1233zd(Z), and one or more additional compounds selected from HFO-1234ze(Z) and HFC-245fa. It will be understood by those skilled in the art, based on the description provided above, that liquid phase preparation of HFO-1233ze(Z)/(E) from HCC-240fa may alternatively be carried out in the absence of a catalyst.

Example 5: Vapor Phase Preparation of Z/E-HFO-1233zd from HCC-240fa

[0489] An inconel tube (1/2 inch {13 mm} OD) was filled with 4 cc of fluorinated Cr_2O_3 catalyst (Newport Cr). A flow of $\text{CCl}_3\text{CH}_2\text{CHCl}_2$ (HCC-240fa) at 0.21 ml/hr was vaporized with anhydrous HF at 1:20 mol ratio at 150°C and fed over the catalyst bed at various temperatures. This reaction could optionally be run in the presence of an oxygen containing gas, such as air. Part of the reactor effluent was passed through a series of valves and analyzed by Agilent® 7890B GC/5977 MS and a Restek® PC2618 5% Krytox® CBK-D/60/80 6-meter x 2mm ID 1/8" OD packed column purged with helium at 20 sccm. The data from the analysis is shown in below Table 11, with the components being expressed as mole percent and the samples having been taken in 1.5 hourly intervals.

Table 11: Example 5

Inj	Unknowns	E-1234ze	245fa + Z-1234ze	1233xf	E-1233zd	Temp °C
1	0.17%	3.66%	31.08%	0.03%	57.31%	250
2	0.14%	3.91%	36.56%	0.03%	52.07%	250
3	0.15%	4.49%	45.14%	0.02%	44.00%	250
4	0.15%	4.81%	49.37%	0.02%	39.97%	250
5	0.36%	4.48%	44.92%	0.03%	43.98%	250
6	0.17%	4.95%	50.13%	0.02%	39.21%	250
7	0.15%	4.45%	44.34%	0.02%	44.73%	250
8	0.16%	7.59%	34.40%	0.02%	50.85%	275
9	0.12%	6.87%	30.34%	0.02%	55.12%	275
10	0.12%	7.25%	33.03%	0.02%	52.43%	275
11	0.33%	7.17%	32.56%	0.02%	52.64%	275
12	0.15%	6.51%	29.65%	0.02%	56.09%	275
13	0.20%	9.35%	20.18%	0.03%	61.69%	300
14	0.15%	9.59%	20.01%	0.03%	61.72%	300
15	0.27%	9.52%	20.13%	0.04%	61.54%	300
16	0.16%	10.03%	21.32%	0.03%	60.12%	300
17	0.17%	10.63%	22.95%	0.03%	58.11%	300
18	0.14%	10.79%	23.32%	0.03%	57.75%	300
19	0.19%	14.76%	16.03%	0.04%	60.42%	325
20	0.15%	13.31%	15.43%	0.05%	62.29%	325
21	0.23%	17.29%	19.31%	0.04%	55.21%	325
22	0.16%	13.56%	14.82%	0.05%	62.54%	325
23	0.22%	15.83%	17.19%	0.04%	58.36%	325
24	0.20%	16.24%	10.40%	0.09%	63.78%	350
25	0.41%	19.02%	12.35%	0.09%	59.41%	350
26	0.21%	16.62%	10.31%	0.09%	63.44%	350
27	0.21%	19.01%	12.82%	0.08%	59.21%	350
28	0.19%	16.99%	10.50%	0.09%	62.96%	350

Inj	Z-1233zd	244fa	243fa	243fb	Temp °C
1	5.60%	1.81%	0.00%	0.34%	250
2	4.98%	1.98%	0.00%	0.33%	250
3	4.30%	1.67%	0.00%	0.24%	250
4	3.94%	1.54%	0.00%	0.21%	250
5	4.28%	1.70%	0.00%	0.25%	250
6	3.87%	1.47%	0.00%	0.19%	250
7	4.35%	1.71%	0.00%	0.25%	250
8	5.40%	1.43%	0.00%	0.15%	275
9	5.82%	1.53%	0.00%	0.18%	275
10	5.51%	1.47%	0.00%	0.16%	275
11	5.59%	1.51%	0.00%	0.18%	275
12	5.86%	1.54%	0.00%	0.19%	275
13	7.03%	1.39%	0.02%	0.13%	300
14	6.99%	1.36%	0.02%	0.13%	300
15	7.03%	1.32%	0.02%	0.13%	300
16	6.87%	1.33%	0.02%	0.12%	300
17	6.68%	1.30%	0.02%	0.12%	300
18	6.58%	1.26%	0.02%	0.11%	300
19	7.32%	1.11%	0.04%	0.08%	325
20	7.50%	1.13%	0.06%	0.09%	325
21	6.74%	1.10%	0.04%	0.06%	325
22	7.56%	1.16%	0.06%	0.08%	325
23	7.09%	1.14%	0.05%	0.07%	325
24	8.07%	1.02%	0.13%	0.06%	350
25	7.59%	0.97%	0.10%	0.05%	350
26	8.06%	1.06%	0.15%	0.07%	350
27	7.57%	0.95%	0.11%	0.05%	350
28	8.02%	1.03%	0.16%	0.06%	350

[0490] The final reaction product, after purification, had a purity of greater than 99.5%. That is, the composition comprised about 99.5% by weight of HCFO-1233zd(E) and HCFO-1233zd(Z), and one or more additional compounds selected from HFO-1234ze(Z) and HFC-245fa.

Example 6: Preparation of Z/E-HFO-1234ze from Z/E-HFO-1233zd

[0491] An inconel tube (1/2 inch {13 mm} OD) was filled with 8 cc of fluorinated Cr₂O₃ catalyst (Newport Cr), and the reaction was performed at various temperatures. A composition of CF₃CH=CHCl (E/Z-HFO-1233zd) and one or more additional compounds selected from HFO-1234ze(Z) and HFC-245fa were fed at 0.41 ml/hr via a vaporizer controlled at 80°C, and anhydrous HF fed was fed at 16 sccm. This reaction could optionally be run in the presence of an oxygen containing gas, such as air. Part of the reactor effluent was passed through a series of valves and analyzed by Agilent® 7890B GC/5977 MS and a Restek® PC2618 5% Krytox® CBK-D/60/80 6-meter x 2mm ID 1/8" OD packed column purged with helium at 20

sccm. The data is shown in Table 12, with the components being expressed as mole percent and samples having been taken in 1.5 hourly intervals.

Table 12: Example 6

Inj	Unknowns	1234 yf	E-1234 ze	236fa +245fa	Z-1234ze	Temp °C
2	0.06%	0.51%	9.46%	11.20%	2.27%	300
3	0.07%	0.21%	9.00%	6.84%	2.21%	300
4	0.07%	0.31%	9.32%	10.26%	2.27%	300
5	0.07%	0.30%	9.60%	10.96%	2.39%	300
6	0.07%	0.31%	9.90%	11.58%	2.48%	300
7	0.07%	0.69%	12.07%	6.65%	2.92%	325
8	0.07%	0.61%	12.01%	6.56%	2.91%	325
9	0.07%	0.54%	11.90%	6.44%	2.90%	325
10	0.06%	0.49%	12.15%	6.70%	2.98%	325
11	0.01%	0.45%	13.08%	7.31%	3.23%	325
12	0.07%	0.87%	13.62%	3.78%	3.41%	350
13	0.07%	0.77%	13.77%	3.83%	3.47%	350
14	0.06%	0.66%	13.68%	3.74%	3.47%	350
15	0.05%	0.60%	13.91%	3.79%	3.54%	350

Inj	1233xf	E-1233zd	Z-1233zd	243fa	Temp °C
2	1.39%	67.03%	7.98%	0.10%	300
3	0.86%	72.28%	8.34%	0.18%	300
4	0.97%	68.36%	8.12%	0.33%	300
5	0.89%	67.45%	8.03%	0.30%	300
6	0.87%	66.56%	7.94%	0.30%	300
7	1.93%	66.48%	8.36%	0.83%	325
8	1.71%	66.96%	8.40%	0.78%	325
9	1.57%	67.35%	8.50%	0.74%	325
10	1.39%	67.09%	8.47%	0.66%	325
11	1.21%	65.80%	8.35%	0.55%	325
12	2.38%	65.54%	8.80%	1.41%	350
13	2.09%	65.82%	8.84%	1.25%	350
14	1.80%	66.45%	8.97%	1.08%	350
15	1.60%	66.48%	9.01%	0.95%	350

[0492] The analysis showed 85-98% conversion of Z/E-HFO-1233zd and a selectivity to E/Z-1234ze is in the range of 10 to 20%. The E/Z ratio was between 5:1 to 3:1.

[0493] The final reaction product, after purification, had a purity of greater than 99.5%. That is, the composition comprised about 99.5% by weight of HFO-1234ze(E) and HFO-1234ze(Z), and one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, HFO-1234ze(Z), CFC-114, trifluoropropylene, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-

263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

Example 7: Isomerization of HFO-1234ze(E) to HFO-1234ze(Z)

[0494] An inconel tube (1/2 inch {13 mm} OD) is filled with 4 cc of fluorinated Cr₂O₃ catalyst. A composition comprising E-HFO-1234ze one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, HFO-1234ze(Z), CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E) is fed at 0.45 ml/hr with 0.91 sccm air. The reaction is performed at 300°C. Contact time is 14 seconds at atmospheric pressure. This reaction could optionally be run in the presence of an oxygen containing gas, such as air. Part of the reactor effluent is passed through a series of valves and analyzed by Agilent® 7890B GC/5977 MS and a Restek® PC2618 5% Krytox® CBK-D/60/80 6-meter x 2mm ID 1/8" OD packed column purged with helium at 20 sccm. The conversion of E-HFO-1234ze to Z-HFO-1234ze is 20%.

[0495] In one embodiment, the final reaction product, after purification, has a purity of greater than 99%, 99.5%. That is, the composition comprises about 99%, 99.5% by weight of HFO-1234ze(Z), and further comprises HFO-245fa, one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, and one or more additional compounds selected from HFC-143a, HFC-1225zc, HFC-236fa, HFO-E/Z-1234ze, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234ze(Z), HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E),

HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

[0496] In one embodiment, the final reaction product, after purification, has a purity of greater than 99.9% and is free of or substantially free of chlorinated compounds, making it suitable for etching gas applications. By “substantially free of” with respect to chlorinated compounds is meant that the amount of chlorinated compounds present in the composition is less than about 100 ppm, preferably less than about 50 ppm, more preferably less than about 10 ppm, and most preferably less than about 1 ppm.

Example 8: Preparation of HFO-1234ze(E)/(Z) from HCC-240fa

[0497] An Inconel® pipe (0.5-inch (1.27 cm) OD, 10-inch (25.4 cm) length, 0.35 in (0.89 cm wall thickness) was used as the reactor and was filled with 4 cc of fluorinated Cr_2O_3 catalyst (Newport Cr). A flow of $\text{CCl}_3\text{CH}_2\text{CHCl}_2$ (HCC-240fa) at 0.21 ml/hr was vaporized with anhydrous HF at 1:20 mol ratio at a temperature of 150°C and fed over the catalyst bed at various temperatures. The reaction was carried out at temperatures ranging from 250°C to 350°C. This reaction could optionally be run in the presence of an oxygen containing gas, such as air. Part of the reactor effluent was passed through a series of valves and analyzed by Agilent® 7890B GC/5977 MS and a Restek® PC2618 5% Krytox® CBK-D/60/80 6-meter x 2mm ID 1/8" OD packed column purged with helium at 20 sccm. Samples were taken in 1.5 hours intervals. Compositions comprising HFO-1234ze(Z) and HFO-1234ze(E) were obtained, as shown in Table 13, with the amounts of components being expressed as mole percent.

Table 13: Example 8

Inj	Unknowns	E-1234ze	245fa + Z-1234ze	1233xf	E-1233zd	Temp °C
1	0.17%	3.66%	31.08%	0.03%	57.31%	250
2	0.14%	3.91%	36.56%	0.03%	52.07%	250
3	0.15%	4.49%	45.14%	0.02%	44.00%	250
4	0.15%	4.81%	49.37%	0.02%	39.97%	250
5	0.36%	4.48%	44.92%	0.03%	43.98%	250
6	0.17%	4.95%	50.13%	0.02%	39.21%	250
7	0.15%	4.45%	44.34%	0.02%	44.73%	250
8	0.16%	7.59%	34.40%	0.02%	50.85%	275

Inj	Unknowns	E-1234ze	245fa + Z-1234ze	1233xf	E-1233zd	Temp °C
9	0.12%	6.87%	30.34%	0.02%	55.12%	275
10	0.12%	7.25%	33.03%	0.02%	52.43%	275
11	0.33%	7.17%	32.56%	0.02%	52.64%	275
12	0.15%	6.51%	29.65%	0.02%	56.09%	275
13	0.20%	9.35%	20.18%	0.03%	61.69%	300
14	0.15%	9.59%	20.01%	0.03%	61.72%	300
15	0.27%	9.52%	20.13%	0.04%	61.54%	300
16	0.16%	10.03%	21.32%	0.03%	60.12%	300
17	0.17%	10.63%	22.95%	0.03%	58.11%	300
18	0.14%	10.79%	23.32%	0.03%	57.75%	300
19	0.19%	14.76%	16.03%	0.04%	60.42%	325
20	0.15%	13.31%	15.43%	0.05%	62.29%	325
21	0.23%	17.29%	19.31%	0.04%	55.21%	325
22	0.16%	13.56%	14.82%	0.05%	62.54%	325
23	0.22%	15.83%	17.19%	0.04%	58.36%	325
24	0.20%	16.24%	10.40%	0.09%	63.78%	350
25	0.41%	19.02%	12.35%	0.09%	59.41%	350
26	0.21%	16.62%	10.31%	0.09%	63.44%	350
27	0.21%	19.01%	12.82%	0.08%	59.21%	350
28	0.19%	16.99%	10.50%	0.09%	62.96%	350

Inj	Z-1233zd	244fa	243fa	243fb	Temp °C
1	5.60%	1.81%	0.00%	0.34%	250
2	4.98%	1.98%	0.00%	0.33%	250
3	4.30%	1.67%	0.00%	0.24%	250
4	3.94%	1.54%	0.00%	0.21%	250
5	4.28%	1.70%	0.00%	0.25%	250
6	3.87%	1.47%	0.00%	0.19%	250
7	4.35%	1.71%	0.00%	0.25%	250
8	5.40%	1.43%	0.00%	0.15%	275
9	5.82%	1.53%	0.00%	0.18%	275
10	5.51%	1.47%	0.00%	0.16%	275
11	5.59%	1.51%	0.00%	0.18%	275
12	5.86%	1.54%	0.00%	0.19%	275
13	7.03%	1.39%	0.02%	0.13%	300
14	6.99%	1.36%	0.02%	0.13%	300
15	7.03%	1.32%	0.02%	0.13%	300
16	6.87%	1.33%	0.02%	0.12%	300
17	6.68%	1.30%	0.02%	0.12%	300
18	6.58%	1.26%	0.02%	0.11%	300
19	7.32%	1.11%	0.04%	0.08%	325
20	7.50%	1.13%	0.06%	0.09%	325
21	6.74%	1.10%	0.04%	0.06%	325
22	7.56%	1.16%	0.06%	0.08%	325
23	7.09%	1.14%	0.05%	0.07%	325
24	8.07%	1.02%	0.13%	0.06%	350
25	7.59%	0.97%	0.10%	0.05%	350
26	8.06%	1.06%	0.15%	0.07%	350
27	7.57%	0.95%	0.11%	0.05%	350
28	8.02%	1.03%	0.16%	0.06%	350

[0498] The analysis showed greater than 99% conversion of HCC-240fa and a selectivity to E/Z-HFO-1234ze in the range of 3 to 25%. The E/Z ratio was in the range of 10:1 to 3:1.

[0499] The final reaction product, after purification, had a purity of greater than 99%, or greater than 99.5%. That is, the composition comprised about 99% or 99.5% by weight of HFO-1234ze(E) and HFO-1234ze(Z), and one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, HFO-1234ze(Z), CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

Examples 9-15

[0500] In Examples 9-15, refrigerant performance has been determined for some exemplary compositions of the present invention in medium temperature refrigeration systems as compared to R-471A. The data are based on the conditions set forth in Table 14. In Table 14, “T_condensor” is condenser temperature, “T_evaporator” is evaporator temperature, and “Return gas T” is return line gas temperature.

[0501] In Tables 15-23, “COP” is coefficient of performance (analogous to energy efficiency), and “CAP” is volumetric cooling capacity.

Table 14: Medium Temperature Refrigeration Conditions

T_condensor (°C)	40
T_evaporator (°C)	7
Return gas T (°C)	18

Example 9

[0502] Compositions comprising HFO-1234ze(Z) and HFO-1234ze(E) are prepared. In one embodiment, the compositions comprise up to about 0.5 wt% of one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-

245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, and one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E).

[0503] Performance of such compositions comprising HFO-1234ze(E) and HFO-1234ze(Z) is explored in a medium temperature refrigeration system as compared to R-471A. The data are based on the conditions set forth in Table 14. Table 15 tabulates the performance metrics and properties of several compositions, particularly compositions of optimal cooling efficiency and capacity.

Table 15: Med Temp Refrig conditions, cycle metric performance and fluid property ranges for 1234zeE/1234zeZ in Example 9

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	GWP AR5	ASHRAE flammability class	Glide (K)	COP _c (% dev from R-471A)	CAP _c (% dev from R-471A)
0.1	0.9	1	2L	2.5	4.8	-52
0.08	0.92	1	2L	2	4.9	-53
0.07	0.93	1	2L	1.8	5	-53.5
0.03	0.97	1	2L	0.8	5.3	-55.5
0.02	0.98	1	2L	0.5	5.4	-56
0.01	0.99	1	2L	0.3	5.5	-56.4
0.11	0.89	1	2L	2.7	4.7	-51.4
0.09	0.91	1	2L	2.3	4.8	-52.5
0.04	0.96	1	2L	1.1	5.2	-55
0.12	0.88	1	2L	2.9	4.6	-50.9
0.06	0.94	1	2L	1.6	5	-54
0.05	0.95	1	2L	1.3	5.1	-54.5
0.14	0.86	1	2L	3.3	4.5	-49.9
0.13	0.87	1	2L	3.1	4.6	-50.4
0.16	0.84	1	2L	3.7	4.4	-48.8
0.15	0.85	1	2L	3.5	4.5	-49.3
0.18	0.82	1	2L	4	4.3	-47.7
0.17	0.83	1	2L	3.9	4.4	-48.2
0.2	0.8	1	2L	4.4	4.3	-46.6
0.19	0.81	1	2L	4.2	4.3	-47.1
0.21	0.79	1	2L	4.5	4.2	-46
0.22	0.78	1	2L	4.7	4.2	-45.4

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	GWP AR5	ASHRAE flammability class	Glide (K)	COP_c (% dev from R-471A)	CAP_c (% dev from R-471A)
0.23	0.77	1	2L	4.8	4.1	-44.9
0.24	0.76	1	2L	5	4.1	-44.3
0.25	0.75	1	2L	5.1	4	-43.7
0.26	0.74	1	2L	5.2	4	-43.1
0.28	0.72	1	2L	5.5	3.9	-42
0.27	0.73	1	2L	5.3	4	-42.6
0.31	0.69	1	2L	5.8	3.8	-40.2
0.3	0.7	1	2L	5.7	3.9	-40.8
0.29	0.71	1	2L	5.6	3.9	-41.4
0.32	0.68	1	2L	5.9	3.8	-39.6
0.34	0.66	1	2L	6	3.7	-38.4
0.33	0.67	1	2L	6	3.7	-39
0.35	0.65	1	2L	6.1	3.7	-37.8
0.36	0.64	1	2L	6.2	3.7	-37.1
0.39	0.61	1	2L	6.4	3.5	-35.3
0.37	0.63	1	2L	6.3	3.6	-36.5
0.4	0.6	1	2L	6.4	3.5	-34.6
0.38	0.62	1	2L	6.3	3.6	-35.9
0.41	0.59	1	2L	6.5	3.5	-34
0.42	0.58	1	2L	6.5	3.4	-33.3
0.43	0.57	1	2L	6.5	3.4	-32.7
0.45	0.55	1	2L	6.6	3.3	-31.4
0.46	0.54	1	2L	6.6	3.2	-30.7
0.47	0.53	1	2L	6.6	3.2	-30.1
0.44	0.56	1	2L	6.6	3.3	-32.1
0.48	0.52	1	2L	6.6	3.2	-29.4
0.5	0.5	1	2L	6.6	3	-28.1
0.51	0.49	1	2L	6.6	3	-27.4
0.49	0.51	1	2L	6.6	3.1	-28.7
0.53	0.47	1	2L	6.5	2.9	-26
0.52	0.48	1	2L	6.6	2.9	-26.7
0.55	0.45	1	2L	6.5	2.8	-24.6
0.54	0.46	1	2L	6.5	2.8	-25.3
0.56	0.44	1	2L	6.4	2.7	-23.9
0.58	0.42	1	2L	6.3	2.6	-22.5
0.57	0.43	1	2L	6.4	2.6	-23.2
0.59	0.41	1	2L	6.3	2.5	-21.8
0.6	0.4	1	2L	6.2	2.5	-21
0.61	0.39	1	2L	6.1	2.4	-20.3
0.62	0.38	1	2L	6.1	2.3	-19.6
0.63	0.37	1	2L	6	2.3	-18.8
0.66	0.34	1	2L	5.7	2.1	-16.5
0.67	0.33	1	2L	5.6	2	-15.8
0.65	0.35	1	2L	5.8	2.1	-17.3

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	GWP AR5	ASHRAE flammability class	Glide (K)	COP _c (%) dev from R-471A)	CAP _c (%) dev from R-471A)
0.68	0.32	1	2L	5.5	2	-15
0.64	0.36	1	2L	5.9	2.2	-18.1
0.7	0.3	1	2L	5.3	1.8	-13.4
0.71	0.29	1	2L	5.2	1.8	-12.6
0.69	0.31	1	2L	5.4	1.9	-14.2
0.73	0.27	1	2L	4.9	1.6	-11
0.74	0.26	1	2L	4.8	1.6	-10.1
0.72	0.28	1	2L	5	1.7	-11.8
0.77	0.23	1	2L	4.3	1.4	-7.6
0.76	0.24	1	2L	4.5	1.5	-8.4
0.78	0.22	1	2L	4.2	1.3	-6.7
0.79	0.21	1	2L	4	1.3	-5.9
0.8	0.2	1	2L	3.9	1.2	-5
0.83	0.17	1	2L	3.3	1	-2.3
0.81	0.19	1	2L	3.7	1.2	-4.1
0.84	0.16	1	2L	3.2	1	-1.3
0.82	0.18	1	2L	3.5	1.1	-3.2
0.85	0.15	1	2L	3	0.9	-0.4
0.86	0.14	1	2L	2.8	0.9	0.5
0.75	0.25	1	2L	4.6	1.5	-9.3
0.87	0.13	1	2L	2.6	0.9	1.5
0.88	0.12	1	2L	2.4	0.8	2.5
0.89	0.11	1	2L	2.2	0.8	3.4
0.9	0.1	1	2L	2	0.7	4.4
0.91	0.09	1	2L	1.8	0.7	5.4
0.92	0.08	1	2L	1.6	0.6	6.4
0.93	0.07	1	2L	1.4	0.6	7.4
0.94	0.06	1	2L	1.2	0.5	8.4
0.95	0.05	1	2L	1	0.5	9.4
0.96	0.04	1	2L	0.8	0.5	10.4
0.98	0.02	1	2L	0.4	0.4	12.5
0.97	0.03	1	2L	0.6	0.4	11.5
0.99	0.01	1	2L	0.2	0.4	13.6

[0504] Broadly, for cooling mode, a composition range of 1.0% to 99.0% of HFO-1234ze(E) and 1.0% to 99.0% of HFO-1234ze(Z) will have a GWP less than 1, a maximum average glide of about 6.6 K, a cooling capacity range that has a deviation range of -56.4% to 13.6% from the cooling capacity of R-471A evaluated with the same conditions set, and the cooling COP range has a deviation range from 0.4% to 5.5% than that of the cooling COP of R-471A evaluated with the same conditions

set. Table 15 lists example compositions within the GWP < 1 range that have ASHRAE flammability classifications of 2L.

[0505] In some embodiments, blend composition ranges for cooling mode within a composition range of 75.0% to 95.0% of HFO-1234ze(E) and 5.0% to 25.0% of HFO-1234ze(Z) will have a GWP < 1, a maximum average heat exchanger glide of 4.6 K, an ASHRAE flammability classification of 2L, the minimum and maximum cooling capacities are -9.3% and 9.4% than that of R-471A evaluated at the same conditions set, and the minimum and maximum cooling COP efficiencies are 0.5% and 1.5% than that of R-471A evaluated at the same conditions set.

[0506] In one embodiment, at the maximum cooling capacity of 9.4%, the composition comprises 95 wt-% HFO-1234ze(E) and 5 wt-% HFO-1234ze(Z). In addition, the COP for cooling is 0.5% than that for R-471A under the same cycle conditions, the maximum average heat exchanger glide is 1.0 K and its ASHRAE flammability classification is 2L.

[0507] In one embodiment, at the maximum cooling COP efficiency, which is 1.5%, the composition comprises 75 wt-% HFO-1234ze(E) and 25 wt-% HFO-1234ze(Z). In addition, the maximum average heat exchanger glide is 4.6 K and its ASHRAE flammability classification is 2L.

[0508] The HFO-1234ze(Z)/HFO-1234ze(E) composition has a lower critical temperature than the incumbent fluid, but has a higher pressure and capacity. Also, the HFO-1234ze(E)/HFO-1234ze(Z) compositions do not exhibit wet compression.

[0509] It will be understood by those skilled in the art that weight percentages of HFO-1234ze(E) and HFO-1234ze(Z) provided for the above compositions are approximate, and the compositions may further comprise one or more of the additional compounds disclosed above.

Example 10

[0510] Compositions comprising HFO-1234ze(Z) and HFO-1336mzz(Z) are prepared. In one embodiment, the compositions comprise up to about 0.5 wt% of one or more additional compounds selected from HFO-1336mzz(E), HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb, and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb,

HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb. Performance of such compositions comprising HFO-1234ze(Z) and HFO-1336mzz(Z) is explored in a medium temperature refrigeration system as compared to R-471A. The data are based on the conditions set forth in Table 14. Table 16 tabulates the performance metrics and properties of several compositions, particularly compositions of optimal cooling efficiency and capacity.

Table 16: Med Temp Refrig conditions, cycle metric performance and fluid property ranges for 1234zeZ/1336mzzZ in Example 10

wt-frac R1234ze(Z)	wt-frac R1336mzz(Z)	GWP AR5	ASHRAE flammability class	Glide (K)	COP _c (%) dev from R-471A)	CAP _c (%) dev from R-471A)
0.01	0.99	2	1	0.2	5.3	-83.1
0.99	0.01	1	2L	0.1	5.6	-57.2
0.98	0.02	1	2L	0.3	5.6	-57.6
0.11	0.89	2	1	2	5.1	-80.8
0.12	0.88	2	1	2.1	5.1	-80.6
0.1	0.9	2	1	1.9	5.1	-81
0.13	0.87	2	1	2.3	5.1	-80.3
0.15	0.85	2	1	2.6	5.1	-79.8
0.16	0.84	2	1	2.7	5.1	-79.6
0.14	0.86	2	1	2.4	5.1	-80.1
0.45	0.55	2	1	4.3	5.3	-72.5
0.83	0.17	1	1	2.1	5.4	-62.2
0.8	0.2	1	1	2.4	5.4	-63.1
0.81	0.19	1	1	2.3	5.4	-62.8
0.82	0.18	1	1	2.2	5.4	-62.5

[0511] Broadly, for cooling mode, a composition range of 1.0% to 99.0% of HFO-1234ze(Z) and 1.0% to 99.0% of HFO-1336mzz(Z) will have a GWP less than 2, a maximum average glide of about 4.3 K, and the cooling COP range has a deviation range from 5.1% to 5.6% than that of the cooling COP of R-471A evaluated with the same conditions set. Table 16 lists example compositions within the GWP < 2 range that have ASHRAE flammability classifications of 1 and 2L.

[0512] In some embodiments, blend composition ranges for cooling mode within a composition range of 1.0% to 83.0% of HFO-1234ze(Z) and 17.0% to 99.0% of HFO-1336mzz(Z) will have a GWP < 2, a maximum average heat exchanger glide of

4.3 K, an ASHRAE flammability classification of 1, and the minimum and maximum cooling COP efficiencies are 5.1% and 5.4% than that of R-471A evaluated at the same conditions set.

[0513] In one embodiment, at the maximum cooling COP efficiency of 5.4%, the composition comprises 80 wt-% HFO-1234ze(Z) and 20 wt-% HFO-1336mzz(Z). In addition, the maximum average heat exchanger glide is 2.4 K and its ASHRAE flammability classification is 1.

[0514] It will be understood by those skilled in the art that weight percentages of HFO-1234ze(Z) and HFO-1336mzz(Z) provided for the above compositions are approximate, and the compositions may further comprise one or more of the additional compounds disclosed above.

[0515] The HFO-1234ze(Z)/HFO-1336mzz(Z) composition has lower pressure and capacity relative to the incumbent fluid, but has a higher critical temperature, making it suitable for use at higher heating temperatures. Also, the HFO-1234ze(Z)/HFO-1336mzz(Z) compositions do not exhibit wet compression.

Example 11

[0516] Compositions comprising HFO-1234ze(Z), HFO-1336mzz(E) and HFO-1336mzz(Z) are prepared. In one embodiment, the compositions comprise up to about 0.5 wt% of one or more additional compounds selected from HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb; one more additional compounds selected from C-30, HCFC-114, HCFC-114a, HCFC-133, HCFC-133a, HFC-245fa, HFC-338mee, HFC-338mf, HFC-347mef, HCO-1140, HCFO-1224 isomers, HCFO-1224yd, HCFO-1224yb, HCFO-1233xf, HCFO-1233zd, HFO-1243zf, HFO-1327mz, HFO-1336ft and HCFO-1326mxz; and one or more additional compounds selected from HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb. Performance of such compositions comprising HFO-1234ze(Z), HFO-1336mzz(E) and HFO-1336mzz(Z) is explored in a medium temperature refrigeration system as compared to R-471A. The data are based on the conditions set forth in Table 14. Table 17 tabulates the

performance metrics and properties of several compositions, particularly compositions of optimal cooling efficiency and capacity.

Table 17: Med Temp Refrig conditions, cycle metric performance and fluid property ranges for 1234zeZ/1336mzzE/1336mzzZ in Example 11

wt-frac R1234ze(Z)	wt-frac R1336mzzE	wt-frac R- R1336mzzZ	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP _c (% dev from R- 471A)	CAP _c (% dev from R- 471A)
0.01	0.98	0.01	16	1	0.2	1.7	-56.6
0.98	0.01	0.01	1	2L	0.2	5.6	-57.2
0.01	0.79	0.2	13	1	2.9	2.2	-63.1
0.23	0.01	0.76	2	1	3.5	5.1	-77.7
0.01	0.01	0.98	2	1	0.4	5.2	-82.9
0.31	0.68	0.01	11	1	0.2	3	-53.2
0.32	0.67	0.01	11	1	0.2	3.1	-53.2
0.33	0.66	0.01	11	1	0.2	3.1	-53.2
0.34	0.65	0.01	11	1	0.3	3.2	-53.2
0.02	0.97	0.01	16	1	0.2	1.7	-56.4
0.12	0.39	0.49	7	1	5.9	3.9	-71.1
0.01	0.23	0.76	5	1	4.2	4.1	-78.5
0.35	0.01	0.64	2	1	4.2	5.2	-74.7
0.85	0.14	0.01	3	2L	0.3	5.2	-56.2
0.01	0.21	0.78	5	1	3.9	4.2	-78.9
0.87	0.01	0.12	1	2L	1.6	5.4	-60.6
0.91	0.08	0.01	2	2L	0.3	5.4	-56.7
0.83	0.14	0.03	3	1	0.7	5.2	-56.9
0.01	0.19	0.8	5	1	3.6	4.2	-79.3
0.12	0.01	0.87	2	1	2.3	5	-80.4
0.29	0.7	0.01	12	1	0.2	2.9	-53.2
0.79	0.01	0.2	1	1	2.5	5.4	-63
0.8	0.01	0.19	1	1	2.4	5.4	-62.7
0.81	0.01	0.18	1	1	2.3	5.4	-62.4
0.82	0.01	0.17	1	1	2.2	5.4	-62.1
0.83	0.02	0.15	1	1	2	5.4	-61.5
0.83	0.01	0.16	1	1	2	5.4	-61.8

[0517] Broadly, for cooling mode, a composition range of 1.0% to 98.0% of HFO-1234ze(Z), 1.0% to 98.0% of HFO-1336mzz(E), and 1.0% to 98.0% of HFO-1336mzz(Z) will have a GWP less than 16, a maximum average glide of about 5.9 K, and the cooling COP range has a deviation range from 1.7% to 5.6% than that of the cooling COP of R-471A evaluated with the same conditions set. Table 17 lists

example compositions within the GWP < 16 range that have ASHRAE flammability classifications of 1 and 2L.

[0518] In some embodiments, blend composition ranges for cooling mode within a composition range of 1.0% to 83.0% of HFO-1234ze(Z), 1.0% to 98.0% of HFO-1336mzz(E), and 1.0% to 98.0% of HFO-1336mzz(Z) will have a GWP < 16, a maximum average heat exchanger glide of 5.9 K, an ASHRAE flammability classification of 1, and the minimum and maximum cooling COP efficiencies are 1.7% and 5.4% than that of R-471A evaluated at the same conditions set.

[0519] In one embodiment, at the maximum cooling COP efficiency of 5.4%, the composition comprises 79 wt-% HFO-1234ze(Z), 1 wt-% HFO-1336mzz(E) and 20 wt-% HFO-1336mzz(Z). In addition, the maximum average heat exchanger glide is 2.5 K and its ASHRAE flammability classification is 1.

[0520] It will be understood by those skilled in the art that weight percentages of HFO-1234ze(Z), HFO-1336mzz(E) and HFO-1336mzz(Z) provided for the above compositions are approximate, and the compositions may further comprise one or more of the additional compounds disclosed above.

Example 12

[0521] Refrigerant performance has been determined for some exemplary compositions of the present invention in medium temperature refrigeration systems as compared to R-471A. More particularly, performance of compositions comprising HFO-1234ze(E), HFO-1234ze(Z) and HFC-134 was explored in a medium temperature refrigeration system as compared to R-471A.

[0522] Compositions comprising HFO-1234ze(Z), HFO-1234ze(E) and HFC-134 are prepared. In one embodiment, the compositions comprise up to about 0.5 wt% of one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and

HCFO-1233zd(E); and one or more additional compounds selected from HFC-134a, HCFC-124, HCFC-124a, HCFO-1122, HFC-143a, HCFC-31, HFC-32, HFC-125, CFC-114, CFC-114a, FCO-1114, HFC-152a, FCO-1318my, HFC-245cb, FC-C318, and HC-161. Performance of such compositions comprising HFO-1234ze(Z), HFO-1234ze(E) and HFC-134 is explored in a medium temperature refrigeration system as compared to R-471A. The data are based on the conditions set forth in Table 14. Table 18 tabulates the performance metrics and properties of several compositions, particularly compositions of optimal cooling efficiency and capacity.

Table 18: Med Temp Refrig conditions, cycle metric performance and fluid property ranges for 1234zeE/1234zeZ/134 in Example 12

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-134	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP _c (% dev from R- 471A)	CAP _c (% dev from R-471A)
0.005	0.786	0.209	235	1	6.8	4	-41
0.005	0.915	0.08	90	2L	3.5	5	-51
0.01	0.73	0.26	292	1	7.5	4	-37
0.01	0.86	0.13	146	2L	5.2	4	-47
0.01	0.985	0.005	7	2L	0.5	5	-56
0.02	0.72	0.26	292	1	7.6	4	-36
0.02	0.85	0.13	146	2L	5.3	4	-46
0.03	0.71	0.26	292	1	7.6	4	-36
0.03	0.84	0.13	146	2L	5.5	4	-46
0.04	0.7	0.26	292	1	7.7	4	-35
0.04	0.83	0.13	146	2L	5.6	4	-45
0.05	0.69	0.26	292	1	7.7	4	-34
0.05	0.82	0.13	146	2L	5.7	4	-45
0.06	0.68	0.26	292	1	7.7	4	-34
0.06	0.81	0.13	146	2L	5.9	4	-44
0.07	0.67	0.26	292	1	7.8	4	-33
0.07	0.8	0.13	146	2L	6	4	-44
0.08	0.66	0.26	292	1	7.8	4	-33
0.08	0.79	0.13	146	2L	6.1	4	-43
0.09	0.65	0.26	292	1	7.8	4	-32
0.09	0.78	0.13	146	2L	6.2	4	-42
0.1	0.64	0.26	292	1	7.9	4	-31
0.1	0.77	0.13	146	2L	6.3	4	-42
0.11	0.63	0.26	292	1	7.9	4	-31
0.11	0.76	0.13	146	2L	6.4	4	-41
0.12	0.62	0.26	292	1	7.9	4	-30
0.12	0.75	0.13	146	2L	6.5	4	-41
0.13	0.61	0.26	292	1	7.9	4	-30

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-134	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP _c (% dev from R- 471A)	CAP _c (%) dev from R-471A)
0.13	0.74	0.13	146	2L	6.6	4	-40
0.14	0.6	0.26	292	1	7.9	4	-29
0.14	0.73	0.13	146	2L	6.7	4	-40
0.15	0.59	0.26	292	1	7.9	4	-28
0.15	0.72	0.13	146	2L	6.8	4	-39
0.16	0.58	0.26	292	1	7.9	4	-28
0.16	0.71	0.13	146	2L	6.9	4	-38
0.17	0.57	0.26	292	1	7.9	4	-27
0.17	0.7	0.13	146	2L	6.9	4	-38
0.18	0.56	0.26	292	1	7.9	4	-26
0.18	0.69	0.13	146	2L	7	4	-37
0.19	0.55	0.26	292	1	7.9	4	-26
0.19	0.68	0.13	146	2L	7.1	4	-37
0.2	0.54	0.26	292	1	7.8	3	-25
0.2	0.67	0.13	146	2L	7.1	4	-36
0.21	0.53	0.26	292	1	7.8	3	-24
0.21	0.66	0.13	146	2L	7.2	4	-35
0.22	0.52	0.26	292	1	7.8	3	-24
0.22	0.65	0.13	146	2L	7.2	4	-35
0.23	0.51	0.26	292	1	7.7	3	-23
0.23	0.64	0.13	146	2L	7.3	4	-34
0.24	0.5	0.26	292	1	7.7	3	-22
0.24	0.63	0.13	146	2L	7.3	4	-33
0.25	0.49	0.26	292	1	7.6	3	-22
0.25	0.62	0.13	146	2L	7.3	4	-33
0.26	0.48	0.26	292	1	7.6	3	-21
0.26	0.61	0.13	146	2L	7.4	4	-32
0.27	0.47	0.26	292	1	7.5	3	-20
0.27	0.6	0.13	146	2L	7.4	4	-32
0.28	0.46	0.26	292	1	7.5	3	-20
0.28	0.59	0.13	146	2L	7.4	4	-31
0.29	0.45	0.26	292	1	7.4	3	-19
0.29	0.58	0.13	146	2L	7.4	3	-30
0.3	0.44	0.26	292	1	7.3	3	-18
0.3	0.57	0.13	146	2L	7.4	3	-30
0.31	0.43	0.26	292	1	7.3	3	-17
0.31	0.56	0.13	146	2L	7.4	3	-29
0.32	0.42	0.26	292	1	7.2	3	-17
0.32	0.55	0.13	146	2L	7.4	3	-28
0.33	0.41	0.26	292	1	7.1	3	-16
0.33	0.54	0.13	146	2L	7.4	3	-28
0.34	0.4	0.26	292	1	7	3	-15
0.34	0.53	0.13	146	2L	7.4	3	-27

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-134	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP _c (% dev from R- 471A)	CAP _c (%) dev from R-471A)
0.35	0.39	0.26	292	1	6.9	3	-14
0.35	0.52	0.13	146	2L	7.4	3	-26
0.36	0.38	0.26	292	1	6.8	3	-14
0.36	0.51	0.13	146	2L	7.4	3	-26
0.37	0.37	0.26	292	1	6.7	2	-13
0.37	0.5	0.13	146	2L	7.3	3	-25
0.38	0.36	0.26	292	1	6.6	2	-12
0.38	0.49	0.13	146	2L	7.3	3	-24
0.39	0.35	0.26	292	1	6.5	2	-11
0.39	0.48	0.13	146	2L	7.3	3	-24
0.4	0.34	0.26	292	1	6.4	2	-11
0.4	0.47	0.13	146	2L	7.2	3	-23
0.41	0.33	0.26	292	1	6.2	2	-10
0.41	0.46	0.13	146	2L	7.2	3	-22
0.42	0.32	0.26	292	1	6.1	2	-9
0.42	0.45	0.13	146	2L	7.1	3	-22
0.43	0.31	0.26	292	1	6	2	-8
0.43	0.44	0.13	146	2L	7.1	3	-21
0.44	0.3	0.26	292	1	5.8	2	-7
0.44	0.43	0.13	146	2L	7	3	-20
0.45	0.29	0.26	292	1	5.7	2	-7
0.45	0.42	0.13	146	2L	6.9	3	-19
0.46	0.28	0.26	292	1	5.5	2	-6
0.46	0.41	0.13	146	2L	6.9	3	-19
0.47	0.27	0.26	292	1	5.4	2	-5
0.47	0.4	0.13	146	2L	6.8	3	-18
0.48	0.26	0.26	292	1	5.2	2	-4
0.48	0.39	0.13	146	2L	6.7	2	-17
0.49	0.25	0.26	292	1	5.1	2	-3
0.49	0.38	0.13	146	2L	6.6	2	-16
0.498	0.498	0.005	7	2L	6.6	3	-28
0.5	0.24	0.26	292	1	4.9	2	-2
0.5	0.37	0.13	146	2L	6.5	2	-16
0.51	0.23	0.26	292	1	4.8	2	-1
0.51	0.36	0.13	146	2L	6.4	2	-15
0.52	0.22	0.26	292	1	4.6	2	-1
0.52	0.35	0.13	146	2L	6.3	2	-14
0.53	0.21	0.26	292	1	4.4	1	0
0.53	0.34	0.13	146	2L	6.2	2	-13
0.54	0.2	0.26	292	1	4.2	1	1
0.54	0.33	0.13	146	2L	6.1	2	-13
0.55	0.19	0.26	292	1	4	1	2
0.55	0.32	0.13	146	2L	6	2	-12

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-134	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP _c (% dev from R- 471A)	CAP _c (%) dev from R-471A)
0.56	0.18	0.26	292	1	3.8	1	3
0.56	0.31	0.13	146	2L	5.8	2	-11
0.57	0.17	0.26	292	1	3.7	1	4
0.57	0.3	0.13	146	2L	5.7	2	-10
0.58	0.16	0.26	292	1	3.5	1	5
0.58	0.29	0.13	146	2L	5.6	2	-9
0.59	0.15	0.26	292	1	3.3	1	6
0.59	0.28	0.13	146	2L	5.4	2	-9
0.59	0.29	0.12	135	2L	5.5	2	-10
0.6	0.14	0.26	292	1	3.1	1	7
0.6	0.27	0.13	146	2L	5.3	2	-8
0.61	0.13	0.26	292	1	2.9	1	8
0.61	0.26	0.13	146	2L	5.1	2	-7
0.62	0.12	0.26	292	1	2.7	1	9
0.62	0.25	0.13	146	2L	5	2	-6
0.63	0.11	0.26	292	1	2.4	1	10
0.63	0.24	0.13	146	2L	4.8	2	-5
0.64	0.1	0.26	292	1	2.2	1	11
0.64	0.23	0.13	146	2L	4.7	1	-4
0.65	0.09	0.26	292	1	2	1	12
0.65	0.22	0.13	146	2L	4.5	1	-3
0.66	0.08	0.26	292	1	1.8	1	13
0.66	0.21	0.13	146	2L	4.3	1	-3
0.67	0.07	0.26	292	1	1.6	1	14
0.67	0.2	0.13	146	2L	4.1	1	-2
0.68	0.06	0.26	292	1	1.4	1	15
0.68	0.19	0.13	146	2L	4	1	-1
0.69	0.05	0.26	292	1	1.2	1	16
0.69	0.18	0.13	146	2L	3.8	1	0
0.69	0.27	0.04	46	2L	5.1	2	-10
0.7	0.04	0.26	292	1	0.9	1	17
0.7	0.17	0.13	146	2L	3.6	1	1
0.71	0.03	0.26	292	1	0.7	1	18
0.71	0.16	0.13	146	2L	3.4	1	2
0.72	0.02	0.26	292	1	0.5	1	19
0.72	0.15	0.13	146	2L	3.2	1	3
0.73	0.01	0.26	292	1	0.3	1	20
0.73	0.14	0.13	146	2L	3	1	4
0.736	0.005	0.259	290	1	0.2	1	21
0.74	0.13	0.13	146	2L	2.8	1	5
0.75	0.12	0.13	146	2L	2.6	1	6
0.76	0.11	0.13	146	2L	2.4	1	7
0.77	0.1	0.13	146	2L	2.2	1	8

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-134	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP _c (% dev from R- 471A)	CAP _c (%) dev from R-471A)
0.78	0.09	0.13	146	2L	2	1	9
0.79	0.08	0.13	146	2L	1.8	1	10
0.8	0.07	0.13	146	2L	1.6	1	11
0.81	0.06	0.13	146	2L	1.4	1	12
0.816	0.005	0.179	201	1	0.2	0	19
0.82	0.05	0.13	146	2L	1.2	1	13
0.83	0.04	0.13	146	2L	0.9	1	14
0.84	0.03	0.13	146	2L	0.7	1	15
0.846	0.149	0.005	7	2L	3	1	0
0.85	0.02	0.13	146	2L	0.5	0	16
0.86	0.01	0.13	146	2L	0.3	0	17
0.866	0.005	0.129	146	2L	0.2	0	18
0.876	0.119	0.005	7	2L	2.4	1	3
0.896	0.005	0.1	112	2L	0.2	0	17
0.93	0.05	0.02	23	2L	1	1	10
0.935	0.005	0.06	68	2L	0.2	0	16
0.94	0.05	0.01	12	2L	1	1	10
0.945	0.005	0.05	57	2L	0.2	0	16
0.945	0.05	0.005	7	2L	1	1	10
0.955	0.005	0.04	46	2L	0.1	0	15
0.96	0.01	0.03	35	2L	0.2	0	14
0.965	0.005	0.03	34	2L	0.1	0	15
0.97	0.01	0.02	23	2L	0.2	0	14
0.975	0.005	0.02	23	2L	0.1	0	15
0.98	0.01	0.01	12	2L	0.2	0	14
0.985	0.005	0.01	12	2L	0.1	0	14
0.985	0.01	0.005	7	2L	0.2	0	14

[0523] Broadly, for cooling mode, a composition range of 0.5% to 98.5% of HFO-1234ze(E), 0.5% to 98.5% of HFO-1234ze(Z), and 0.5% to 26.0% of HFC-134 will have a GWP less than 300, a maximum average glide of about 7.9 K, a cooling capacity range that has a deviation range of -56% to 21% from the cooling capacity of R-471A evaluated with the same conditions set, and the cooling COP range has a deviation range from 0% to 5% than that of the cooling COP of R-471A evaluated with the same conditions set. Table 19 lists example compositions within the GWP < 300 range that have ASHRAE flammability classifications of 1 and 2L.

[0524] In some embodiments, for cooling mode, a composition range of 0.5% to 98.5% of HFO-1234ze(E), 0.5% to 98.5% of HFO-1234ze(Z), and 0.5% to 13.0% of

HFC-134 will have a GWP less than 150, a maximum average glide of about 7.4 K, an ASHRAE flammability classification of 2L, a cooling capacity range has a deviation of -56% to 18% from the cooling capacity of R-471A evaluated with the same conditions set, and the cooling COP range has a deviation of 0% to 5% than that of the cooling COP of R-471A evaluated with the same conditions set.

[0525] In some embodiments, blend composition ranges for cooling mode within a composition range of 58.0% to 94.5% of HFO-1234ze(E), 5.0% to 29.0% of HFO-1234ze(Z), and 0.5% to 13.0% of HFC-134 will have a GWP < 150, a maximum average heat exchanger glide of 5.6 K, an ASHRAE flammability classification of 2L, the minimum and maximum cooling capacities are -10% and 10% than that of R-471A evaluated at the same conditions set, and the minimum and maximum cooling COP efficiencies are 1% and 2% than that of R-471A evaluated at the same conditions set.

[0526] In some embodiments, blend composition ranges for cooling mode within a composition range of 58.0% to 94.5% of HFO-1234ze(E), 5.0% to 29.0% of HFO-1234ze(Z), and 0.5% to 13.0% of HFC-134 will have a GWP < 150, a maximum average heat exchanger glide of 5.6 K, an ASHRAE flammability classification of 2L, the minimum and maximum cooling capacities are -10% and 10% than that of R-471A evaluated at the same conditions set, and the minimum and maximum cooling COP efficiencies are 1% and 2% than that of R-471A evaluated at the same conditions set.

[0527] In one embodiment, at the maximum cooling capacity of 10%, the composition comprises about 93 wt-% HFO-1234ze(E), about 5 wt-% HFO-1234ze(Z) and about 2 wt-% HFC-134, where the COP for cooling is 1% than that for R-471A under the same cycle conditions, the maximum average heat exchanger glide is 1.0 K and its ASHRAE flammability classification is 2L.

[0528] In one embodiment, at the maximum cooling COP efficiency of 2%, the composition comprises 58 wt-% HFO-1234ze(E), 29 wt-% HFO-1234ze(Z) and 13 wt-% HFC-134, and the maximum average heat exchanger glide is 5.6 K and its ASHRAE flammability classification is 2L.

Example 13

[0529] Refrigerant performance has been determined for some exemplary compositions of the present invention in medium temperature refrigeration systems as compared to R-471A. More particularly, performance of compositions comprising HFO-1234ze(E), HFO-1234ze(Z) and HFO-1336mzz(E) was explored in a medium temperature refrigeration system as compared to R-471A.

[0530] Compositions comprising HFO-1234ze(E), HFO-1234ze(Z) and HFO-1336mzz(E) are prepared. In one embodiment, the compositions comprise up to about 0.5 wt% of one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from C-30, HCFC-114, HCFC-114a, HCFC-133, HCFC-133a, HFC-245fa, HFC-338mee, HFC-338mf, HFC-347mef, HCO-1140, HCFO-1224 isomers, HCFO-1224yd, HCFO-1224yb, HCFO-1233xf, HCFO-1233zd, HFO-1243zf, HFO-1327mz, HFO-1336ft and HCFO-1326mxz. Performance of such compositions comprising HFO-1234ze(Z), HFO-1234ze(E) and HFC-134 is explored in a medium temperature refrigeration system as compared to R-471A. The data are based on the conditions set forth in Table 14. Table 19 tabulates the performance metrics and properties of several compositions, particularly compositions of optimal cooling efficiency and capacity.

Table 19: Med Temp Refrig conditions, cycle metric performance and fluid property ranges for 1234zeE/1234zeZ/1336mzzE in Example 13

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-1336mzzE	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP _c (% dev from R- 471A)	CAP _c (% dev from R- 471A)
0.01	0.01	0.98	16	1	0.3	2	-56
0.98	0.01	0.01	1	2L	0.4	0	13
0.01	0.85	0.14	3	2L	0.4	5	-55
0.01	0.98	0.01	1	2L	0.3	6	-56
0.33	0.01	0.66	11	1	4.7	1	-35

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-1336mzzE	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP _c (% dev from R- 471A)	CAP _c (% dev from R- 471A)
0.06	0.93	0.01	1	2L	1.6	5	-54
0.71	0.01	0.28	5	1	3.7	0	-9
0.72	0.01	0.27	5	1	3.6	0	-8
0.73	0.01	0.26	5	1	3.5	0	-7
0.74	0.01	0.25	5	1	3.4	0	-7
0.75	0.01	0.24	5	1	3.3	0	-6
0.76	0.01	0.23	4	1	3.2	0	-5
0.77	0.01	0.22	4	1	3.1	0	-4
0.78	0.01	0.21	4	1	3	0	-3
0.79	0.01	0.2	4	1	2.9	0	-3
0.8	0.01	0.19	4	1	2.8	0	-2
0.81	0.01	0.18	4	1	2.7	0	-1
0.82	0.01	0.17	4	1	2.6	0	0
0.83	0.01	0.16	3	2L	2.4	0	0
0.84	0.01	0.15	3	2L	2.3	0	1
0.85	0.01	0.14	3	2L	2.2	0	2
0.86	0.01	0.13	3	2L	2.1	0	3
0.87	0.01	0.12	3	2L	1.9	0	4
0.88	0.01	0.11	3	2L	1.8	0	4
0.48	0.51	0.01	1	2L	6.5	3	-29
0.01	0.79	0.2	4	1	0.5	5	-55
0.91	0.01	0.08	2	2L	1.4	0	7
0.7	0.01	0.29	5	1	3.8	0	-10
0.95	0.02	0.03	1	2L	0.9	0	10
0.7	0.1	0.2	4	1	3.8	1	-10
0.74	0.25	0.01	1	2L	4.7	2	-10
0.79	0.2	0.01	1	2L	3.9	1	-6
0.71	0.15	0.14	3	2L	4	1	-10
0.95	0.04	0.01	1	2L	1	0	10
0.75	0.24	0.01	1	2L	4.5	1	-9

[0531] Broadly, for cooling mode, a composition range of 1.0% to 98.0% of HFO-1234ze(E), 1.0% to 98.0% of HFO-1234ze(Z), and 1.0% to 98.0% of HFO-1336mzz(E) will have a GWP less than 16, a maximum average glide of about 6.5 K, a cooling capacity range that has a deviation range of -56% to 13% from the cooling capacity of R-471A evaluated with the same conditions set, and the cooling COP range has a deviation range from 0% to 6% than that of the cooling COP of R-471A evaluated with the same conditions set. Table 19 lists example compositions within the GWP < 16 range that have ASHRAE flammability classifications of 1 and 2L.

[0532] In some embodiments, for cooling mode, a composition range of 1.0% to 98.0% of HFO-1234ze(E), 1.0% to 98.0% of HFO-1234ze(Z), and 1.0% to 26.0% of HFO-1336mzz(E) will have a GWP less than 5, a maximum average glide of about 6.5 K, an ASHRAE flammability classification of 1 and 2L, a cooling capacity range has a deviation of -56% to 13% from the cooling capacity of R-471A evaluated with the same conditions set, and the cooling COP range has a deviation of 0% to 6% than that of the cooling COP of R-471A evaluated with the same conditions set.

[0533] In some embodiments, blend composition ranges for cooling mode within a composition range of 70.0% to 95.0% of HFO-1234ze(E), 1.0% to 25.0% of HFO-1234ze(Z), and 1.0% to 26.0% of HFO-1336mzz(E) will have a GWP < 5, a maximum average heat exchanger glide of 4.7 K, an ASHRAE flammability classification of 1 and 2L, the minimum and maximum cooling capacities are -10% and 10% than that of R-471A evaluated at the same conditions set, and the minimum and maximum cooling COP efficiencies are 0% and 2% than that of R-471A evaluated at the same conditions set.

[0534] In some embodiments, blend composition ranges for cooling mode within a composition range of 70.0% to 82.0% of HFO-1234ze(E), 1.0% to 12.0% of HFO-1234ze(Z), and 17.0% to 26.0% of HFO-1336mzz(E) will have a GWP < 5, a maximum average heat exchanger glide of 3.8 K, an ASHRAE flammability classification of 1, the minimum and maximum cooling capacities are -10% and -0% than that of R-471A evaluated at the same conditions set, and the minimum and maximum cooling COP efficiencies are 0% and 1% than that of R-471A evaluated at the same conditions set.

[0535] In one embodiment, at the maximum cooling capacity of 0%, the composition comprises 82 wt-% HFO-1234ze(E), 1 wt-% HFO-1234ze(Z) and 17 wt-% HFO-1336mzz(E), where the COP for cooling is 0% than that for R-471A under the same cycle conditions, the maximum average heat exchanger glide is 2.6 K and its ASHRAE flammability classification is 1.

[0536] In one embodiment, at the maximum cooling COP efficiency of 1%, the composition comprises 71 wt-% HFO-1234ze(E), 12 wt-% HFO-1234ze(Z) and 17 wt-% HFO-1336mzz(E), and the maximum average heat exchanger glide is 3.8 K and its ASHRAE flammability classification is 1.

Example 14

[0537] Refrigerant performance has been determined for some exemplary compositions of the present invention in medium temperature refrigeration systems as compared to R-471A. More particularly, performance of compositions comprising HFO-1234ze(E), HFO-1234ze(Z) and HFC-134a was explored in a medium temperature refrigeration system as compared to R-471A.

[0538] Compositions comprising HFO-1234ze(Z), HFO-1234ze(E) and HFC-134a are prepared. In one embodiment, the compositions comprise up to about 0.5 wt% of one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from HFC-143a, HFO-1225zc, HFC-245cb, HFC-134, HFC-152a, HFO-1225ye, HFC-161, E-HFO-1234ze, HCFC-22, HFO-1243zf, CHFC-124, HCC-40, CHFO-1122, HCFC-31, CFC-114, CFC-114a and HCO-1140. Performance of such compositions comprising HFO-1234ze(Z), HFO-1234ze(E) and HFC-134a is explored in a medium temperature refrigeration system as compared to R-471A. The data are based on the conditions set forth in Table 14. Table 20 tabulates the performance metrics and properties of several compositions, particularly compositions of optimal cooling efficiency and capacity.

Table 20: Med Temp Refrig conditions, cycle metric performance and fluid property ranges for 1234zeE/1234zeZ/134a in Example 14

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-R134a	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP_c (% dev from R- 471A)	CAP_c (% dev from R- 471A)
0.01	0.76	0.23	300	1	6.8	3.9	-40.6
0.02	0.75	0.23	300	1	6.9	3.8	-40
0.03	0.74	0.23	300	1	7.1	3.8	-39.3
0.04	0.73	0.23	300	1	7.2	3.8	-38.7

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-R134a	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP_c (% dev from R- 471A)	CAP_c (% dev from R- 471A)
0.05	0.72	0.23	300	1	7.3	3.7	-38.1
0.06	0.71	0.23	300	1	7.4	3.7	-37.4
0.07	0.7	0.23	300	1	7.5	3.7	-36.8
0.08	0.69	0.23	300	1	7.6	3.7	-36.1
0.09	0.68	0.23	300	1	7.7	3.7	-35.5
0.1	0.67	0.23	300	1	7.8	3.6	-34.8
0.11	0.66	0.23	300	1	7.9	3.6	-34.2
0.12	0.65	0.23	300	1	8	3.6	-33.5
0.13	0.64	0.23	300	1	8.1	3.5	-32.8
0.14	0.63	0.23	300	1	8.1	3.5	-32.1
0.15	0.62	0.23	300	1	8.2	3.4	-31.4
0.16	0.61	0.23	300	1	8.2	3.4	-30.8
0.17	0.6	0.23	300	1	8.3	3.4	-30.1
0.18	0.59	0.23	300	1	8.3	3.3	-29.4
0.19	0.58	0.23	300	1	8.4	3.3	-28.7
0.2	0.57	0.23	300	1	8.4	3.2	-28
0.21	0.56	0.23	300	1	8.4	3.2	-27.3
0.22	0.55	0.23	300	1	8.4	3.2	-26.5
0.23	0.54	0.23	300	1	8.5	3.1	-25.8
0.24	0.53	0.23	300	1	8.5	3.1	-25.1
0.25	0.52	0.23	300	1	8.5	3	-24.4
0.26	0.51	0.23	300	1	8.5	3	-23.6
0.27	0.5	0.23	300	1	8.5	2.9	-22.9
0.28	0.49	0.23	300	1	8.5	2.9	-22.1
0.29	0.48	0.23	300	1	8.4	2.8	-21.4
0.3	0.47	0.23	300	1	8.4	2.8	-20.6
0.31	0.46	0.23	300	1	8.4	2.7	-19.9
0.32	0.45	0.23	300	1	8.3	2.6	-19.1
0.33	0.44	0.23	300	1	8.3	2.6	-18.3
0.34	0.43	0.23	300	1	8.2	2.6	-17.5
0.35	0.42	0.23	300	1	8.2	2.5	-16.7
0.36	0.41	0.23	300	1	8.1	2.4	-15.9
0.37	0.4	0.23	300	1	8	2.3	-15.2
0.38	0.39	0.23	300	1	8	2.3	-14.3
0.39	0.38	0.23	300	1	7.9	2.2	-13.5
0.4	0.37	0.23	300	1	7.8	2.1	-12.7
0.41	0.36	0.23	300	1	7.7	2.1	-11.9
0.42	0.35	0.23	300	1	7.6	2	-11
0.43	0.34	0.23	300	1	7.5	1.9	-10.2
0.44	0.33	0.23	300	1	7.4	1.9	-9.3
0.45	0.32	0.23	300	1	7.3	1.8	-8.5
0.46	0.31	0.23	300	1	7.2	1.7	-7.6
0.47	0.3	0.23	300	1	7	1.6	-6.7

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-R134a	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP_c (% dev from R- 471A)	CAP_c (% dev from R- 471A)
0.48	0.29	0.23	300	1	6.9	1.6	-5.8
0.49	0.28	0.23	300	1	6.7	1.5	-4.9
0.5	0.27	0.23	300	1	6.6	1.4	-4
0.51	0.26	0.23	300	1	6.4	1.3	-3.1
0.52	0.25	0.23	300	1	6.3	1.3	-2.1
0.53	0.24	0.23	300	1	6.1	1.2	-1.2
0.54	0.23	0.23	300	1	5.9	1.1	-0.2
0.55	0.22	0.23	300	1	5.7	1	0.7
0.56	0.21	0.23	300	1	5.6	1	1.7
0.57	0.2	0.23	300	1	5.4	0.9	2.7
0.58	0.19	0.23	300	1	5.2	0.8	3.7
0.59	0.18	0.23	300	1	5	0.8	4.8
0.6	0.17	0.23	300	1	4.8	0.7	5.8
0.61	0.16	0.23	300	1	4.5	0.6	6.8
0.62	0.15	0.23	300	1	4.3	0.6	7.9
0.63	0.14	0.23	300	1	4.1	0.5	9
0.64	0.13	0.23	300	1	3.9	0.4	10.1
0.65	0.12	0.23	300	1	3.6	0.4	11.2
0.66	0.11	0.23	300	1	3.4	0.4	12.3
0.67	0.1	0.23	300	1	3.1	0.3	13.5
0.68	0.09	0.23	300	1	2.9	0.3	14.6
0.69	0.08	0.23	300	1	2.6	0.2	15.8
0.7	0.07	0.23	300	1	2.4	0.2	17
0.71	0.06	0.23	300	1	2.1	0.1	18.2
0.72	0.05	0.23	300	1	1.9	0.1	19.4
0.73	0.04	0.23	300	1	1.6	0	20.6
0.74	0.03	0.23	300	1	1.3	0	21.9
0.75	0.02	0.23	300	1	1.1	0	23.1
0.76	0.01	0.23	300	1	0.8	-0.1	24.4
0.98	0.01	0.01	14	2L	0.2	0.3	14
0.01	0.98	0.01	14	2L	0.6	5.4	-55.8
0.95	0.01	0.04	53	2L	0.4	0.3	15.5
0.32	0.67	0.01	14	2L	6.1	3.7	-38.8
0.77	0.01	0.22	287	1	0.8	-0.1	23.9
0.01	0.88	0.11	144	2L	3.9	4.4	-49.4
0.02	0.87	0.11	144	2L	4.1	4.3	-48.8
0.03	0.86	0.11	144	2L	4.3	4.3	-48.3
0.04	0.85	0.11	144	2L	4.5	4.3	-47.7
0.05	0.84	0.11	144	2L	4.7	4.2	-47.1
0.06	0.83	0.11	144	2L	4.8	4.2	-46.6
0.07	0.82	0.11	144	2L	5	4.2	-46
0.08	0.81	0.11	144	2L	5.2	4.1	-45.4
0.09	0.8	0.11	144	2L	5.3	4.1	-44.8

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-R134a	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP_c (% dev from R- 471A)	CAP_c (% dev from R- 471A)
0.1	0.79	0.11	144	2L	5.5	4	-44.3
0.11	0.78	0.11	144	2L	5.6	4	-43.7
0.12	0.77	0.11	144	2L	5.8	4	-43.1
0.13	0.76	0.11	144	2L	5.9	3.9	-42.5
0.14	0.75	0.11	144	2L	6.1	3.9	-41.9
0.15	0.74	0.11	144	2L	6.2	3.9	-41.3
0.16	0.73	0.11	144	2L	6.3	3.8	-40.7
0.17	0.72	0.11	144	2L	6.4	3.8	-40
0.18	0.71	0.11	144	2L	6.6	3.8	-39.4
0.19	0.7	0.11	144	2L	6.7	3.7	-38.8
0.2	0.69	0.11	144	2L	6.8	3.7	-38.2
0.21	0.68	0.11	144	2L	6.9	3.7	-37.6
0.22	0.67	0.11	144	2L	6.9	3.7	-36.9
0.23	0.66	0.11	144	2L	7	3.6	-36.3
0.24	0.65	0.11	144	2L	7.1	3.6	-35.6
0.25	0.64	0.11	144	2L	7.2	3.6	-35
0.26	0.63	0.11	144	2L	7.2	3.5	-34.3
0.27	0.62	0.11	144	2L	7.3	3.5	-33.7
0.28	0.61	0.11	144	2L	7.4	3.4	-33
0.29	0.6	0.11	144	2L	7.4	3.4	-32.4
0.3	0.59	0.11	144	2L	7.5	3.4	-31.7
0.31	0.58	0.11	144	2L	7.5	3.3	-31
0.32	0.57	0.11	144	2L	7.5	3.3	-30.3
0.33	0.56	0.11	144	2L	7.6	3.2	-29.7
0.34	0.55	0.11	144	2L	7.6	3.2	-29
0.35	0.54	0.11	144	2L	7.6	3.2	-28.3
0.36	0.53	0.11	144	2L	7.6	3.1	-27.6
0.37	0.52	0.11	144	2L	7.6	3.1	-26.9
0.38	0.51	0.11	144	2L	7.6	3	-26.2
0.39	0.5	0.11	144	2L	7.6	3	-25.5
0.4	0.49	0.11	144	2L	7.6	2.9	-24.8
0.41	0.48	0.11	144	2L	7.6	2.9	-24.1
0.42	0.47	0.11	144	2L	7.5	2.8	-23.3
0.43	0.46	0.11	144	2L	7.5	2.7	-22.6
0.44	0.45	0.11	144	2L	7.5	2.7	-21.9
0.45	0.44	0.11	144	2L	7.4	2.6	-21.1
0.46	0.43	0.11	144	2L	7.4	2.6	-20.4
0.47	0.42	0.11	144	2L	7.3	2.5	-19.6
0.48	0.41	0.11	144	2L	7.3	2.5	-18.9
0.49	0.4	0.11	144	2L	7.2	2.4	-18.1
0.5	0.39	0.11	144	2L	7.1	2.3	-17.3
0.51	0.38	0.11	144	2L	7	2.3	-16.6
0.52	0.37	0.11	144	2L	7	2.2	-15.8

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-R134a	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP_c (% dev from R- 471A)	CAP_c (% dev from R- 471A)
0.53	0.36	0.11	144	2L	6.9	2.1	-15
0.54	0.35	0.11	144	2L	6.8	2.1	-14.2
0.55	0.34	0.11	144	2L	6.7	2	-13.4
0.56	0.33	0.11	144	2L	6.6	1.9	-12.6
0.57	0.32	0.11	144	2L	6.4	1.9	-11.7
0.58	0.31	0.11	144	2L	6.3	1.8	-10.9
0.59	0.3	0.11	144	2L	6.2	1.7	-10.1
0.6	0.29	0.11	144	2L	6.1	1.6	-9.2
0.61	0.28	0.11	144	2L	5.9	1.6	-8.4
0.62	0.27	0.11	144	2L	5.8	1.5	-7.5
0.63	0.26	0.11	144	2L	5.7	1.5	-6.6
0.64	0.25	0.11	144	2L	5.5	1.4	-5.7
0.65	0.24	0.11	144	2L	5.3	1.3	-4.8
0.66	0.23	0.11	144	2L	5.2	1.2	-3.9
0.67	0.22	0.11	144	2L	5	1.2	-3
0.68	0.21	0.11	144	2L	4.8	1.1	-2.1
0.69	0.2	0.11	144	2L	4.7	1	-1.2
0.7	0.19	0.11	144	2L	4.5	1	-0.2
0.71	0.18	0.11	144	2L	4.3	0.9	0.8
0.72	0.17	0.11	144	2L	4.1	0.9	1.7
0.73	0.16	0.11	144	2L	3.9	0.8	2.7
0.74	0.15	0.11	144	2L	3.7	0.7	3.7
0.75	0.14	0.11	144	2L	3.5	0.7	4.7
0.76	0.13	0.11	144	2L	3.3	0.6	5.7
0.77	0.12	0.11	144	2L	3.1	0.6	6.8
0.78	0.11	0.11	144	2L	2.9	0.5	7.8
0.79	0.1	0.11	144	2L	2.6	0.5	8.9
0.8	0.09	0.11	144	2L	2.4	0.4	10
0.81	0.08	0.11	144	2L	2.2	0.4	11
0.82	0.07	0.11	144	2L	2	0.4	12.1
0.83	0.06	0.11	144	2L	1.7	0.3	13.2
0.84	0.05	0.11	144	2L	1.5	0.3	14.3
0.85	0.04	0.11	144	2L	1.3	0.3	15.5
0.86	0.03	0.11	144	2L	1	0.2	16.6
0.87	0.02	0.11	144	2L	0.8	0.2	17.7
0.88	0.01	0.11	144	2L	0.6	0.1	18.9
0.01	0.97	0.02	27	2L	1	5.3	-55.2
0.96	0.01	0.03	40	2L	0.3	0.3	15
0.69	0.3	0.01	14	2L	5.4	1.8	-13.1
0.94	0.05	0.01	14	2L	1.1	0.5	9.9
0.8	0.19	0.01	14	2L	3.8	1.1	-3.7
0.66	0.28	0.06	79	2L	5.6	1.6	-9.9
0.62	0.29	0.09	118	2L	5.9	1.7	-9.8

wt-frac R1234ze(E)	wt-frac R1234ze(Z)	wt-frac R-R134a	GWP AR5	ASHRAE flamma- bility class	Glide (K)	COP _c (% dev from R- 471A)	CAP _c (% dev from R- 471A)
0.84	0.08	0.08	105	2L	2.1	0.4	9.8
0.61	0.29	0.1	131	2L	6	1.6	-9.5
0.79	0.2	0.01	14	2L	3.9	1.2	-4.6

[0539] Broadly, for cooling mode, a composition range of 1.0% to 98.0% of HFO-1234ze(E), 1.0% to 98.0% of HFO-1234ze(Z), and 1.0% to 23.0% of HFC-134a will have a GWP less than 300, a maximum average glide of about 8.5 K, a cooling capacity range that has a deviation range of -55.8% to 24.4% from the cooling capacity of R-471A evaluated with the same conditions set, and the cooling COP range has a deviation range from -0.1% to 5.4% than that of the cooling COP of R-471A evaluated with the same conditions set. Table 20 lists example compositions within the GWP < 300 range that have ASHRAE flammability classifications of 2L.

[0540] In some embodiments, for cooling mode, a composition range of 1.0% to 98.0% of HFO-1234ze(E), 1.0% to 98.0% of HFO-1234ze(Z), and 1.0% to 11.0% of HFC-134a will have a GWP less than 144, a maximum average glide of about 7.6 K, an ASHRAE flammability classification of 2L, a cooling capacity range has a deviation of -55.8% to 18.9% from the cooling capacity of R-471A evaluated with the same conditions set, and the cooling COP range has a deviation of 0.1% to 5.4% than that of the cooling COP of R-471A evaluated with the same conditions set.

[0541] In some embodiments, blend composition ranges for cooling mode within a composition range of 60.0% to 94.0% of HFO-1234ze(E), 5.0% to 29.0% of HFO-1234ze(Z), and 1.0% to 11.0% of HFC-134a will have a GWP < 144, a maximum average heat exchanger glide of 6.1 K, an ASHRAE flammability classification of 2L, the minimum and maximum cooling capacities are -9.9% and 10.0% than that of R-471A evaluated at the same conditions set, and the minimum and maximum cooling COP efficiencies are 0.4% and 1.7% than that of R-471A evaluated at the same conditions set.

[0542] In one embodiment, at a maximum cooling capacity of 10.0%, the composition comprises 80 wt-% HFO-1234ze(E), 9 wt-% HFO-1234ze(Z) and 11 wt-% HFC-134a, where the COP for cooling is 0.4% than that for R-471A under

the same cycle conditions, the maximum average heat exchanger glide is 2.4 K and its ASHRAE flammability classification is 2L.

[0543] In one embodiment, at a maximum cooling COP efficiency of 1.7%, the composition comprises 62 wt-% HFO-1234ze(E), 29 wt-% HFO-1234ze(Z) and 9 wt-% HFC-134a, and the maximum average heat exchanger glide is 5.9 K and its ASHRAE flammability classification is 2L.

Example 15

[0544] Compositions comprising HFO-1234ze(Z), HFO-1234ze(E), HFO-1336mzz(E) and HFO-1336mzz(Z) are prepared. In one embodiment, the compositions comprise up to about 0.5 wt% of one or more additional compounds selected from HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb; one more additional compounds selected from C-30, HCFC-114, HCFC-114a, HCFC-133, HCFC-133a, HFC-245fa, HFC-338mee, HFC-338mf, HFC-347mef, HCO-1140, HCFO-1224 isomers, HCFO-1224yd, HCFO-1224yb, HCFO-1233xf, HCFO-1233zd, HFO-1243zf, HFO-1327mz, HFO-1336ft and HCFO-1326mxz; one or more additional compounds selected from HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb; and one or more additional compounds selected from HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E). Performance of such compositions comprising HFO-1234ze(Z), HFO-1234ze(E), HFO-1336mzz(E) and HFO-1336mzz(Z) is explored in a medium temperature refrigeration system as compared to R-471A. The data are based on the conditions set forth in Table 14. Table 21 tabulates the performance metrics and properties of several compositions, particularly compositions of optimal cooling efficiency and capacity.

Table 21: Med Temp Refrig conditions, cycle metric performance and fluid property ranges for 1234zeZ/1336mzzE/1336mzzZ in Example 15

wt-frac R1234ze (E)	wt-frac R1234ze (Z)	wt-frac R- R1336mzz (E)	wt-frac R- R1336mzz (Z)	GWP AR5	ASHRAE flam- mability class	Glide (K)	COP _c (% dev from R- 471A)	CAP _c (% dev from R- 471A)
0.01	0.01	0.97	0.01	16	1	0.4	1.6	-56.1
0.97	0.01	0.01	0.01	1	2L	1.2	0.1	10.3
0.01	0.08	0.57	0.34	10	1	5.5	3.1	-66.4
0.01	0.97	0.01	0.01	1	2L	0.4	5.5	-56.7
0.19	0.01	0.38	0.42	7	1	11.8	2.4	-61.3
0.1	0.62	0.01	0.27	1	1	6.6	4.2	-60.7
0.01	0.01	0.01	0.97	2	1	1.5	4.6	-82.4
0.07	0.41	0.51	0.01	9	1	1.7	3.2	-50
0.04	0.4	0.4	0.16	7	1	3.8	-15.8	-66.2
0.45	0.01	0.01	0.53	2	1	19.2	3.9	-52.3
0.01	0.43	0.53	0.03	9	1	1	3.5	-53.9
0.29	0.01	0.09	0.61	3	1	16.6	3.3	-62.5
0.6	0.1	0.01	0.29	1	1	15.4	2.1	-36.1
0.65	0.18	0.16	0.01	3	1	5	1.2	-15.3
0.71	0.01	0.27	0.01	5	1	4.2	0.2	-9.7
0.71	0.05	0.23	0.01	4	1	4.1	0.4	-9.8
0.75	0.23	0.01	0.01	1	2L	5	1.3	-9.9
0.76	0.01	0.19	0.04	4	1	5.2	0	-9.1
0.88	0.02	0.01	0.09	1	2L	6.8	-0.5	-6.4
0.87	0.01	0.01	0.11	1	2L	7.9	-0.6	-8.8
0.74	0.11	0.14	0.01	3	2L	4.1	0.7	-8.4
0.74	0.2	0.05	0.01	2	2L	4.8	1.2	-10
0.8	0.06	0.07	0.07	2	2L	6.6	0	-10
0.88	0.01	0.01	0.1	1	2L	7.3	-0.6	-7.2
0.89	0.01	0.01	0.09	1	2L	6.7	-0.6	-5.6
0.9	0.01	0.01	0.08	1	2L	6.1	-0.6	-3.8
0.86	0.02	0.01	0.11	1	2L	8	-0.5	-9.6
0.82	0.01	0.09	0.08	2	1	6.7	-0.3	-9.1
0.71	0.02	0.26	0.01	5	1	4.1	0.2	-9.7
0.72	0.11	0.16	0.01	3	1	4.2	0.8	-9.7
0.8	0.01	0.17	0.02	4	1	3.8	0	-4.1
0.81	0.02	0.09	0.08	2	1	6.8	-0.3	-9.8
0.81	0.01	0.1	0.08	3	1	6.8	-0.3	-9.7
0.76	0.03	0.2	0.01	4	1	3.7	0.3	-6.1
0.82	0.01	0.16	0.01	3	1	3.1	0.1	-1.5
0.75	0.04	0.17	0.04	4	1	5.3	0.1	-10

[0545] Broadly, for cooling mode, a composition range of 1.0% to 97.0% of HFO-1234ze(E), 1.0% to 97.0% of HFO-1234ze(Z), 1.0% to 97.0% of HFO-1336mzz(E),

and 1.0% to 97.0% of HFO-1336mzz(Z) will have a GWP less than 16, a maximum average glide of about 19.2 K, a cooling capacity range that has a deviation range of -82.4% to 10.3% from the cooling capacity of R-471A evaluated with the same conditions set, and the cooling COP range has a deviation range from -15.8% to 5.5% than that of the cooling COP of R-471A evaluated with the same conditions set. Table 21 lists example compositions within the GWP < 16 range that have ASHRAE flammability classifications of 1 and 2L.

[0546] In some embodiments, blend composition ranges for cooling mode within a composition range of 71.0% to 97.0% of HFO-1234ze(E), 1.0% to 23.0% of HFO-1234ze(Z), 1.0% to 27.0% of HFO-1336mzz(E), and 1.0% to 11.0% of HFO-1336mzz(Z) will have a GWP < 16, a maximum average heat exchanger glide of 8.0 K, an ASHRAE flammability classification of 1 and 2L, the minimum and maximum cooling capacities are -10.0% and 10.3% than that of R-471A evaluated at the same conditions set, and the minimum and maximum cooling COP efficiencies are -0.6% and 1.3% than that of R-471A evaluated at the same conditions set.

[0547] In one embodiment, at a maximum cooling capacity of 10.3%, the composition comprises 97 wt-% HFO-1234ze(E), 1 wt-% HFO-1234ze(Z), 1 wt-% HFO-1336mzz(E) and 1 wt-% HFO-1336mzz(Z). In addition, the COP for cooling is 0.1% than that for R-471A under the same cycle conditions, the maximum average heat exchanger glide is 1.2 K and its ASHRAE flammability classification is 2L.

[0548] In one embodiment, at a maximum cooling COP efficiency of 1.3%, the composition comprises 75 wt-% HFO-1234ze(E), 23 wt-% HFO-1234ze(Z), 1 wt-% HFO-1336mzz(E), and 1 wt-% HFO-1336mzz(Z). In addition, the maximum average heat exchanger glide is 5.0 K and its ASHRAE flammability classification is 2L.

[0549] In some embodiments, blend composition ranges for cooling mode within a composition range of 71.0% to 82.0% of HFO-1234ze(E), 1.0% to 11.0% of HFO-1234ze(Z), 9.0% to 27.0% of HFO-1336mzz(E), and 1.0% to 8.0% of HFO-1336mzz(Z) will have a GWP < 16, a maximum average heat exchanger glide of 6.8 K, an ASHRAE flammability classification of 1, and the minimum and maximum cooling COP efficiencies are -0.3% and 0.8% than that of R-471A evaluated at the same conditions set.

[0550] In one embodiment, at a maximum cooling COP efficiency of 0.8%, the composition comprises 72 wt-% HFO-1234ze(E), 11 wt-% HFO-1234ze(Z), 16 wt-% HFO-1336mzz(E), and 1 wt-% HFO-1336mzz(Z), and the maximum average heat exchanger glide is 4.2 K and its ASHRAE flammability classification is 1.

CLAIMS OF THE INVENTION

What is claimed is:

1. A process of preparing a mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene, the process comprising:
 - (i) reacting vinyl chloride ($\text{CH}_2=\text{CHCl}$) and carbon tetrachloride (CCl_4) in the presence of catalyst system comprising a metal-containing compound and a phosphorus-containing compound to make a product comprising 1,1,1,3,3-pentachloropropane ($\text{CCl}_3\text{CH}_2\text{CHCl}_2$, HCC-240fa);
 - (ii) fluorinating the HCC-240fa with a fluorination agent in the presence of a fluorination catalyst to produce a product comprising 1,1,1,3,3-pentafluoropropane ($\text{CF}_3\text{CH}_2\text{CHF}_2$, HFC-245fa); and
 - (iii) contacting HFC-245fa in the gas phase with a catalyst, in the presence of an oxygen containing gas, to form a reaction mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene.
2. A process of preparing a mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene, the process comprising:
 - (i) reacting vinyl chloride ($\text{CH}_2=\text{CHCl}$) and carbon tetrachloride (CCl_4) in the presence of catalyst system comprising a metal-containing compound and a phosphorus-containing compound to make a product comprising 1,1,1,3,3-pentachloropropane ($\text{CCl}_3\text{CH}_2\text{CHCl}_2$, HCC-240fa);
 - (ii) fluorinating the HCC-240fa with a fluorination agent in the presence of a fluorination catalyst to produce a product comprising ($\text{CF}_3\text{CH}=\text{CHCl}$, E/Z-HFO-1233zd); and
 - (iii) fluorinating the HFO-1233zd with a fluorination agent in the presence of a fluorination catalyst to form a reaction mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene.
3. A process of preparing a mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene, the process comprising:
 - (i) reacting vinyl chloride ($\text{CH}_2=\text{CHCl}$) and carbon tetrachloride (CCl_4) in the presence of catalyst system comprising a metal-containing compound

- and a phosphorus-containing compound to make a product comprising 1,1,1,3,3-pentachloropropane ($\text{CCl}_3\text{CH}_2\text{CHCl}_2$, HCC-240fa); and
- (ii) fluorinating the HCC-240fa with a fluorination agent in the presence of a fluorination catalyst to form a reaction mixture comprising Z-1,3,3,3-tetrafluoropropene and E-1,3,3,3-tetrafluoropropene.
4. The process of claim 2, wherein the (ii) fluorination of the HCC-240fa with a fluorination agent is conducted in the vapor phase in the presence of a fluorination catalyst.
 5. The process of claim 2, wherein the (ii) fluorination of the HCC-240fa with a fluorination agent is conducted in the liquid phase in the presence or absence of a fluorination catalyst.
 6. The process of any of claims 1, 2 or 3, wherein a feed composition comprising the carbon tetrachloride further comprises one or more additional compounds selected from the group consisting of trichloroethylene (CClH=CCl_2), tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$), hexachloroethane (CCl_3CCl_3), bromotrichloromethane (CCl_3Br), chloroform (CCl_3H), 1,1,1-trichloroethane (CCl_3CH_3), 1,1,2-trichloroethane ($\text{CHCl}_2\text{CH}_2\text{Cl}$), trans-1,2-dichloroethylene (E- CHCl=CHCl), cis-1,2-dichloroethylene (Z- CHCl=CHCl) and 1,1-dichloroethylene ($\text{CH}_2=\text{CCl}_2$).
 7. The process of any of claims 1, 2 or 3, wherein the product comprising HCC-240fa further comprises one or more additional compounds selected from the group consisting of 1-chlorobutane; 1,2,3-trichloropropene ($\text{CHCl=CCl-CH}_2\text{Cl}$, HCO-1240xd); HCO-1230xd (CHCl=CCl-CHCl_2 , 1,2,3,3-tetrachloropropene); 1,1,1,3-tetrachloropropane ($\text{CCl}_3\text{-CH}_2\text{-CH}_3$, HCC-250fb); 1,4 dichlorobutane; 1,2-dichloro-cyclobutane, 1,1,4,4-tetrachlorobutadiene; 1,1,3,4 tetrachlorobutadiene; 1,1,1,2,3-pentachloropropane (HCC-240db); $\text{C}_5\text{H}_7\text{Cl}_3$ isomer(s) and $\text{C}_4\text{H}_7\text{Cl}_3$ isomer(s).
 8. The process of claim 7, wherein a total amount of the additional compounds is greater than 0 wt.% and less than or equal to about 5 wt.%, preferably less than or equal to about 1 wt.%, based on the total weight of the composition.

9. The process of any of claims 1, 2 or 3, wherein the metal-containing compound of the catalyst system of step (i) comprises an iron-containing compound.
10. The process of any of claims 1, 2 or 3, wherein the phosphorous-containing compound of the catalyst system comprises a phosphine, preferably triphenyl phosphine or tributyl phosphine, or a phosphate, preferably tributyl phosphate.
11. The process of claim 1, wherein the fluorination catalyst is a Lewis acid catalyst, preferably selected from the group consisting of SbCl_5 , SbCl_3 , SbF_5 , SnCl_4 , TiCl_4 , NiF_5 , FeCl_3 , and combinations of two or more thereof.
12. The process of claim 1, wherein the product comprising HFC-245fa further comprises two or more additional compounds selected from the group consisting of:
 - (i) HFC-143a, HFC-1225zc, HFC-236fa, HFO-E/Z-1234ze, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa;
or
 - (ii) HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234ze(Z), HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.
13. The process of claim 12, wherein a total amount of the additional compounds is greater than 0 wt.% and less than or equal to about 5 wt.%, preferably less than or equal to about 1 wt.%, based on the total weight of the composition.
14. The process of claim 1, wherein the catalyst of step (iii) comprises chromium.
15. The process of any of claims 1, 2 or 3, wherein an E:Z ratio of the reaction mixture is from about 10:1 to about 3:1.
16. The process of any of claims 1, 2 or 3, the process further comprising separating HFO-1234ze(E) and HFO-1234ze(Z) from the reaction mixture.

17. The process of claim 1, the process further comprising separating HFO-1234ze(E), HFO-1234ze(Z) and HFC-245fa from the reaction mixture.
18. The process of claim 2, the process further comprising separating HFO-1233zd(E), HFO-1234ze(Z) and HFC-245fa from the reaction mixture.
19. The process of claim 2, the process further comprising separating HFO-1233zd(E) and HFO-1234ze(Z) from the reaction mixture.
20. The process of claim 2, the process further comprising separating HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E) from the reaction mixture.
21. The process of claim 2, the process further comprising separating HFO-1233zd(E), HFO-1234ze(Z), HFO-1234ze(E) and HFC-245fa from the reaction mixture.
22. The process of claim 3, the process further comprising separating HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E) from the reaction mixture.
23. The process of any of claims 16 to 17, 20, 21 or 22, the process further comprising separating the HFO-1234ze(Z) from the HFO-1234ze(E).
24. The process of claim 23, the process further comprising isomerizing the HFO-1234ze(E) to HFO-1234ze(Z).
25. The process of claim 24, wherein isomerization of the HFO-1234ze(E) to HFO-1234ze(Z) is carried out in the presence of an oxygen containing gas.
26. The process of claim 24 or claim 25, wherein the isomerization of the HFO-1234ze(E) to HFO-1234ze(Z) is carried out in the presence of an isomerization catalyst.
27. The process of claim 26, wherein the isomerization catalyst comprises a metal compound selected from the group consisting of chromium, aluminum, zinc, magnesium, and combinations thereof, preferably wherein the isomerization catalyst is selected from the group consisting of Cr_2O_3 , Al_2O_3 , and combinations thereof.

28. A high purity etching gas composition comprising HFO-1234ze(Z), the composition having a purity of greater than 99.5 wt.% and being free of or substantially free of chlorinated compounds.
29. A composition comprising HFO-1234ze(E) and HFO-1234ze(Z), the composition being produced by the process of any of claims 1, 2 or 3.
30. The composition of claim 29, the composition further comprising one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.
31. A composition comprising (a) HFO-1234ze(E), HFO-1234ze(Z) and HFC-245fa; (b) HFO-1234ze(Z), HFO-1234ze(E), HFO-1233zd(E) and HFC-245fa; or (c) HFO-1234ze(Z) and HFC-245fa.
32. The composition of claim 31, wherein the composition is produced by the process of claim 1.
33. The composition of any of claims 31 to 32,
wherein the composition (a) further comprises (i) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); (ii) one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; and (iii) one or more additional compounds selected from the

group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130;

wherein the composition (b) further comprises (i) one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; (ii) one or more additional compounds selected from the group consisting of Z-HFO-1234ze, E-HFO-1234ze and HFC-245fa; (iii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb and HFO-1243zf; and (iv) one or more additional compounds selected from the group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130; or

wherein the composition (c) further comprises (i) one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-

263fb, HFO-1234zc, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; and (ii) one or more additional compounds selected from the group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HFO-1234ze(E), HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFC-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.

34. A composition comprising HFO-1233zd(E), HFO-1234ze(Z) and HFC-245fa.
35. The composition of claim 34, wherein the composition is produced by the process of claim 2.
36. The composition of any of claims 34 to 35, the composition further comprising (i) one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; (ii) an additional compound of E-HFO-1234ze; and (iii) one or more additional compounds selected from the group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HFO-1234ze(E), HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFC-338mf, HFC-356mff, HFO-1234ze(Z), HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-1224zc, HCC-160, HCFC-

- 244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.
37. A blowing agent composition comprising HFO-1233zd(E) and HFO-1234ze(Z).
38. The blowing agent composition of claim 37, wherein the composition is produced by the process of claim 2.
39. The blowing agent composition of any of claims 37 to 38, the composition further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; and one or more additional compounds selected from the group consisting of E-HFO-1234ze and HFC-245fa.
40. A composition comprising HFO-1233zd(E), HFO-1234ze(Z) and HFO-1234ze(E).
41. The composition of claim 30, wherein the composition is produced by the process of claim 2 or claim 3.
42. The composition of any of claims 40 to 41, the composition further comprising (i) one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; (ii) an additional compound of HFC-245fa; and (iii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb and HFO-1243zf.
43. A composition comprising HFO-1233zd(E), HFO-1234ze(Z), HFO-1234ze(E) and HFC-245fa.
44. The composition of claim 43, wherein the composition is produced by the process of claim 2.

45. The composition of any of claims 42 to 44, the composition further comprising (i) one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; (ii) one or more additional compounds selected from the group consisting of Z-HFO-1234ze, E-HFO-1234ze and HFC-245fa; (iii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb and HFO-1243zf; and (iv) one or more additional compounds selected from the group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFC-338mf, HFC-356mff, HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130.
46. A composition comprising HFO-1234ze(Z) and at least one compound selected from the group consisting of HFO-1234ze(E), HFO-1233zd(E), HFC-245fa, HFO-1336mzz(E), HFO-1336mzz(Z), HFC-227ea, HFC-134a and HFC-134.
47. The composition of claim 46, wherein the HFO-1234ze(Z) is produced by any of claims 1 to 27.
48. The composition of any of claims 46 to 47, the composition further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.

49. A composition comprising HFO-1234ze(Z) and at least one compound selected from the group consisting of HFO-1234ze(E), HFO-1233zd(E) and HFC-245fa.
50. The composition of claim 49, wherein the composition is produced by any of claims 1 to 27.
51. The composition of any of claims 49 to 50, the composition further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb.
52. A blowing agent composition comprising (i) HFO-1234ze(Z), or (ii) HFO-1234ze(Z) and at least one compound selected from the group consisting of HFO-1336mzz(E), HFO-1336mzz(Z), HCFO-1224yd(Z) and HFO-1233zd(E).
53. A blowing agent composition comprising HFO-1234ze(Z) and one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.
54. A blowing agent composition comprising HFO-1234ze(Z) and HFO-1336mzz(E), and further comprising one or more additional compounds selected from the group consisting of HCFO-1233xf, HFO-1336ft, HCFC-133a, CO-1140, HCFO-1233zd(E), HFC-245fa, HFO-1327mz, HFC-347mef, HFO-1243zf, and further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.
55. A blowing agent composition comprising HFO-1234ze(Z) and HFO-1336mzz(Z), and further comprising one or more additional compounds selected from the group consisting of HFO-1336mzz(E), HFO-1327mz, HFO-

- 1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb, and further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.
56. A blowing agent composition comprising HFO-1234ze(Z) and HFO-1233zd(E), and further comprising one or more additional compounds selected from the group consisting of Z-HFO-1234ze, E-HFO-1234ze and HFC-245fa, and further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.
57. A blowing agent composition comprising HFO-1234ze(Z) and HCFO-1224yd(Z), and further comprising one or more additional compounds selected from HFO-1234yf, HFO-1234ze(E), HFO-1243zf, HFC-263fb, HFC-254eb, CFC-1215yb, HCFC-244bb, HFO-1224 isomer(s) other than 1224yd(Z), HCFO-1224yd(E), CFC-1112a, HCFC-225ca, HCFC-225cb and HCFC-234bb, and further comprising one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.
58. The blowing agent composition of any of claims 53 to 57, wherein the HFO-1234ze(Z) is produced by any of claims 1-27.
59. A composition comprising HFO-1234ze(Z), HFO-1234ze(E) and HFC-227ea, and further comprising (i) one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb; (ii) one or more additional

compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, HFO-1234ze(Z), CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E); and (iii) one or more additional compounds selected from the group consisting of FC-1216 and HCFC-124.

60. A composition comprising HFO-1234ze(Z), HFO-1234ze(E), and HFC-134a, and further comprising (i) one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf, HFC-134 and HFC-245cb, (ii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, HFO-1234ze(Z), CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E), and (iii) one or more additional compounds selected from the group consisting of HFC-134, HCFC-124, HCFO-1122, HFC-143a, HCFC-31, HFC-32, HFC-125, CFC-114 and CFC-114a.
61. A composition comprising HFO-1234ze(Z) and HFO-1336mzz(Z), and further comprising (i) one or more additional compounds selected from the group consisting of HFO-1336mzz(E), HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb, and (ii) one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.
62. A composition comprising HFO-1234ze(Z), HFO-1336mzz(E) and HFO-1336mzz(Z), and further comprising (i) one or more additional compounds selected from the group consisting of HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb, (ii) one or more

additional compounds selected from the group consisting of C-30, HCFC-114, HCFC-114a, HCFC-133, HCFC-133a, HFC-245fa, HFC-338mee, HFC-338mf, HFC-347mef, HCO-1140, HCFO-1224 isomers, HCFO-1224yd, HCFO-1224yb, HCFO-1233xf, HCFO-1233zd, HFO-1243zf, HFO-1327mz, HFO-1336ft and HCFO-1326mxz, and (iii) one or more additional compounds selected from the group consisting of HFO-1234ze(E), HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb.

63. A composition comprising HFO-1234ze(Z), HFO-1234ze(E) and HFC-134, and further comprising (i) one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, (ii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E), and (iii) one or more additional compounds selected from the group consisting of HFC-134a, HCFC-124, HCFC-124a, HCFO-1122, HFC-143a, HCFC-31, HFC-32, HFC-125, CFC-114, CFC-114a, FCO-1114, HFC-152a, FCO-1318my, HFC-245cb, FC-C318, and HC-161.
64. A composition comprising HFO-1234ze(Z), HFO-1234ze(E) and HFO-1336mzz(E), and further comprising (i) one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, (ii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E), and (iii) one or

more additional compounds selected from the group consisting of C-30, HCFC-114, HCFC-114a, HCFC-133, HCFC-133a, HFC-245fa, HFC-338mee, HFC-338mf, HFC-347mef, HCO-1140, HCFO-1224 isomers, HCFO-1224yd, HCFO-1224yb, HCFO-1233xf, HCFO-1233zd, HFO-1243zf, HFO-1327mz, HFO-1336ft and HCFO-1326mxz.

65. A composition comprising HFO-1234ze(Z), HFO-1234ze(E), HFO-1336mzz(E) and HFO-1336mzz(E), and further comprising (i) one or more additional compounds selected from the group consisting of HFC-263fb, HFO-1234zc, HFC-245fa, HCFO-1233zd(E), HCFO-1233zd(Z), HCFO-1233xf, HCFC-124, HCC-40, CFC-114, HCFC-1131(E), CFC-114a, HCFC-124a, HFC-227ca, HFO-1234yf, HFC-152a, HFO-1234zf and HFC-245cb, (ii) one or more additional compounds selected from the group consisting of HFC-134a, HFO-1225zc, HFO-1234yf, HFC-245cb, HFC-236fa, HFC-1225ye(E), HFO-1234zc, HFC-245fa, HCFC-124, CFC-114, trifluoropropyne, HFC-152a, HFC-1225ye(Z), HFC-1225ye(E), HCFO-1233xf, HFC-263fb, HFO-1243zf and HCFO-1233zd(E), (iii) one or more additional compounds selected from the group consisting of C-30, HCFC-114, HCFC-114a, HCFC-133, HCFC-133a, HFC-245fa, HFC-338mee, HFC-338mf, HFC-347mef, HCO-1140, HCFO-1224 isomers, HCFO-1224yd, HCFO-1224yb, HCFO-1233xf, HCFO-1233zd, HFO-1243zf, HFO-1327mz, HFO-1336ft and HCFO-1326mxz, and (iv) one or more additional compounds selected from the group consisting of HFO-1327mz, HFO-1326mxz(Z), HFO-1326mxz(E), HFC-356mff, CHFC-346mdf, and HFC-263fb.
66. The composition of any of claims 59 to 65, wherein the HFO-1234ze(Z) is produced from any of claims 1 to 27.
67. The composition of claim 59, claim 60, claim 63 or claim 64 or claim 65, wherein a mixture of the HFO-1234ze(Z) and the HFO-1234ze(E) is produced from any of claims 1 to 27.
68. The composition of any of claims 28 to 67, wherein the composition has a GWP of 300 or less, preferably 150 or less.

69. The composition of any of claims 28 to 68, wherein the composition has a flammability classification of 1, 2L or 2 as determined by ASHRAE Standard 34 and ASTM E681-09.
70. The composition of any of claims 28 to 69, the composition further comprising at least one lubricant.
71. The composition of claim 70, wherein the lubricant is selected from the group consisting of polyalkylene glycols, polyol esters, polyvinyl ethers, poly-alpha-olefins, and combinations thereof.
72. A system for cooling or heating comprising an evaporator, compressor, condenser, and expansion device, said system containing the composition of any of claims 28 to 71.
73. A method for producing heating in a high temperature heat pump, the method comprising condensing the composition of any of claims 28 to 71 in a condenser, wherein the high temperature heat pump uses condenser operating temperatures greater than about 55°C, preferably from about 55°C to about 150°C.
74. A high temperature heat pump comprising a condenser and the composition of any of claims 28 to 71, wherein an operating temperature of the condenser is greater than about 55°C, preferably from about 55°C to about 150°C, more preferably greater than about 150°C.
75. The composition of any of claims 28 to 71, 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.
76. The process of claim 1, wherein a feed composition for (iii) comprises HFC-245fa, and one or more additional compounds selected from the group consisting of HFC-143a, HFC-1225zc, HFC-236fa, HFO-E/Z-1234ze, HCFC-22, CFC-12, HCFC-142b, HCFC-133a, HCFC-1224, HCFC-235fa, HCFC-1233, HCFC-235da, HCFC-123, HCFC-141b, HCFC-234fb, HCFC-1223xd, HCC-20, HCFC-224aa, CFC-1213xa, HCFC-233da, and HCFC-223aa, or one or more additional compounds selected from the group consisting of HFO-1234ze(E),

HFC-338mf, HFC-356mff, HFO-1234ze(Z), HFO-1234zc, HFC-347 isomer, HCFC-133a, HCFC-244bb, HCFC-235fa, HCFO-1326mxz(Z), HCFO-1224yd, HCFO-123zd(E), HCFO-1224zc, HCC-160, HCFC-244, HCFO-1335, HCFC-123, HCFC-123a, HCFO-123zd(Z), 1233zd (Br), CFO-1214ya, HCC-30, CFC-113, HCFO-1223xd, HCO-1130a and HCO-1130, and

wherein the feed composition has a moisture content of less than about 50 ppm, preferably less than about 20 ppm, more preferably less than about 10 ppm, and a non-absorbable gases (NAG) content of greater than zero and less than about 10%, preferably less than about 5%, more preferably less than about 3%, most preferably less than about 1.5%.

77. The process of any of claims 1, 2 or 3, the process further comprising a step of adding one or more compounds to the reaction mixture.
78. A process comprising using a composition as a dielectric gas, wherein the composition is a composition comprising Z-HFO-1234ze produced by the process of any of claims 1 to 27, preferably wherein the Z-HFO-1234ze has a purity of greater than 99.5%.
79. A process comprising using a composition as an etching gas, wherein the composition is a composition of claim 28.
80. A process comprising using a composition as a propellant in a sprayable composition of a medical product, wherein the composition is a composition comprising Z-HFO-1234ze produced by the process of any one of claims 1 to 2, the Z-HFO-1234ze having a purity of 99.9% or greater.