

**TITLE OF THE INVENTION**

BLEND COMPOSITIONS CONTAINING DIFLUOROPROPENE

**FIELD**

**[0001]** The present disclosure relates to compositions useful as refrigerants, and in particular, for air-conditioning and heat pump systems. The compositions of the present disclosure are useful in methods for producing cooling and heating, and methods for replacing refrigerants and air-conditioning and heat pump systems.

**BACKGROUND**

**[0002]** 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 1,430 and 3,500 according to the UN's IPCC Fourth Assessment Report (AR4).

**[0003]** 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 provide superior performance in a variety of applications and which meet the standards of evolving regulations.

**[0004]** The instant invention solves certain problems associated with conventional refrigerants and provides refrigerant blends containing 1,1-difluoropropene, which meets the evolving regulatory landscape.

### SUMMARY

[0005] In order to meet the rapidly changing regulatory environment, the present inventors have identified a fluoroolefin compound that provides performance relative to existing refrigerants that will allow its use going forward even in view of the standards of the evolving regulatory landscape.

[0006] Certain embodiments disclosed herein relate to a fluoropropene composition comprising 1,1-difluoropropene (also called HFO-1252zc, or R-1252zc). This compound is shown herein to have advantageous properties for its use in refrigerant applications.

[0007] In one embodiment, disclosed herein are compositions comprising HFO-1252zc and at least one of HFO-1234ze-E (i.e., the E-isomer) or HFC-32.

[0008] According to any of the foregoing embodiments, disclosed herein are compositions comprising from about 20 to 83 weight percent HFO-1252zc and from about 17 to 80 weight percent of at least one of HFO-1234ze-E or HFC-32.

[0009] According to any of the foregoing embodiments, disclosed herein are compositions comprising from about 20 to 81 weight percent HFO-1252zc and from about 19 to 80 weight percent of at least one of HFO-1234ze-E or HFC-32.

[0010] According to any of the foregoing embodiments, disclosed herein are compositions comprising from about 20 to 83 weight percent HFO-1252zc and from about 17 to 80 weight percent HFC-32.

[0011] According to any of the foregoing embodiments, disclosed herein are compositions comprising from about 20 to 81 weight percent HFO-1252zc and from about 19 to 80 weight percent HFO-1234ze-E.

[0012] According to any of the foregoing embodiments, disclosed herein are compositions comprising from about 50 to 81 weight percent HFO-1252zc and from about 19 to 50 weight percent HFO-1234ze-E.

[0013] According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc and HFC-32, wherein: a concentration of the HFO-1252zc in the composition is in a range of from about  $X_1$  weight percent to about  $Y_1$  weight percent based upon a weight of the HFO-1252zc and the HFC-32; a

concentration of the HFC-32 in the composition is in a range of from about  $X_2$  weight percent to about  $Y_2$  weight percent based upon the weight of the HFO-1252zc and the HFC-32;  $X_1$  is any number selected from 20, 50, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, and 70;  $Y_1$  is any number selected from 50, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, and 83;  $X_2$  is any number selected from 17, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, and 50;  $Y_2$  is any number selected from 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 50, and 80;; and a sum of the weight percentages of the HFO-1252zc and the HFC-32 is 100.

[0014] According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc and HFO-1234ze-E, wherein: a concentration of the HFO-1252zc in the composition is in a range of from about  $X_1$  weight percent to about  $Y_1$  weight percent based upon a weight of the HFO-1252zc and the HFO-1234ze-E; a concentration of the HFO-1234ze-E in the composition is in a range of from about  $X_3$  weight percent to about  $Y_3$  weight percent based upon the weight of the HFO-1252zc and the HFO-1234ze-E;  $X_1$  is any number selected from 1, 4, 7, 10, 13, 16, 19, 20, 22, 25, 28, 31, 34, 37, 40, 43, 46, 49, and 50;  $Y_1$  is any number selected from 4, 7, 10, 13, 16, 19, 20, 22, 25, 28, 31, 34, 37, 40, 43, 46, 49, 50, and 81;  $X_3$  is any number selected from 19, 50, 51, 54, 57, 60, 63, 66, 69, 72, 75, 78, 80, 81, 84, 87, 90, 93, and 96;  $Y_3$  is any number selected from 50, 51, 54, 57, 60, 63, 66, 69, 72, 75, 78, 80, 81, 84, 87, 90, 93, 96, and 99; and a sum of the weight percentages of the HFO-1252zc and the HFO-1234ze-E is 100.

[0015] According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc, HFC-32, and HFO-1234ze-E, wherein: a concentration of the HFO-1252zc in the composition is in a range of from about  $X_1$  weight percent to about  $Y_1$  weight percent based upon a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; a concentration of the HFC-32 in the composition is in a range of from about  $X_2$  weight percent to about  $Y_2$  weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; a concentration of the HFO-1234ze-E is in a range of from about  $X_3$  weight percent to about  $Y_3$  weight percent based upon a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E;  $X_1$  is any number selected from 0.5, 5, 10, 14, 17, 21, 22, 24, 27, 28, 30, 32, 33, 35, 37, 39, 40, 42, 44, 45, 46, 47, 48, 49, 51, 52, 54, 55, 56, 57, 58, 59, 60, 62, and 63;  $Y_1$  is any number selected from 5, 10, 14, 17, 21, 22, 24, 27, 28,

30, 32, 33, 35, 37, 39, 40, 42, 44, 45, 46, 47, 48, 49, 51, 52, 54, 55, 56, 57, 58, 59, 60, 62, 63, and 64;  $X_2$  is any number selected from 17, 18, 19, 20, 21, 23, 24, 28, 29, 32, 33, 34, 35, 36, 38, 41, 42, 43, 44, 45, 46, 47, 48, 49, 51, 52, 54, 55, 56, 57, 58, 59, 60, 62, 63, and 64;  $Y_2$  is any number selected from ;  $X_3$  is any number selected from 4, 5, 14, 17, 19, 21, 22, 23, 24, 26, 27, 28, 30, 32, 34, 35, 36, 37, 38, 39, 42, 43, 44, 45, 47, 51, 54, 55, 55.72, and 56;  $Y_3$  is any number selected from 5, 14, 17, 19, 21, 22, 23, 24, 26, 27, 28, 30, 32, 34, 35, 36, 37, 38, 39, 42, 43, 44, 45, 47, 51, 54, 55, 55.72, 56, and 62; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

[0016] According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc and HFC-32, wherein: the HFO-1252zc is present at a concentration from about 56 weight percent to about 70 weight percent based upon a weight of the HFO-1252zc and the HFC-32; and the HFC-32 is present at a concentration of from about 30 weight percent to about 44 weight percent based upon a weight of the HFO-1252zc and the HFC-32.

[0017] According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc and HFC-32, wherein: the HFO-1252zc is present at a concentration from about 56 weight percent to about 68 weight percent based upon a weight of the HFO-1252zc and the HFC-32; and the HFC-32 is present at a concentration of from about 32 weight percent to about 44 weight percent based upon a weight of the HFO-1252zc and the HFC-32.

[0018] According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc and HFC-32, wherein: the HFO-1252zc is present at a concentration from about 56 weight percent to about 65 weight percent based upon a weight of the HFO-1252zc and the HFC-32; and the HFC-32 is present at a concentration of from about 35 weight percent to about 44 weight percent based upon a weight of the HFO-1252zc and the HFC-32.

[0019] According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc, HFC-32, and HFO-1234ze-E, wherein: the HFO-1252zc is present at a concentration of from about 33 weight percent to about 45 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, HFC-32 is present at a concentration of from about 18 weight percent to about 20 weight percent based upon the weight of the HFO-1252zc, HFC-32, and

HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 19 weight percent to about 47 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

**[0020]** According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc, HFC-32, and HFO-1234ze-E, wherein: the HFO-1252zc is present at a concentration of from about 0.05 weight percent to about 24 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 34 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 37 weight percent to about 62 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

**[0021]** According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc, HFC-32, and HFO-1234ze-E, wherein: the HFO-1252zc is present at a concentration of from about 51 weight percent to about 63 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 23 weight percent to about 38 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 4 weight percent to about 21 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

**[0022]** According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc, HFC-32, and HFO-1234ze-E, wherein: the HFO-1252zc is present at a concentration of from about 31 weight percent to about 64 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 17 weight percent to about 43 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 1 weight percent to about 31 weight percent based upon the weight of the HFO-1252zc, HFC-

32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

**[0023]** According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc, HFC-32, and HFO-1234ze-E, wherein: the HFO-1252zc is present at a concentration of from about 0.05 weight percent to about 25 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 36 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 39 weight percent to about 57 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

**[0024]** According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc, HFC-32, and HFO-1234ze-E, wherein: the HFO-1252zc is present at a concentration of from about 36 weight percent to about 60 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 17 weight percent to about 22 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 18 weight percent to about 42 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

**[0025]** According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc and HFO-1234ze-E, wherein: the HFO-1252zc is present at a concentration of from about 1 weight percent to about 16 weight percent based upon a weight of the HFO-1252zc and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 84 weight percent to about 99 weight percent based upon the weight of the HFO-1252zc and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc and the HFO-1234ze-E is 100.

**[0026]** According to any of the foregoing embodiments, disclosed herein are compositions comprising HFO-1252zc, HFC-32, and HFO-1234ze-E, wherein: the HFO-125zc is present a concentration of from about 19 weight percent to about 23

percent based upon a weight of the HFO-1252zc, the HFC-32, and the HFO-1234zc; the HFC-32 is present at a concentration of from about 18 weight percent to about 22 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 57 weight percent to about 61 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E.

**[0027]** According to any of the foregoing embodiments, disclosed herein are compositions further comprising at least one additional compound selected from HCFC-22, HFC-23, HCC-30, HCFC-31, HCC-40, HFC-41, methane, HFC-125, HFC-143, HFC-143a, HFC-152a, HFC-245cb, HCFC-253dc, HFC-254fb, HCC-260fb, HCFC-261fc, HCFC-262fc, HFC-263fb, HFC-272fb, propane, HFO-374, n-butane, allene, 2-butene, cyclobutene, 2-methyl propene, HCFO-1122, HFO-1132, HFO-1132a, HFO-1141, ethylene, HCFO-1233xf, HFO-1234yf, HCFO-1242zf, HFO-1243zf, HCFO-1251, HFO-1260zf, HFO-1261zf, propylene, HFO-1345, HFO-1252zc, HFO-1252yf, HFO-1252zf, HFO-1252ye, and E/Z-t-BuO-CF=CH-CH<sub>3</sub>.

**[0028]** According to any of the foregoing embodiments, disclosed herein are compositions further comprising at least one additional compound selected from HCFC-22, HCC-40, HFO-1234yf, HFO-1243zf, HFC-263fb, HFO-1252zc, HFO-1252yf, HFO-1252zf, and HFO-1252ye.

**[0029]** According to any of the foregoing embodiments, disclosed herein are compositions wherein said composition further comprises from 0.1 to 200 ppm by weight of water; from about 10 ppm by volume to about 0.35 volume percent oxygen; and/or from about 100 ppm by volume to about 1.5 volume percent air or NAG.

**[0030]** According to any of the foregoing embodiments, disclosed herein are compositions wherein said composition comprises a stabilizer.

**[0031]** According to any of the foregoing embodiments, disclosed herein are compositions wherein the stabilizer is selected from the group consisting of nitromethane, ascorbic acid, terephthalic acid, azoles, phenolic compounds, cyclic monoterpenes, terpenes, phosphites, phosphates, phosphonates, thiols, and lactones.

[0032] According to any of the foregoing embodiments, disclosed herein are compositions wherein the stabilizer is selected from toluotriazole, benzotriazole, tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-terbutyl-4-methylphenol, fluorinated epoxides, n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, d-limonene,  $\alpha$ -terpinene,  $\beta$ -terpinene,  $\alpha$ -pinene,  $\beta$ -pinene, or butylated hydroxytoluene.

[0033] According to any of the foregoing embodiments, disclosed herein are compositions wherein the stabilizer is present in an amount from about 0.001 to 1.0 weight percent based on the weight of the refrigerant.

[0034] According to any of the foregoing embodiments, disclosed herein are compositions wherein the composition further comprises a lubricant. wherein said lubricant is at least one selected from the group consisting of polyalkylene glycol, polyol ester, poly- $\alpha$ -olefin, and polyvinyl ether.

[0035] According to any of the foregoing embodiments, disclosed herein are compositions wherein said lubricant is a polyol ester or a polyvinyl ether.

[0036] According to any of the foregoing embodiments, disclosed herein are compositions wherein said lubricant has at least one property selected from the group consisting of volume resistivity of greater than  $10^{10}$   $\Omega$ -m at 20 °C; surface tension of from about 0.02 N/m to 0.04 N/m at 20 °C; kinematic viscosity of from about 20 cSt to about 500 cSt at 40 °C; a breakdown voltage of at least 25 kV; and a hydroxy value of at most 0.1 mg KOH/g.

[0037] According to any of the foregoing embodiments, disclosed herein are compositions wherein the composition comprises at least one tracer.

[0038] According to any of the foregoing embodiments, disclosed herein are compositions wherein said tracer is present in an amount from about 1.0 ppm by weight to about 1000 ppm by weight.

[0039] According to any of the foregoing embodiments, disclosed herein are compositions wherein said at least one tracer is selected from the group consisting of hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons,

hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof.

**[0040]** According to any of the foregoing embodiments, disclosed herein are compositions wherein said at least one tracer is selected from the group consisting of HFC-23, HCFC-31, HFC-41, HFC-161, HFC-143a, HFC-134a, HFC-125, HFC-236fa, HFC-236ea, HFC-245cb, HFC-245fa, HFC-254eb, HFC-263fb, HFC-272ca, HFC-281ea, HFC-281fa, HFC-329p, HFC-329mmz, HFC338mf, HFC-338pcc, CFC-12, CFC-11, CFC-114, CFC-114a, HCFC-22, HCFC-123, HCFC-124, HCFC-124a, HCFC-141b, HCFC-142b, HCFC-151a, HCFC-244bb, HCC-40, HFO-1141, HCFO-1130, HCFO-1130a, HCFO-1131, HCFO-1122, HFO-1123, HFO-1234yf, HFO-1234ye, HFO-1243zf, HFO-1225ye, HFO-1225zc, PFC-116, PFC-C216, PFC-218, PFC-C318, PFC-1216, PFC-31-10mc, PFC-31-10my, and combinations thereof.

**[0041]** According to any of the foregoing embodiments, disclosed herein are compositions 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.

**[0042]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein: the HFO-1252zc is present at a concentration of from about 56 weight percent to about 70 weight percent based upon a weight of the HFO-1252zc and the HFC-32; and the HFC-32 is present at a concentration of from about 30 weight percent to about 44 weight percent based upon a weight of the HFO-1252zc and the HFC-32.

**[0043]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein: the HFO-1252zc is present at a concentration from about 56 weight percent to about 68 weight percent based upon a weight of the HFO-1252zc and the HFC-32; and the HFC-32 is present at a concentration of from about 32 weight percent to about 44 weight percent based upon a weight of the HFO-1252zc and the HFC-32.

**[0044]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein: the HFO-1252zc is present at a concentration from about 56 weight percent to about 65 weight percent based upon a weight of the HFO-1252zc and the HFC-32; and the HFC-32 is present at a concentration of from about 35

weight percent to about 44 weight percent based upon a weight of the HFO-1252zc and the HFC-32.

**[0045]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein: the HFO-1252zc is present at a concentration of from about 33 weight percent to about 45 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 18 weight percent to about 20 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 19 weight percent to about 47 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; and the composition has a GWP < 160.

**[0046]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein: the HFO-1252zc is present at a concentration of from about 0.05 weight percent to about 24 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 34 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 37 weight percent to about 62 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; and the composition has a flammability rating of 2L (when measured in accordance with ANSI/ASHRAE Standard 34).

**[0047]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein: the HFO-1252zc is present at a concentration of from about 51 weight percent to about 63 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 23 weight percent to about 38 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 4 weight percent to about 21 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

[0048] According to any of the foregoing embodiments, disclosed herein are compositions, wherein: the HFO-1252zc is present at a concentration of from about 31 weight percent to about 64 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, HFC-32 is present at a concentration of from about 17 weight percent to about 43 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 1 weight percent to about 31 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

[0049] According to any of the foregoing embodiments, disclosed herein are compositions, wherein: the HFO-1252zc is present at a concentration of from about 0.05 weight percent to about 25 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, HFC-32 is present at a concentration of from about 36 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 39 weight percent to about 57 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; and the composition has a flammability rating of 2L (when measured in accordance with ANSI/ASHRAE Standard 34).

[0050] According to any of the foregoing embodiments, disclosed herein are compositions, wherein: the HFO-1252zc is present at a concentration of from about 36 weight percent to about 60 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, HFC-32 is present at a concentration of from about 17 weight percent to about 22 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 18 weight percent to about 42 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; and said composition has a GWP < 160.

[0051] According to any of the foregoing embodiments, disclosed herein are compositions, wherein the HFO-1252zc is present at a concentration of from about 1

weight percent to about 16 weight percent based upon a weight of the HFO-1252zc and HFO-1234ze-E, HFO-1234ze-E is present at a concentration of from about 84 weight percent to about 99 weight percent based upon the weight of the HFO-1252zc and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc and the HFO-1234ze-E is 100; and the composition has a flammability rating of 2L (when measured in accordance with ANSI/ASHRAE Standard 34).

**[0052]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein the HFO-125zc is present at a concentration of from about 19 weight percent to about 23 percent based upon a weight of the HFO-1252zc, the HFC-32, and the HFO-1234zc; the HFC-32 is present at a concentration of from about 18 weight percent to about 22 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 57 weight percent to about 61 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

**[0053]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein HFO-1252zc is present at a concentration of from about 56 weight percent to about 70 weight percent based upon a weight of the HFO-1252zc and the HFC-32; the HFC-32 is present at a concentration of from about 30 weight percent to about 44 weight percent based upon the weight of the HFO-1252zc and the HFC-32; and a sum of the weight percentages of the HFO-1252zc and the HFC-32 is 100; and they also show that a heat pump operated in a cooling mode

**[0054]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein: HFO-1252zc is present at a concentration of from about 0.5 weight percent to about 63 weight percent based upon a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; HFC-32 is present at a concentration of from about 18 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 4 weight percent to about 62 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; and a

sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

**[0055]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein: HFO-1252zc is present at a concentration of from about 0.5 weight percent to about 64 weight percent based upon a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; HFC-32 is present at a concentration of from about 17 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 1 weight percent to about 57 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

**[0056]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein: HFO-1252zc is present at a concentration of from about 18 weight percent to about 20 weight percent based on a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; HFC-32 is present at a concentration of from about 6 weight percent to about 21 weight percent upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 59 weight percent to about 76 weight percent upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; a sum of the weight percentages of the HFO-1252ze, the HFC-32, and the HFO-1234ze-E is 100; and the composition exhibits a GWP < 160 and a flammability rating of 2L.

**[0057]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein: HFO-1252zc is present at a concentration of about 20 weight percent based on a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; HFC-32 is present at a concentration of about 21 weight percent upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of about 59 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252ze, the HFC-32, and the HFO-1234ze-E is 100.

**[0058]** According to any of the foregoing embodiments, disclosed herein are compositions, wherein: HFO-1252zc is present at a concentration of from about 18

weight percent to about 22 weight percent based on a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; HFC-32 is present at a concentration of from about 19 weight percent to about 23 weight percent upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 57 weight percent to about 61 weight percent upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; a sum of the weight percentages of the HFO-1252ze, the HFC-32, and the HFO-1234ze-E is 100.

**[0059]** According to any of the foregoing embodiments, disclosed herein are methods for cooling comprising evaporating the composition in the vicinity of a body to be cooled and thereafter condensing said composition, wherein said cooling is provided by an air-conditioner or heat pump.

**[0060]** According to any of the foregoing embodiments, disclosed herein are compositions method for heating comprising evaporating the composition and thereafter condensing said composition in the vicinity of a body to be heated, wherein said heating is provided by a heat pump.

**[0061]** According to any of the foregoing embodiments, disclosed herein are systems for cooling or heating comprising the composition of any of the foregoing embodiments. In another embodiment, the systems comprise an evaporator, compressor, condenser, and expansion device, each operably connected to perform a vapor compression cycle. In another embodiment, the system may be a secondary loop system.

**[0062]** According to any of the foregoing embodiments, disclosed herein are methods of replacing R-454C or propane in air-conditioning or heat pump systems comprising providing the composition of any of the foregoing embodiments to the system in place of R-454C or propane.

**[0063]** According to any of the foregoing embodiments, disclosed herein is the use of the composition of any of the foregoing embodiments as refrigerant in air-conditioning or heat pump systems.

### **DETAILED DESCRIPTION**

**[0064]** This invention relates to compositions containing 1,1-difluoropropene (HFO-1252zc), and at least one of difluoromethane (HFC-32) or E-1,3,3,3-tetrafluoropropene (HFO-1234ze-E). The compositions may potentially be candidates to replace refrigerants such as R-454C, R-410A, or propane with low Global Warming Potential (GWP), improved environmental fate characteristics, and improved energy efficiency (COP).

**[0065]** The compositions comprise HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E. These compositions provide refrigerant blends with low global warming potential, improved glide as compared to other suggested refrigerant blends, and improved coefficient of performance as compared to existing refrigerants and other proposed replacements, as well as meeting the evolving regulatory landscape.

**[0066]** 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.

**[0067]** 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.

**[0068]** Examples of heat transfer systems are any type of refrigeration systems and air conditioning systems including, but not limited to, stationary heat transfer systems, air conditioners, freezers, refrigerators, heat pumps, flooded evaporator heat pumps, direct expansion heat pumps, chillers, flooded evaporator chillers, direct expansion chillers, walk-in coolers, mobile refrigerators, mobile heat transfer systems, mobile heat pumps (including heat pumps for cabin comfort cooling and heating in automobiles), mobile air conditioning units (for cooling of passenger compartments in automobiles), dehumidifiers, and combinations thereof. The focus of the present application is air-conditioning and heat pump systems.

**[0069]** Volumetric capacity is the amount of heat absorbed or rejected divided by the theoretical compressor displacement. Heat removed or absorbed is the enthalpy difference across a heat exchanger multiplied by the refrigerant mass flowrate. Theoretical compressor displacement is the refrigerant mass flowrate divided by the

density of the gas entering the compressor (i.e., compressor suction density). More simply, volumetric capacity is the density at the suction of the compressor (e.g.,  $\text{kg/m}^3$ ) multiplied by the heat exchanger enthalpy difference. Higher volumetric capacity allows the use of a smaller compressor for the same heat load. Herein, cooling capacity refers to the volumetric capacity in cooling mode and heating capacity refers to the volumetric capacity in heating mode.

**[0070]** Coefficient of performance (COP) is the amount of heat absorbed or rejected divided by the required energy input to operate the cycle (approximated by the compressor power). COP is specific to the mode of operation of a heat pump, thus COP for heating or COP for cooling. COP is directly related to the energy efficiency ratio (EER).

**[0071]** Subcooling refers to the reduction of the temperature of a liquid below that liquid's saturation point for a given pressure. The liquid saturation point is the temperature at which the vapor is completely condensed to a liquid. By cooling a liquid below the saturation temperature (or bubble point temperature), the net refrigeration effect can be increased. Subcooling thereby improves refrigeration capacity and energy efficiency of a system. The subcool amount is the amount of cooling below the saturation temperature (in degrees).

**[0072]** Superheating refers to the increase of the temperature of a vapor above that vapor's saturation point for a given pressure. The vapor saturation point is the temperature at which the liquid is completely evaporated to a vapor. Superheating continues to heat the vapor to a higher temperature vapor at the given pressure. By heating the vapor above the saturation temperature (or dew point temperature), the net refrigeration effect can be increased. Superheating thereby improves refrigeration capacity and energy efficiency of a system when it occurs in the evaporator. Suction line superheat does not add to the net refrigeration effect and can reduce efficiency and capacity. The superheat amount is the amount of heating above the saturation temperature (in degrees).

**[0073]** Temperature glide (sometimes referred to simply as "glide") is the absolute value of the difference between the starting and ending temperatures of a phase-change process by a refrigerant within a condenser of a refrigerant system, exclusive of any subcooling or superheating. For an evaporator, the glide is the difference in

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

**[0074]** The net refrigeration effect is the quantity of heat that each kilogram of refrigerant absorbs in the evaporator to produce useful cooling.

**[0075]** 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.

**[0076]** 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.

**[0077]** 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. Herein, the GWP values are those reported in the United Nations Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (AR4). The GWP of 1252zc is estimated at 1.

**[0078]** 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. Hydrofluorocarbons (HFCs) and the hydrofluoro-olefins (HFO's) described herein have zero ODP

because they do not contain chlorine, bromine or iodine, species known to contribute to ozone breakdown and depletion. HFO-1252zc has zero ozone depletion potential.

**[0079]** 1,1-Difluoropropene (HFO-1252zc or R-1252zc) may be prepared by hydrogenation of 3,3,3-trifluoropropene (HFO-1243zf) over palladium on carbon catalyst to form 1,1,1-trifluoropropane (HFC-263fb), followed by dehydrofluorination of the HFC-263fb over chrome catalyst or by pyrolysis at high temperatures (see attorney docket number FL2084, filed herewith, and herein incorporated by reference).

**[0080]** E-1,3,3,3-Tetrafluoropropene (HFO-1234ze-E or R-1234ze-E) is available commercially from Honeywell (Charlotte, North Carolina, USA). And difluoromethane (HFC-32 or R-32) is available commercially from various sources worldwide.

**[0081]** 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.

**[0082]** 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.

**[0083]** 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.

**[0084]** 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.

**[0085]** 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.

#### **REFRIGERANT COMPOSITION**

**[0086]** In one embodiment, compositions comprise, consist of, or consist essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E. These compositions provide low Global Warming Potential (GWP), improved environmental fate characteristics, and improved energy efficiency (COP). The presently claimed compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E also provide flammability classified as class 2 by ASHRAE.

**[0087]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 20 to 83 weight percent HFO-1252zc and from about 17 to 80 weight percent of at least one of HFO-1234ze-E or HFC-32.

**[0088]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 20 to 81 weight percent HFO-1252zc and from about 19 to 80 weight percent of at least one of HFO-1234ze-E or HFC-32.

**[0089]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 20 to 83 weight percent HFO-1252zc and from about 17 to 80 weight percent HFC-32.

**[0090]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 20 to 50 weight percent HFO-1252zc and from about 50 to 80 weight percent HFC-32. These compositions provide lower average glide, and higher capacity. These compositions also provide improved COP as compared to R-410A and R-454C.

**[0091]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 50 to 83 weight percent HFO-1252zc and from about 17 to 50 weight percent HFC-32. These compositions provide lower compressor discharge temperatures, capacity more similar to R-454C and still improved COP compared to both R-410A and R-454C.

**[0092]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 20 to 81 weight percent HFO-1252zc and from about 19 to 80 weight percent HFO-1234ze-E.

**[0093]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 50 to 81 weight percent HFO-1252zc and from about 19 to 50 weight percent HFO-1234ze-E. These compositions provide higher capacity. Additionally, these compositions provide improved COP as compared to both R-410A and R-454C.

**[0094]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 56 weight percent to about 70 weight percent HFO-1252zc based upon a weight of the HFO-1252zc and HFC-32; and from about 30 weight percent to about 44 weight percent HFC-32 based upon the weight of the HFO-1252zc and HFC-32. When these compositions are used in a heat pump in cooling (or heating mode), the heat pump exhibits a cooling (or heating) capacity of at least 90% of the volumetric cooling capacity of R-454C.

**[0095]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 56 weight percent to about 68 weight percent HFO-1252zc based upon a weight of the HFO-1252zc and HFC-32; and from about 32 weight percent to about 44 weight percent HFC-32 based upon the weight of the HFO-1252zc and HFC-32. When these compositions are used in a heat pump in cooling (or heating mode), the heat pump exhibits a glide  $< 8$  K.

**[0096]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 56 weight percent to about 65 weight percent HFO-1252zc based upon a weight of the HFO-1252zc and HFC-32; and from about 35 weight percent to about 44 weight percent HFC-32 based upon the weight of the HFO-1252zc and HFC-32. When these compositions are used in a heat pump in cooling mode, the heat pump exhibits a glide  $< 8$  K.

**[0097]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 33 weight percent to about 45 weight percent HFO-1252zc based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 18 weight percent to about 20 weight percent HFC-32 based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 19 weight percent to about 47 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100. Such compositions exhibit a GWP  $< 160$ .

**[0098]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 0.05 weight percent to about 24 weight percent HFO-1252zc based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, from about 34 weight percent to about 43.78 weight percent HFC-32 based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 37 weight percent to about 62 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100. Such compositions exhibit a flammability rating of 2L (when measured in accordance with ANSI/ASHRAE Standard 34).

**[0099]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 51 weight percent to about 63 weight percent HFO-1252zc

based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, of from about 23 weight percent to about 38 weight percent HFC-32 based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 4 weight percent to about 21 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100. When such compositions are used in a heat pump in cooling mode, the heat pump exhibits a glide < 8 K.

**[0100]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 31 weight percent to about 64 weight percent HFO-1252zc based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 17 weight percent to about 43 weight percent HFC-32 based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 1 weight percent to about 31 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100. When such compositions are used in a heat pump in heating mode, the heat pump exhibits a glide < 8 K.

**[0101]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 0.05 weight percent to about 25 weight percent HFO-1252zc is present at a concentration of based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 36 weight percent to about 43.78 weight percent HFC-32 based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 39 weight percent to about 57 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100. Such compositions exhibit a flammability rating of 2L (when measured in accordance with ANSI/ASHRAE Standard 34).

**[0102]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 36 weight percent to about 60 weight percent HFO-1252zc based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, from about 17 weight percent to about 22 weight percent HFC-32 based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 18 weight percent to about 42 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-

32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100. Such compositions exhibit a GWP < 160.

**[0103]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 1 weight percent to about 16 weight percent HFO-1252zc based upon a weight of the HFO-1252zc and HFO-1234ze-E; from about 84 weight percent to about 99 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc and the HFO-1234ze-E is 100. Such compositions have a flammability rating of 2L (when measured in accordance with ANSI/ASHRAE Standard 34).

**[0104]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 19 weight percent to about 23 percent HFO-125zc based upon a weight of the HFO-1252zc, the HFC-32, and the HFO-1234zc; from about 18 weight percent to about 22 weight percent HFC-32 based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 57 weight percent to about 61 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

**[0105]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 0.5 weight percent to about 63 weight percent HFO-1252zc based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 18 weight percent to about 43.78 weight percent HFC-32 based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 4 weight percent to about 62 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100. When such compositions are used in a heat pump in cooling mode, the heat pump exhibits a cooling capacity within 20% of a cooling capacity of R-454C

**[0106]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 0.5 weight percent to about 64 weight percent HFO-1252zc based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 17 weight percent to about 43.78 weight percent HFC-32 based upon the weight of

the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 1 weight percent to about 57 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100. When such compositions are used in a heat pump in heating mode, the heat pump exhibits a heating capacity within 20% of a heating capacity of R-454C

**[0107]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 18 weight percent to about 20 weight percent HFO-1252zc based on a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 6 weight percent to about 21 weight percent HFC-32 upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; from about 59 weight percent to about 76 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252ze, the HFC-32, and the HFO-1234ze-E is 100. Such compositions exhibit a GWP < 160 and a flammability rating of 2L.

**[0108]** In another embodiment, the compositions comprise, consist of, or consist essentially of about 20 weight percent HFO-1252zc based on a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; about 21 weight percent HFC-32 upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; about 59 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252ze, the HFC-32, and the HFO-1234ze-E is 100.

**[0109]** In another embodiment, the compositions comprise, consist of, or consist essentially of from about 18 weight percent to about 22 weight percent HFO-1252zc based on a weight of the HFO-1252zc, HFC-32, the HFO-1234ze-E; about 19 weight percent to about 23 weight percent HFC-32 based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; from about 57 weight percent to about 61 weight percent HFO-1234ze-E based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252ze, the HFC-32, and the HFO-1234ze-E is 100.

**[0110]** Flammability is a term used to mean the ability of a composition to ignite and/or propagate a flame. For refrigerants and other heat transfer compositions or

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

**[0111]** In order for a refrigerant to be classified by ANSI/ASHRAE as low flammability (class 2L), it must: 1) exhibit flame propagation when tested at 140°F (60°C) and 14.7 psia (101.3 kPa); 2) have an LFL >0.0062 lb/ft<sup>3</sup> (0.10 kg/m<sup>3</sup>); 3) have a heat of combustion <8169 Btu/lb (19,000 kJ/kg); and 4) have a maximum burning velocity of ≤3.9 in./s (10 cm/s) when tested at 73.4°F (23.0°C) and 14.7 psia (101.3 kPa) in dry air.

**[0112]** In order for a refrigerant to be classified by ANSI/ASHRAE as flammable (class 2), it must: 1) exhibit flame propagation when tested at 140°F (60°C) and 14.7 psia (101.3 kPa); 2) have an LFL >0.0062 lb/ft<sup>3</sup> (0.10 kg/m<sup>3</sup>); and 3) have a heat of combustion <8169 Btu/lb (19,000 kJ/kg).

**[0113]** ASHRAE Standard 34 provides a methodology to calculate the heat of combustion for refrigerant blends using a balanced stoichiometric equation based on the complete combustion of one mole of refrigerant with enough oxygen for a stoichiometric reaction.

**[0114]** HFO-1252zc can be combined with HFC-32 or HFO-1234ze-E and provide estimated class 2 or class 2L flammability as defined by ANSI/ASHRAE standard 34 and ISO 817. Class 2 and class 2L flammability may be manageable in air-conditioning and heat pumps. Specific applications may have different requirements, with regards to flammability.

**[0115]** The compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E may further comprise at least one additional compound from the list in Table 1.

TABLE 1

| Code    | Name-ASHRAE Designation                      | Formula                                        |
|---------|----------------------------------------------|------------------------------------------------|
| R-22    | chlorodifluoromethane                        | $\text{CHF}_2\text{Cl}$                        |
| R-23    | trifluoromethane (HFC-23)                    | $\text{CHF}_3$                                 |
| R-30    | dichloromethane (HCC-30)                     | $\text{CH}_2\text{Cl}_2$                       |
| R-31    | chlorofluoromethane (HCFC-31)                | $\text{CH}_2\text{FCl}$                        |
| R-40    | methyl chloride (HCC-40)                     | $\text{CH}_3\text{Cl}$                         |
| R-41    | fluoromethane (HFC-41)                       | $\text{CH}_3\text{F}$                          |
| R-50    | methane                                      | $\text{CH}_4$                                  |
| R-125   | 1,1,2,2,2-pentafluoroethane (HFC-125)        | $\text{CF}_2\text{CF}_3$                       |
| R-143   | 1,1,2-trifluoroethane (HFC-143)              | $\text{CF}_2\text{CH}_2\text{F}$               |
| R-143a  | 1,1,1-trifluoroethane (HFC-143a)             | $\text{CF}_3\text{CH}_3$                       |
| R-152a  | 1,1,1-difluoroethane (HFC-152a)              | $\text{CHF}_2\text{CH}_3$                      |
| R-245cb | 1,1,1,2,2-pentafluoropropane (HFC-245cb)     | $\text{CF}_3\text{CF}_2\text{CH}_3$            |
| R-253dc | 2-chloro-1,1,1-trifluoropropane (HCFC-253dc) | $\text{CF}_3\text{CHClCH}_3$                   |
| R-254fb | 1,1,1,3-tetrafluoropropane (HFC-254fb)       | $\text{CF}_3\text{CH}_2\text{CH}_2\text{F}$    |
| R-260fb | 1,1,1-trichloropropane (HCC-260fb)           | $\text{CCl}_3\text{CH}_2\text{CH}_3$           |
| R-261fc | 1,1-dichloro-1-fluoropropane (HCFC-261fc)    | $\text{CCl}_2\text{FCH}_2\text{CH}_3$          |
| R-262fc | 1-chloro-1,1-difluoropropane (HCFC-262fc)    | $\text{CClF}_2\text{CH}_2\text{CH}_3$          |
| R-263fb | 1,1,1-trifluoropropane (HFC-263fb)           | $\text{CF}_3\text{CH}_2\text{CH}_3$            |
| R-272fb | 1,1-difluoropropane (HFC-272fb)              | $\text{CHF}_2\text{CH}_2\text{CH}_3$           |
| R-290   | propane (HC-290)                             | $\text{CH}_3\text{CH}_2\text{CH}_3$            |
| R-374   | tetrafluorobutene (HFO-374)                  | $\text{C}_4\text{H}_6\text{F}_4$               |
| R-600   | butane (HC-600)                              | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ |
|         | allene                                       | $\text{H}_2\text{C}=\text{C}=\text{CH}_2$      |
|         | 2-butene                                     | $\text{CC}_3\text{CH}=\text{CHCH}_3$           |
|         | cyclobutene                                  | $\text{C}_4\text{H}_6$                         |
|         | 2-methylpropene                              | $\text{CH}_3(\text{CH}_3)\text{C}=\text{CF}_3$ |
| R-1122  | 1-chloro-2,2-difluoroethylene (HCFO-1122)    | $\text{CHCl}=\text{CF}_2$                      |

| Code     | Name-ASHRAE Designation                       | Formula                                  |
|----------|-----------------------------------------------|------------------------------------------|
| R-1132   | 1,2-difluoroethene (HFO-1132)                 | $\text{CHF}=\text{CHF}$                  |
| R-1132a  | 1,1-difluoroethene ((HFO-1132a)               | $\text{CH}=\text{CF}_2$                  |
| R-1141   | fluoroethene (HFO-1141)                       | $\text{CH}_2=\text{CHF}$                 |
| R-1150   | ethylene (HO-1150)                            | $\text{CH}_2=\text{CH}_2$                |
| R-1233xf | 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) | $\text{CF}_3\text{CCl}=\text{CH}_2$      |
| R-1234yf | 2,3,3,3-tetrafluoropropene(HFO-1234yf)        | $\text{CF}_3\text{CH}=\text{CHF}$        |
| R-1242zf | 3-chloro-3,3-difluoropropene (HCFO-1242zf)    | $\text{CClF}_2\text{CH}=\text{CH}_2$     |
| R-1243zf | 3,3,3-trifluoropropene (HFO-1243zf)           | $\text{CF}_3\text{CH}=\text{CH}_2$       |
| R-1251   | HCFO-1251 isomer                              | $\text{C}_3\text{H}_4\text{FCl}$         |
| R-1251   | HCFO-1251 isomer                              | $\text{C}_3\text{H}_4\text{FCl}$         |
| R-1252zc | 1,3-difluoropropene (HFO-1252zc)              | $\text{CH}_2\text{FCH}=\text{CHF}$       |
| R-1252yf | 2,3-difluoropropene (HFO-1252yf)              | $\text{CH}_2\text{FCF}=\text{CH}_2$      |
| R-1252zf | 3,3-difluoropropene (HFO-1252zf)              | $\text{CHF}_2\text{CH}=\text{CH}_2$      |
| R-1252ye | 1,2-difluoropropene (HFO1252ye)               | $\text{CH}_3\text{CF}=\text{CHF}$        |
| R-1260zf | 3-chloropropene (HCO-1260zf)                  | $\text{CH}_2\text{ClCH}=\text{CH}_2$     |
| R-1261   | 3-fluoro-1-propene (HFO-1261)                 | $\text{CH}_2\text{FCH}=\text{CH}_2$      |
| R-1270   | propylene (HO-1270)                           | $\text{CH}_3\text{CH}=\text{CH}_2$       |
| R-1345   | pentafluorobutene (HFO-1345)                  | $\text{C}_4\text{H}_3\text{F}_5$         |
|          | E/Z- <i>t</i> -BuO-CF=CH-CH <sub>3</sub>      | E/Z- <i>t</i> -BuO-CF=CH-CH <sub>3</sub> |

[0116] In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E may further comprise at least one additional compound selected from HCFC-22, HCC-40, HFO-1234yf, HFO-1243zf, HFO-263fb, HFO-1252zc, HFO-1252yf, HFO-1252zf, and HFO-1252ye. In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E may further comprise at least one additional compound comprising HFO-1234yf. In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E

may further comprise at least one additional compound comprising HFO-1243zf. In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E may further comprise at least one additional compound comprising HFO-263fb.

**[0117]** Some of the compounds present in the compositions of the present invention identified in Table 1 may exist as different configurational isomers or stereoisomers. The present invention is intended to include all single configurational isomers, single stereoisomers or any combination or mixture thereof. For instance, 1,2-difluoroethene (HFO-1132) is meant to represent the cis-isomer (Z), trans-isomer (E), or any combination or mixture of both isomers in any ratio. Single isomers or multiple isomers of the same compound may be used in any proportion.

**[0118]** The amount of additional compounds present in any of the foregoing refrigerant compositions can be greater than 0 ppm and less than 5,000 ppm and, in particular, can range from greater than zero to about 1,000 ppm, about 5 to about 500 ppm and about 1 to about 100 ppm.

**[0119]** In one embodiment, the amount of additional compounds present in any of the foregoing refrigerant compositions can be greater than 0 and less than 1 wt% of the refrigerant composition, preferably less than 0.5 weight percent, or more preferably less than 0.1 weight percent.

**[0120]** The compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E will perform more consistently and be more stable with only minor amounts of water present. Thus, the compositions may further comprise less than 100 ppm (by weight) water, preferably less than 20 ppm (by weight) water, and even more preferably less than 10 ppm (by weight) water.

**[0121]** Additionally, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E will perform more consistently and be more stable with only minor amounts of oxygen or air present. Therefore, the presently claimed compositions may further comprise less than about 5 volume percent non-adsorbable gases (NAG), preferably less than 3 volume percent NAG, and more preferably less than 1.5 volume percent NAG. Further, the presently claimed compositions, due to the presence of air or NAG, will

contain less than 1 volume percent oxygen, preferably less than 0.5 volume percent oxygen, and more preferably less than 0.3 volume percent oxygen.

**[0122]** In another embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E may contain a stabilizer. Such stabilizer compounds are intended to be present in a small amount and prevent decomposition due to the presence of water, air, NAG, or oxygen in a system while in use or while the composition is stored. HFO type refrigerants, due to the presence of a double bond, may be subject to thermal instability and decompose under extreme use, handling or storage situations also. Therefore, there may be advantages to adding stabilizers to HFO type refrigerants. Stabilizers may notably include nitromethane, ascorbic acid, terephthalic acid, azoles such as tolutriazole or benzotriazole, phenolic compounds such as tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-tertbutyl-4-methylphenol, epoxides (possibly fluorinated or perfluorinated alkyl epoxides or alkenyl or aromatic epoxides) such as n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, cyclic monoterpenes, terpenes, such as d-limonene,  $\alpha$ -terpinene,  $\beta$ -terpinene,  $\gamma$ -terpinene,  $\alpha$ -pinene, or  $\beta$ -pinene, phosphites, phosphates, phosphonates, thiols and lactones. Examples of suitable stabilizers are disclosed in WO2019213004, WO2020222864, and WO2020222865; the disclosures of which are hereby incorporated by reference.

**[0123]** If the composition does include a stabilizer, it may include any amount from 0.001 wt% up to 1 wt%, preferably from about 0.001 to about 0.5 weight percent, more preferably, from about 0.001 to about 0.3 weight percent of any of the stabilizers listed above.

**[0124]** In some embodiments, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E may contain a tracer compound or tracers. The tracer may comprise two or more tracer compounds. In some embodiments, the tracer is present in the compositions at a total concentration of about 50 parts per million by weight (ppm) to about 1000 ppm, based on the weight of the total composition. In other embodiments, the tracer is present at a total concentration of about 50 ppm to about 500 ppm. Alternatively, the tracer is present at a total concentration of about 100 ppm to about 300 ppm.

**[0125]** The tracer may be present in compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E in predetermined quantities to allow detection of any dilution, contamination or other alteration of the composition. The presence of certain compounds in the composition may indicate by what method or process one of the components has been produced. The tracer may also be added to the composition in a specified amount in order to identify the source of the composition. In this manner, detection of infringement on patent rights may be accomplished. The tracers may be refrigerant compounds but are present in the composition at levels that are unlikely to impact performance of the refrigerant component of the composition.

**[0126]** Tracer compounds may be hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof. Examples of tracer compounds include, but are not limited to HFC-23 (trifluoromethane), HCFC-31 (chlorofluoromethane), HFC-41 (fluoromethane), HFC-161 (fluoroethane), HFC-143a (1,1,1-trifluoroethane), HFC-134a (1,1,1,2-tetrafluoroethane), HFC-125 (pentafluoroethane), HFC-236fa (1,1,1,3,3,3-hexafluoropropane), HFC-236ea (1,1,1,2,3,3-hexafluoropropane), HFC-245cb (1,1,1,2,2-pentafluoropropane), HFC-245fa (1,1,1,3,3-pentafluoropropane), HFC-254eb (1,1,1,2-tetrafluoropropane), HFC-263fb (1,1,1 trifluoropropane), HFC-272ca (2,2-difluoropropane), HFC-281ea (2-fluoropropane), HFC-281fa (1-fluoropropane), HFC-329p (1,1,1,2,2,3,3,4,4-nonafluorobutane), HFC-329mmz (1,1,1-trifluoro-2-methylpropane), HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane), HFC-338pcc (1,1,2,2,3,3,4,4-octafluorobutane), CFC-12 (dichlorodifluoromethane), CFC-11 (trichlorofluoromethane), CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane), CFC-114a (1,1,-dichloro-1,2,2,2-tetrafluoroethane), HCFC-22 (chlorodifluoromethane), HCFC-123 (1,1-dichloro-2,2,2-trifluoroethane), HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane), HCFC-124a (1-chloro-1,1,2,2-tetrafluoroethane), HCFC-141b (1,1-dichloro-1-fluoroethane), HCFC-142b (1-chloro-1,1-difluoroethane), HCFC-151a (1-chloro-1-fluoroethane), HCFC-244bb (2-chloro-1,1,1,2-tetrafluoropropane), HCC-40 (chloromethane), HFO-1141 (fluoroethene), HCFO-1130 (1,2-dichloroethene), HCFO-1130a (1,1-dichloroethene),

HCFO-1131 (1-chloro-2-fluoroethene), HCFO-1122 (2-chloro-1,1-difluoroethene), HFO-1123 (1,1,2-trifluoroethene), HFO-1234ye (1,2,3,3-tetrafluoropropene), HFO-1243zf (3,3,3-trifluoropropene), HFO-1225ye (1,2,3,3,3-pentafluoropropene), HFO-1225zc (1,1,3,3,3-pentafluoropropene), PFC-116 (hexafluoroethane), PFC-C216 (hexafluorocyclopropane), PFC-218 (octafluoropropane), PFC-C318 (octafluorocyclobutane), PFC-1216 (hexafluoroethane), PFC-31-10mc (1,1,1,2,2,3,3,4,4,4-decafluorobutane), PFC-31-10my (1,1,1,2,3,3,3-heptafluoro-2-trifluoromethylpropane), and combinations thereof.

**[0127]** In another embodiment of the present disclosure, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E further comprise at least one lubricant. Lubricants may be selected from polyol ester, polyvinyl ether, and polyalkylene glycol. Lubricants may also 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.

**[0128]** 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. 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.

**[0129]** In one particular embodiment, the compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E are combined with a PAG lubricant or a PVE lubricant or a POE lubricant for usage in an air-conditioning system or heat pump system.

**[0130]** In the compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E 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.

**[0131]** In another aspect of the invention, the inventive composition comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E is used to introduce lubricant into the air-conditioning or heat pump 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.

**[0132]** 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.

**[0133]** 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.

[0134] 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.

[0135] 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.

[0136] 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-triadiazole 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).

[0137] 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.

[0138] 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.

**[0139]** 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, HFC-227ea, HFC-236fa, CF<sub>3</sub>I, and/or Krytox® lubricants, also incorporated by reference and described in patent application "Refrigerant compositions comprising fluoroolefins and uses thereof WO2009018117A1."

**[0140]** In one embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that (i) contains at least one fully fluorinated methyl (–CF<sub>3</sub>) or methylene (–CF<sub>2</sub>–) 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).

**[0141]** 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 (–CF<sub>3</sub>) or methylene (–CF<sub>2</sub>–) 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.

**[0142]** Thus, according to some embodiments, compositions of the present invention which comprise, consist of, or consist essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E 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  $\leq 5$  wt.%, or  $> 0$  wt.% and  $\leq 4$  wt.%, or  $> 0$  wt.% and  $\leq 3$  wt.%, or  $> 0$  wt.% and  $\leq 2$  wt.%, or  $> 0$  wt.% and  $\leq 1$  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. In some embodiments, the stabilized compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E are free of Group A fluorinated Substances, meaning that these substances are non-detectable by the methods and techniques described herein.

**[0143]** Further, in some embodiments, degradation products of such compositions of the present invention which comprise, consist of, or consist essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E 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. In some embodiments, degradation products of such compositions of the present invention which comprise, consist of, or consist essentially of stabilized compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E are free of Group A Fluorinated Substances, such as TFA, meaning that these substances are non-detectable by the methods and techniques described herein.

#### **METHODS AND SYSTEMS**

**[0144]** The compositions comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E are useful in numerous methods and systems that provide air-conditioning and heating.

**[0145]** In one embodiment, provided is a method of cooling comprising evaporating a composition comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E in the vicinity of a body to be cooled and thereafter condensing said composition, wherein said cooling is provided by an air-conditioner or heat pump.

**[0146]** In one embodiment, the air conditioner may be a residential, commercial, or industrial air-conditioning system. These may include, but are not limited to, window, ducted, ductless, packaged terminal, and those exterior to, but connected to the building, such as rooftop systems. The present method may be particularly useful in high ambient temperature regions, due to the high critical temperature of blends containing HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E.

[0147] In another embodiment, provided is a method of heating comprising evaporating a composition comprising HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E and thereafter condensing said composition in the vicinity of a body to be heated, wherein said heating is provided by a heat pump.

[0148] In one embodiment, the heat pump is a residential, light commercial or industrial heat pump system. These may include, but are not limited to, residential heat pumps that provide comfort air-conditioning and heating, hot water heat pumps for heating air (by secondary loop) or for heating water for residential or commercial use, heat pumps for heating manufacturing process equipment, and high temperature heat pumps. Due to the high critical temperature of blends containing HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E it is possible to heat water to higher temperatures than propane or R-454C.

[0149] In another embodiment, the method for producing cooling is particularly useful in regions where the ambient temperature can exceed at least 35°C.

[0150] In geographic areas with high ambient temperatures, where air conditioning becomes essential, refrigerant compositions with high critical temperatures and high thermal stability are desirable. Currently available hydrofluorocarbon (HFC) refrigerants such as R-410A, R-407C or R-32 have relatively low critical temperatures. As a consequence, these refrigerants do not perform well in extreme hot environments. The energy efficiency of a refrigerant generally decreases as the condensing temperature approaches the refrigerant critical temperature during operation at high ambient temperatures. In hot climates, R-22 has remained the refrigerant of choice for much air conditioning and refrigeration applications as it is not flammable and has a higher critical temperature so that it delivers higher cooling capacity and higher energy efficiency in hot climates as compared to R-410A or R-32. However, R-22 is an ozone depleting substance in the Montreal Protocol to reduce ozone depletion. As such, R-22 has been mandated and legislated for phase out for manufacture for and use in air conditioning and refrigeration. There is interest in finding a refrigerant with the lowest possible direct GWP and also that performs well in hot climate (or high ambient) temperature regions.

[0151] In the method for producing cooling the body to be cooled may be defined as any space, location, object or body for which it is desirable to provide cooling.

Examples include spaces, open or enclosed, that require cooling such as a residence, such as an apartment or apartment building, university dormitory, townhouse or other attached house, or a single family home; or the body to be cooled may be any other building, such as an office building, supermarket, college or university classroom or administration buildings.

**[0152]** In another embodiment, a method for producing air conditioning in high ambient temperatures is provided. The method comprises evaporating a composition comprising, consisting essentially of, or consisting of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E and thereafter condensing said composition. The method is particularly useful in regions where ambient temperatures can exceed 35°C or more.

**[0153]** In another embodiment, a method is provided for replacing HCFC-22 in high ambient air conditioning apparatus comprising providing a composition comprising, consisting essentially of, or consisting of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E to said apparatus. The method of replacing HCFC-22 is particularly useful in regions where ambient temperatures can exceed 35°C or more.

**[0154]** Similarly, in some industrial air conditioning applications heat must be released in high ambient temperature environments. HCFC-124 has been used as the working fluid in such applications. HCFC-124 is also controlled under the Montreal protocol as an ozone depleting substance and more environmentally sustainable replacements are desirable. Thus, a method is provided for replacing HCFC-124 in industrial air conditioning apparatus, comprising providing a composition comprising, consisting essentially of, or consisting of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E to said apparatus. The method of replacing HCFC-124 is particularly useful in regions where ambient temperatures can exceed 35°C or more.

**[0155]** In another embodiment, the method for producing cooling and method for replacing HCFC-22 or HCFC-124 are useful for systems operating in ambient temperatures of 40°C or higher. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures of 45°C or higher. In another embodiment, the method for producing cooling is useful for systems

operating in ambient temperatures of 50°C or higher. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures of 55°C or higher. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures of 60°C or higher. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures from 35- 50°C. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures from 35- 60°C. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures from 40- 60°C. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures from 45- 60°C. In another embodiment, the method for producing cooling is useful for systems operating in ambient temperatures from 50- 60°C.

**[0156]** In another embodiment, is provided a system for cooling or heating comprising a composition comprising, consisting of, or consisting essentially of HFO-1252zc and at least one of HFC-32 or HFO-1234ze-E and optionally a lubricant. The system comprises an evaporator, compressor, condenser, and expansion device, each operably connected to perform a vapor compression cycle.

**[0157]** The air-conditioner or heat pump system may be a residential, light commercial, or industrial air-conditioner or heat pump. Various such systems are described previously herein. In another embodiment, the air-conditioning or heat pump system containing a composition comprising, consisting of, or consisting essentially of HFO-1234ze-E and at least one of HFC-32 or HFO-1234ze-E may be a secondary loop system.

**[0158]** The following Examples are provided to illustrate certain aspects of the invention and shall not limit the scope of the appended claims.

## **EXAMPLES**

### **Example 1**

**[0159]** Cooling and heating performance for compositions containing HFO-1252zc and HFO-1234ze-E as well as compositions containing HFO-1252zc and HFC-32 is

compared to that for R-454C (ASHRAE designation for a refrigerant containing 78.5 wt% HFO-1234yf and 21.5 wt% HFC-32) and R-410A (ASHRAE designation for a refrigerant containing 50 wt% HFC-125 and 50 wt% HFC-32) for evaporator temperature at -10 degC. Results are shown in Table 2A and Table 2B.

[0160] The conditions used for the calculations are:

|                                                         |
|---------------------------------------------------------|
| T_condenser = 65.0 degC                                 |
| T_evaporator = -10.0 degC                               |
| subcool = 10.0 K                                        |
| superheat = 5.0 K                                       |
| compressor efficiency = 0.7                             |
| Average Heat Exchanger Temperature Set Points           |
| 100 % of superheat is included in refrigeration effect. |
| Vapor Molar Quality Entering Evaporator: q_4            |
| cooling load = 3.517 kW                                 |
| compressor displacement = 0.1 (m <sup>3</sup> / min)    |

TABLE 2A – EVAPORATOR – 10 °C, COMPARED TO R-454C

| Composition            | Critical temp (C) | Discharge temperature (C) | avg glide (K) | Cooling CAP vs 454C | Cooling COP vs 454C | Heating CAP vs 454C | Heating COP vs 454C |
|------------------------|-------------------|---------------------------|---------------|---------------------|---------------------|---------------------|---------------------|
| R-454C                 | 85.67             | 99.16                     | 4.65          | -                   | -                   | -                   | -                   |
| 1252zc / 1234ze-E, wt% |                   |                           |               |                     |                     |                     |                     |
| 81 / 19                | 108.64            | 97.63                     | 0.28          | 70.07               | 112.31              | 67.07               | 107.50              |
| 50 / 50                | 109.42            | 91.86                     | 0.47          | 62.75               | 111.09              | 60.31               | 106.76              |
| 20 / 80                | 109.49            | 86.31                     | 0.32          | 55.28               | 109.42              | 53.43               | 105.74              |
| 1252zc / R32, wt%      |                   |                           |               |                     |                     |                     |                     |
| 83 / 17                | 95.93             | 117.1                     | 5.74          | 98.78               | 108.14              | 95.87               | 104.96              |
| 50 / 50                | 81.44             | 132.56                    | 3.33          | 143.55              | 103.01              | 141.91              | 101.84              |
| 20 / 80                | 77.42             | 145.88                    | 0.44          | 178.95              | 103.65              | 176.49              | 102.23              |

TABLE 2B– EVAPORATOR – 10 °C, COMPARED TO R-410A

| Composition            | Crit temp (C) | Discharge temp (C) | avg glide (K) | Cooling CAP vs 410A | Cooling COP vs 410A | Heating CAP vs 410A | Heating COP vs 410A |
|------------------------|---------------|--------------------|---------------|---------------------|---------------------|---------------------|---------------------|
| R410A                  | 71.34         | 120.85             | 0.0629        | -                   | -                   | -                   | -                   |
| 1252zc / 1234ze-E, wt% |               |                    |               |                     |                     |                     |                     |
| 81 / 19                | 108.64        | 97.63              | 0.2804        | 42.3                | 114.4               | 40.2                | 108.7               |
| 50 / 50                | 109.42        | 91.86              | 0.4721        | 37.9                | 113.1               | 36.1                | 107.9               |
| 20 / 80                | 109.49        | 86.31              | 0.3168        | 33.3                | 111.4               | 32.0                | 106.9               |

| Composition       | Crit temp (C) | Discharge temp (C) | avg glide (K) | Cooling CAP vs 410A | Cooling COP vs 410A | Heating CAP vs 410A | Heating COP vs 410A |
|-------------------|---------------|--------------------|---------------|---------------------|---------------------|---------------------|---------------------|
| 1252zc / R32, wt% |               |                    |               |                     |                     |                     |                     |
| 83 / 17           | 95.93         | 117.1              | 5.7391        | 59.6                | 110.1               | 57.4                | 106.1               |
| 50 / 50           | 81.44         | 132.56             | 3.3298        | 86.6                | 104.9               | 85.0                | 103.0               |
| 20 / 80           | 77.42         | 145.88             | 0.4387        | 107.9               | 105.5               | 105.7               | 103.4               |

**[0161]** The data demonstrates improved COP for all compositions of the present invention as compared to R-410A and R-454C. Additionally, some of the inventive compositions have cooling capacity and heating capacity similar to R-410A or R-454C and the average temperature glide is reasonable. Additionally, the critical temperatures, particularly for the compositions containing HFO-1252zc and HFO-1234ze-E, are high enough for these blends to function well for cooling in high ambient regions, such as the Middle East, and could be used to provide high temperature water in a water heating heat pump as well.

### **Example 2**

**[0162]** Cooling and heating performance for compositions containing HFO-1252zc and HFO-1234ze-E as well as compositions containing HFO-1252zc and HFC-32 is compared to that for R-454C (ASHRAE designation for a refrigerant containing 78.5 wt% HFO-1234yf and 21.5 wt% HFC-32) and R-410A (ASHRAE designation for a refrigerant containing 50 wt% HFC-125 and 50 wt% HFC-32) for evaporator temperature at -15 deg C. Results are shown in Table 3A and Table 3B.

**[0163]** The conditions used for the calculations are:

|                                                         |
|---------------------------------------------------------|
| T <sub>condenser</sub> = 65.0 degC                      |
| T <sub>evaporator</sub> = -15.0 degC                    |
| subcool = 10.0 K                                        |
| superheat = 5.0 K                                       |
| compressor efficiency = 0.7                             |
| Average Heat Exchanger Temperature Set Points           |
| 100 % of superheat is included in refrigeration effect. |
| Vapor Molar Quality Entering Evaporator: q <sub>4</sub> |
| cooling load = 3.517 kW                                 |
| compressor displacement = 0.1 (m <sup>3</sup> / min)    |

TABLE 3A – EVAPORATOR – 15 °C, COMPARED TO R-454C

| Composition            | Discharge temp (C) | average glide (K) | Cooling CAP vs 454C | Cooling COP vs 454C | Heating CAP vs 454C | Heating COP vs 454C |
|------------------------|--------------------|-------------------|---------------------|---------------------|---------------------|---------------------|
| R-410A                 | 125.84             | 0.061             | -                   | -                   | -                   | -                   |
| R-454C                 | 101.74             | 4.56              | -                   | -                   | -                   | -                   |
| 1252zc / 1234ze-E, wt% |                    |                   |                     |                     |                     |                     |
| 81 / 19                | 100.37             | 0.28              | 70.22               | 112.84              | 66.86               | 107.46              |
| 50 / 50                | 94.19              | 0.48              | 62.45               | 111.40              | 59.77               | 106.62              |
| 20 / 80                | 88.25              | 0.32              | 54.53               | 109.38              | 52.56               | 105.45              |
| 1252zc / R32, wt%      |                    |                   |                     |                     |                     |                     |
| 83 / 17                | 121.16             | 5.61              | 99.33               | 108.80              | 95.96               | 105.11              |
| 50 / 50                | 138.32             | 3.32              | 146.39              | 103.97              | 144.06              | 102.31              |
| 20 / 80                | 153.43             | 0.42              | 183.89              | 104.83              | 180.30              | 102.81              |

TABLE 3B – EVAPORATOR -15 °C, COMPARED TO R-410A

| Composition            | Discharge temp (C) | average glide (K) | Cooling CAP vs 410A | Cooling COP vs 410A | Heating CAP vs 410A | Heating COP vs 410A |
|------------------------|--------------------|-------------------|---------------------|---------------------|---------------------|---------------------|
| R-410A                 | 125.84             | 0.0611            | -                   | -                   | -                   | -                   |
| R-454C                 | 101.74             | 4.5568            | 59.1                | 101.0               | 58.9                | 100.6               |
| 1252zc / 1234ze-E, wt% |                    |                   |                     |                     |                     |                     |
| 81 / 19                | 100.37             | 0.28              | 41.5                | 114.0               | 39.4                | 108.1               |
| 50 / 50                | 94.19              | 0.4764            | 36.9                | 112.5               | 35.2                | 107.3               |
| 20 / 80                | 88.25              | 0.3186            | 32.2                | 110.5               | 30.9                | 106.1               |
| 1252zc / R32, wt%      |                    |                   |                     |                     |                     |                     |
| 83 / 17                | 121.16             | 5.6084            | 58.7                | 109.9               | 56.5                | 105.7               |
| 50 / 50                | 138.32             | 3.3175            | 86.6                | 105.0               | 84.8                | 102.9               |
| 20 / 80                | 153.43             | 0.4245            | 108.7               | 105.9               | 106.1               | 103.4               |

**[0164]** The data demonstrates improved COP for all compositions of the present invention as compared to R-410A and R-454C. Additionally, some of the inventive compositions have cooling capacity and heating capacity similar to R-410A or R-454C and the average temperature glide is reasonable. Results show that a heat pump operated in a heating mode (or cooling mode), using a composition of 20-83 wt% HFO-1252z and 17-80 wt% HFC-32 exhibits a heating (or cooling) capacity of at least 80% of a heating (or cooling) capacity of R-454C.

**Example 3**

[0165] Cooling and heating performance for compositions containing HFO-1252zc and HFO-1234ze-E as well as compositions containing HFO-1252zc and HFC-32 is compared to that for R-454C (ASHRAE designation for a refrigerant containing 78.5 wt% HFO-1234yf and 21.5 wt% HFC-32) and R-410A (ASHRAE designation for a refrigerant containing 50 wt% HFC-125 and 50 wt% HFC-32) for evaporator temperature at -20 deg C. Results are shown in Table 4A and Table 4B.

[0166] The conditions used for the calculations are:

|                                                         |
|---------------------------------------------------------|
| T_condenser = 65.0 degC                                 |
| T_evaporator = -20.0 degC                               |
| subcool = 10.0 K                                        |
| superheat = 5.0 K                                       |
| compressor efficiency = 0.7                             |
| Average Heat Exchanger Temperature Set Points           |
| 100 % of superheat is included in refrigeration effect. |
| Vapor Molar Quality Entering Evaporator: q <sub>4</sub> |
| cooling load = 3.517 kW                                 |
| compressor displacement = 0.1 (m <sup>3</sup> / min)    |

**TABLE 4A – EVAPORATOR -20 °C, COMPARED TO R-454C**

| Composition            | Discharge temp (C) | avg glide (K) | Cooling CAP vs 454C | Cooling COP vs 454C | Heating CAP vs 454C | Heating COP vs 454C |
|------------------------|--------------------|---------------|---------------------|---------------------|---------------------|---------------------|
| R-454C                 | 104.54             | 4.4599        | -                   | -                   | -                   | -                   |
| 1252zc / 1234ze-E, wt% |                    |               |                     |                     |                     |                     |
| 81 / 19                | 103.35             | 0.2799        | 70.36               | 113.45              | 66.63               | 107.43              |
| 50 / 50                | 96.75              | 0.4807        | 62.11               | 111.67              | 59.19               | 106.45              |
| 20 / 80                | 90.39              | 0.3199        | 53.73               | 109.40              | 51.66               | 105.19              |
| 1252zc / R32, wt%      |                    |               |                     |                     |                     |                     |
| 83 / 17                | 125.51             | 5.478         | 99.90               | 109.48              | 96.03               | 105.24              |
| 50 / 50                | 144.46             | 3.3055        | 149.45              | 104.94              | 146.29              | 102.73              |
| 20 / 80                | 161.46             | 0.4105        | 189.23              | 106.16              | 184.31              | 103.40              |

TABLE 4B – EVAPORATOR –20 °C, COMPARED TO R-410A

| Composition            | Discharge temp (C) | avg glide (K) | Cooling CAP vs 410A | Cooling COP vs 410A | Heating CAP vs 410A | Heating COP vs 410A |
|------------------------|--------------------|---------------|---------------------|---------------------|---------------------|---------------------|
| R-410A                 | 131.17             | 0.0594        | -                   | -                   | -                   | -                   |
| 1252zc / 1234ze-E, wt% |                    |               |                     |                     |                     |                     |
| 81 / 19                | 103.35             | 0.2799        | 40.7                | 113.7               | 38.5                | 107.6               |
| 50 / 50                | 96.75              | 0.4807        | 36.0                | 111.9               | 34.2                | 106.6               |
| 20 / 80                | 90.39              | 0.3199        | 31.1                | 109.7               | 29.9                | 105.3               |
| 1252zc / R32, wt%      |                    |               |                     |                     |                     |                     |
| 83 / 17                | 125.51             | 5.478         | 57.8                | 109.7               | 55.5                | 105.4               |
| 50 / 50                | 144.46             | 3.3055        | 86.5                | 105.2               | 84.6                | 102.9               |
| 20 / 80                | 161.46             | 0.4105        | 109.6               | 106.4               | 106.6               | 103.5               |

[0167] The data demonstrates improved COP for all compositions of the present invention as compared to R-410A and R-454C. Additionally, some of the inventive compositions have cooling capacity and heating capacity similar to R-410A or R-454C and the average temperature glide is reasonable.

#### Example 4

[0168] Flammability estimates for the compositions containing HFO-1252zc and HFO-1234ze-E as well as compositions containing HFO-1252zc and HFC-32 are provided in Table 5. HOC is heat of combustion.

TABLE 5

| Composition, wt% |          |    | HOC, kJ/kg | Flam Class | Est LFL, vol% | GWP (AR4) |
|------------------|----------|----|------------|------------|---------------|-----------|
| 1252zc           | 1234ze-E | 32 |            |            |               |           |
| 81               | 19       | 0  | 18,972     | 2          | 4.0           | 1.95      |
| 50               | 50       | 0  | 16,019     | 2          | 5.0           | 3.5       |
| 20               | 80       | 0  | 12,653     | 2          | 6.0           | 5.0       |
| 83               | 0        | 17 | 18,904     | 2          | 5.5           | 115       |
| 50               | 0        | 50 | 15,257     | 2          | 9.0           | 336       |
| 20               | 0        | 80 | 11,942     | 2          | 12.3          | 536       |

[0169] The compositions claimed herein all fall within ASHRAE flammability class 2, with HOC less than 19,000 kJ/kg.

**Residential Heat Pump Systems**

[0170] In the below Tables 6 through 17B, “T\_condensor” is condenser temperature, “T\_evaporator” is evaporator temperature, “COP” is coefficient of performance (analogous to energy efficiency), and “CAP” is volumetric cooling capacity. In Examples 5-8, refrigerant performance has been determined for exemplary compositions of the present invention in residential heat pump systems as compared to R-410A and R-454C, in cooling and heating modes. The cooling mode data are based on the conditions set forth in Table 6. The heating mode data are based on the conditions set forth in Table 7.

**TABLE 6: RESIDENTIAL HEAT PUMP COOLING MODE CONDITIONS**

|                       |       |
|-----------------------|-------|
| T_condensor           | 47°C  |
| T_evaporator          | 7°C   |
| Subcool temp.         | 12.0K |
| Superheat temp.       | 3.0K  |
| Compressor Efficiency | 0.7   |

**TABLE 7: RESIDENTIAL HEAT PUMP HEATING MODE CONDITIONS**

|                       |        |
|-----------------------|--------|
| T_condensor           | 35°C   |
| T_evaporator          | -5°C   |
| Subcool temp.         | 11.11K |
| Superheat temp.       | 8.33K  |
| Compressor Efficiency | 0.7    |

**Example 5: HFO-1252zc/HFC-32 (cooling mode)**

[0171] Refrigerant performance has been determined for exemplary compositions of the present invention comprising HFO-1252zc and HFC-32 in residential heat pump systems as compared to R-410A and R-454C, in cooling mode. Performance metric and composition property ranges are summarized in Table 8, where the ASHRAE flammability class remains 2, the average temperature glide is < 10 K, the cooling capacity is no less than 90% of the cooling capacity of R-454C, and the GWP < 300. Tables 9A and 9B tabulate several compositions of optimal cooling efficiency and capacity.

**TABLE 8: RESIDENTIAL HEAT PUMP COOLING MODE CONDITION, SUMMARY  
OF CYCLE METRIC PERFORMANCE AND FLUID PROPERTY RANGES FOR  
1252ZC/32 IN EX. 5**

|                                     | MAXIMA | MINIMA |
|-------------------------------------|--------|--------|
| w_R1252zc (nominal weight fraction) | 0.7    | 0.56   |
| W_R32 (nominal weight fraction)     | 0.44   | 0.3    |
| average glide (K)                   | 8.1    | 6.0    |
| GWP AR5                             | 298    | 204    |
| COP (relative to R-410A)            | 1.04   | 1.02   |
| CAP (relative to R-410A)            | 0.82   | 0.72   |
| COP (relative to R-454C)            | 1.00   | 0.98   |
| CAP (relative to R-454C)            | 1.24   | 1.09   |

**TABLE 9A: RESIDENTIAL HEAT PUMP COOLING MODE CONDITION, CYCLE  
METRIC PERFORMANCE AND FLUID PROPERTY RANGES FOR 1252ZC/32 IN  
EX. 5**

| w_R-1252zc | w_R32 | average<br>glide (K) | GWP<br>AR5 | ASHRAE<br>flammability class |
|------------|-------|----------------------|------------|------------------------------|
| 0.56       | 0.44  | 5.98                 | 298.4      | 2                            |
| 0.57       | 0.43  | 6.17                 | 291.7      | 2                            |
| 0.58       | 0.42  | 6.36                 | 284.9      | 2                            |
| 0.59       | 0.41  | 6.54                 | 278.2      | 2                            |
| 0.6        | 0.4   | 6.72                 | 271.4      | 2                            |
| 0.61       | 0.39  | 6.90                 | 264.6      | 2                            |
| 0.62       | 0.38  | 7.06                 | 257.9      | 2                            |
| 0.63       | 0.37  | 7.22                 | 251.1      | 2                            |
| 0.64       | 0.36  | 7.38                 | 244.4      | 2                            |
| 0.65       | 0.35  | 7.52                 | 237.6      | 2                            |
| 0.66       | 0.34  | 7.66                 | 230.8      | 2                            |
| 0.67       | 0.33  | 7.79                 | 224.1      | 2                            |
| 0.68       | 0.32  | 7.90                 | 217.3      | 2                            |
| 0.69       | 0.31  | 8.01                 | 210.6      | 2                            |
| 0.7        | 0.3   | 8.10                 | 203.8      | 2                            |

**TABLE 9B: RESIDENTIAL HEAT PUMP COOLING MODE CONDITION, CYCLE METRIC PERFORMANCE AND FLUID PROPERTY RANGES FOR 1252ZC/32 IN**

**EX. 5**

| w_R-1252zc | w_R32 | COP (rel R-410A) | CAP (rel to R-410A) | COP (rel to R-454C) | CAP (rel to R-454C) |
|------------|-------|------------------|---------------------|---------------------|---------------------|
| 0.56       | 0.44  | 1.02             | 0.82                | 0.98                | 1.24                |
| 0.57       | 0.43  | 1.02             | 0.81                | 0.98                | 1.23                |
| 0.58       | 0.42  | 1.02             | 0.81                | 0.98                | 1.22                |
| 0.59       | 0.41  | 1.02             | 0.80                | 0.99                | 1.21                |
| 0.6        | 0.4   | 1.03             | 0.79                | 0.99                | 1.20                |
| 0.61       | 0.39  | 1.03             | 0.78                | 0.99                | 1.19                |
| 0.62       | 0.38  | 1.03             | 0.78                | 0.99                | 1.18                |
| 0.63       | 0.37  | 1.03             | 0.77                | 0.99                | 1.17                |
| 0.64       | 0.36  | 1.03             | 0.76                | 0.99                | 1.16                |
| 0.65       | 0.35  | 1.03             | 0.76                | 1.00                | 1.15                |
| 0.66       | 0.34  | 1.04             | 0.75                | 1.00                | 1.14                |
| 0.67       | 0.33  | 1.04             | 0.74                | 1.00                | 1.13                |
| 0.68       | 0.32  | 1.04             | 0.74                | 1.00                | 1.12                |
| 0.69       | 0.31  | 1.04             | 0.73                | 1.00                | 1.10                |
| 0.7        | 0.3   | 1.04             | 0.72                | 1.00                | 1.09                |

**[0172]** Results show that the HFO-1252zc and HFC-32 compositions of the present invention provide improved COP relative to R-410A and improved capacity relative to R-454C, for cooling using residential heat pump systems. Results also show that a heat pump operated in cooling mode, using a composition of 56-68 wt% HFO-1252zc and 32-44 wt% HFC-32, exhibits a glide of < 8 °K. They also show that a heat pump operated in a cooling mode, using a composition of 56-70 wt% HFO-1252z and 30-44 wt% HFC-32 exhibits a cooling capacity of at least 80% of a cooling capacity of R-454C.

**Example 6: HFO-1252zc/HFC-32 (heating mode)**

**[0173]** Refrigerant performance has been determined for exemplary compositions of the present invention comprising HFO-1252zc and HFC-32 in residential heat pump systems as compared to R-410A and R-454C, in heating mode. Performance metric and composition property ranges are summarized in Table 10, where the ASHRAE flammability class remains 2, the average temperature glide is < 10 K, the heating capacity is least 10% less than heating capacity of R-454C, and GWP < 300. Table 11 tabulates several compositions of optimal cooling efficiency and capacity.

**TABLE 10: RESIDENTIAL HEAT PUMP HEATING MODE CONDITION, CYCLE  
METRIC PERFORMANCE AND FLUID PROPERTY RANGES FOR 1252ZC/32 IN**

**EX. 6**

|                                     | MAXIMA | MINIMA |
|-------------------------------------|--------|--------|
| w_R1252zc (nominal weight fraction) | 0.7    | 0.56   |
| W_R32 (nominal weight fraction)     | 0.44   | 0.3    |
| average glide (K)                   | 8.5    | 6.3    |
| GWP AR5                             | 298    | 204    |
| COP (relative to R-410A)            | 1.03   | 1.01   |
| CAP (relative to R-410A)            | 0.81   | 0.71   |
| COP (relative to R-454C)            | 1.00   | 0.98   |
| CAP (relative to R-454C)            | 1.24   | 1.09   |

**TABLE 11A: RESIDENTIAL HEAT PUMP HEATING MODE CONDITION,  
SUMMARY OF CYCLE METRIC PERFORMANCE AND FLUID PROPERTY  
RANGES FOR 1252ZC/32 IN EX. 6**

| w_R-<br>1252zc | w_R32 | average glide<br>(K) | GWP AR5 | ASHRAE<br>flammability<br>class |
|----------------|-------|----------------------|---------|---------------------------------|
| 0.7            | 0.3   | 8.54                 | 203.8   | 2                               |
| 0.69           | 0.31  | 8.45                 | 210.6   | 2                               |
| 0.68           | 0.32  | 8.34                 | 217.3   | 2                               |
| 0.67           | 0.33  | 8.22                 | 224.1   | 2                               |
| 0.66           | 0.34  | 8.09                 | 230.8   | 2                               |
| 0.65           | 0.35  | 7.95                 | 237.6   | 2                               |
| 0.64           | 0.36  | 7.80                 | 244.4   | 2                               |
| 0.63           | 0.37  | 7.64                 | 251.1   | 2                               |
| 0.62           | 0.38  | 7.48                 | 257.9   | 2                               |
| 0.61           | 0.39  | 7.31                 | 264.6   | 2                               |
| 0.6            | 0.4   | 7.13                 | 271.4   | 2                               |
| 0.59           | 0.41  | 6.94                 | 278.2   | 2                               |
| 0.58           | 0.42  | 6.75                 | 284.9   | 2                               |
| 0.57           | 0.43  | 6.55                 | 291.7   | 2                               |
| 0.56           | 0.44  | 6.35                 | 298.4   | 2                               |

**TABLE 11B: RESIDENTIAL HEAT PUMP HEATING MODE CONDITION,  
SUMMARY OF CYCLE METRIC PERFORMANCE AND FLUID PROPERTY  
RANGES FOR 1252ZC/32 IN EX. 6**

| w_R-1252zc | w_R32 | COP_(rel to R-410A) | CAP_(rel to R-410A) | COP_(rel to R-454C)) | CAP_(rel to R-454C) |
|------------|-------|---------------------|---------------------|----------------------|---------------------|
| 0.7        | 0.3   | 1.03                | 0.71                | 1.00                 | 1.09                |
| 0.69       | 0.31  | 1.03                | 0.71                | 1.00                 | 1.10                |
| 0.68       | 0.32  | 1.03                | 0.72                | 1.00                 | 1.11                |
| 0.67       | 0.33  | 1.02                | 0.73                | 0.99                 | 1.12                |
| 0.66       | 0.34  | 1.02                | 0.74                | 0.99                 | 1.13                |
| 0.65       | 0.35  | 1.02                | 0.74                | 0.99                 | 1.14                |
| 0.64       | 0.36  | 1.02                | 0.75                | 0.99                 | 1.15                |
| 0.63       | 0.37  | 1.02                | 0.76                | 0.99                 | 1.17                |
| 0.62       | 0.38  | 1.02                | 0.77                | 0.99                 | 1.18                |
| 0.61       | 0.39  | 1.02                | 0.77                | 0.99                 | 1.19                |
| 0.6        | 0.4   | 1.02                | 0.78                | 0.99                 | 1.20                |
| 0.59       | 0.41  | 1.01                | 0.79                | 0.99                 | 1.21                |
| 0.58       | 0.42  | 1.01                | 0.79                | 0.98                 | 1.22                |
| 0.57       | 0.43  | 1.01                | 0.80                | 0.98                 | 1.23                |
| 0.56       | 0.44  | 1.01                | 0.81                | 0.98                 | 1.24                |

**[0174]** Results show that the HFO-1252zc and HFC-32 compositions of the present invention provide improved COP relative to R-410A and improved capacity (upwards of 25% more in some cases) relative to R-454C, for heating using residential heat pump systems. Results also show that a heat pump operated in heating mode, using a composition of 56-65 wt% HFO-1252zc and 36-44 wt% HFC-32, exhibits a glide of < 8 °K. They also show that a heat pump operated in a heating mode, using a composition of 56-70 wt% HFO-1252z and 30-44 wt% HFC-32 exhibits a heating capacity of at least 80% of a heating capacity of R-454C.

**Example 7: HFO-1252zc/HFO-1234ze(E)/HFC-32 (cooling mode)**

**[0175]** Refrigerant performance has been determined for exemplary compositions of the present invention comprising HFO-1252zc, HFO-1234ze(E), and HFC-32 in residential heat pump systems as compared to R-410A and R-454C, in cooling mode. Performance metric and composition property ranges are summarized in Table 12, where the ASHRAE flammability class remains 2L or 2, the average

temperature glide is < 10 K, the cooling capacity is least 10% less than cooling capacity of R-454C, and GWP < 300. Performance metric and composition property ranges are summarized in Table 13, where the ASHRAE flammability class remains 2L or 2, the average temperature glide is < 10 K, the cooling capacity is at least 10% less than cooling capacity of R-454C, and GWP < 150. Table 14 tabulates several compositions about the compositions of optimal cooling efficiency and capacity.

**TABLE 12: RESIDENTIAL HEAT PUMP COOLING MODE CONDITION, SUMMARY OF CYCLE METRIC PERFORMANCE AND FLUID PROPERTY RANGES FOR CERTAIN COMPOSITIONAL RANGES OF 1252ZC/1234ZE-E/32 IN EX. 7**

|                                       | MAXIMA | MINIMA |
|---------------------------------------|--------|--------|
| w_R1252zc (nominal weight fraction)   | 0.7    | 0      |
| w_R1234ze-E (nominal weight fraction) | 0.68   | 0      |
| W_R32 (nominal weight fraction)       | 0.44   | 0.16   |
| average glide (K)                     | 10     | 5.7    |
| GWP AR5                               | 298    | 109    |
| COP (relative to R-410A)              | 1.07   | 1.02   |
| CAP (relative to R-410A)              | 0.82   | 0.59   |
| COP (relative to R-454C)              | 1.03   | 0.98   |
| CAP (relative to R-454C)              | 1.24   | 0.90   |

**TABLE 13: RESIDENTIAL HEAT PUMP COOLING MODE CONDITION, CYCLE METRIC PERFORMANCE AND FLUID PROPERTY RANGES FOR CERTAIN COMPOSITIONAL RANGES OF 1252ZC/1234ZE-E/32 IN EX. 7**

|                                       | MAXIMA | MINIMA |
|---------------------------------------|--------|--------|
| w_R1252zc (nominal weight fraction)   | 0.65   | 0.15   |
| w_R1234ze-E (nominal weight fraction) | 0.63   | 0.13   |
| W_R32 (nominal weight fraction)       | 0.22   | 0.16   |
| average glide (K)                     | 10     | 7.3    |
| GWP AR5                               | 150    | 109    |
| COP (relative to R-410A)              | 1.07   | 1.06   |
| CAP (relative to R-410A)              | 0.66   | 0.59   |
| COP (relative to R-454C)              | 1.03   | 1.02   |
| CAP (relative to R-454C)              | 0.99   | 0.90   |

**TABLE 14A: RESIDENTIAL HEAT PUMP COOLING MODE CONDITION,  
SUMMARY OF CYCLE METRIC PERFORMANCE AND FLUID PROPERTY  
RANGES FOR 1252ZC/1234ZE-E/32 IN EX. 7**

| w_R-<br>1252zc | w_R1234<br>ze(E) | w_R32  | average<br>glide (K) | GWP AR5 | ASHRAE<br>flammability<br>class |
|----------------|------------------|--------|----------------------|---------|---------------------------------|
| 0.005          | 0.5572           | 0.4378 | 8.39                 | 297.0   | 2L                              |
| 0.05           | 0.62             | 0.33   | 9.67                 | 224.1   | 2L                              |
| 0.1            | 0.55             | 0.35   | 9.15                 | 237.6   | 2L                              |
| 0.14           | 0.45             | 0.41   | 7.93                 | 278.2   | 2L                              |
| 0.17           | 0.54             | 0.29   | 9.42                 | 197.0   | 2L                              |
| 0.21           | 0.37             | 0.42   | 7.23                 | 284.9   | 2L                              |
| 0.24           | 0.42             | 0.34   | 8.38                 | 230.8   | 2L                              |
| 0.27           | 0.45             | 0.28   | 8.89                 | 190.3   | 2                               |
| 0.3            | 0.47             | 0.23   | 8.96                 | 156.5   | 2                               |
| 0.33           | 0.47             | 0.2    | 8.73                 | 136.2   | 2                               |
| 0.37           | 0.19             | 0.44   | 5.90                 | 298.4   | 2                               |
| 0.39           | 0.43             | 0.18   | 8.27                 | 122.7   | 2                               |
| 0.42           | 0.39             | 0.19   | 8.21                 | 129.4   | 2                               |
| 0.45           | 0.35             | 0.2    | 8.14                 | 136.2   | 2                               |
| 0.48           | 0.28             | 0.24   | 8.11                 | 163.2   | 2                               |
| 0.51           | 0.21             | 0.28   | 7.87                 | 190.3   | 2                               |
| 0.54           | 0.14             | 0.32   | 7.51                 | 217.3   | 2                               |
| 0.57           | 0.05             | 0.38   | 6.86                 | 257.9   | 2                               |
| 0.6            | 0.04             | 0.36   | 7.20                 | 244.4   | 2                               |
| 0.63           | 0.14             | 0.23   | 7.96                 | 156.5   | 2                               |

**TABLE 14B: RESIDENTIAL HEAT PUMP COOLING MODE CONDITION,  
SUMMARY OF CYCLE METRIC PERFORMANCE AND FLUID PROPERTY  
RANGES FOR 1252ZC/1234ZE-E/32 IN EX. 7**

| w_R-<br>1252zc | w_R12<br>34ze(E) | w_R32  | COP_(rel<br>to R-<br>410A) | CAP_(rel<br>to R-<br>410A) | COP_(rel<br>to R-<br>454C) | CAP_(rel<br>to R-<br>454C) |
|----------------|------------------|--------|----------------------------|----------------------------|----------------------------|----------------------------|
| 0.005          | 0.5572           | 0.4378 | 1.04                       | 0.73                       | 1.00                       | 1.11                       |
| 0.05           | 0.62             | 0.33   | 1.06                       | 0.66                       | 1.02                       | 1.01                       |
| 0.1            | 0.55             | 0.35   | 1.05                       | 0.69                       | 1.01                       | 1.05                       |
| 0.14           | 0.45             | 0.41   | 1.04                       | 0.74                       | 1.00                       | 1.13                       |
| 0.17           | 0.54             | 0.29   | 1.05                       | 0.66                       | 1.02                       | 1.00                       |
| 0.21           | 0.37             | 0.42   | 1.03                       | 0.77                       | 0.99                       | 1.16                       |
| 0.24           | 0.42             | 0.34   | 1.04                       | 0.71                       | 1.00                       | 1.08                       |
| 0.27           | 0.45             | 0.28   | 1.05                       | 0.67                       | 1.01                       | 1.01                       |
| 0.3            | 0.47             | 0.23   | 1.06                       | 0.63                       | 1.02                       | 0.95                       |

| w_R-1252zc | w_R1234ze(E) | w_R32 | COP_(rel to R-410A) | CAP_(rel to R-410A) | COP_(rel to R-454C) | CAP_(rel to R-454C) |
|------------|--------------|-------|---------------------|---------------------|---------------------|---------------------|
| 0.33       | 0.47         | 0.2   | 1.06                | 0.61                | 1.02                | 0.92                |
| 0.37       | 0.19         | 0.44  | 1.02                | 0.81                | 0.99                | 1.22                |
| 0.39       | 0.43         | 0.18  | 1.06                | 0.60                | 1.02                | 0.90                |
| 0.42       | 0.39         | 0.19  | 1.06                | 0.61                | 1.02                | 0.92                |
| 0.45       | 0.35         | 0.2   | 1.06                | 0.62                | 1.02                | 0.94                |
| 0.48       | 0.28         | 0.24  | 1.05                | 0.66                | 1.01                | 1.00                |
| 0.51       | 0.21         | 0.28  | 1.05                | 0.70                | 1.01                | 1.06                |
| 0.54       | 0.14         | 0.32  | 1.04                | 0.73                | 1.00                | 1.11                |
| 0.57       | 0.05         | 0.38  | 1.03                | 0.78                | 0.99                | 1.18                |
| 0.6        | 0.04         | 0.36  | 1.03                | 0.76                | 0.99                | 1.16                |
| 0.63       | 0.14         | 0.23  | 1.05                | 0.66                | 1.02                | 1.01                |

[0176] Results show that the HFO-1252zc, HFO-1234ze(E), and HFC-32 compositions of the present invention provide improved COP or similar energy efficiency relative to R-454C, for cooling using residential heat pump systems. Additionally, in many cases, the HFO-1252zc, HFO-1234ze(E), and HFC-32 compositions of the present invention provide improved cooling capacity relative to R-454C. Results also show that a composition of 0.5-24 wt% HFO-1252zc, 29-43.78 wt% HFC-32, and 37-62 wt% HFO-1234ze-E has a flammability rating of 2L. They also show that a heat pump operated in cooling mode, using a composition of 14-63 wt% HFO-1252zc, 23-44 wt% HFC-32, and 4-37 wt% HFO-1234ze-E, exhibits a glide of < 8 °K. Finally, they also show that a composition of 30-63 wt% HFO-1252zc, 18-23 wt% HFC-32, and 14-47 wt% HFO-1234ze-E has a GWP < 160. They also show that a heat pump operated in a cooling mode, using a composition of 0.5-63 wt% HFO-1252zc, 18-43.78 wt% HFC-32, and 4-62 wt% HFO-1234ze-E exhibits a cooling capacity of at least 80% of a cooling capacity of R-454C.

**Example 8: HFO-1252zc/HFO-1234ze(E)/HFC-32 (heating mode)**

[0177] Refrigerant performance has been determined for exemplary compositions of the present invention comprising HFO-1252zc, HFO-1234ze(E), and HFC-32 in residential heat pump systems as compared to R-410A and R-454C, in heating mode. Performance metric and composition property ranges are summarized in Table 15, where the ASHRAE flammability class remains 2L or 2, the average temperature glide is < 10 K, the heating capacity is least 10% less than heating capacity of R-454C, and GWP < 300. Performance metric and composition property

ranges are summarized in Table 16, where the ASHRAE flammability class remains 2L or 2, the average temperature glide is < 10 K, the heating capacity is at least 10% less than heating capacity of R-454C, and GWP < 150. Table 17 tabulates several compositions of optimal cooling efficiency and capacity.

**TABLE 15: RESIDENTIAL HEAT PUMP HEATING MODE CONDITION,  
SUMMARY OF CYCLE METRIC PERFORMANCE AND FLUID PROPERTY  
RANGES FOR CERTAIN COMPOSITIONAL RANGES OF 1252ZC/1234ZE-E/32 IN  
EX. 8**

|                                       | MAXIMA | MINIMA |
|---------------------------------------|--------|--------|
| w_R1252zc (nominal weight fraction)   | 0.7    | 0      |
| w_R1234ze-E (nominal weight fraction) | 0.63   | 0      |
| W_R32 (nominal weight fraction)       | 0.44   | 0.17   |
| average glide (K)                     | 10     | 6.1    |
| GWP AR5                               | 298    | 116    |
| COP (relative to R-410A)              | 1.04   | 1.01   |
| CAP (relative to R-410A)              | 0.81   | 0.59   |
| COP (relative to R-454C)              | 1.01   | 0.98   |
| CAP (relative to R-454C)              | 1.24   | 0.90   |

**TABLE 16: RESIDENTIAL HEAT PUMP HEATING MODE CONDITION,  
SUMMARY OF CYCLE METRIC PERFORMANCE AND FLUID PROPERTY  
RANGES FOR CERTAIN COMPOSITIONAL RANGES OF 1252ZC/1234ZE-E/32 IN  
EX. 8**

|                                       | MAXIMA | MINIMA |
|---------------------------------------|--------|--------|
| w_R1252zc (nominal weight fraction)   | 0.65   | 0.22   |
| w_R1234ze-E (nominal weight fraction) | 0.56   | 0.13   |
| W_R32 (nominal weight fraction)       | 0.22   | 0.17   |
| average glide (K)                     | 10     | 7.87   |
| GWP AR5                               | 150    | 116    |
| COP (relative to R-410A)              | 1.04   | 1.04   |
| CAP (relative to R-410A)              | 0.64   | 0.59   |
| COP (relative to R-454C)              | 1.01   | 1.01   |
| CAP (relative to R-454C)              | 0.98   | 0.90   |

**TABLE 17A: RESIDENTIAL HEAT PUMP HEATING MODE CONDITION, CYCLE  
METRIC PERFORMANCE AND FLUID PROPERTY RANGES FOR  
1252ZC/1234ZE-E/32 IN EX. 8**

| w_R-<br>1252zc | w_R1234<br>ze(E) | w_R32      | average<br>glide (K) | GWP AR5 | ASHRAE<br>flammability<br>class |
|----------------|------------------|------------|----------------------|---------|---------------------------------|
| 0.005          | 0.5572           | 0.437<br>8 | 8.89                 | 297.0   | 2L                              |
| 0.07           | 0.57             | 0.36       | 9.74                 | 244.4   | 2L                              |
| 0.13           | 0.52             | 0.35       | 9.51                 | 237.6   | 2L                              |
| 0.18           | 0.45             | 0.37       | 8.84                 | 251.1   | 2L                              |
| 0.22           | 0.41             | 0.37       | 8.55                 | 251.1   | 2L                              |
| 0.25           | 0.39             | 0.36       | 8.50                 | 244.4   | 2L                              |
| 0.28           | 0.36             | 0.36       | 8.30                 | 244.4   | 2                               |
| 0.31           | 0.31             | 0.38       | 7.75                 | 257.9   | 2                               |
| 0.34           | 0.24             | 0.42       | 6.81                 | 284.9   | 2                               |
| 0.36           | 0.42             | 0.22       | 9.14                 | 149.7   | 2                               |
| 0.39           | 0.34             | 0.27       | 8.80                 | 183.5   | 2                               |
| 0.42           | 0.23             | 0.35       | 7.72                 | 237.6   | 2                               |
| 0.45           | 0.12             | 0.43       | 6.28                 | 291.7   | 2                               |
| 0.47           | 0.27             | 0.26       | 8.53                 | 176.8   | 2                               |
| 0.5            | 0.13             | 0.37       | 7.28                 | 251.1   | 2                               |
| 0.52           | 0.27             | 0.21       | 8.41                 | 143.0   | 2                               |
| 0.55           | 0.13             | 0.32       | 7.94                 | 217.3   | 2                               |
| 0.57           | 0.26             | 0.17       | 7.93                 | 115.9   | 2                               |
| 0.6            | 0.18             | 0.22       | 8.33                 | 149.7   | 2                               |
| 0.64           | 0.01             | 0.35       | 7.90                 | 237.6   | 2                               |

**TABLE 17B: RESIDENTIAL HEAT PUMP HEATING MODE CONDITION, CYCLE  
METRIC PERFORMANCE AND FLUID PROPERTY RANGES FOR  
1252ZC/1234ZE-E/32 IN EX. 8**

| w_R-<br>1252zc | w_R1234<br>ze(E) | w_R3<br>2  | COP_(rel<br>to R-<br>410A) | CAP_(rel<br>to R-<br>410A) | COP_(rel<br>to R-<br>454C) | CAP_(rel<br>to R-<br>454C) |
|----------------|------------------|------------|----------------------------|----------------------------|----------------------------|----------------------------|
| 0.005          | 0.5572           | 0.437<br>8 | 1.02                       | 0.71                       | 1.00                       | 1.09                       |
| 0.07           | 0.57             | 0.36       | 1.03                       | 0.67                       | 1.00                       | 1.03                       |
| 0.13           | 0.52             | 0.35       | 1.03                       | 0.67                       | 1.00                       | 1.04                       |
| 0.18           | 0.45             | 0.37       | 1.02                       | 0.70                       | 1.00                       | 1.08                       |
| 0.22           | 0.41             | 0.37       | 1.02                       | 0.71                       | 0.99                       | 1.09                       |
| 0.25           | 0.39             | 0.36       | 1.02                       | 0.71                       | 0.99                       | 1.09                       |

| w_R-1252zc | w_R1234ze(E) | w_R32 | COP_(rel to R-410A) | CAP_(rel to R-410A) | COP_(rel to R-454C) | CAP_(rel to R-454C) |
|------------|--------------|-------|---------------------|---------------------|---------------------|---------------------|
| 0.28       | 0.36         | 0.36  | 1.02                | 0.71                | 0.99                | 1.10                |
| 0.31       | 0.31         | 0.38  | 1.02                | 0.74                | 0.99                | 1.13                |
| 0.34       | 0.24         | 0.42  | 1.02                | 0.77                | 0.99                | 1.19                |
| 0.36       | 0.42         | 0.22  | 1.04                | 0.61                | 1.01                | 0.94                |
| 0.39       | 0.34         | 0.27  | 1.03                | 0.66                | 1.00                | 1.01                |
| 0.42       | 0.23         | 0.35  | 1.02                | 0.73                | 0.99                | 1.12                |
| 0.45       | 0.12         | 0.43  | 1.01                | 0.79                | 0.98                | 1.22                |
| 0.47       | 0.27         | 0.26  | 1.03                | 0.66                | 1.00                | 1.01                |
| 0.5        | 0.13         | 0.37  | 1.02                | 0.75                | 0.99                | 1.16                |
| 0.52       | 0.27         | 0.21  | 1.04                | 0.62                | 1.01                | 0.95                |
| 0.55       | 0.13         | 0.32  | 1.03                | 0.72                | 1.00                | 1.10                |
| 0.57       | 0.26         | 0.17  | 1.04                | 0.59                | 1.01                | 0.90                |
| 0.6        | 0.18         | 0.22  | 1.04                | 0.64                | 1.01                | 0.98                |
| 0.64       | 0.01         | 0.35  | 1.02                | 0.74                | 0.99                | 1.14                |

[0178] Results show that the HFO-1252zc, HFO-1234ze(E), and HFC-32 compositions of the present invention provide improved COP or similar energy efficiency relative to R-454C, for heating using residential heat pump systems. Additionally, in many cases, the HFO-1252zc, HFO-1234ze(E), and HFC-32 compositions of the present invention provide improved heating capacity relative to R-454C. Results also show that a composition of 0.5-25 wt% HFO-1252zc, 35-43.78 wt% HFC-32, and 39-57 wt% HFO-1234ze-E has a flammability rating of 2L. They also show that a heat pump operated in heating mode, using a composition of 31-64 wt% HFO-1252zc, 17-43 wt% HFC-32, and 1-31 wt% HFO-1234ze-E, exhibits a glide of < 8 °K. Finally, they also show that a composition of 36-60 wt% HFO-1252zc, 17-22 wt% HFC-32, and 18-42 wt% HFO-1234ze-E has a GWP < 160. They also show that a heat pump operated in a heating mode, using a composition of 0.5-64 wt% HFO-1252zc, 17-43.78 wt% HFC-32, and 1-57 wt% HFO-1234ze-E exhibits a heating capacity of at least 80% of a heating capacity of R-454C.

#### **Example 9: HFO-1252zc/HFO-1234ze-E (cooling mode)**

[0179] Refrigerant performance has been determined for exemplary compositions of the present invention comprising HFO-1252zc and HFO-1234ze-E in residential heat pump systems as compared to R-410A and R-454C, in cooling mode. Performance metric and composition property ranges are summarized in Table 18,

where the ASHRAE flammability class remains 2L or 2, the average temperature glide is < 2 K, the cooling capacity is least 10% less than cooling capacity of R-454C, and GWP < 300. There are no composition ranges where the ASHRAE flammability class remains 2L or 2, the average temperature glide is < 10 K, the cooling capacity is at least 50% of cooling capacity of R-454C, and GWP ~ 1. Table 19 tabulates several compositions of optimal cooling efficiency and capacity.

**TABLE 18: RESIDENTIAL HEAT PUMP COOLING MODE CONDITION,  
SUMMARY OF CYCLE METRIC PERFORMANCE AND FLUID PROPERTY  
RANGES FOR 1252ZC/1234ZE-E IN EX. 9**

|                                       | MAXIMA | MINIMA |
|---------------------------------------|--------|--------|
| w_R1252zc (nominal weight fraction)   | 0.49   | 0      |
| W_R1234ze-E (nominal weight fraction) | 1      | 0.51   |
| average glide (K)                     | 1.1    | 0      |
| GWP AR5                               | 1      | 1      |
| COP (relative to R-410A)              | 1.08   | 1.07   |
| CAP (relative to R-410A)              | 0.42   | 0.33   |
| COP (relative to R-454C)              | 1.04   | 1.03   |
| CAP (relative to R-454C)              | 0.63   | 0.51   |

**TABLE 19A: RESIDENTIAL HEAT PUMP COOLING MODE CONDITION, CYCLE  
METRIC PERFORMANCE AND FLUID PROPERTY RANGES FOR  
1252ZC/1234ZE-E IN EX. 9**

| w_R-1252zc | w_R1234ze(E) | average glide<br>(K) | GWP AR5 | ASHRAE<br>flammability<br>class |
|------------|--------------|----------------------|---------|---------------------------------|
| 0.01       | 0.99         | 0.08                 | 1       | 2L                              |
| 0.04       | 0.96         | 0.31                 | 1       | 2L                              |
| 0.07       | 0.93         | 0.51                 | 1       | 2L                              |
| 0.1        | 0.9          | 0.68                 | 1       | 2L                              |
| 0.13       | 0.87         | 0.82                 | 1       | 2L                              |
| 0.16       | 0.84         | 0.92                 | 1       | 2L                              |
| 0.19       | 0.81         | 0.99                 | 1       | 2                               |
| 0.22       | 0.78         | 1.04                 | 1       | 2                               |
| 0.25       | 0.75         | 1.06                 | 1       | 2                               |
| 0.28       | 0.72         | 1.06                 | 1       | 2                               |
| 0.31       | 0.69         | 1.03                 | 1       | 2                               |
| 0.34       | 0.66         | 0.99                 | 1       | 2                               |

| w_R-1252zc | w_R1234ze(E) | average glide<br>(K) | GWP AR5 | ASHRAE<br>flammability<br>class |
|------------|--------------|----------------------|---------|---------------------------------|
| 0.37       | 0.63         | 0.94                 | 1       | 2                               |
| 0.4        | 0.6          | 0.87                 | 1       | 2                               |
| 0.43       | 0.57         | 0.79                 | 1       | 2                               |
| 0.46       | 0.54         | 0.71                 | 1       | 2                               |
| 0.49       | 0.51         | 0.63                 | 1       | 2                               |

**TABLE 19B: RESIDENTIAL HEAT PUMP COOLING MODE CONDITION, CYCLE  
METRIC PERFORMANCE AND FLUID PROPERTY RANGES FOR  
1252ZC/1234ZE-E IN EX. 9**

| w_R-1252zc | w_R1234ze(E) | COP_(rel<br>to R-<br>410A) | CAP_(rel<br>to R-<br>410A) | COP_(rel<br>to R-<br>454C) | CAP_(rel<br>to R-<br>454C) |
|------------|--------------|----------------------------|----------------------------|----------------------------|----------------------------|
| 0.01       | 0.99         | 1.08                       | 0.33                       | 1.04                       | 0.51                       |
| 0.04       | 0.96         | 1.08                       | 0.34                       | 1.04                       | 0.52                       |
| 0.07       | 0.93         | 1.08                       | 0.35                       | 1.04                       | 0.53                       |
| 0.1        | 0.9          | 1.08                       | 0.35                       | 1.04                       | 0.54                       |
| 0.13       | 0.87         | 1.08                       | 0.36                       | 1.04                       | 0.55                       |
| 0.16       | 0.84         | 1.08                       | 0.37                       | 1.04                       | 0.55                       |
| 0.19       | 0.81         | 1.07                       | 0.37                       | 1.03                       | 0.56                       |
| 0.22       | 0.78         | 1.07                       | 0.38                       | 1.03                       | 0.57                       |
| 0.25       | 0.75         | 1.07                       | 0.38                       | 1.03                       | 0.58                       |
| 0.28       | 0.72         | 1.07                       | 0.39                       | 1.03                       | 0.59                       |
| 0.31       | 0.69         | 1.07                       | 0.39                       | 1.03                       | 0.60                       |
| 0.34       | 0.66         | 1.07                       | 0.40                       | 1.03                       | 0.60                       |
| 0.37       | 0.63         | 1.07                       | 0.40                       | 1.03                       | 0.61                       |
| 0.4        | 0.6          | 1.07                       | 0.41                       | 1.03                       | 0.62                       |
| 0.43       | 0.57         | 1.07                       | 0.41                       | 1.03                       | 0.62                       |
| 0.46       | 0.54         | 1.07                       | 0.41                       | 1.03                       | 0.63                       |
| 0.49       | 0.51         | 1.07                       | 0.42                       | 1.03                       | 0.63                       |

**[0180]** Results show that the HFO-1252zc and HFO-1234ze-E compositions of the present invention provide improved COP relative to R-410A and R-454C, for cooling using residential heat pump systems. Results also show that a composition of 1-16 wt% HFO-1252zc and 84-99 wt% HFO-1234ze-E has a flammability rating of 2L. They also show that a heat pump operated in cooling mode, using a composition of 1-49 wt% HFO-1252zc and 51-99 wt% HFO-1234ze-E, exhibits a glide of < 1.1 °K

**Example 10: HFO-1252zc/HFO-1234ze(E)/HFC-32 (heating mode)**

[0181] In Example 10, refrigerant performance has been determined for exemplary compositions of the present invention in residential heat pump systems as compared to R-454C, in cooling and heating modes. The data are based on the conditions set forth in Table 20.

**TABLE 20: CONDITIONS USED FOR CALCULATIONS**

|                                                         |
|---------------------------------------------------------|
| T_condenser = 47.0 degC                                 |
| T_evaporator = 7.0 degC                                 |
| subcool = 12 K                                          |
| superheat = 3.0 K                                       |
| compressor efficiency = 0.7                             |
| Average Heat Exchanger Temperature Set Points           |
| 100 % of superheat is included in refrigeration effect. |
| Vapor Molar Quality Entering Evaporator: q_4            |
| cooling load = 3.517 kW                                 |
| compressor displacement = 0.1 (m^3 / min)               |

[0182] Tables 21A and 21B tabulate compositions of optimal cooling efficiency and capacity.

**TABLE 21A: RESIDENTIAL HEAT PUMP, CYCLE METRIC PERFORMANCE AND FLUID PROPERTY RANGES FOR 1252ZC/1234ZE-E/32 IN EX. 10**

| w_R-1252zc | w_R1234ze(E) | w_R32 | average glide (K) | GWP (AR5) | ASHRAE flammability class |
|------------|--------------|-------|-------------------|-----------|---------------------------|
| 0.2        | 0.59         | 0.21  | 9.49              | 142.96    | 2L                        |
| 0.18       | 0.76         | 0.06  | 5.50              | 41.56     | 2L                        |

**TABLE 21B: RESIDENTIAL HEAT PUMP, CYCLE METRIC PERFORMANCE AND  
FLUID PROPERTY RANGES FOR 1252ZC/1234ZE-E/32 IN EX. 10**

| w_R-1252zc | w_R1234ze(E) | w_R32 | CAP_cooling<br>(rel to R-454C) | CAP_heating<br>(rel to R-454C) |
|------------|--------------|-------|--------------------------------|--------------------------------|
| 0.2        | 0.59         | 0.21  | 0.90                           | 0.90                           |
| 0.18       | 0.76         | 0.06  | 0.67                           | 0.66                           |

**[0183]** Results show that compositions containing 18-20 weight percent HFO-1252zc, 6-21 weight percent HFC-32, and 59-76 weight percent HFO-1234ze(E) exhibit a GWP < 160 and a flammability rating of 2L. They also show that heat pumps operated with such compositions exhibit a glide < 10 K. They also show that heat pumps operated with a composition containing about 20 weight percent HFO-1252zc, about 21 weight percent R-32, and about 59 weight percent HFO-1234ze-E exhibit a cooling (or heating) capacity of at least 90% of a cooling (or heating) capacity of R-454C.

### CLAIMS

What is claimed is:

1. A composition comprising HFO-1252zc and at least one of HFO-1234ze-E or HFC-32.
2. The composition of claim 1 comprising from about 20 to 83 weight percent HFO-1252zc and from about 17 to 80 weight percent of at least one of HFO-1234ze-E or HFC-32.
3. The composition of claim 1 or 2 comprising from about 20 to 81 weight percent HFO-1252zc and from about 19 to 80 weight percent of at least one of HFO-1234ze-E or HFC-32.
4. The composition of claim 1 or 2 comprising from about 20 to 83 weight percent HFO-1252zc and from about 17 to 80 weight percent HFC-32.
5. The composition of claim 1 or 2 comprising from about 20 to 81 weight percent HFO-1252zc and from about 19 to 80 weight percent HFO-1234ze-E.
6. The composition of any of claims 1 to 5, further comprising at least one additional compound selected from HCFC-22, HFC-23, HCC-30, HCFC-31, HCC-40, HFC-41, methane, HFC-125, HFC-143, HFC-143a, HFC-152a, HFC-245cb, HCFC-253dc, HFC-254fb, HCC-260fb, HCFC-261fc, HCFC-262fc, HFC-263fb, HFC-272fb, propane, HFO-374, n-butane, allene, 2-butene, cyclobutene, 2-methyl propene, HCFO-1122, HFO-1132, HFO-1132a, HFO-1141, ethylene, HCFO-1233xf, HFO-1234yf, HCFO-1242zf, HFO-1243zf, HCFO-1251, HCO-1260zf, HFO-1261zf, propylene, HFO-1345, HFO-1252zc, HFO-1252yf, HFO-1252zf, HFO-1252ye, and E/Z-t-BuO-CF=CH-CH<sub>3</sub>.
7. The composition of any of claims 1 to 6, further comprising at least one additional compound selected from HCFC-22, HCC-40, HFO-1234yf, HFO-1243zf, HFC-263fb, HFO-1252zc, HFO-1252yf, HFO-1252zf, and HFO-1252ye.
8. The composition of any of claims 1 to 7, wherein said composition further comprises from 0.1 to 200 ppm by weight of water; from about 10 ppm by volume to about 0.35 volume percent oxygen; and/or from about 100 ppm by volume to about 1.5 volume percent air or NAG.

9. The composition of any of claims 1 to 8, wherein said composition comprises a stabilizer.
10. The composition of claim 9, wherein the stabilizer is selected from the group consisting of nitromethane, ascorbic acid, terephthalic acid, azoles, phenolic compounds, cyclic monoterpenes, terpenes, phosphites, phosphates, phosphonates, thiols, and lactones.
11. The composition of any of claims 9 or 10, wherein the stabilizer is selected from toluotriazole, benzotriazole, tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-terbutyl-4-methylphenol, fluorinated epoxides, n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, d-limonene,  $\alpha$ -terpinene,  $\beta$ -terpinene,  $\alpha$ -pinene,  $\beta$ -pinene, or butylated hydroxytoluene.
12. The composition of any of claims 7 to 9, wherein the stabilizer is present in an amount from about 0.001 to 1.0 weight percent based on the weight of the refrigerant.
13. The composition of any of claims 1 to 12, wherein the composition further comprises a lubricant.
14. The composition of claim 13, wherein said lubricant is at least one selected from the group consisting of polyalkylene glycol, polyol ester, poly- $\alpha$ -olefin, and polyvinyl ether.
15. The composition of claim 13 or 14, wherein said lubricant is a polyol ester or a polyvinyl ether.
16. The composition of any of claims 13 to 15, wherein said lubricant has at least one property selected from the group consisting of volume resistivity of greater than  $10^{10}$   $\Omega$ -m at 20 °C; surface tension of from about 0.02 N/m to 0.04 N/m at 20 °C; kinematic viscosity of from about 20 cSt to about 500 cSt at 40 °C; a breakdown voltage of at least 25 kV; and a hydroxy value of at most 0.1 mg KOH/g.
17. The composition of any of claims 1 to 16, wherein the composition comprises at least one tracer.

18. The composition of claim 17, wherein said tracer is present in an amount from about 1.0 ppm by weight to about 1000 ppm by weight.
19. The composition of any of claims 17 or 18, wherein said at least one tracer is selected from the group consisting of hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof.
20. The composition of any of claims 17 to 19, wherein said at least one tracer is selected from the group consisting of HFC-23, HCFC-31, HFC-41, HFC-161, HFC-143a, HFC-134a, HFC-125, HFC-236fa, HFC-236ea, HFC-245cb, HFC-245fa, HFC-254eb, HFC-263fb, HFC-272ca, HFC-281ea, HFC-281fa, HFC-329p, HFC-329mmz, HFC338mf, HFC-338pcc, CFC-12, CFC-11, CFC-114, CFC-114a, HCFC-22, HCFC-123, HCFC-124, HCFC-124a, HCFC-141b, HCFC-142b, HCFC-151a, HCFC-244bb, HCC-40, HFO-1141, HCFO-1130, HCFO-1130a, HCFO-1131, HCFO-1122, HFO-1123, HFO-1234yf, HFO-1234ye, HFO-1243zf, HFO-1225ye, HFO-1225zc, PFC-116, PFC-C216, PFC-218, PFC-C318, PFC-1216, PFC-31-10mc, PFC-31-10my, and combinations thereof.
21. The composition of any of claims 1 to 20, 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.
22. The composition of any of claims 1 or 6 to 21, wherein: the HFO-1252zc is present at a concentration of from about 56 weight percent to about 70 weight percent based upon a weight of the HFO-1252zc and the HFC-32; and the HFC-32 is present at a concentration of from about 30 weight percent to about 44 weight percent based upon a weight of the HFO-1252zc and the HFC-32.
23. The composition of any of claims 1 or 6 to 21, wherein: the HFO-1252zc is present at a concentration from about 56 weight percent to about 68 weight percent based upon a weight of the HFO-1252zc and HFC-32; and the HFC-32

is present at a concentration of from about 32 weight percent to about 44 weight percent based upon a weight of the HFO-1252zc and HFC-32.

24. The composition of any of claims 1 or 6 to 21, wherein: the HFO-1252zc is present at a concentration of from about 56 weight percent to about 65 weight percent based upon a weight of the HFO-1252zc and HFC-32; and the HFC-32 is present at a concentration of from about 35 weight percent to about 44 weight percent based upon a weight of the HFO-1252zc and HFC-32.
25. The composition of any of claims 1 or 6 to 21, wherein: the HFO-1252zc is present at a concentration of from about 33 weight percent to about 45 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 18 weight percent to about 20 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 19 weight percent to about 47 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; and the composition has a GWP < 160.
26. The composition of any of claims 1 or 6 to 21, wherein: the HFO-1252zc is present at a concentration of from about 0.05 weight percent to about 24 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, HFC-32 is present at a concentration of from about 34 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 37 weight percent to about 62 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; and the composition has a flammability rating of 2L (when measured in accordance with ANSI/ASHRAE Standard 34).
27. The composition of any of claims 1 or 6 to 21, wherein: the HFO-1252zc is present at a concentration of from about 51 weight percent to about 63 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, HFC-32 is present at a concentration of from about 23 weight percent to about

38 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 4 weight percent to about 21 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

28. The composition of any of claims 1 or 6 to 21, wherein: the HFO-1252zc is present at a concentration of from about 31 weight percent to about 64 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, HFC-32 is present at a concentration of from about 17 weight percent to about 43 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 1 weight percent to about 31 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.
29. The composition of any of claims 1 or 6 to 21, wherein: the HFO-1252zc is present at a concentration of from about 0.05 weight percent to about 25 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, HFC-32 is present at a concentration of from about 36 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 39 weight percent to about 57 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; and the composition has a flammability rating of 2L (when measured in accordance with ANSI/ASHRAE Standard 34).
30. The composition of any of claims 1 or 6 to 21, wherein: the HFO-1252zc is present at a concentration of from about 36 weight percent to about 60 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, HFC-32 is present at a concentration of from about 17 weight percent to about 22 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 18 weight percent to about 42 weight percent based upon the weight of the HFO-

1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; and said composition has a GWP < 160.

31. The composition of any of claims 1 or 6 to 21, wherein the HFO-1252zc is present at a concentration of from about 1 weight percent to about 16 weight percent based upon a weight of the HFO-1252zc and HFO-1234ze-E, HFO-1234ze-E is present at a concentration of from about 84 weight percent to about 99 weight percent based upon the weight of the HFO-1252zc and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc and the HFO-1234ze-E is 100; and the composition has a flammability rating of 2L (when measured in accordance with ANSI/ASHRAE Standard 34).
32. The composition of any of claims 1 or 6 to 21, wherein the HFO-125zc is present a concentration of from about 19 weight percent to about 23 percent based upon a weight of the HFO-1252zc, the HFC-32, and the HFO-1234zc; the HFC-32 is present at a concentration of from about 18 weight percent to about 22 weight percent based upon the weight of the HFO-1252zc, HFC-32, and te HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 57 weight percent to about 61 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.
33. The composition of any of claims 1 or 6 to 21, wherein HFO-1252zc is present at a concentration of from about 56 weight percent to about 70 weight percent based upon a weight of the HFO-1252zc and HFC-32; HFC-32 is present a concentration of from about 30 weight percent to about 44 weight percent based upon the weight of the HFO-1252zc and HFC-32; and a sum of the weight percentages of the HFO-1252zc and the HFC-32 is 100.
34. The composition of any of claims 1 or 6 to 21, wherein: HFO-1252zc is present at a concentration of from about 0.5 weight percent to about 63 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 18 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 4

weight percent to about 62 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.

35. The composition of any of claims 1 or 6 to 21, wherein: HFO-1252zc is present at a concentration of from about 0.5 weight percent to about 64 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 17 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 1 weight percent to about 57 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100.
36. The composition of any of claims 1 or 6 to 21, wherein: HFO-1252zc is present at a concentration of from about 18 weight percent to about 20 weight percent based on a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 6 weight percent to about 21 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 59 weight percent to about 76 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252ze, the HFC-32, and the HFO-1234ze-E is 100; and the composition exhibits a GWP < 160 and a flammability rating of 2L.
37. The composition of any of claims 1 or 6 to 21, wherein: HFO-1252zc is present at a concentration of about 20 weight percent based on a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of about 21 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of about 59 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252ze, the HFC-32, and the HFO-1234ze-E is 100.
38. The composition of any of claims 1 or 6 to 21, wherein: HFO-1252zc is present at a concentration of from about 18 weight percent to about 22 weight percent

based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFC-32 is present at a concentration of from about 19 weight percent to about 23 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 57 weight percent to about 61 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252ze, the HFC-32, and the HFO-1234ze-E is 100.

39. A method for cooling comprising evaporating a composition of any of claims 1 to 38 in the vicinity of a body to be cooled and thereafter condensing said composition, wherein said cooling is provided by an air-conditioner or heat pump.
40. The method of claim 39, wherein: the HFO-1252zc is present at a concentration from about 56 weight percent to about 68 weight percent based upon a weight of the HFO-1252zc and the HFC-32; the HFC-32 is present at a concentration of from about 32 weight percent to about 44 weight percent based upon a weight of the HFO-1252zc and the HFC-32; said cooling is provided by a heat pump; and said heat pump exhibits a glide of  $< 8^{\circ}\text{K}$ .
41. The method of claim 39, wherein: the HFO-1252zc is present at a concentration of from about 51 weight percent to about 63 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, HFC-32 is present at a concentration of from about 23 weight percent to about 38 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 4 weight percent to about 21 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; said cooling is provided by a heat pump; and said heat pump exhibits a glide of  $< 8^{\circ}\text{K}$ .
42. The method of claim 39, wherein: HFO-1252zc is present at a concentration of from about 56 weight percent to about 70 weight percent based upon a weight of the HFO-1252zc and the HFC-32; the HFC-32 is present a concentration of from about 30 weight percent to about 44 weight percent based upon the weight of the HFO-1252zc and the HFC-32; a sum of the weight percentages of

the HFO-1252zc and the HFC-32 is 100; said cooling is provided by a heat pump; and said heat pump exhibits a cooling capacity of at least 80% of a cooling capacity of R-454C.

43. The method of claim 39, wherein: HFO-1252zc is present at a concentration of from about 0.5 weight percent to about 63 weight percent based upon a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; HFC-32 is present at a concentration of from about 18 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 4 weight percent to about 62 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; said cooling is provided by a heat pump; and said heat pump exhibits a cooling capacity of at least 80% of a cooling capacity of R-454C.
44. The method of claim 39, wherein: HFO-1252zc is present at a concentration of from about 20 weight percent to about 83 weight percent based upon a weight of the HFO-1252zc and the HFC-32; HFC-32 is present at a concentration of about 17 weight percent to about 80 weight percent based upon a weight of the HFO-1252zc and the HFC-32; a sum of the weight percentages of the HFO-1252zc and the HFC-32 is 100; said cooling is provided by a heat pump; and said heat pump exhibits a cooling capacity of at least 80% of a cooling capacity of R-454C.
45. The method of claim 39, wherein: HFO-1252zc is present at a concentration of from about 0.5 weight percent to about 64 weight percent based upon a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; HFC-32 is present at a concentration of from about 17 weight percent to about 43.78 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 1 weight percent to about 57 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; and said heat pump exhibits a cooling capacity of at least 80% of a cooling capacity of R-454C.

46. The method of claim 39, wherein: HFO-1252zc is present at a concentration of from about 18 weight percent to about 20 weight percent based on a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; HFC-32 is present at a concentration of from about 6 weight percent to about 21 weight percent upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of from about 59 weight percent to about 76 weight percent upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; a sum of the weight percentages of the HFO-1252ze, the HFC-32, and the HFO-1234ze-E is 100; said cooling is provided by a heat pump; and said heat pump exhibits a glide of  $< 10^{\circ}\text{K}$ .
47. The method of claim 39, wherein HFO-1252zc is present at a concentration of about 20 weight percent based on a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; HFC-32 is present at a concentration of about 21 weight percent upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of about 59 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252ze, the HFC-32, the HFO-1234ze-E is 100; the cooling is provided by a heat pump; and said heat pump exhibits a cooling capacity of at least 90% of a cooling capacity of R-454C.
48. A method for heating comprising evaporating a composition of any of claims 1 to 38 and thereafter condensing said composition in the vicinity of a body to be heated, wherein said heating is provided by a heat pump.
49. The method of claim 48, wherein: the HFO-1252zc is present at a concentration from about 56 weight percent to about 65 weight percent based upon a weight of the HFO-1252zc and the HFC-32; the HFC-32 is present at a concentration of from about 35 weight percent to about 44 weight percent based upon a weight of the HFO-1252zc and the HFC-32; and said heat pump exhibits a glide of  $< 8^{\circ}\text{K}$ .
50. The method of claim 48, wherein: the HFO-1252zc is present at a concentration of from about 31 weight percent to about 64 weight percent based upon a weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E, HFC-32 is present at

a concentration of from about 17 weight percent to about 43 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; HFO-1234ze-E is present at a concentration of from about 1 weight percent to about 31 weight percent based upon the weight of the HFO-1252zc, HFC-32, and HFO-1234ze-E; a sum of the weight percentages of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E is 100; and said heat pump exhibits a glide of < 8 °K.

51. The method of claim 48, wherein: HFO-1252zc is present at a concentration of from about 56 weight percent to about 70 weight percent based upon a weight of the HFO-1252zc and the HFC-32; HFC-32 is present at a concentration of from about 30 weight percent to about 40 weight percent based upon the weight of the HFO-1252zc and the HFC-32; a sum of the weight percentages of the HFO-1252zc and the HFC-32 is 100; and said heat pump exhibits a heating capacity of at least 80% of a heating capacity of R-454C.
52. The method of claim 48, wherein HFO-1252zc is present at a concentration of from about 20 weight percent to about 83 weight percent based upon a weight of the HFO-1252zc and the HFC-32; HFC-32 is present at a concentration of from about 17 weight percent to about 80 weight percent based upon the weight of the HFO-1252zc and the HFC-32; a sum of the weight percentages of the HFO-1252zc and the HFC-32 is 100; and said heat pump exhibits a heating capacity of at least 80% of a heating capacity of R-454C.
53. The method of claim 48, wherein HFO-1252zc is present at a concentration of about 20 weight percent based on a weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; HFC-32 is present at a concentration of about 21 weight percent upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; the HFO-1234ze-E is present at a concentration of about 59 weight percent based upon the weight of the HFO-1252zc, the HFC-32, and the HFO-1234ze-E; and a sum of the weight percentages of the HFO-1252ze, the HFC-32, the HFO-1234ze-E is 100; and said heat pump exhibits a heating capacity of at least 90% of a heating capacity of R-454C.
54. A system for cooling or heating comprising a composition of any of claims 1 to 38.

55. The system of claim 54, comprising an evaporator, compressor, condenser, and expansion device, each operably connected to perform a vapor compression cycle.
56. The system of claim 54 or 55, wherein said air-conditioner or heat pump is a residential, light commercial, or industrial air-conditioner or heat pump.
57. A method of replacing R-454C or propane in air-conditioning or heat pump systems comprising providing the composition of any of claims 1 to 38 to the system in place of R-454C or propane.
58. Use of the composition of any of claims 1 to 38 as refrigerant in air-conditioning or heat pump systems.
59. The system of any of claims 54 to 56, wherein the system is a secondary loop system.