

TITLE OF THE INVENTION

METHODS OF TREATING DIFLUOROPROPENE COMPOSITIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application 63/527,140 filed July 17, 2023, and U.S. Provisional Application 63/565,045 filed March 14, 2024, the disclosure of each of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention is directed to processes for treating, particularly drying and/or purifying, compositions containing difluoropropene, and more particularly 1,1-difluoropropene. The processes comprise contacting such difluoropropene-containing compositions with molecular sieves having specific pore sizes.

BACKGROUND OF THE INVENTION

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

[0004] This regulatory landscape is continuously evolving, taking into consideration properties beyond just ODP and GWP. More particularly, there is a

need for refrigerant compositions that not only meet low ODP standards and have low global warming potentials, but that also exhibit low or no flammability, provide superior performance in a variety of applications and which meet the standards of evolving regulations.

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

[0006] Some fluoropropenes, particularly difluoropropenes (HFO-1252) such as HFO-1252zf, HFO-1252yf, HFO-1252ye HFO-1252ze and HFO-1252zc are such potential new refrigerants.

[0007] Manufacturing processes to make difluoropropenes, particularly 1,1-difluoropropene (HFO-1252zc) result in moisture (e.g., water) and other impurities, such as inorganic compounds, acids, gases, oils, particulates and the like, being incorporated into the HFO-1252zc. Such manufacturing processes also result in additional organic compounds, other than the HFO-1252 isomer, being present in the difluoropropene composition. For the sake of brevity, such additional organic compounds may be referred to herein as impurities which are removed or reduced by treatment of the difluoropropene composition.

[0008] For a variety of reasons, it is desirable to reduce the water content and/or impurity content of such compositions to low concentrations. For example, for storage and handling of compositions containing HFO-1252zc, low moisture content is advantageous for minimizing corrosion of the storage tank. When HFO-1252zc is to be used as a neat refrigerant or blend in a heat transfer/refrigeration system, reduced water and/or impurities content is required because high moisture levels can negatively impact system performance. For these same reasons, it also is desirable to reduce the water and/or impurities content of reclaimed refrigerant compositions containing HFO-1252zc, as these reclaimed compositions may also have high concentrations of water which must be removed or reduced before the reclaimed composition can be used again in a heat transfer/refrigeration system.

[0009] Desiccants, such as molecular sieves, are known to be effective for drying other types of refrigerant materials, such as 2,3,3,3-tetrafluoropropene (HFO-1234yf). However, such known drying processes may not prove compatible and

effective for drying difluoropropenes, such as HFO-1252zc which is more reactive than 1234yf. It was found that certain reactive olefins can trigger oligomerization upon contact with molecular sieve. Also, due to the smaller molecular size of difluoropropenes, such as HFO-1252zc, more material can more easily enter the pores of the molecular desiccant sieve during the drying process, thereby reducing the capacity of the sieve and/or forming tars during regeneration which degrade the performance of the sieve.

[0010] There is therefore a need to provide effective treatment, namely drying and/or purifying, of difluoropropenes such as HFO-1252zc, or blends comprising difluoropropenes such as HFO-1252zc, utilizing a compatible desiccant material, particularly a molecular sieve desiccant.

SUMMARY OF THE INVENTION

[0011] In some embodiments, the present invention relates to a method of treating a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting the composition with an aluminum containing adsorbent to remove impurities from the difluoropropene.

[0012] In some embodiments, examples of the impurities that may be present in the difluoropropene-containing compositions include, but are not limited to, water, organic compounds such as vinyl chloride (VCM), HFO-1261 and HFC-152a, inorganic compounds such as NaCl or other metal compounds, acids such as HF and/or HCl, gases such as CO₂, oils such as certain polyolester oils (POEs) (e.g., Castrol® 100), particulates such as non-volatile residue (NVR), and the like.

[0013] In some embodiments, the present invention relates to a method of reducing a water content of a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting the composition with an aluminum containing adsorbent, wherein the reduced water content of the composition is about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, about 8 ppmw or less, about 6 ppmw or less, about 4 ppmw or less.

[0014] In some embodiments, the present invention relates to a method of treating a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, to reduce the content of additional organic compounds and increase the purity of the difluoropropene composition, the method comprising contacting the composition with an aluminum containing adsorbent until the difluoropropene composition reaches a purity of at least about 99%, or at least about 99.5%.

[0015] In some embodiments, the present invention relates to a method of treating a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, to reduce the content of additional organic compounds and increase the purity of the difluoropropene composition, the method comprising contacting the composition with an aluminum containing adsorbent until the organic impurities content is reduced by about 5% to about 100%, or by about 10% to about 80% relative to a starting content of the organic impurities, which reflects a corresponding increase in the purity of the difluoropropene composition.

[0016] In some embodiments, the present invention relates to a method of treating a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, to reduce the acidity content and increase the purity of the difluoropropene composition, the method comprising contacting the composition with an aluminum containing adsorbent until the acidity content is reduced by about 90% or greater relative to a starting acidity content. In some embodiments, the treated composition has a reduced acid content equivalent to about 10 ppm HCl or less, or about 9 ppm HCl or less, or about 8 ppm HCl or less, or about 7 ppm HCl or less, or about 6 ppm HCl or less, or about 5 ppm HCl or less, preferably about 4.6 ppm or less.

[0017] In some embodiments, the present invention relates to a method of treating a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, to reduce the acidity content, water content, and the content of other organic compounds contained within the composition, and increase the purity of the difluoropropene composition, the method comprising contacting the composition with an aluminum

containing adsorbent for a predetermined duration. In some embodiments, the contents of other impurities, such as inorganic compounds and oils may also be reduced.

[0018] In any of the embodiments disclosed herein, the contacting of the composition with the adsorbent may occur in the liquid phase or the vapor phase. Preferably, the contacting is in the liquid phase.

[0019] In some embodiments, the present invention relates to use of an aluminum containing adsorbent for treating a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, by contacting the composition with an aluminum containing adsorbent to remove impurities from the difluoropropene. In some embodiments, the impurities include, but are not limited to, water, acids, organic compounds (other than HFO-1252 isomers), inorganic compounds, oils and the like.

[0020] In some embodiments, the present invention relates to use of an aluminum containing adsorbent for reducing a water content of a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, by contacting the composition with an aluminum containing adsorbent.

[0021] In some embodiments, the treated composition has a reduced water content of about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, about 8 ppmw or less, about 6 ppmw or less, about 4 ppmw or less.

[0022] In some embodiments, contacting of the difluoropropene composition with an aluminum containing adsorbent simultaneously reduces a water content of the composition and removes other impurities, particularly organic compounds such as hydrofluorocarbons (HFCs), hydrofluorocarbons, chlorofluorocarbons (CFCs), hydrofluorochlorocarbons (HCFCs), and hydrofluoroolefins (HFOs) other than HFO-1252 isomers, from the composition.

[0023] In some embodiments, the present invention relates to use of an aluminum containing adsorbent for reducing acidity content of a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf,

HFO-1252ye, HFO-1252ze and HFO-1252zc, by contacting the composition with an aluminum containing adsorbent.

[0024] In some embodiments, the present invention relates to use of an aluminum containing adsorbent for increasing the purity of a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, by contacting the composition with an aluminum containing adsorbent.

[0025] In some embodiments, the present invention relates to a method of regenerating a molecular sieve having a nominal pore size of about 3 Å and configured for treating a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising: flowing dry nitrogen across the molecular sieve at a first temperature; increasing the temperature to a second temperature of about 150°C to about 350°C; and decreasing the temperature back to the first temperature under a dry nitrogen flow or under vacuum.

[0026] In some embodiments, the present invention relates to a method of regenerating a molecular sieve having a nominal pore size of greater than about 3 Å and configured for treating a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising: flowing a stream of one of water vapor, wet nitrogen or wet air, across the molecular sieve at a first temperature; increasing the temperature to a second temperature of about 150°C to about 350°C; switching to a dry nitrogen flow at the second temperature; and decreasing the temperature back to the first temperature under a dry nitrogen flow or under vacuum.

[0027] In some embodiments, the present invention relates to a method of manufacturing a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting a product stream comprising the difluoropropene with an aluminum containing adsorbent to reduce a water content of the difluoropropene and/or remove other impurities, such as acids, from the difluoropropene.

[0028] In some embodiments, the present invention relates to a method of reclaiming a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting a stream comprising used difluoropropene with an aluminum containing adsorbent to reduce a water content of the difluoropropene and/or remove other impurities from the difluoropropene.

[0029] In some embodiments, the present invention relates to a method of storing a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting the composition with an aluminum containing adsorbent in a closed container for a predetermined duration to reduce a water content of the composition, and/or reduce an acidity content of the composition, and/or increase a purity of the difluoropropene in the composition.

[0030] In some embodiments, the present invention relates to a container configured to store a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, wherein the difluoropropene has a reduced water content of about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, or about 8 ppmw or less, or about 6 ppmw or less, preferably about 4 ppmw or less.

[0031] Embodiment 1. A method of treating a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting the composition with an aluminum containing adsorbent to remove impurities from the difluoropropene.

[0032] Embodiment 2. The method of Embodiment 1, wherein the impurities are one or more impurities selected from the group consisting of water, organic compounds, inorganic compounds, acids, gases, particulates and oils.

[0033] Embodiment 3. The method of Embodiment 2, wherein the organic compounds are selected from the group consisting of HFC-152a, HFO-1261ze(E), HFO-1261ze(Z), difluorodimethylsilane, HF, HCl, acetic acid, formic acid, nitric acid, sulfuric acid and trifluoro acetic.

[0034] Embodiment 4. The method of any of Embodiments 1 to 3, wherein contacting of the composition with the aluminum containing adsorbent reduces a water content of the composition to about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, about 8 ppmw or less, about 6 ppmw or less, about 4 ppmw or less; and/or contacting of the composition with the aluminum containing adsorbent occurs until an organic impurities content of the composition is reduced by about 5% to about 100% relative to a starting content of the organic impurities; and/or contacting of the composition with the aluminum containing adsorbent reduces an acidity content of the composition.

[0035] Embodiment 5. A method of treating a composition comprising HFO-1252zc and one or more additional compounds selected from the group consisting of HFC-152a, HFO-1243zf, difluorodimethylsilane, E-HFO-1261ze, Z-HFO-1261ze, HF, HCl, acetic acid, formic acid, nitric acid, sulfuric acid and trifluoro acetic, the method comprising contacting the composition with an aluminum containing adsorbent and reducing a content of at least one of the additional compounds from the composition.

[0036] Embodiment 6. A method of reducing a water content of a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting the composition with an aluminum containing adsorbent, wherein the reduced water content of the composition is about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, about 8 ppmw or less, about 6 ppmw or less, about 4 ppmw or less.

[0037] Embodiment 7. A method of reducing an amount of organic impurities in a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting the composition with an aluminum containing adsorbent until an amount of the organic impurities is reduced by about 5% to about 100% relative to a starting amount of the organic impurities.

[0038] Embodiment 8. A method of reducing an acidity content of a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf,

HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting the composition with an aluminum containing adsorbent.

[0039] Embodiment 9. The method of any of Embodiments 1 to 8, wherein the aluminum containing adsorbent is selected from the group consisting of zeolite Y, zeolite X, zeolite beta, zeolite A, zeolite ZK-20, zeolite ZSM-3, faujasite, LZ-10, AW-500, ZSM-5-type zeolites, crystalline silicates such as silicalite, erionite, mordenite, offretite, chabazite, FU-1-type zeolite, NU-type zeolites and LZ-210-type zeolite.

[0040] Embodiment 10. The method of any of Embodiments 1 to 9, wherein the aluminum containing adsorbent is a molecular sieve.

[0041] Embodiment 11. The method of Embodiment 10, wherein the molecular sieve has openings which have a nominal pore size of about 3 Å to about 10 Å, or wherein the molecular sieve has openings which have a nominal pore size of about 3 Å to about 5 Å, preferably about 3 Å, or wherein the molecular sieve has openings which have a nominal pore size of about 9 Å to 10 Å, preferably about 10 Å.

[0042] Embodiment 12. The method of any of Embodiments 1 to 11, wherein the aluminum containing adsorbent is zeolite 3A or molecular sieve 13X.

[0043] Embodiment 13. The method of any of Embodiments 10 to 12, wherein the composition comprises HFO-1252zc and one or more additional compounds selected from the group consisting of HFC-152a, HFO-1243zf, difluorodimethylsilane, E-HFO-1261ze, Z-HFO-1261ze, HF and HCl; and wherein contacting of the composition with the molecular sieve reduces a content of at least one of the additional compounds, preferably reduces a content of at least one of HFC-152a, E-HFO-1261ze and Z-HFO-1261ze.

[0044] Embodiment 14. The method according to any of Embodiments 1 to 13, wherein the difluoropropene is HFO-1252zc.

[0045] Embodiment 15. The method according to any of Embodiments 1 to 14, wherein the composition comprises at least one other refrigerant component.

[0046] Embodiment 16. The method according to any of Embodiments 1 to 15, wherein the composition is in the liquid state.

[0047] Embodiment 17. The method according to any of Embodiments 1 to 16, wherein the composition is in the gaseous state.

[0048] Embodiment 18. The method according to any of Embodiments 1 to 17, wherein the composition is free of or substantially free of Group A Fluorinated Substances.

[0049] Embodiment 19. The method according to any of Embodiments 1 to 18, wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.

[0050] Embodiment 20. The method according to any of Embodiments 1 to 19, wherein contacting of the composition with the adsorbent is carried out more than once or for a predetermined duration.

[0051] Embodiment 21. The method according to Embodiment 20, wherein the adsorbent is regenerated and reused between one or more contacts.

[0052] Embodiment 22. The method according to Embodiment 21, wherein the adsorbent is regenerated by a heated dry nitrogen flow, a water vapor flow, a water vapor in nitrogen flow, an air flow, and/or a heated dry air flow.

[0053] Embodiment 23. The method according to any of Embodiments 1 to 22, wherein the water content of the composition is reduced by about 90% to about 100% relative to the starting water content, preferably about 93% to about 100%, or about 93% to about 98%, or about 94% to about 98%, or about 94% to about 97%, or about 94% to about 96%, or about 95% to about 96%, preferably about 96%.

[0054] Embodiment 24. The method according to any of Embodiments 1 to 23, wherein the treated composition has a reduced water content of about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, about 8 ppmw or less, about 6 ppmw or less, about 4 ppmw or less.

[0055] Embodiment 25. The method according to Embodiment 24, wherein the treated composition has a reduced water content of about 20 ppmw or less.

[0056] Embodiment 26. The method according to Embodiment 25, wherein the treated composition has a reduced water content of about 4 ppmw or less.

[0057] Embodiment 27. The method of any of Embodiments 1 to 26, wherein a purity of the composition after treatment is at least 99%, preferably at least 99.5%.

[0058] Embodiment 28. The method of any of Embodiments 1 to 27, wherein an acidity content of the composition is reduced by about 90% or greater.

[0059] Embodiment 29. The method of any of Embodiments 1 to 28, wherein the treated composition has a reduced acid content of about 10 ppm HCl equivalent or less, preferably about 5 ppm HCl equivalent or less.

[0060] Embodiment 30. The method according to any of Embodiments 1 to 29, wherein the composition is a reclaimed refrigerant composition.

[0061] Embodiment 31. The method according to any of Embodiments 1 to 30, wherein the adsorbent comprises an aluminosilicate.

[0062] Embodiment 32. The method according to any of Embodiments 1 to 31, wherein the aluminum containing adsorbent is a molecular sieve having a surface area of from about 600 to about 1000 m²/g.

[0063] Embodiment 33. The method according to any of Embodiments 1 to 32, wherein the aluminum containing adsorbent is molecular sieve that is pre-treated by a heated dry nitrogen flow.

[0064] Embodiment 34. The method according to any of Embodiments 1 to 33, wherein contacting of the composition with the adsorbent is in the liquid phase or vapor phase, preferably the liquid phase.

[0065] Embodiment 35. The method according to any of Embodiments 1 to 34, wherein contacting of the composition in a liquid state with the molecular sieve occurs at a temperature of about -40°C to about 55°C, or about -40°C to about 50°C, or about 5°C to about 55°C, or about -30°C to about 40°C, or about 15°C to about 45°C, or at room temperature.

[0066] Embodiment 36. The method according to any of Embodiments 1 to 35, wherein contacting of the composition in a gaseous state with the molecular sieve occurs at a temperature of about -20°C to about 95°C, or about -20°C to about 60°C, or about 5°C to about 95°C, or about -10°C to about 80°C, or about -10°C to about 45°C, or about 15°C to about 80°C, or at room temperature.

[0067] Embodiment 37. A method of regenerating a molecular sieve having a nominal pore size of about 3 Å and configured for treating a composition comprising water and a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising: flowing dry nitrogen across the molecular sieve at a first temperature; increasing the temperature to a second temperature of about 150°C to about 350°C; and decreasing the temperature back to the first temperature under a dry nitrogen flow or under vacuum.

[0068] Embodiment 38. The method of Embodiment 37, wherein the temperature is maintained at the second temperature until the dewpoint of the nitrogen effluent indicates the water has been removed, such as <-20°C.

[0069] Embodiment 39. A method of regenerating a molecular sieve having a nominal pore size of greater than about 3 Å and configured for treating a composition comprising water and a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising: flowing a stream of one of water vapor, wet nitrogen or wet air, across the molecular sieve at a first temperature; increasing the temperature to a second temperature of about 150°C to about 350°C; switching to a dry nitrogen flow at the second temperature; and decreasing the temperature back to the first temperature under a dry nitrogen flow or under vacuum.

[0070] Embodiment 40. The method of Embodiment 39, wherein the temperature is maintained at the second temperature under the dry nitrogen flow until the dewpoint of the nitrogen effluent indicates the water has been removed, such as <-20°C.

[0071] Embodiment 41. A method of manufacturing a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting a product stream comprising the difluoropropene with an aluminum containing adsorbent to reduce at least one of (i) a water content of the difluoropropene, (ii) an acidity content of the composition, and (iii) an organic impurities content of the composition.

[0072] Embodiment 42. A method of reclaiming a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting a stream comprising used difluoropropene with an aluminum containing adsorbent to reduce at least one of (i) a water content of the difluoropropene, (ii) an acidity content of the composition, and (iii) an organic impurities content of the composition.

[0073] Embodiment 43. A method of storing a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising mixing a composition comprising the difluoropropene with an aluminum containing adsorbent to form a mixture and storing the mixture for a predetermined duration to reduce at least one of (i) a water content of the difluoropropene, (ii) an acidity content of the composition, and (iii) an organic impurities content of the composition.

[0074] Embodiment 44. A container configured to store a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, wherein the composition has a reduced water content of about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, or about 8 ppmw or less, or about 6 ppmw or less, preferably about 4 ppmw or less; and/or wherein the difluoropropene has a purity of at least about 99%, preferably at least about 99.55%; and/or wherein the composition has a reduced acids content equivalent to about 10 ppm HCl or less, preferably about 5 ppm HCl or less.

[0075] Embodiment 45. The method according to any of Embodiments 37 to 43 or the container according to Embodiment 44, wherein the difluoropropene is HFO-1252zc.

[0076] Embodiment 46. The method according to any of Embodiments 37 to 43, wherein the aluminum containing adsorbent is a molecular sieve.

[0077] Embodiment 47. The method of Embodiment 46, wherein the molecular sieve has openings which have a nominal pore size of about 3 Å to about 10 Å, or wherein the molecular sieve has openings which have a nominal pore size of about 3 Å to about 5 Å, preferably about 3 Å, or wherein the molecular sieve has openings which have a nominal pore size of about 9 Å to 10 Å, preferably about 10 Å

[0078] Embodiment 48. The method of any of Embodiments 46 to 47, wherein the composition comprises HFO-1252zc and one or more additional compounds selected from the group consisting of HFC-152a, HFO-1243zf, difluorodimethylsilane, E-HFO-1261ze, Z-HFO-1261ze, HF and HCl; and wherein contacting of the composition with the molecular sieve reduces a content of at least one of the additional compounds, preferably reduces a content of at least one of HFC-152a, E-HFO-1261ze and Z-HFO-1261ze.

[0079] The various aspects and embodiments of the invention can be used alone or in combinations with each other. Other features and advantages of the present invention will be apparent from the following more detailed description, taken in conjunction with the accompanying drawings which illustrate, by way of example, the principles of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0080] The present invention provides a method of treating a composition (liquid or gas) comprising a difluoropropene, particularly HFO-1252zc. In some embodiments, the treatment is drying or purification or a combination of both drying and purifying. In some embodiments, the treatment is purification to remove impurities from the difluoropropene. The impurities may include, but are not limited to, water; organic compounds other than HFO-1252zc, such as vinyl chloride (VCM), HFO-1261 and HFC-152a; inorganic compounds such as NaCl or other metal compounds; acids such as HF and/or HCl; gases such as CO₂; oils such as certain polyolester oils (POEs) (e.g., Castrol® 100); particulates such as non-volatile residue (NVR), and the like. In some embodiments, the impurities which are removed from the difluoropropene composition include at least one of water, acids and organic compounds other than HFO-1252zc.

[0081] The treatment method of the present invention may be carried out as a step in a process to make HFO-1252zc, as a step in a process to make a composition (neat or blend) comprising HFO-1252zc, as a step in a process for storing a composition (neat or blend) comprising HFO-1252zc, for example during handling and transport or storage at a facility.

[0082] The composition may be a neat difluoropropene (e.g., HFO-1252zc) composition or a blend comprising a difluoropropene such as HFO-1252zc. The method comprises contacting the fluid composition with a desiccant, and more preferably a molecular sieve. In some embodiments, the molecular sieve has pore sizes (more particularly, pore diameter) of about 3 Å to 10 Å, or about 3 Å to 5 Å, or about 3 Å, or greater than 0 and less than about 3 Å. In some embodiments, the molecular sieve has pore sizes (more particularly, pore diameter) of about 5 Å to 10 Å, or about 5 Å to about 9 Å, or about 9 Å to about 10 Å, or about 10 Å.

[0083] As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a composition, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, process, method, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0084] 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.

[0085] The transitional phrase “consisting essentially of” is used to define a composition, method that includes materials, steps, features, components, or elements, in addition to those literally disclosed provided that these additional included materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention, especially the mode of action to achieve the desired result of any of the processes of the present invention. The term “consisting essentially of” occupies a middle ground between “comprising” and “consisting of.”

[0086] Where applicants have defined an invention or a portion thereof with an open-ended term such as “comprising,” it should be readily understood that (unless otherwise stated) the description should be interpreted to also include such an invention using the terms “consisting essentially of” or “consisting of.”

[0087] 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.

[0088] Compounds referred to in this disclosure may be referred to by code, based on fluorochemical naming convention, chemical structure and/or chemical name. For convenience and reference, selected compounds with codes, structures and chemical names are provided in Table 1.

Table 1

Code	Name-ASHRAE Designation	Formula
R-23	trifluoromethane (HFC-23)	CHF ₃
R-30	dichloromethane (HCC-30)	CH ₂ Cl ₂
R-31	chlorofluoromethane (HCFC-31)	CH ₂ ClF
R-40	methyl chloride (HCC-40)	CH ₃ Cl
R-50	Methane (HC-50)	CH ₄
R-125	1,1,2,2,2-pentafluoroethane (HFC-125)	CHF ₂ CF ₃
R-143	1,1,2-trifluoroethane (HFC-143)	CHF ₂ CH ₂ F
R-143a	1,1,1-trifluoroethane(HFC-143a)	CF ₃ CH ₃
R-152a	1,1,difluoroethane (HFC-152a)	CHF ₂ CH ₃
R-245cb	1,1,1,2,2-pentafluoropropane (HFC-245cb)	CF ₃ CF ₂ CH ₃
R-253dc	2-chloro-1,1,1-trifluoropropane (HCFC-253dc)	CF ₃ CHClCH ₃
R-254fb	1,1,1,3-tetrafluoropropane (HFC-254fb)	CF ₃ CH ₂ CH ₂ F
R-260fb	1,1,1-trichloropropane (HCC-260fb)	CCl ₃ CH ₂ CH ₃
R-261fc	1,1-dichloro-1-fluoropropane (HCFC-261fc)	CCl ₂ FCH ₂ CH ₃
R-262fc	1-chloro-1,1-difluoropropane (HCFC-262fc)	CClF ₂ CH ₂ CH ₃
R-263fb	1,1,1-trifluoropropane (HFC-263fb)	CF ₃ CH ₂ CH ₃
R-272fb	1,1-difluoropropane (HFC-272fb)	CHF ₂ CH ₂ CH ₃
R-290	propane (HC-290)	CH ₃ CH ₂ CH ₃
R-374	Tetrafluorobutane (HFC-374)	C ₄ H ₆ F ₄
	butane	CH ₃ CH ₂ CH ₂ CH ₃
	allene	H ₂ C=C=CH ₂
	2-butene	CH ₃ CH=CHCH ₃
	cyclobutene	C ₄ H ₆
	2-methylpropene	CH ₃ (CH ₃)C=CF ₂
R-1122	1-chloro-2,2-difluoroethylene (HCFO-1122)	CHCl=CF ₂
R-1132	1,2-difluoroethene (E/Z-HFO-1132)	CHF=CHF
R-1132a	1,1-difluoroethene ((HFO-1132a)	CH=CF ₂

Code	Name-ASHRAE Designation	Formula
R-1141	fluoroethene (HFO-1141)	$\text{CH}_2=\text{CHF}$
R-1150	ethylene (HO-1150)	$\text{CH}_2=\text{CH}_2$
R-1225zc	1,1,3,3,3-pentafluoropropene (HFO-1252zc)	$\text{CF}_3\text{CH}=\text{CF}_2$
R-1243zf	3,3,3-trifluoropropene (HFO-1243zf)	$\text{CF}_3\text{CH}=\text{CH}_2$
R-1233xf	2-chloro-3,3,3-trifluoropropene (HCFO-1233xf)	$\text{CF}_3\text{CCl}=\text{CH}_2$
R-1234yf	2,3,3,3-tetrafluoropropene (HFO-1234yf)	$\text{CF}_3\text{CF}=\text{CH}_2$
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-1252ze,	1,3-difluoropropene (HFO-1252ze)	$\text{CH}_2\text{FCH}=\text{CHF}$
R-1252yf,	2,3-difluoropropene (HFO-1252yf)	$\text{CH}_2\text{FCF}=\text{CH}_2$
R-1252zf	3,3-difluoropropene (HFO-1252zf)	$\text{CHF}_2\text{CH}=\text{CH}_2$
R-1252ye	1,2-difluoropropene (HFO-1252ye)	$\text{CH}_3\text{CF}=\text{CHF}$
R-1252zc	1,1-difluoropropene (HFO-1252zc)	$\text{CH}_3\text{CH}=\text{CF}_2$
R-1260zf	3-chloropropene (HFO-1260zf)	$\text{CH}_2\text{ClCH}=\text{CH}_2$
R-1261ze	1-fluoropropene (E/Z-HFO-1261ze)	$\text{CH}_3\text{CH}=\text{CHF}$
R-1261zf	3-fluoro-1-propene (HFO-1261zf)	$\text{CH}_2\text{FCH}=\text{CH}_2$
R-1270	propylene (HO-1270)	$\text{CH}_3\text{CH}=\text{CH}_2$
R-1345	pentafluorobutene (HFO-1345)	$\text{C}_4\text{H}_3\text{F}_5$
	E/Z- <i>t</i> -BuO-CF=CH-CH ₃	E/Z- <i>t</i> -BuO-CF=CH-CH ₃

[0089] 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.

Compositions

[0090] In one embodiment, the composition according to the present invention comprises, consists of or consists essentially of a difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, and mixtures thereof. In one embodiment, the composition according to the present invention comprises, consists of or consists essentially of HFO-1252zc.

[0091] It will be understood by those skilled in the art that the compositions described herein refer to compositions which have been treated (i.e., dried and/or purified) or may be treated (i.e., dried and/or purified) according to processes of the present invention.

[0092] The composition according to the present invention may be a neat composition comprising, consisting of or consisting essentially of HFO-1252zc and optionally one or more additional compounds in minor amounts, or may be a blend composition comprising, consisting of or consisting essentially of HFO-1252zc, one or more other refrigerant compounds, and optionally one or more additional compounds in minor amounts.

[0093] The compositions to be treated, and more particularly dried and/or purified, according to processes of the present invention are fluid compositions which may be in either the liquid state or the vapor (gas) state.

[0094] In one embodiment, the composition according to the present invention comprises, consists of or consists essentially of a difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, each having a purity of at least about 98 wt%, at least about 99 wt% pure, and in some cases at least about 99% to at least about 99.5 wt% pure, and in some cases at least about 99.5%.

[0095] In certain embodiments disclosed herein, the compositions comprise at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional compounds or members, such as one or more of the compounds identified in Table 1, wherein each additional compound is present in an amount of between:

- a. greater than 0 and less than 4 wt. percent,
- b. greater than 0 and less than 3 wt. percent,
- c. greater than 0 and less than 2 wt. percent,
- d. greater than 0 and less than 1 wt. percent,
- e. greater than 0 and less than 0.5 wt. percent,
- f. greater than 0 and less than 0.1 wt. percent,
- g. greater than 0 and less than 0.01 wt. percent,
- h. greater than 0 and less than 0.005 wt. percent,
- i. greater than 0.001 and less than 4 wt. percent,
- j. greater than 0.001 and less than 3 wt. percent,

- k. greater than 0.001 and less than 2 wt. percent,
- l. greater than 0.001 and less than 1 wt. percent,
- m. greater than 0.001 and less than 0.5 wt. percent,
- n. greater than 0.001 and less than 0.1 wt. percent,
- o. greater than 0.001 and less than 0.01 wt. percent, or
- p. greater than 0.001 and less than 0.005 wt. percent,

based on the total amount of the composition *with the proviso* that the total amount of additional compounds other than HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze or HFO-1252zc is greater than 0.0001 and less than 10 wt.%, greater than 0.0001 and less than 9 wt.%, greater than 0.0001 and less than 8 wt.%, greater than 0.0001 and less than 7 wt.%, greater than 0.0001 and less than 6 wt.%, greater than 0.0001 and less than 5 wt.%, greater than 0.0001 and less than 4 wt.%, greater than 0.0001 and less than 3 wt.%, greater than 0.0001 and less than 2 wt.%, greater than 0.0001 and less than 1 wt.%, greater than 0.0001 and less than 0.5 wt.%, or greater than 0.0001 and less than 0.1 wt.%.

[0096] A further embodiment of the invention disclosed herein is a composition comprising, consisting essentially of, or consisting of a difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and at least one additional member or compound, wherein the total amount of the additional members is between greater than 0 and less than about 15%, 14%, 13%, 12%, 11%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2% or 1%, and all values and ranges therebetween.

[0097] A still further embodiment of the invention disclosed herein is a composition comprising, consisting essentially of, or consisting of a difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and at least one additional compound, wherein the total amount of additional compounds is between greater than 0 and less than about 10%, between greater than 0.001% and less than 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2% or 1%, including all values and ranges therebetween.

[0098] In certain embodiments of the invention disclosed herein is a composition comprising, consisting essentially of, or consisting of a difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional compound selected from the compounds of Table 1 in any combination.

[0099] In certain embodiments disclosed herein, the compositions comprise at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional compounds such as C₂-C₄ alkenes selected from ethylene, propylene, butene, allene, and cyclobutene.

[0100] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional members or compounds selected from methane, ethylene, trifluoromethane (HFC-23), fluoroethene (HFO-1141), propane (HC-290), propylene (HO-1270), 2,3,3,3-tetrafluoropropene (HFO-1234yf), allene, allene, C₃H₄F₂, 1-fluoro-1-propene (HFO-1261ze), 1,1,1-trifluoropropane (HFC-263fb), 2-butene, cyclobutene, 2-methyl-1-propene, 1,1-difluoropropane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 3-chloropropene (HCO-1260zf), C₃H₄FCI (I) (HCFO-1251), and C₃H₄FCI (II) (HCFO-1251).

[0101] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of 1,1-difluoropropene (HFO-1252zc), optionally 1,1,1-trifluoropropane (HFC-263fb), and (i) one or more additional members or compounds selected from methane, ethylene, trifluoromethane (HFC-23), fluoroethene (HFO-1141), propane (HC-290), propylene (HO-1270), 2,3,3,3-tetrafluoropropene (HFO-1234yf), allene, allene, C₃H₄F₂, 1-fluoro-1-propene (HFO-1261ze), 1,1,1-trifluoropropane (HFC-263fb), 2-butene, cyclobutene, 2-methyl-1-propene, 1,1-difluoropropane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 3-chloropropene (HCO-1260zf), C₃H₄FCI (I) (HCFO-1251), and C₃H₄FCI (II) (HCFO-1251), or (2) one or more additional members selected from HFO-1132a, HFC-125, HFC-143a, HFO-1225zc, HFC-152a, HFO-1252ze, HFO-1252yf, HFO-1252zf, and HFO-1252ye.

[0102] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, optionally 1-chloro-1,1-difluoropropane (HCFC-262fc) or 1,1,1-trifluoropropane (HFC-263fb), and one or more additional members or compounds selected from methane, ethylene, trifluoromethane (HFC-23), fluoroethene (HFO-1141), propane (HC-290), propylene (HO-1270), 2,3,3,3-tetrafluoropropene (HFO-1234yf), allene, $C_3H_4F_2$, 1-fluoro-1-propene (HFO-1261ze), 2-butene, cyclobutene, 2-methyl-1-propene, 1,1-difluoropropane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 3-chloropropene (HCO-1260zf), C_3H_4FCI (I) (HCFO-1251), and C_3H_4FCI (II) (HCFO-1251).

[0103] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, optionally 1,1,1-trifluoropropane (HFC-263fb), and one or more additional members selected from methane, ethylene, trifluoromethane (HFC-23), fluoroethene (HFO-1141), propane (HC-290), propylene (HO-1270), 2,3,3,3-tetrafluoropropene (HFO-1234yf), allene, $C_3H_4F_2$, 1-fluoro-1-propene (HFO-1261ze), 2-butene, cyclobutene, 2-methyl-1-propene, 1,1-difluoropropane, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 3-chloropropene (HCO-1260zf), C_3H_4FCI (I) (HCFO-1251), and C_3H_4FCI (II) (HCFO-1251).

[0104] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, optionally 1-chloro-1,1-difluoropropane (HCFC-262fc), optionally 1,1,1-trifluoropropane (HFC-263fb), and one or more additional members selected from ethylene, trifluoromethane (HFC-23), 1,1-difluoroethene (HFO-1132a), fluoroethene (HFO-1141), 1,1,2,2,2-pentafluoroethane (HFC-125), propane (HC-290), 1,1,2-trifluoroethane (HFC-143), 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,1,1-difluoroethane (HFC-152a), 1-fluoro-1-propene (HFO-1261ze), 1,1,1-trifluoropropane (HFC-263fb), 1,1,1-trifluoroethane (HFC-143a), difluoropropane, chlorotrifluoropropene, pentafluorobutene (HFO-1345) and $C_4H_6F_4$ (HFC-374).

[0105] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, optionally 1,1,1-trifluoropropane (HFC-263fb), and one or more additional members selected from ethylene, trifluoromethane (HFC-23), 1,1-difluoroethene (HFO-1132a), fluoroethene (HFO-1141), 1,1,2,2,2-pentafluoroethane (HFC-125), propane (HC-290), 1,1,2-trifluoroethane (HFC-143), 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,1,1-difluoroethane (HFC-152a), 1-fluoro-1-propene (HFO-1261ze), 1,1,1-trifluoropropane (HFC-263fb), 1,1,1-trifluoroethane (HFC-143a), difluoropropane, chlorotrifluoropropene, pentafluorobutene (HFO-1345) and C₄H₆F₄ (HFC-374).

[0106] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, optionally 1-chloro-1,1-difluoropropane (HCFC-262fc) and/or 1,1,1-trifluoropropane (HFC-263fb), and one or more additional members selected from trifluoromethane (HFC-23), dichloromethane (HCC-30), chlorofluoromethane (HCFC-31), methyl chloride (HCC-40), methane, 1,1,2,2,2-pentafluoroethane (HFC-125), 1,1,2-trifluoroethane (HFC-143), 1,1,1-trifluoroethane (HFC-143a), 1,1,1-difluoroethane (HFC-152a), 1,1,1,2,2-pentafluoropropane (HFC-245cb), 2-chloro-1,1,1-trifluoropropane (HCFC-253dc), 1,1,1,3-tetrafluoropropane (HFC-254fb), 1,1,1-trichloropropane (HCC-260fb), 1,1-dichloro-1-fluoropropane (HCFC-261fc), 1,1-difluoropropane (HFC-272fb), propane (HC-290), tetrafluorobutene (HFO-374), butane (HC-600), allene, 2-butene, cyclobutene, 2-methylpropene, 1-chloro-2,2-difluoroethylene (HCFO-1122), 1,2-difluoroethene (HFO-1132), 1,1-difluoroethene (HFO-1132a), fluoroethene (HFO-1141), ethylene (HFO-1150), 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 2,3,3,3-tetrafluoropropene (HFO-1234yf), 3-chloro-3,3-difluoropropene (HCFO-1242zf), 3,3,3-trifluoropropene (HFO-1243zf), CFO-1251 isomer (I), HCFO-1251 isomer (II), 3-chloropropene (HCO-1260zf), 1-fluoro-1-propene (HFO-1261ze), propylene (HFO-1270), pentafluorobutene (HFO-1345), and E/Z-t-BuO-CF=CH-CH₃.

[0107] In certain embodiments disclosed herein the composition comprises, consists essentially of, or consists of 1,1-difluoropropene (HFO-1252zc), optionally

1,1,1-trifluoropropane (HFC-263fb), and one or more additional members HFO-1243zf, HFO-1234yf, allene, HFO-1252ye, HFO-1252yf, and HFO-1252zf.

[0108] In certain embodiments disclosed herein the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, optionally at least one of HFC-263fb, HCFC-262fc, and one or more additional members selected from ethylene, HFC-23, HFO-1132a, propane, HFO-1234yf, HFO-1261ze, HFC-143a, HCFO-1233xf, and HFC-374.

[0109] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional members selected from HCFO-1233xf, HFC-152a, HFC-263fb, HFC-254fb, HFC-253dc, HFC-252dc and HCFO-1230xa.

[0110] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional members selected from HCFC-262fc, HCC-250fb, HFC-263fb, HFO-1243zf, other HCFO-1252 isomers, ethane, ethylene, HFC-23, HCFC-22, HFO-1132a, propane, HFC-143a, HCFC-142b, HFO-1234yf, HFO-1234ze, HFO-1225zc, HCFO-1242zf and HCFC-252fc.

[0111] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional members selected from at least one of HCC-250fb, HCFC-252fc and HCFC-262fc, and one or more additional compounds selected from HFC-263fb, HFO-1243zf, other 1252 isomers, ethane, ethylene, HFC-23, HCFC-22, HFO-1132a, propane, HFC-143a, HCFC-142b, HFO-1234yf, HFO-1234ze, HFO-1225zc, and HCFO-1242zf.

[0112] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more

additional members selected from HCC-250fb, HFC-263fb, HFO-1243zf, other 1252 isomers, ethane, ethylene, HFC-23, HCFC-22, HFO-1132a, propane, HFC-143a, HCFC-142b, HFO-1234yf, HFO-1234ze, HFO-1225zc, HCFO-1242zf and HCFC-252fc.

[0113] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional members selected from HCC-250fb, HFC-263fb, HFO-1243zf, other 1252 isomers, ethane, ethylene, HFC-23, HCFC-22, HFO-1132a, propane, HCC-143a, HCC-142b, HFO-1234yf, HFO-1234ze, HFO-1225zc and HCFO-1242zf.

[0114] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional members selected from HCFC-262fc, HCC-250fb, HFC-263fb, HCFO-1242zf, HFO-1252zf, HFO-1243zf and HCFC-252fc.

[0115] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of (i) at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, (ii) optionally at least one of HCC-250fb and HCFO-1242zf; and (iii) one or more additional compounds selected from HCFC-262fc, HFC-263fb, HFO-1252zf, HFO-1243zf and HCFC-252fc.

[0116] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional compounds selected from HCFO-1242zf, HCFC-262fc, HCC-250fb, HFC-263fb, HFO-1252zf, HFO-1243zf and HCFC-252fc.

[0117] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional compounds selected from HCC-250fb, HCFC-252fc, HCFC-262fc, HCFO-1242zf, HFC-263fb, other 1252 isomers, ethane, ethylene, HFC-23, HCFC-22, HFO-

1132a, propane, HCC-143a, HCC-142b, HFO-1234yf, HFO-1234ze, and HFO-1225zc and HFO-1243zf.

[0118] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional compounds selected from HFC-152a, HFO-1243zf, difluorodimethylsilane ($\text{C}_2\text{H}_6\text{F}_2\text{Si}$), HF, HCl, E-HFO-1261ze and Z-HFO-1261ze.

[0119] In certain embodiment disclosed herein, the total amount of additional compounds/members in any of the foregoing stabilized HFO-1252 refrigerant compositions is selected from between: greater than 0 and less than 0.5 wt. percent, greater than 0 and less than 0.4 wt. percent, greater than 0 and less than 0.2 wt. percent, greater than 0 and less than 0.2 wt. percent, greater than 0 and less than about 0.1 wt. percent, or greater than 0 and less than about 0.01 wt. percent based on the total amount of the composition, with the *proviso* that the total amount of the composition is 100 wt.%; and/or the respective amount of an additional compound/member is selected from one of greater than 0 and less than about 0.2 wt. percent, greater than 0 and less than about 0.1 wt. percent, greater than 0 and less than about 0.01 wt. percent, greater than 0 and less than about 0.001 wt. percent, or greater than 0 and less than about 0.02001 percent based on the total amount of the composition, with the *proviso* that the total amount of the composition is 100 wt.%; and/or the respective amount of an additional compound/member is independently selected from one of greater than 0 and less than about 0.2 wt. percent, greater than 0 and less than about 0.1 wt. percent, greater than 0 and less than about 0.01 wt. percent, greater than 0 and less than about 0.001 wt. percent, or greater than 0 and less than about 0.0001 wt. percent based on the total amount of the composition, with the *proviso* that the total amount of the composition is 100 wt.%; and/or the total amount of the additional compounds/members in any of the foregoing stabilized HFO-1252 refrigerant compositions is selected from between greater than 0.0001 and less than 10 wt.%, greater than 0.0001 and less than 9 wt.%, greater than 0.0001 and less than 8 wt.%, greater than 0.0001 and less than 7 wt.%, greater than 0.0001 and less than 6 wt.%, greater than 0.0001 and less than 5 wt.%, greater than 0.0001 and less than 4 wt.%, greater than 0.0001 and less than 3

wt.%, greater than 0.0001 and less than 2 wt.%, greater than 0.0001 and less than 1 wt.%, greater than 0.0001 and less than 0.5 wt.%, or greater than 0.0001 and less than 0.1 wt.%, based on the total amount of the composition, with the *proviso* that the total amount of the composition is 100 wt.%.

[0120] In some embodiments, the composition comprises a refrigerant blend including at least one difluoropropene and at least one other refrigerant compound. Such a composition may further comprise one or more of any of the refrigerant compounds listed in Table 1. The at least one difluoropropene is selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, and is preferably HFO-1252zc.

[0121] In one embodiment, the at least one other compound of the refrigerant blends may be selected from fluoroolefins, hydrofluorocarbons, hydrocarbons, dimethyl ether, CF₃I, ammonia, and mixtures thereof, meaning mixtures of any of the additional compounds listed in this paragraph. The amount of the other refrigerant compound can range from about 1 to about 90 wt%, about 5 to about 75 wt%, and in some cases about 10 to about 50 wt%, inclusive of all intervening values and ranges.

[0122] In one embodiment, the at least one other compound of the refrigerant blends may be carbon dioxide (CO₂). The amount of CO₂ can range from about 1 to about 90 wt%, about 1 to about 50 wt%, about 1 to about 10 wt%, and in some cases about 1 to about 5 wt%, inclusive of all intervening values and ranges.

[0123] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and at least one other compound selected from, CO₂, HFO-1234ze(E), HFO-1234ze(Z), HFO-1336mzz(E), HFO-1336mzz(Z), HFC-32, HFC-152a, HFC-125, HFC-134a, HFO-1132(E), HFO-1132(Z), HCFO-1233zd(E), HCFO-1233zd(Z), HFO-1234yf, HFC-143, HFC-143a, HFC-134, CFC-12, HFO-1243zf, HCFO-1224yd(Z), HCFO-1233xf, HCFO-1131a, HCFO-1122a(Z), HFO-1234yc, HFO-1234ye(E), HFO-1234ye(Z), HFO-1234zc, HFO-1243yc, HFO-1243zc, HFO-1243ye(E), HFO-1243ye(Z), HFO-1243ze(E), HFO-1243ze(Z), HFC-227ea, HFO-1252zc, HFO-1252zf, HFO-

1252ye(E), HFO-1252ye(Z), HFO-1252ze(E), HFO-1252ze(Z), HFO-1252yf, ethane, propane, butane and combinations thereof.

[0124] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and selected from CO₂, HFO-1132(E), HFO-1132(Z), HFO-1234ze(E), HFO-1234ze(Z), HFO-1336mzz(E), HFO-1336mzz(Z), HFC-32, HFC-152a, HFC-125, HCFO-1233zd(E), HCFO-1233zd(Z), HFC-143a, HFC-134, CFC-12, HFO-1243zf, HCFO-1131a, HCFO-1122a(Z), HFO-1234yc, HFO-1234ye(E), HFO-1234ye(Z), HFO-1234zc, HFO-1243yc, HFO-1243zc, HFO-1243ye(E), HFO-1243ye(Z), HFO-1243ze(E), HFO-1243ze(Z), HFO-1252zc, HFO-1252zf, HFO-1252ye(E), HFO-1252ye(Z), HFO-1252ze(E), HFO-1252ze(Z), HFO-1252yf, ethane, propane, butane and combinations thereof.

[0125] In some embodiments, the at least one other compound includes a fluoroolefin, such as any of the fluoroolefins listed above. The amount of the other fluoroolefins can range from about 1 to about 90 wt%, about 5 to about 75 wt%, and in some cases about 10 to about 50 wt%, inclusive of all intervening values and ranges.

[0126] In one embodiment, the at least one other compound comprises hydrofluorocarbons. The hydrofluorocarbon (HFC) compounds of the present invention comprise saturated compounds containing carbon, hydrogen, and fluorine. Of particular utility are hydrofluorocarbons having 1-7 carbon atoms and having a normal boiling point of from about -90°C to about 80°C. Hydrofluorocarbons are commercial products available from a number of sources, or may be prepared by methods known in the art. Representative hydrofluorocarbon compounds include but are not limited to fluoromethane (CH₃F, HFC-41), difluoromethane (CH₂F₂, HFC-32), trifluoromethane (CHF₃, HFC-23), pentafluoroethane (CF₃CHF₂, HFC-125), 1,1,2,2-tetrafluoroethane (CHF₂CHF₂, HFC-134), 1,1,1,2-tetrafluoroethane (CF₃CH₂F, HFC-134a), 1,1,1-trifluoroethane (CF₃CH₃, HFC-143a), 1,1-difluoroethane (CHF₂CH₃, HFC-152a), fluoroethane (CH₃CH₂F, HFC-161), 1,1,1,2,2,3,3-heptafluoropropane (CF₃CF₂CHF₂, HFC-227ca), 1,1,1,2,3,3,3-heptafluoropropane (CF₃CHFCF₃, HFC-227ea), 1,1,2,2,3,3,3-hexafluoropropane

(CHF₂CF₂CHF₂, HFC-236ca), 1,1,1,2,2,3-hexafluoropropane (CF₃CF₃CH₂F, HFC-236cb), 1,1,1,2,3,3-hexafluoropropane (CF₃CHFCHF₂, HFC-236ea), 1,1,1,3,3,3-hexafluoropropane (CF₃CH₂CF₃, HFC-236fa), 1,1,2,2,3-pentafluoropropane (CHF₂CF₂CH₂F, HFC-245ca), 1,1,1,2,2-pentafluoropropane (CF₃CF₂CH₃, HFC-245cb), 1,1,2,3,3-pentafluoropropane (CHF₂CHFCHF₂, HFC-245ea), 1,1,1,2,3-pentafluoropropane (CF₃CHFCH₂F, HFC-245eb), 1,1,1,3,3-pentafluoropropane (CF₃CH₂CHF₂, HFC-245fa), 1,2,2,3-tetrafluoropropane (CH₂FCF₂CH₂F, HFC-254ca), 1,1,2,2-tetrafluoropropane (CHF₂CF₂CH₃, HFC-254cb), 1,1,2,3-tetrafluoropropane (CHF₂CHFCH₂F, HFC-254ea), 1,1,1,2-tetrafluoropropane (CF₃CHFCH₃, HFC-254eb), 1,1,3,3-tetrafluoropropane (CHF₂CH₂CHF₂, HFC-254fa), 1,1,1,3-tetrafluoropropane (CF₃CH₂CH₂F, HFC-254fb), 1,1,1-trifluoropropane (CF₃CH₂CH₃, HFC-263fb), 2,2-difluoropropane (CH₃CF₂CH₃, HFC-272ca), 1,2-difluoropropane (CH₂FCHFCH₃, HFC-272ea), 1,3-difluoropropane (CH₂FCH₂CH₂F, HFC-272fa), 1,1-difluoropropane (CHF₂CH₂CH₃, HFC-272fb), 2-fluoropropane (CH₃CHFCH₃, HFC-281ea), 1-fluoropropane (CH₂FCH₂CH₃, HFC-281fa), 1,1,2,2,3,3,4,4-octafluorobutane (CHF₂CF₂CF₂CHF₂, HFC-338pcc), 1,1,1,2,2,4,4,4-octafluorobutane (CF₃CH₂CF₂CF₃, HFC-338mf), 1,1,1,3,3-pentafluorobutane (CF₃CH₂CHF₂, HFC-365mfc), 1,1,1,2,3,4,4,5,5,5-decafluoropentane (CF₃CHFCHFCF₂CF₃, HFC-43-10mee), and 1,1,1,2,2,3,4,5,5,6,6,7,7,7-tetradecafluoroheptane (CF₃CF₂CHFCHFCF₂CF₂CF₃, HFC-63-14mee).

[0127] In one embodiment, examples of suitable hydrofluorocarbons comprise at least one member selected from HFC-32, HFC-125, HFC-134a, HFC-152a, HFC-236fa, and HFC-227ea. The amount of hydrofluorocarbon can range from about 1 to about 90 wt%, about 5 to about 75 wt%, and in some cases about 10 to about 50 wt%, inclusive of all intervening values and ranges.

[0128] In another embodiment, the at least one other compound of the blend comprises hydrocarbons. The hydrocarbons of the present invention comprise compounds having only carbon and hydrogen. Of particular utility are compounds having 3-7 carbon atoms. Hydrocarbons are commercially available through numerous chemical suppliers. Representative hydrocarbons include but are not limited to propane, n-butane, isobutane, cyclobutane, n-pentane, 2-methylbutane, 2,2-dimethylpropane, cyclopentane, n-hexane, 2-methylpentane, 2,2-

dimethylbutane, 2,3-dimethylbutane, 3-methylpentane, cyclohexane, n-heptane, and cycloheptane.

[0129] In another embodiment, the at least one other compound of the blend comprises hydrocarbons containing heteroatoms, such as dimethylether (DME, CH_3OCH_3). DME is commercially available. The amount of the hydrocarbon can range from about 1 to about 90 wt%, about 5 to about 75 wt%, and in some cases about 10 to about 50 wt%, inclusive of all intervening values and ranges.

[0130] In another embodiment, the at least one other compound of the blend comprises iodotrifluoromethane (CF_3I), which is commercially available from various sources or may be prepared by methods known in the art. The amount of CF_3I can range from about 1 to about 90 wt%, about 5 to about 75 wt%, and in some cases about 10 to about 50 wt%, inclusive of all intervening values and ranges.

[0131] In another embodiment, the at least one other compound of the blend comprises at least one member selected from HFC-23, HFC-41, HFC-134a, HCFC-22, CFC-12, HCC-40, and HFC-143a, in an amount ranging from about 1 to about 90 wt%, about 5 to about 75 wt%, and in some cases about 10 to about 50 wt%, inclusive of all intervening values and ranges.

[0132] In another embodiment, the at least one other compound comprises at least one member selected from air (N_2/O_2 78/21 ratio), O_2 , N_2 , Ar, CO_2 , CH_4 , and He.

[0133] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and at least one other refrigerant compound selected from 2,3,3,3-tetrafluoropropene (HFO-1234yf), difluoromethane (HFC-32), 1,3,3,3-tetrafluoropropene (HFO-1234ze(E)), and 1,1-difluoroethane (HFC-152a). The at least one difluoropropene is selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, and is preferably HFO-1252zc. In some embodiments, the refrigerant blend further includes at least one refrigerant compound selected from trifluoroethylene (HFO-1123), trifluoroiodomethane (CF_3I), carbon dioxide (R-744, CO_2), 1,1,1,2-tetrafluoroethane (HFC-134a), and 1,1,2,2-tetrafluoroethane (HFC-134).

[0134] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and at least one other refrigerant compound selected from HFC-227ca, HFC-134, HFC-152a, HFC-32, HFC-41, R1311 (CF₃I), CO₂, HFO-1123, HFO-1132a, HFO-1132(E), HFO-1132(Z), HCFO-1131a, HCFO-1122a(Z), and HCFO-1122a(E).

[0135] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and at least one other refrigerant compound selected from HFC-227ca, HFC-134, HFC-152a, HFC-32, HFC-41, R1311 (CF₃I), CO₂, HFO-1123, HFO-1132a, HFO-1132(E), HFO-1132(Z), HCFO-1131a, HCFO-1122a(Z), HCFO-1122a(E), HFO-1234yc, HFO-1234ye(E), HFO-1234ye(Z), HFO-1234zc, HFO-1243yc, HFO-1243zf, HFO-1243zc, HFO-1243ye(E), HFO-1243ye(Z), HFO-1243ze(E), HFO-1243z(-)Z, HFO-1336mzz(Z), HFO-1336mzz(E), HCFO-1233zd(E), and HCFO-1233zd(Z).

[0136] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and HFC-32 (i.e., as the other refrigerant compound).

[0137] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and HFO-1132(E) (i.e., as the other refrigerant compound).

[0138] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and HFC-32 and HFC-152a (i.e., as the other refrigerant compounds).

[0139] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and HFC-32 and HFC-134 (i.e., as the other refrigerant compounds).

[0140] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and HFC-32 and HFC-227ca (i.e., as the other refrigerant compounds).

[0141] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and HFC-32 and CF₃I (i.e., as the other refrigerant compounds).

[0142] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and HFC-1132(E) and HFC-152a (i.e., as the other refrigerant compounds).

[0143] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and HFC-1132(E) and HFC-134 (i.e., as the other refrigerant compounds).

[0144] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and HFC-1132(E) and HFC-227ca (i.e., as the other refrigerant compounds).

[0145] In one embodiment, the composition comprises a refrigerant blend comprising at least one difluoropropene selected from HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and HFC-1132(E) and CF₃I (i.e., as the other refrigerant compounds).

[0146] In some embodiments, the refrigerant blend which makes up the refrigerant portion of the composition comprises from about 1 to about 96 wt% difluoropropene and from about 4 wt% to about 99 wt% of at least one other refrigerant compound, alternatively about 1 to about 20 wt% difluoropropene and from about 80 wt% to about 99 wt% of at least one other refrigerant compound, alternatively about 2 to about 14 wt% difluoropropene and from about 86 wt% to about 98 wt% of at least one other refrigerant compound, alternatively about 20 wt% or greater

difluoropropene and up to about 80 wt% of at least one other refrigerant compound, alternatively about 72 to about 96 wt% difluoropropene and from about 4 wt% to about 28 wt% of at least one other refrigerant compound, or any value, range, or sub-range therebetween.

[0147] In some particular embodiments, the refrigerant blend which makes up the refrigerant portion of the composition comprises from 2 to 35 wt% difluoropropene, from 2 to 96 wt% of a second refrigerant compound, and from 2 to 96 wt% of a third refrigerant compound, such as, for example, from 4 to 10 wt% difluoropropene, from 2 to 30 wt% of the second refrigerant compound, and from 60 to 94 wt% of the third refrigerant compound.

[0148] In some particular embodiments, the refrigerant blend which makes up the refrigerant portion of the composition comprises from about 1 wt% to about 35 wt% difluoropropene, from about 1 wt% to about 40 wt% of a second refrigerant compound, and from about 40 wt% to about 98 wt% of a third refrigerant compound.

[0149] According to one embodiment, some of the compositions of the present invention are free of or substantially free of Group A Fluorinated Substances, such as trifluoroacetic acid (TFA). In one embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that (i) contains at least one fully fluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) carbon atom (without any H/Cl/Br/I attached to it); and (ii) meets the criterion for persistence in soil/sediment and water established in Annex XIII (Section 1.1.1) of the European Union's REACH Regulation (<https://reachonline.eu/reach/en/annex-xiii-1-1.1-1.1.1.html> as accessed on May 2, 2023) and referenced in the Annex XV Restriction Report dated March 22, 2023, the disclosure of which is hereby incorporated by reference (<https://echa.europa.eu/documents/10162/f605d4b5-7c17-7414-8823-b49b9fd43aea> as accessed on May 2, 2023).

[0150] In another embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that has a Henry's Law constant $\leq 250 \text{ Pa}\cdot\text{m}^3/\text{mol}$ and contains at least one fully fluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) carbon atom (without any H/Cl/Br/I attached to it).

[0151] In embodiments, Group A Fluorinated Substances include, but are not limited to, TFA.

[0152] The phrase "free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by gas chromatography with a flame ionization detector, gas chromatography with a mass detector by analysis of a gas sample or liquid sample, and/or ion chromatography by analysis of a water sample after bubbling the thermal fluid through water. Such methodologies are well known to those skilled in the art. The phrase "substantially free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is > 0 wt.% and ≤ 5 wt.%, or > 0 wt.% and ≤ 4 wt.%, or > 0 wt.% and ≤ 3 wt.%, or > 0 wt.% and ≤ 2 wt.%, or > 0 wt.% and ≤ 1 wt.%, and all values and ranges therebetween, when measured by gas chromatographic (GC) techniques, for example gas chromatography (GC) with a flame ionization or electron-capture detector, or GC coupled with a mass detector (gas chromatography/mass spectral (GC/MS) method), by ion chromatograph(IC) or ion chromatography mass spectrometry (IC-MS) techniques, or by high-performance liquid chromatography (HPLC) or high-performance liquid chromatography mass spectrometry (HPLC-MS) techniques. The TFA analytical standard may be used in either gas chromatography or ion chromatography and is available from, for example, Sigma Aldrich.

[0153] In one embodiment, the composition according to the present invention comprises at least one difluoropropene, such as HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze or HFO-1252zc, preferably HFO-1252zc; and optionally one or more of the additional members or additional compounds disclosed herein; and the composition is free of or substantially free of Group A Fluorinated Substances, such as TFA.

[0154] In one embodiment, the composition according to the present invention comprises at least one difluoropropene, such as HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze or HFO-1252zc, preferably HFO-1252zc; at least one other refrigerant selected from CO₂, HFO-1132(E), HFO-1132(Z), HFO-1234ze(E), HFO-1234ze(Z), HFO-1336mzz(E), HFO-1336mzz(Z), HFC-32, HFC-152a, HFC-125, HCFO-1233zd(E), HCFO-1233zd(Z), HFC-143a, HFC-134, CFC-12, HFO-1243zf, HCFO-1131a, HCFO-1122a(Z), HFO-1234yc, HFO-1234ye(E), HFO-1234ye(Z),

HFO-1234zc, HFO-1243yc, HFO-1243zc, HFO-1243ye(E), HFO-1243ye(Z), HFO-1243ze(E), HFO-1243ze(Z), HFO-1252zc, HFO-1252zf, HFO-1252ye(E), HFO-1252ye(Z), HFO-1252ze(E), HFO-1252ze(Z), HFO-1252yf, ethane, propane, butane and combinations thereof; and optionally one or more of the additional members or additional compounds disclosed herein, and the composition is free of or substantially free of Group A Fluorinated Substances, such as TFA.

[0155] In one embodiment, degradation products of some of the compositions according to the present invention are free of or substantially free of Group A Fluorinated Substances, such as TFA. The phrase "free of" as used herein with respect to the formation of Group A Fluorinated Substances as degradation products of the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during tropospheric degradation of the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by GC techniques, for example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques. The phrase "substantially free of" as used herein with respect to the formation of Group A Fluorinated Substances by the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during tropospheric degradation of the compositions is $> 0\%$ and $\leq 5\%$, or $> 0\%$ and $\leq 4\%$, or $> 0\%$ and $\leq 3\%$, or $> 0\%$ and $\leq 2\%$, or $> 0\%$ and $\leq 1\%$, and all values and ranges therebetween, when measured by GC techniques, for example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques.

[0156] In one embodiment, the composition according to the present invention comprises at least one difluoropropene, such as HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze or HFO-1252zc, preferably HFO-1252zc; and optionally one or more of the additional members or additional compounds disclosed herein; wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances, such as TFA.

[0157] In one embodiment, the composition according to the present invention comprises at least one difluoropropene, such as HFO-1252zf, HFO-1252yf, HFO-

1252ye, HFO-1252ze or HFO-1252zc, preferably HFO-1252zc; at least one other refrigerant selected from CO₂, HFO-1132(E), HFO-1132(Z), HFO-1234ze(E), HFO-1234ze(Z), HFO-1336mzz(E), HFO-1336mzz(Z), HFC-32, HFC-152a, HFC-125, HCFO-1233zd(E), HCFO-1233zd(Z), HFC-143a, HFC-134, CFC-12, HFO-1243zf, HCFO-1131a, HCFO-1122a(Z), HFO-1234yc, HFO-1234ye(E), HFO-1234ye(Z), HFO-1234zc, HFO-1243yc, HFO-1243zc, HFO-1243ye(E), HFO-1243ye(Z), HFO-1243ze(E), HFO-1243ze(Z), HFO-1252zc, HFO-1252zf, HFO-1252ye(E), HFO-1252ye(Z), HFO-1252ze(E), HFO-1252ze(Z), HFO-1252yf, ethane, propane, butane and combinations thereof; and optionally one or more of the additional members or additional compounds disclosed herein, wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances, such as TFA.

[0158] In some embodiments, any of the refrigerant compositions described herein may further comprise at least one lubricant. The optional lubricant component of the refrigerant compositions can comprise those suitable for use with refrigeration or air-conditioning apparatus. Among these lubricants are those conventionally used in compression refrigeration apparatus utilizing chlorofluorocarbon refrigerants. Such lubricants and their properties are discussed in the 1990 ASHRAE Handbook, Refrigeration Systems and Applications, chapter 8, titled "Lubricants in Refrigeration Systems", pages 8.1 through 8.21, herein incorporated by reference. Lubricants of the present invention may comprise those commonly known as "mineral oils" in the field of compression refrigeration lubrication. Mineral oils comprise paraffins (i.e. straight-chain and branched-carbon-chain, saturated hydrocarbons), naphthenes (i.e. cyclic or ring structure saturated hydrocarbons, which may be paraffins) and aromatics (i.e. unsaturated, cyclic hydrocarbons containing one or more rings characterized by alternating double bonds). Lubricants of the present invention further comprise those commonly known as "synthetic oils" in the field of compression refrigeration lubrication. Synthetic oils comprise alkylaryls (i.e. linear and branched alkyl alkylbenzenes), synthetic paraffins and naphthenes, silicones, and poly-alpha-olefins. 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.

[0159] In another embodiment, the optional lubricant component of the difluoropropene refrigerant compositions treated, and more particularly dried and/or purified, according to the processes of the present invention can comprise those which have been designed for use with hydrofluorocarbon refrigerants and are miscible with refrigerants and inhibitors of the present invention under compression refrigeration and air-conditioning apparatus' operating conditions. Such lubricants and their properties are discussed in "Synthetic Lubricants and High-Performance Fluids", R. L. Shubkin, editor, Marcel Dekker, 1993. Such lubricants include, but are not limited to, polyol esters (POEs) such as Castrol® 100 (Castrol, United Kingdom), polyalkylene glycols (PAGs) such as RL-488A from Dow (Dow Chemical, Midland, Michigan), and polyvinyl ethers (PVEs).

[0160] Lubricants of the present invention are selected by considering a given compressor's requirements and the environment to which the lubricant will be exposed. The amount of lubricant can range from about 1 to about 50, about 1 to about 20 and in some cases about 1 to about 3. In one particular embodiment, the foregoing refrigerant compositions are combined with a PAG lubricant for usage in an automotive A/C system having an internal combustion engine. In another particular embodiment, the foregoing stabilized difluoropropene refrigerant compositions are combined with a POE lubricant for usage in an automotive A/C system having an electric or hybrid electric drive train.

[0161] In some embodiments, the compositions treated, and more particularly dried and/or purified, by processes of the present invention (e.g., any of the neat or blend compositions comprising HFO-1252zc described herein) may further comprise one or more members or additives which can improve the refrigerant and air-conditioning system lifetime and compressor durability are desirable. In one aspect of the invention, any of the difluoropropene refrigerant compositions described herein may further comprise at least one member selected from performance enhancers,

flame suppressants, stabilizers, polymerization inhibitors, antioxidants, and acid scavengers.

[0162] Examples of suitable polymerization inhibitors include, but are not limited to, limonene, α -terpinene, tocopherol including α -tocopherol, butylated hydroxytoluene, phenols such as 4-methoxyphenol, and aromatic organic compounds having the chemical formula $C_6H_4(OH)$ including benzene-1,4-diol. While any suitable effective amount can be employed, effective amounts comprise from about 0.001 wt% to about 10 wt%, about 0.01 wt% to about 5 wt%, about 0.3 wt% to about 4 wt%, about 0.3 wt% to about 1 wt% based on the total weight of HFO-1252 refrigerant compositions as described herein. In one embodiment, an effective amount comprises about 10 to about 2,000 ppm by weight, about 10 to about 1,000 ppm and in some cases about 10 to about 500 ppm of at least one inhibitor. The polymerization inhibitor is preferably present in any of the difluoropropene refrigerant compositions described herein in an amount such that the composition comprises less than about 0.03 wt.% of oligomeric, homopolymers or other polymeric products.

[0163] While any suitable antioxidant can be employed, examples of suitable antioxidants comprise at least one member selected from butylated hydroxytoluene, butylated hydroxyanisole, tertiary-butylhydroquinone, gallate, 2-phenyl-2-propanol, 1-(2,4,5-trihydroxyphenyl)-1-butanone, bisphenol methane derivatives, 2,2'-methylene bis (4-methyl-6-*t*-butyl phenol), among other phenolics, and combinations thereof.

[0164] In one embodiment of the invention, limonene or α -terpinene optionally with an antioxidant has unique fragrance even at a few ppm level. This pleasant odor can be utilized for refrigerant leakage detection with refrigerant and blends based on hydrofluoroolefins (e.g., comprising at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, and mixtures thereof). This is especially beneficial for early refrigerant leakage detection in household air conditioner or mobile air conditioner as paraprofessional electronic leak detectors often are not available in either location.

[0165] In some embodiments, an acid scavenger may comprise a butyl oxide, a siloxane, an activated aromatic compound, or a combination thereof. Serrano et al. (paragraph 38 of US 2011/0272624 A1), which is hereby incorporated by reference,

discloses that the siloxane may be any molecule having a siloxyfunctionality. The siloxane may include an alkyl siloxane, an aryl siloxane, or a siloxane containing mixtures of aryl and alkyl substituents. For example, the siloxane may be an alkyl siloxane, including a dialkylsiloxane or a polydialkylsiloxane. Preferred siloxanes include an oxygen atom bonded to two silicon atoms, i.e., a group having the structure: SiOSi. For example, the siloxane may be a siloxane of Formula IV: $R_1[Si(R_2R_3)_4O]_nSi(R_2R_3)_4R_4$, Where n is 1 or more. Siloxanes of Formula IV have n that is preferably 2 or more, more preferably 3 or more, (e.g., about 4 or more). Siloxanes of formula IV have n that is preferably about 30 or less, more preferably about 12 or less, and most preferably about 7 or less. Preferably the R₄ group is an aryl group or an alkyl group. Preferably the R₂ groups are aryl groups or alkyl groups or mixtures thereof. Preferably the R₃ groups are aryl groups or alkyl groups or mixtures thereof. Preferably the R₄ group is an aryl group or an alkyl group. Preferably R₁, R₂, R₃, R₄, or any combination thereof are not hydrogen. The R₂ groups in a molecule may be the same or different. Preferably the R₂ groups in a molecule are the same. The R₂ groups in a molecule may be the same or different from the R₃ groups. Preferably, the R₂ groups and R₃ groups in a molecule are the same. Preferred siloxanes include siloxanes of Formula IV, wherein R₁, R₂, R₃, R₄, R₅, or any combination thereof is a methyl, ethyl, propyl, or butyl group, or any combination thereof. Exemplary siloxanes that may be used include hexamethyldisiloxane, polydimethylsiloxane, polymethylphenylsiloxane, dodecamethylpentasiloxane, decamethylcyclo-pentasiloxane, decamethyltetrasiloxane, octamethyltrisiloxane, or any combination thereof.

[0166] Incorporated by previous reference from paragraph 38 of Serrano et al., in one aspect of the invention, the siloxane is an alkylsiloxane containing from about 1 to about 12 carbon atoms, such as hexamethyldisiloxane. The siloxane may also be a polymer such as polydialkylsiloxane, Where the alkyl group is a methyl, ethyl, propyl, butyl, or any combination thereof. Suitable polydialkylsiloxanes have a molecular weight from about 100 to about 10,000. Highly preferred siloxanes include hexamethyldisiloxane, polydimethylsiloxane, and combinations thereof. The siloxane may consist essentially of polydimethylsiloxane, hexamethyldisiloxane, or a combination thereof.

[0167] The activated aromatic compound may be any aromatic molecule activated towards a Friedel-Crafts addition reaction, or mixtures thereof. An aromatic molecule activated towards a Friedel-Crafts addition reaction is defined to be any aromatic molecule capable of an addition reaction with mineral acids. Especially aromatic molecules capable of addition reactions with mineral acids either in the application environment (AC system) or during the ASHRAE 97: 2007 "Sealed Glass Tube Method to Test the Chemical Stability of Materials for Use within Refrigerant Systems" thermal stability test. Such molecules or compounds are typically activated by substitution of a hydrogen atoms of the aromatic ring with one of the following groups: NH₂, NHR, NR₂, ADH, AD, NHCOCH₃, NHCOR, 4OCH₃, OR, CH₃, 4C₂H₅, R, or C₆H₅, where R is a hydrocarbon (preferably a hydrocarbon containing from about 1 to about 100 carbon atoms). The activated aromatic molecule may be an alcohol, or an ether, where the oxygen atom (i.e., the oxygen atom of the alcohol or ether group) is bonded directly to an aromatic group. The activated aromatic molecule may be an amine Where the nitrogen atom (i.e., the nitrogen atom of the amine group) is bonded directly to an aromatic group. By way of example, the activated aromatic molecule may have the formula ArXR_n, Where X is O (i.e., oxygen) or N (i.e., nitrogen); n:1 When X:O; n:2 When x:N; Ar is an aromatic group (i.e., group, C₆H₅); R may be H or a carbon containing group; and When n:2, the R groups may be the same or different. For example, R may be H (i.e., hydrogen), Ar, an alkyl group, or any combination thereof, Exemplary activated aromatic molecules that may be employed in a refrigerant composition according to the teachings herein include diphenyl oxide (i.e., diphenyl ether), methyl phenyl ether (e.g., anisole), ethyl phenyl ether, butyl phenyl ether or any combination thereof. One highly preferred aromatic molecule activated to Wards a Friedel-Crafts addition reaction is diphenyl oxide.

[0168] In one embodiment, the acid scavenger is preferably a butyl oxide.

[0169] Incorporated by previous reference from Serrano et al., the acid scavenger (e.g., the activated aromatic compound, the siloxane, or both) may be present in any concentration that results in a relatively low total acid number, a relatively low total halides concentration, a relatively low total organic acid concentration, or any combination thereof. 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 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.

[0170] Additional examples of acid scavengers which may be included in the refrigerant composition and preferably are excluded from the refrigerant composition include those described by Kaneko (U.S. patent application Ser. No. 11/575,256, published as U.S. Patent Publication 2007/0290164, paragraph 42, expressly incorporated herein by reference), such as one or more of: phenyl glycidyl ethers, alkyl glycidyl ethers, alkylene glycol glycidylethers, cyclohexeneoxides, otolenoxides, or epoxy compounds such as epoxidized soybean oil, and those described by Singh et al. (U.S. patent application Ser. No. 11/250,219, published as 20060116310, paragraphs 34-42, expressly incorporated herein by reference).

[0171] Preferred additives include those described in U.S. Pat. Nos. 5,152,926; 4,755,316, which are hereby incorporated by reference. In particular, the preferred extreme pressure additives include mixtures of (A) tolyltriazole or substituted derivatives thereof, (B) an amine (e.g. Jeffamine M-600) and (C) a third component which is (i) an ethoxylated phosphate ester (e.g. Antara LP-700 type), or (ii) a phosphate alcohol (e.g. ZELEC 3337 type), or (iii) a Zinc dialkyldithiophosphate (e.g. Lubrizol 5139, 5604, 5178, or 5186 type), or (iv) a mercaptobenzothiazole, or (v) a 2,5-dimercapto-1,3,4-triazole derivative (e. g. Curvan 826) or a mixture thereof. Additional examples of additives which may be used are given in U.S. Pat. No. 5,976,399 (Schnur, 5:12-6:51, hereby incorporated by reference).

[0172] 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.

[0173] Mouli et al. (WO 2008/027595 and WO 2009/042847) teaches 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.

[0174] Preferred flame suppressants include those described in patent application "Refrigerant compositions containing fluorine substituted olefins CA 2557873 A1" and incorporated by reference along with fluorinated products such as HFC-125 and/or Krytox® lubricants, also incorporated by reference and described in patent application "Refrigerant compositions comprising fluoroolefins and uses thereof WO2009018117A1."

[0175] In one embodiment, any of the difluoropropene compositions of the present invention further comprises a tracer. The tracer may be a single compound or two or more tracer compounds from the same class of compounds or from different classes of compounds. In some embodiments, the tracer is present in the compositions at a total concentration of about 1 part per million by weight (ppm) to about 5000 ppm, based on the weight of the total composition. In other embodiments, the tracer is present at a total concentration of about 10 ppm to about 1000 ppm. In other embodiments, the tracer is present at a total concentration of about 20 ppm to about 500 ppm. In other embodiments, the tracer is present at a total concentration of about 25 ppm to about 500 ppm. 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.

[0176] The tracer may be selected from hydrofluorocarbons (HFCs), deuterated hydrofluorocarbons, chlorofluorocarbons (CFCs), hydrofluorochlorocarbons (HCFCs), chlorocarbons, perfluorocarbons, fluoroethers, brominated compounds, iodated compounds, alcohols, aldehydes and ketones, nitrous oxide and combinations thereof. Alternatively, the tracer may be selected from trifluoromethane (HFC-23), dichlorodifluoromethane (CFC-12), chlorodifluoromethane HCFC-22),

methyl chloride (HCC-40), chlorofluoromethane (HCFC-31), fluoroethane (HFC-161), 1,1,-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a), chloropentafluoroethane (CFC-115), 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114), 1,1-dichloro-1,2,2,2-tetrafluoroethane (CFC-114a), 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,2,2,3,3-heptafluoropropane (HFC-227ea), 1,1,1,3,3-pentafluoropropane (HFC-245fa), 1,1,1,2,2-pentafluoropropane (HFC-245cb), 1,1,1,2,3-pentafluoropropane (HFC-245eb), 1,1,2,2-tetrafluoropropane (HFC-254cb), 1,1,1,2-tetrafluoropropane (HFC-254eb), 1,1,1-trifluoropropane (HFC-263fb), 1,1-difluoro-2-chloroethylene (HCFC-1122), 2-chloro-1,1,2-trifluoroethylene (CFC-1113), 1,1,1,3,3-pentafluorobutane (HFC-365mfc), 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-43-10mee), 1,1,1,2,2,3,4,5,5,6,6,7,7,7-tetradecafluoroheptane, hexafluorobutadiene, 3,3,3-trifluoropropyne, iodotrifluoromethane, deuterated hydrocarbons, deuterated hydrofluorocarbons, perfluorocarbons, fluoroethers, brominated compounds, iodated compounds, alcohols, aldehydes, ketones, nitrous oxide (N₂O) and mixtures thereof. In some embodiments, the tracer is a blend containing two or more hydrofluorocarbons, or one hydrofluorocarbon in combination with one or more perfluorocarbons. In other embodiments, the tracer is a blend of at least one CFC and at least one HCFC, HFC, or PFC.

[0177] The tracer may be added to the difluoropropene compositions of the present invention in predetermined quantities to allow detection of any dilution, contamination or other alteration of the composition. Additionally, the tracers may allow detection of product that infringes existing patent rights, by identification of the patent owner's product versus competitive infringing product. Further, in one embodiment, the tracer compounds may allow detection of a manufacturing process by which a product is produced, thus, allowing detection of infringement of a patent to specific manufacturing process chemistry.

Processes

[0178] All of the difluoropropene-containing compositions disclosed herein, neat or blends, will contain some amount of impurities, such as, but not limited to, moisture

(water), acids, organic compounds (other than HFO-1252zc), inorganic compounds, oils and/or particulates. Such impurities may be a result of, for example, the manufacturing process for making HFO-1252zc, the blending process for making a composition, and/or storage/handling/transport of such compositions. Thus, the present invention provides processes for treating a difluoropropene, particularly HFO-1252zc.

[0179] In some embodiments, the present invention provides processes for drying and/or purifying a difluoropropene, particularly HFO-1252zc. In some embodiments, the process comprises contacting any of the difluoropropene-containing compositions disclosed herein with a desiccant, such as an aluminum containing adsorbent. In some embodiments, the aluminum containing adsorbent is a molecular sieve, and more particularly an aluminosilicate molecular sieve (zeolite).

[0180] In any of the embodiments disclosed herein, the contacting of the composition with the adsorbent may occur in the liquid phase or the vapor phase. Preferably, the contacting is in the liquid phase.

[0181] Examples of the zeolitic aluminosilicates which may be utilized in the processes according to the present invention include, but are not limited to, zeolite Y (including steam stabilized, e.g., ultra-stable Y or dealuminated-Y), zeolite X, zeolite beta, zeolite A, zeolite ZK-20, zeolite ZSM-3, faujasite, LZ-10, AW-500, ZSM-5-type zeolites (e.g., ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48), crystalline silicates such as silicalite, erionite, mordenite, offretite, chabazite, FU-1-type zeolite, NU-type zeolites, LZ-210-type zeolite, and mixtures thereof.

[0182] In some embodiments, the molecular sieve is selected from zeolite 3A, zeolite 4A, zeolite 5A and zeolite 13X.

[0183] In some embodiments, the molecular sieve is zeolite 3A.

[0184] In some embodiments, the molecular sieve is zeolite 13X.

[0185] In some embodiments, the process comprises contacting any of the difluoropropene-containing compositions disclosed herein with a molecular sieve having a pore size of about 3 Å to 10 Å. In some embodiments, the process comprises contacting any of the difluoropropene-containing compositions disclosed herein with a molecular sieve having a pore size of about 3 Å to 5 Å, or about 3 Å, or

greater than 0 to about 3 Å. In some embodiments, the process comprises contacting any of the difluoropropene-containing compositions disclosed herein with a molecular sieve having a pore size of about 5 Å to 10 Å, or about 5 Å to about 9 Å, or about 9 Å to about 10 Å, or about 10 Å.

[0186] In some embodiments, the contacting step may be carried out repeatedly, and preferably as many times as necessary to achieve the desired reduced impurities content, and more preferably the desired reduced water content and/or the desired reduced acidity content.

[0187] In some embodiments, the treatment process comprises drying of the composition and reducing the water content of the composition by about 90% to about 100% relative to the starting water content, preferably about 93% to about 100%, or about 93% to about 98%, or about 94% to about 98%, or about 94% to about 97%, or about 94% to about 96%, or about 95% to about 96%, preferably about 96%.

[0188] In some embodiments, the treatment process comprises drying of the composition and results in the difluoropropene-containing composition having a reduced water content of about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, about 8 ppmw or less, about 6 ppmw or less, about 4 ppmw or less, inclusive of all ranges and values therebetween including a water content level of 0 ppm. In some embodiments, the treatment process results in the difluoropropene-containing composition having a reduced water content of about 4 ppmw.

[0189] In some embodiments, the treatment process comprises purification of the composition and results in reduced content of certain HFCs and HFOs other than HFO-1252zc and in increased purity of the HFO-1252zc. In some embodiments, the water content in the composition may be reduced simultaneously with the reduction in the content of certain HFCs and HFOs other than HFO-1252zc.

[0190] In some embodiments, the treatment process comprises purification of the composition and results in reduced acids content. In some embodiments, the water content in the composition may be reduced and the purity increased simultaneously with the reduction in the acidity content.

[0191] In certain embodiments disclosed herein, the composition comprises, consists essentially of, or consists of at least one of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, preferably HFO-1252zc, and one or more additional compounds selected from HFC-152a, HFO-1243zf, difluorodimethylsilane ($C_2H_6F_2Si$), HF, HCl, E-HFO-1261ze and Z-HFO-1261ze. In one embodiment, contacting of the composition with an aluminum containing adsorbent (e.g., a molecular sieve) reduces the amount of at least one of the additional compounds selected from HFC-152a, HFO-1243zf, difluorodimethylsilane, HF, HCl, E-HFO-1261ze and Z-HFO-1261ze, from the composition. In one embodiment, contacting of the composition with an aluminum containing adsorbent (e.g., a molecular sieve) reduces the amount of at least one of the additional compounds selected from HFC-152a, difluorodimethylsilane, HF, HCl, E-HFO-1261ze and Z-HFO-1261ze, from the composition. In one embodiment, contacting of the composition with an aluminum containing adsorbent (e.g., a molecular sieve) reduces the amount of at least one of the additional compounds selected from HFC-152a, E-HFO-1261ze and Z-HFO-1261ze, from the composition.

[0192] In one embodiment, the treatment process comprises contacting the difluoropropene composition with an aluminum containing adsorbent (e.g., a molecular sieve), preferably an aluminosilicate molecular sieve (zeolite), and reducing a content of HFC-152a in the composition by about 20% to about 90%, or about 30% to about 90%, relative to the starting content of HFC-152a.

[0193] In one embodiment, the treatment process comprises contacting the difluoropropene composition with an aluminum containing adsorbent (e.g., a molecular sieve), preferably an aluminosilicate molecular sieve (zeolite), and reducing a content of HFO-1261ze(E) in the composition by about 1% to about 30%, or about 1.5% to about 30%, or about 2% to about 30%, or about 3% to about 26%, relative to the starting content of HFO-1261ze(E).

[0194] In one embodiment, the treatment process comprises contacting the difluoropropene composition with an aluminum containing adsorbent (e.g., a molecular sieve), preferably an aluminosilicate molecular sieve (zeolite), and reducing a content of HFO-1261ze(Z) in the composition by about 10% to about

45%, or about 20% to about 40%, or about 20% to about 32%, relative to the starting content of HFO-1261ze(Z).

[0195] In some embodiments, the present invention relates to a method of treating a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, to increase the purity of the difluoropropene composition, the method comprising contacting the composition with an aluminum containing adsorbent, wherein the purity of the difluoropropene composition is increased by about 0.03% to about 0.15%, or by about 0.04% to about 0.14%, or by about 0.039% to about 0.137%, or by about 0.05% to about 0.136%, relative to a starting purity of the composition.

[0196] In some embodiments, the treated composition has a purity of about 99% (e.g., about 99 wt.% of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze or HFO-1252zc, preferably HFO-1252zc) or greater, or at least about 99.1%, or at least about 99.2%, or at least about 99.3%, or at least about 99.4%, or at least about 99.5%, or at least about 99.51%, or at least about 99.52%, or at least about 99.53%, or at least about 99.54%, or at least about 99.55%, or at least about 99.56%, or at least about 99.57%, or at least about 99.58%, or at least about 99.59%, or at least about 99.6%, or at least about 99.61%, or at least about 99.62%, or at least about 99.63%, or at least about 99.64%, or at least about 99.65%, or at least about 99.66%, or at least about 99.67%, or at least about 99.68%, or at least about 99.69%, or at least about 99.70%, or at least about 99.71%, or at least about 99.72%, or at least about 99.73%, or at least about 99.74%, or at least about 99.75%, or at least about 99.76%, or at least about 99.77%, or at least about 99.78%, or at least about 99.79%, or at least about 99.80%, or at least about 99.81%, or at least about 99.82%, or at least about 99.83%, or at least about 99.84%, or at least about 99.85%, or at least about 99.86%, or at least about 99.87%, or at least about 99.88%, or at least about 99.89%, or at least about 99.9%.

[0197] In some embodiments, the treatment process may be integrated with a manufacturing process for making HFO-1252zc or a blend comprising HFO-1252zc. In some embodiments, the treatment process may be performed independently and downstream of a manufacturing process for making HFO-1252zc.

[0198] In some embodiments, the treatment process may be integrated with a process for reclaiming HFO-1252zc or a blend comprising HFO-1252zc. In some embodiments, the treatment process may be performed independently and downstream of a process for reclaiming HFO-1252zc or a blend comprising HFO-1252zc. More particularly, the treatment process may be utilized for drying and/or purification of a reclaimed refrigerant comprising HFO-1252zc.

[0199] In some embodiments, the treatment process may be performed on any of the neat compositions disclosed herein which comprise, consist of or consist essentially of a difluoropropene, such as HFO-1252zc, and optionally one or more additional compounds or members such as those listed in Table 1. In some embodiments, one or more lubricants and/or one or more additives, as described herein, may be combined with the neat difluoropropene composition either before the composition is treated (i.e., dried and/or purified) or after the composition has been treated. In some embodiments, the neat refrigerant is a reclaimed refrigerant.

[0200] In some embodiments, the treatment process may be performed on any of the blend compositions disclosed herein which comprise, consist of or consist essentially of a difluoropropene, such as HFO-1252zc; one or more other refrigerant compounds; and optionally one or more additional compounds or members such as those listed in Table 1. In some embodiments, one or more lubricants and/or one or more additives, as described herein, may be combined with the difluoropropene blend composition either before the composition is treated (i.e., dried and/or purified) or after the composition has been treated. In some embodiments, the refrigerant blend is a reclaimed refrigerant.

[0201] In some embodiments, the refrigerant composition is treated (i.e., dried and/or purified) while in a liquid state. In some embodiments, the refrigerant composition is treated (i.e., dried and/or purified) while in a gaseous (vapor) state.

[0202] In one embodiment, the molecular sieves used in the processes of the present invention are preferably aluminosilicate molecular sieves (zeolites). In some embodiments, the treatment process comprises contacting HFO-1252zc with a molecular sieve having a pore size of about 3 Å to 10 Å. In some embodiments, the molecular sieve has openings which have a nominal pore size of about 3 Å to 5 Å, or about 3 Å, or greater than 0 to about 3 Å. In some embodiments, the molecular

sieve has openings which have a nominal pore size of 5 Å to about 10 Å, or 5 Å to about 9 Å, or about 9 Å to about 10 Å, or about 10 Å.

[0203] In a preferred embodiment, the molecular sieve has pores which have openings having a size across their largest dimension of about 3 Å. In a preferred embodiment, the molecular sieve has pores which have openings having a size across their largest dimension of about 10 Å.

[0204] The inventors have surprisingly found that openings having a size across their largest dimension of about 3 Å provide peak drying performance as they are sufficiently large to allow the undesired compounds, such as water, to enter into the interior of the zeolite where they are retained, while also excluding the desired compound, namely HFO-1252zc, from entering the interior of the zeolite. Thus, it has been found that pores of a size of about 3 Å or less are particularly effective for selectively removing moisture from HFO-1252zc.

[0205] The inventors have also surprisingly found that openings having a size across their largest dimension of about 10 Å provide peak impurity removal performance. Without wishing to be bound by theory, it is believed that pores of such sizes are sufficiently large to allow undesired organic compounds, such as HFC-152a and E/Z-HFO-1261ze, to enter into the interior of the zeolite where they are retained, while also excluding the desired compound, namely HFO-1252zc, from entering the interior of the zeolite. Thus, it is believed that pores of a size of about 10 Å are particularly effective for selectively removing undesired organic compounds from the HFO-1252zc composition.

[0206] It has also been found that treatment processes utilizing a molecular sieve according to the present invention may also remove impurities molecules and/or acidic impurities, and more generally impurities such as organic compounds, inorganic compounds, gases, oils, acids, particulates and the like), as such impurities tend to strongly bond to the surface or interior of the molecular sieve cage where they are retained.

[0207] The pore size referred to herein relates to the open end or mouth of the pore through which the water enters the body of the pore, where it may be retained. The openings to the pores may have any shape, but preferably are generally

elliptical or circular. The term “pore size” used herein refers to a size across the largest dimension of the opening of a pore.

[0208] The molecular sieve may contain more than one distribution of pore sizes, so that in addition to the pores of the required dimension (i.e., openings to the pores having a size across their largest dimension of about 3 Å to 10 Å), the molecular sieve may also contain pores which are either larger or smaller. Preferably, pores having openings of a size which is larger or smaller than the desired pore size (e.g., 3 Å to 10 Å) constitute a minority of the pores (i.e., less than 50%, less than 40%, less than 30%, less than 20%, less than 10%, less than 5% and all integers and ranges therebetween, inclusive of 0%). In one embodiment, pores having openings of a size which is larger or smaller than about 3 Å constitute a minority of the pores (i.e., less than 50%, less than 40%, less than 30%, less than 20%, less than 10%, less than 5% and all integers and ranges therebetween, inclusive of 0%), since pores of a size of about 3 Å are believed to be most effective at selectively removing moisture from HFO-1252zc. In another embodiment, pores having openings of a size which is larger or smaller than about 10 Å constitute a minority of the pores (i.e., less than 50%, less than 40%, less than 30%, less than 20%, less than 10%, less than 5% and all integers and ranges therebetween, inclusive of 0%), since pores of a size of about 10 Å are believed to be most effective at selectively removing impurities, particularly organic impurities, from HFO-1252zc compositions.

[0209] In one embodiment, particularly when used in the manufacture of difluoropropenes or for preparing a reclaimed difluoropropene composition, particularly a composition comprising HFO-1252zc, the molecular sieve is preferably arranged as a bed or layer in an adsorption column and the product stream containing the difluoropropene, particularly HFO-1252zc, is conveyed over or through the adsorbent bed. The molecular sieve adsorbent bed may be a moving bed or may be a fixed bed. In another embodiment, the molecular sieve may be in the form of a solid, porous core comprising a zeolite of the present invention, a binder and any auxiliary desiccants or adsorbents such as silica gel, calcium sulfate, alumina or activated carbon. In use, the core is contained within a cartridge and the circulating refrigeration fluid is caused to pass through the cartridge and the method comprises passing the difluoropropene composition, either in a liquid or vapor state, through the cartridge in contact with the core (i.e., the molecular sieve).

[0210] In some embodiments, the molecular sieve has a surface area in the range of from about 600 to about 1000 m²/g.

[0211] In some embodiments, the molecular sieve is pre-treated prior to use. In some embodiments, pre-treatment comprises heating the molecular sieve in a dry gas stream, such as dry air or dry nitrogen, preferably dry nitrogen. In some embodiments, temperatures for the pre-treatment are in the range of from about 100°C to about 350°C, or about 150°C to about 350°C, or about 320°C, or about 100°C to about 250°C, or about 175°C to about 315°C, or about 200°C to about 250°C, or about 200°C, or about 220°C.

[0212] In some embodiments, the pre-treatment comprises flowing dry nitrogen across the molecular sieve at a first temperature of about 100°C to about 200°C, preferably about 150°C, for a defined period of time; then increasing the temperature to a second temperature of about 200°C to about 250°C, preferably about 220°C, for a defined period of time; and then decreasing the temperature back to the first temperature for a defined period of time under a dry nitrogen flow.

[0213] In some embodiments, in a difluoropropene manufacturing and/or reclaim process, the difluoropropene product stream exiting the reactor or the reclaimed difluoropropene may be pre-treated, such as by distillation, in order to reduce the overall level of impurities such as organics, inorganics, gases, oil and solid particles, before it is subjected to the treatment process of the present invention by which the difluoropropene is dried and/or further purified.

[0214] In some embodiments, the treatment process comprises recirculating the difluoropropene composition several times through the same molecular sieve in order to achieve the desired low level of water and/or to achieve the desired reduced impurities content.

[0215] In some embodiments, the treatment process comprises mixing or contacting the difluoropropene composition with the molecular sieve for a predetermined duration, optionally with incremental agitation, to achieve the desired purity, the desired low level of water and/or the desired reduced acidity content.

[0216] The process of the invention may be operated in a batch or continuous manner.

[0217] When the difluoropropene composition is in the liquid state, the present process of which the difluoropropene composition is in contact with the molecular sieve is preferably operated at a temperature in the range of about -40°C to about 55°C, or about -40°C to about 50°C, or about 5°C to about 55°C, or about -30°C to about 40°C, or about 15°C to about 45°C, or about 21°C, including all integers and ranges therebetween.

[0218] When the difluoropropene composition is in the gaseous state, the present process of which the difluoropropene composition is in contact with the molecular sieve is preferably operated at a temperature in the range of about -20°C to about 95°C, or about -20°C to about 60°C, or about 5°C to about 95°C, or about -10°C to about 80°C, or about -10°C to about 45°C, or about 15°C to about 80°C, or about 21°C, including all integers and ranges therebetween.

[0219] When the difluoropropene composition is in the liquid state, the preferred operating pressures (absolute pressure) for contact of the difluoropropene composition with the molecular sieve are in the range of from about 2.6 to about 14 bara, more preferably in the range of from about 4 to about 10 bara and particularly in the range of from about 4.5 to about 8 bara.

[0220] When the difluoropropene composition is in the gaseous state, the preferred operating pressures for contact of the difluoropropene composition with the molecular sieve are in the range of from about 1 to about 15 bar, more preferably in the range of from about 1.1 to about 14 bar and particularly in the range of from about 1.5 to about 10 bar.

[0221] When the difluoropropene composition is in the liquid, the preferred feed rate to the molecular sieve is such that the residence time in the bed, calculated based on the empty bed volume, is between 0.5 minutes and 24 hours. In one embodiment, the residence time is between 0.5 and 60 minutes, more preferably in the range of about 1 to about 45 minutes, and particularly in the range of about 2 to about 30 minutes.

[0222] When the difluoropropene composition is in the vapor state, the preferred feed rate to the molecular sieve is such that the residence time in the bed, calculated based on the empty bed volume, is between 1 second and 15 minutes, more

preferably in the range of about 1 second to about 10 minutes, and particularly in the range of about 1 second to about 5 minutes.

[0223] In some embodiments, when the difluoropropene composition is in the liquid state, the contact time between the difluoropropene composition and the molecular sieve is in the range of from about 5 seconds to about 48 hours, about 5 seconds to about 1 minute, about 1 minute to about 48 hours, or about 5 minutes to about 24 hours.

[0224] Generally, where the process is carried out as a continuous treatment, the contact time is preferably shorter than if the process is carried out as a batch treatment.

[0225] In some embodiments, the cartridge or column containing the molecular sieve may be agitated or shaken while in contact with the difluoropropene composition.

[0226] During operation of the present process, the adsorption capability of the molecular sieve is gradually consumed as the pores become occupied with water and/or impurities, such that the sieve must be regenerated. Regeneration may be performed using a stream of water vapor, air and water vapor, air, and/or by heating the used sieve in a dry gas stream, such as dry air or dry nitrogen, preferably dry nitrogen.

[0227] In some embodiments, the regeneration process first comprises stopping the flow into the sieve bed and then venting the bulk of the difluoropropene to less than about 1.5 bara, optionally to less than 1 bara.

[0228] In some embodiments, particularly for 3A sieves, after the venting of the difluoropropene, the regeneration process further comprises flowing dry nitrogen across the molecular sieve at a first temperature of about 10°C to about 40°C, preferably about 21°C, for a defined period of time; then increasing the temperature to a second temperature of about 100°C to about 350°C, or about 150°C to about 350°C, or about 100°C to about 250°C, or about 175°C to about 315°C, or about 200°C to about 250°C, or about 200°C, or about 220°C, for a defined period of time or until the dewpoint of the nitrogen effluent indicates the water has been removed, such as a dew point of <-20°C; and then decreasing the temperature back to the first

temperature for a defined period of time under a dry nitrogen flow or under vacuum. It will be understood by those skilled in the art that the defined periods of time will be based upon factors such as the scale of operation, and thus may vary accordingly.

[0229] In some embodiments, particularly for sieves having pore sizes greater than 3 Å, the regeneration process further comprises, after the venting of the difluoropropene, flowing a stream of water vapor, water vapor in nitrogen (i.e., wet nitrogen), or water vapor in air (i.e., wet air), preferably wet nitrogen or wet air, across the molecular sieve at a first temperature of about 10°C to about 40°C, preferably about 21°C, for a defined period of time; then increasing the temperature to a second temperature of about 100°C to about 350°C, or about 150°C to about 350°C, or about 100°C to about 250°C, or about 175°C to about 315°C, or about 200°C to about 250°C, or about 200°C, or about 220°C, for a defined period of time, then switching the flow to dry nitrogen for an additional defined period of time or until the dewpoint of the nitrogen effluent indicates the water has been removed, such as a dew point of <-20°C; and then decreasing the temperature back to the first temperature for a defined period of time under a dry nitrogen flow. The initial flow of water vapor, water vapor in nitrogen, or air across the molecular sieve bonds strongly with organic impurities retained in the sieve and thus enhances removal of such organics and reduces tar formation for regeneration of the sieve. It will be understood by those skilled in the art that the defined periods of time will be based upon factors such as the scale of operation, and thus may vary accordingly.

[0230] In some embodiments, the amount of water adsorbed on the sieve before regeneration is needed is about 2% to about 20% of the weight of the sieve, preferably about 5% to about 18%, and most preferably about 7% to about 16%.

[0231] After being treated (and more particularly, purified and/or dried) according to processes of the present invention, the refrigerant compositions may have a variety of utilities such as heat transfer mediums (e.g., heat transfer fluids and refrigerants for use in refrigeration systems, refrigerators, air conditioning systems, heat pumps, chillers, and the like), among others. The compositions are particularly suited for use in mobile or stationary air conditioning systems and heat pump systems and as a component for making a refrigerant blend for use in mobile or stationary heat transfer systems and heat pump systems.

[0232] A heat transfer medium (also referred to herein as a heat transfer fluid, a heat transfer composition or a heat transfer fluid composition) is a working fluid used to carry heat from a heat source to a heat sink.

[0233] In some embodiments of the invention, there is provided a method of manufacturing a composition comprising a difluoropropene, such as HFO-1252zc, wherein the method comprises treating at least the difluoropropene component by contact with a molecular sieve.

[0234] In some embodiments of the invention, there is provided a method of providing cooling using a heat transfer fluid comprising a difluoropropene, such as HFO-1252zc, wherein the composition or at least the difluoropropene component has been treated by contact with a molecular sieve. In some embodiments, the molecular sieve has a pore size of about 3 Å to 10 Å. In some embodiments, the molecular sieve has a pore size of about 3 Å to 5 Å, or about 3 Å, or greater than 0 and less than about 3 Å. In some embodiments, the molecular sieve has a pore size of about 5 Å to 10 Å, or about 5 Å to 9 Å, or about 9 Å to 10 Å, or about 10 Å.

[0235] In some embodiments of the invention, there is provided a method of providing heating using a heat transfer fluid comprising a difluoropropene, such as HFO-1252zc, wherein the composition or at least the difluoropropene component has been treated by contact with a molecular sieve. In some embodiments, the molecular sieve has a pore size of about 3 Å to 10 Å. In some embodiments, the molecular sieve has a pore size of about 3 Å to 5 Å, or about 3 Å, or greater than 0 to about 3 Å. In some embodiments, the molecular sieve has a pore size of about 5 Å to 10 Å, or about 5 Å to 9 Å, or about 9 Å to 10 Å, or about 10 Å.

[0236] In some embodiments of the invention, there is provided a heat transfer device comprising a heat transfer fluid comprising a difluoropropene, such as HFO-1252zc, and a desiccant comprising a molecular sieve. In some embodiments, the molecular sieve has a pore size of about 3 Å to 10 Å. In some embodiments, the molecular sieve has a pore size of about 3 Å to 5 Å, or about 3 Å, or greater than 0 and less than about 3 Å. In some embodiments, the molecular sieve has a pore size of about 5 Å to 10 Å, or about 5 Å to 9 Å, or about 9 Å to 10 Å, or about 10 Å.

[0237] The difluoropropene refrigerant compositions of the present invention may be prepared by any convenient method to combine the desired amount of the individual components. A preferred method is to weigh the desired component amounts and thereafter combine the components in an appropriate vessel. Agitation may be used, if desired.

[0238] In some embodiments, the compositions containing difluoropropene which are to be treated according to processes of the present invention are reclaimed refrigerant compositions. Refrigerant reclaim constitutes removing oil, water, acidity, particulates, residues and other impurities which can negatively impact refrigerant quality and hence performance. Reclamation involves reprocessing the used (or recovered) refrigerant such that reprocessed refrigerants meet AHRI 700 quality specifications. Refrigerant quality is verified by analytical techniques such as GC-FID, GC-TCD, GC-MS, FTIR, Goetz Bulb, Karl Fischer, Byk-Garner Color and various other analytical methods.

[0239] In some embodiments of the invention, there is provided a method of reclaiming a composition comprising a difluoropropene, such as HFO-1252zc, wherein the method comprises treating at least the difluoropropene component of a used (or recovered) refrigerant by contact with a molecular sieve. In some embodiments, the molecular sieve has a pore size of about 3 Å to 10 Å. In some embodiments, the molecular sieve has a pore size of about 3 Å to 5 Å, or about 3 Å, or greater than 0 and less than about 3 Å. In some embodiments, the molecular sieve has a pore size of about 5 Å to 10 Å, or about 5 Å to 9 Å, or about 9 Å to 10 Å, or about 10 Å.

[0240] Another embodiment of the invention relates to an air-conditioning or refrigeration apparatus comprising the any of the refrigerant (neat or blend) compositions containing a difluoropropene, as described herein, wherein the composition has been subjected to a treatment process according to the present invention.

[0241] Another embodiment of the invention relates to storing any of the refrigerant compositions described herein in gaseous and/or liquid phases within a sealed container, wherein the composition has been treated according to the processes described herein and wherein the oxygen concentration in the gas and/or

liquid phases ranges from less than about 0.4 vol%, less than about 0.315 vol%, and in some cases less than about 0.3 vol%, about 0.0003 vol% to less than about 0.3 vol%, 0.0003 vol% to less than about 0.3 vol%, about 0.0005 vol% to less than about 0.1 vol% and in some cases about 0.0005 vol% to less than about 0.05 vol%, at a temperature of about 25°C, inclusive of all values and ranges therebetween and inclusive of non-detectable or zero amounts.

[0242] Another embodiment of the invention relates to storing any of the foregoing refrigerant compositions in gaseous and/or liquid phases within a sealed container, wherein the composition has been treated according to the processes described herein and wherein the non-absorbable gas (NAG) concentration in the gas and/or liquid phases ranges from less than about 3 vol%, less than about 2 vol%, less than about 1.5 vol%, and in some cases less than about 1 vol%, about 0.005 vol% to less than about 0.2 vol%, 0.01 vol% to less than about 1.5 vol%, at a temperature of about 25°C, inclusive of all values and ranges therebetween and inclusive of non-detectable or zero amounts.

[0243] Another embodiment of the invention relates to storing any of the foregoing refrigerant compositions in gaseous and/or liquid phases within a sealed container, wherein the composition has been treated according to the processes described herein and wherein the acidity (e.g., total acid number) of the composition in the gas and/or liquid phases ranges from less than about 20, less than about 10, less than about 15, less than about 3 ppm, preferably less than about 2 ppm, more preferably less than about 1 ppm, at a temperature of about 25°C, inclusive of all values and ranges therebetween and inclusive of non-detectable or zero amounts.

[0244] Another embodiment of the invention relates to storing any of the foregoing refrigerant compositions in gaseous and/or liquid phases within a sealed container, wherein the composition has been treated, and more particularly dried, according to the processes described herein and wherein the water content in the gas and/or liquid phases ranges from about 10 ppmw or less, about 8 ppmw or less, about 6 ppmw or less, about 4 ppmw or less, at a temperature of about 25°C, inclusive of all values and ranges therebetween and inclusive of non-detectable or zero amounts.

[0245] The container for storing any of the difluoropropene refrigerant compositions described herein can be constructed of any suitable material and

design that is capable of sealing the stabilized difluoropropene refrigerant compositions therein while maintaining gaseous and liquids phases. Examples of suitable containers comprise pressure resistant containers such as a tank, a filling cylinder, and a secondary filling cylinder. The container can be constructed from any suitable material such as carbon steel, manganese steel, chromium-molybdenum steel, among other low-alloy steels, stainless steel and in some case an aluminum alloy. The container can include a pierce top or valves suitable for dispensing flammable substances.

EXAMPLES

Example 1

[0246] Cylinders are loaded with 5g of different A series molecular sieves – 3A, 4A, and 5A. The sieves in each cylinder are pre-treated by flowing dry (<10 ppmw water) nitrogen at 21°C. After 30 minutes, the temperature is ramped up to 220°C over a period of 5 hours, and the cylinder is held for another 10 hours at this temperature. The dew point of the nitrogen leaving each cylinder is measured and found to be <40°C indicating that no more water is being removed from the sieves. The temperature is then decreased to 21°C over 5 hrs under a dry nitrogen flow. The nitrogen flow is then stopped and each cylinder is evacuated to a pressure of <1 psia.

[0247] At this point, a 100 g sample of HFO-1234yf containing 100 ppmw of water is added to a cylinder loaded with the activated 3A molecular sieve, a 100 g sample of HFO-1234yf containing 100 ppmw of water is added to a cylinder loaded with the activated 4A molecular sieve, and a 100 g sample of HFO-1234yf containing 100 ppmw of water is added to a cylinder loaded with the activated 5A molecular sieve. Also, at this point, a 100 g sample of HFO-1252zc containing 100 ppmw of water is added to a cylinder loaded with the activated 3A molecular sieve, a 100 g sample of HFO-1252zc containing 100 ppmw of water is added to a cylinder loaded with the activated 4A molecular sieve, and a 100 g sample of HFO-1252zc containing 100 ppmw of water is added to a cylinder loaded with the activated 5A molecular sieve. Each of the samples of HFO-1234yf and sample of HFO-1252zc is in a liquid state.

[0248] Each cylinder is shaken for 10 minutes and then allowed to sit for 48 hours at 21°C. A sample of liquid from each cylinder is taken after 48 hours and analyzed for water by Karl Fischer method. These results are in Table 2 as the First Exposure.

[0249] Then, the refrigerant is vented from the cylinders and another dry (<10 ppmw water) nitrogen purge flow is started through each cylinder at 21°C to remove bulk organics. After 30 minutes, the temperature is ramped up to 220°C over a period of 5 hours, and each cylinder is held for another 10 hours at this temperature to drive water and any adsorbed organics out of the sieves. The dew point of the nitrogen leaving each cylinder is measured and found to be <40°C, indicating that no more water is being removed from the sieves. The temperature is then decreased to 21°C over a duration of 5 hours under a dry nitrogen flow. The nitrogen flow is then stopped and each cylinder is evacuated to a pressure of <1 psia.

[0250] Finally, each respectively cylinder is again charged with 100 g of liquid HFO-1234yf and 100 g of liquid HFO-1252zc containing 100 ppmw of water. Each cylinder is shaken for 10 minutes and then allowed to sit for 48 hours at 21°C. A sample of liquid from each cylinder is taken after 48 hours and analyzed for water by Karl Fischer method. These results are in Table 2 as the Second Exposure.

Table 2

	First Exposure			Second Exposure		
Refrigerant	3A Sieve	4A Sieve	5A Sieve	3A Sieve	4A Sieve	5A Sieve
HFO-1234yf	4 ppmw	4 ppmw	15 ppmw	4 ppmw	4 ppmw	25 ppmw
HFO-1252zc	4 ppmw	15 ppmw	15 ppmw	4 ppmw	25 ppmw	30 ppmw

Example 2

[0251] A series of sieve beds are pre-treated as described above. Then 1252zc vapor containing 100 ppmw of water is fed to each bed at 30 deg C and 50 psig such that the residence time in the bed is 1 minute. The water in the effluent from each bed is monitored and the time to breakthrough is measured, where breakthrough is defined as >12 ppmw. The results for 3A, 4A, and 5A sieves is shown in Table 3.

[0252] Then, the sieve beds are regenerated by the procedure described above and the vapor flow experiment is repeated. The results from the second use are also shown in Table 3.

[0253] The first exposure, regeneration, and second exposure are then repeated for 1234yf vapor containing 100 ppmw water. The results for 1234yf are shown in Table 3.

Table 3

Refrigerant	First Exposure			Second Exposure		
	3A Sieve	4A Sieve	5A Sieve	3A Sieve	4A Sieve	5A Sieve
HFO-1234yf	48 hrs	48 hrs	35 hrs	48 hrs	48 hrs	25 hrs
HFO-1252zc	48 hrs	40 hrs	35 hrs	48 hrs	30 hrs	25 hrs

Example 3

[0254] A series of sieve beds is pre-treated as described in Example 1. At this point, a 100 g sample of HFO-1234yf containing 100 ppmw of HCO-1140 (VCM) (typical organic impurity), 100 ppmw of HCl (typical acidic impurity), and 100 ppm of FeCl3 (typical inorganic impurity from corrosion) is added to cylinders loaded with the activated 3A, 4A, and 5A molecular sieves. Also, at this point, a 100 g sample of HFO-1252zc containing 100 ppmw of HCO-1140 (VCM) (typical organic impurity), 100 ppmw of HCl (typical acidic impurity), and 100 ppm of FeCl3 (typical inorganic impurity from corrosion) is added to additional cylinders loaded with the activated 3A, 4A, and 5A molecular sieves. Each of the samples of HFO-1234yf and samples of HFO-1252zc are in a liquid state. Each of the samples may represent a new refrigerant or a reclaimed (used) refrigerant.

[0255] Each cylinder is shaken for 10 minutes and then allowed to sit for 48 hours at 21°C. A sample of liquid from each cylinder is taken after 48 hours and analyzed for VCM, HCl, and FeCl3. These results are in Table 4.

Table 4

Refrigerant	VCM			HCl			FeCl3		
	3A Sieve	4A Sieve	5A Sieve	3A Sieve	4A Sieve	5A Sieve	3A Sieve	4A Sieve	5A Sieve
HFO-1234yf	40 ppmw	40 ppmw	50 ppmw	40 ppmw	40 ppmw	50 ppmw	40 ppmw	40 ppmw	50 ppmw
HFO-1252zc	40 ppmw	50 ppmw	50 ppmw	40 ppmw	50 ppmw	50 ppmw	40 ppmw	50 ppmw	50 ppmw

Example 4

[0256] A series of sieve beds is again pre-treated as described in Example 1. At this point, a 100 g sample of HFO-1234yf containing 100 ppmw of CO₂ (typical gaseous impurity), 100 ppmw of particulates measured by a non-volatile residue (NVR) analysis, and 100 ppm of Castrol™ 100 oil (typical oil impurity) is added to cylinders loaded with the activated 3A, 4A, and 5A molecular sieves. Also, at this point, a 100 g sample of HFO-1252zc containing 100 ppmw of CO₂ (typical gaseous impurity), 100 ppmw of particulates measured by a non-volatile residue (NVR) analysis, and 100 ppm of Castrol™ 100 oil (typical oil impurity) is added to additional cylinders loaded with the activated 3A, 4A, and 5A molecular sieves. Each of the samples of HFO-1234yf and samples of HFO-1252zc are in a liquid state. Each of the samples may represent a new refrigerant or a reclaimed (used) refrigerant.

[0257] Each cylinder is shaken for 10 minutes and then allowed to sit for 48 hours at 21°C. A sample of liquid from each cylinder is taken after 48 hours and analyzed for CO₂, non-volatile residue (NVR), and Castrol™ 100 oil. These results are in Table 5.

Table 5

Refrigerant	CO ₂			NVR			Castrol™ 100		
	3A Sieve	4A Sieve	5A Sieve	3A Sieve	4A Sieve	5A Sieve	3A Sieve	4A Sieve	5A Sieve
HFO-1234yf	40 ppmw	40 ppmw	50 ppmw	40 ppmw	40 ppmw	50 ppmw	40 ppmw	40 ppmw	50 ppmw
HFO-1252zc	40 ppmw	50 ppmw	50 ppmw	40 ppmw	50 ppmw	50 ppmw	40 ppmw	50 ppmw	50 ppmw

[0258] The results indicate that 3A sieves show superior performance for treating of HFO-1252zc compared to 4A and 5A sieves.

[0259] Without intending to be bound by this theory, it is believed that the smaller molecular diameter of HFO-1252zc allows it to enter to pores of the 4A and 5A sieves which, in turn, reduces the water removal capacity during the First Exposure. It also reduces the capacity to remove organic impurities, acids, inorganic impurities, gaseous impurities, particulates, and oils. HFO-1234yf, on the other hand, due to its larger molecular size is not able to enter the pores of 4A sieves, such that both 3A

and 4A are suitable for use with the larger molecule. Further, since HFO-1252zc can enter the pores of the 4A sieves, quantities of HFO-1252zc become adsorbed in the pores of the molecular sieve, which can degrade and form tars which permanently reduce the water removal capacity. As a result, the performance of the 4A sieves is worse during the second exposure than the first.

[0260] This same behavior and benefit from using 3A molecular sieves is expected when treating blends containing HFO-1252zc, such as any of the blends disclosed herein.

Example 5: Purification of 1252zc by adsorption of mol sieve 4A

[0261] A 4A mol sieve was preactivated by heating at 320°C for 16 hours under a 100 sccm N2 purge before use. The 1.0 g preactivated mol sieve was mixed with 10.9 g HFO-1252zc in a pre-dried 75 ml cylinder. The mixture was shaken well and then allowed to sit at room temperature. The liquid phase of the mixture was analyzed by GC-MS-FID at intervals of 2 hours and 24 hours. The GC analysis of the results is provided in Table 6.

Table 6

Compound	FID area%		
	Starting material	2hrs	24 hrs
152a	0.0024%	0.0020%	0.0019%
1243zf	0.0069%	0.0069%	0.0071%
1252zc	99.5394%	99.5692%	99.5891%
difluorodimethylsilane	0.0156%	0.0119%	0.0017%
E-1261ze	0.3389%	0.3337%	0.3333%
Z-1261ze	0.0756%	0.0655%	0.0601%
others	0.0212%	0.0108%	0.0069%

[0262] The results show reduced contents of E-HFO-1261ze, Z-HFO-1261ze, difluorodimethylsilane and HFC-152a after contact with 4A mol sieve for 24 hours. Also, the purity of the HFO-1252zc was improved from 99.5394% to 99.5891% after contact with the 4A mol sieve for 24 hours.

Example 6: Purification of 1252zc by adsorption of mol sieve 5A

[0263] A 5A mol sieve was preactivated by heating at 320°C for 16 hours under a 100 sccm N₂ purge before use. The 1.0 g preactivated mol sieve was mixed with 10.13 g HFO-1252zc in a pre-dried 75 ml cylinder. The mixture was shaken well and then allowed to sit at room temperature. The liquid phase of the mixture was analyzed by GC-MS-FID at intervals of 2 hours and 24 hours. The GC analysis of the results is provided in Table 7.

Table 7

Compound	FID area%		
	Starting material	2hrs	24 hrs
152a	0.0024%	0.0019%	0.0017%
1243zf	0.0069%	0.0072%	0.0074%
1252zc	99.5394%	99.5827%	99.5783%
difluorodimethylsilane	0.0156%	0.0178%	0.0196%
E-1261ze	0.3389%	0.3244%	0.3295%
Z-1261ze	0.0756%	0.0471%	0.0450%
others	0.0212%	0.0188%	0.0184%

[0264] The results show reduced contents of E-HFO-1261ze, Z-HFO-1261ze and HFC-152a after contact with 5A mol sieve for 24 hours. Also, the purity of the HFO-1252zc was improved from 99.5394% to 99.5783% after contact with the 5A mol sieve for 24 hours. The results show that the mol sieve 5A is more efficient at removing HFO-152a, E-HFO-1261ze and Z-HFO-1261ze than the mol sieve 4A.

Example 7: Purification of 1252zc by adsorption of mol sieve 13X

[0265] A mol sieve 13X was preactivated by heating at 320°C for 16 hours under a 100 sccm N₂ purge before use. The 1.02 g preactivated mol sieve was mixed with 10.00 g HFO-1252zc in a pre-dried 75ml cylinder. The mixture was shaken well and then allowed to sit at room temperature. The liquid phase of the mixture was analyzed by GC-MS-FID at intervals of 2 hours and 24 hours. The GC analysis of the results is provided in Table 8.

Table 8

Compound	FID area%		
	Starting material	2hrs	24 hrs
152a	0.0024%	0.0005%	0.0003%
1243zf	0.0069%	0.0076%	0.0109%
1252zc	99.5394%	99.6777%	99.6758%
difluorodimethylsilane	0.0156%	0.0000%	0.0000%
E-1261ze	0.3389%	0.2506%	0.2508%
Z-1261ze	0.0756%	0.0538%	0.0518%
others	0.0212%	0.0099%	0.0105%

[0266] The results show reductions in the contents of E-HFO-1261ze, Z-HFO-1261ze, difluorodimethylsilane and HFC-152a after contact with 13X mol sieve for 24 hours. Also, the purity of the HFO-1252zc was improved from 99.5394% to 99.6758% after contact with the 13X mol sieve for 24 hours. The results show that the mol sieve 13X is more efficient at removing E-HFO-1261ze, difluorodimethylsilane and HFC-152a than the mol sieve 4A and mol sieve 5A.

Example 8: Purification of 1252zc by adsorption of mol sieve 3A

[0267] 100 grams of HFO-1252zc was mixed with 10 grams of preactivated 3A mol sieve. The mixture was stored in a closed vessel at room temperature for 10 weeks. The GC analysis showed the purity of the HFO-1252zc increased from 99.77% to 99.81% during this storage time.

Example 9: Purification of 1252zc by adsorption of mol sieve 3A

[0268] The acidity content of a 250 g sample of HFO-1252zc was measured (starting material). A 450mL carbon steel cylinder was dried at 110°C for >10 hours. The cylinder was then loaded with approximately 40 g 3Å molecular sieves, and a valve fitted with a mesh screen was installed. The 3Å molecular sieves loaded in the cylinder were dried in a tube furnace at 320°C in N₂ purge of 100 sccm for 16 hours. The cylinder was pulled under high vacuum around 150 microns and then chilled with dry ice to transfer the 250 g of HFO-1252zc into the cylinder. The mixture in the cylinder was occasionally shaken and kept at room temperature for 72 hours.

[0269] Then, the acidity of the mixture was analyzed and compared with the acidity measurement of the HFO-1252zc taken before storage. The acidity analysis

was performed by flowing HFO-1252zc from the liquid side of each cylinder into DI water to scrubbing the acid into aqueous, and then the aqueous sample was titrated for acidity and IC for fluoride. The results of the acidity analysis are listed in Table 9 below. The acidity determined by titration is reported as equivalent of HCl.

Table 9

Sample	Condition	Fluoride (ug/g)	Acidity (Equiv. HCl ppm)
1252zc-1	Starting material	37	224.2
1252zc-2	After treatment by 3A mol sieve	0.65	4.6

[0270] The water scrubbing sample of the starting HFO-1252zc was also further analyzed by IC-MS to determine the type of acids present in the starting HFO-1252zc. It was found that HF, acetic acid, formic acid, HCl, nitric acid, sulfuric acid and trifluoro acetic were present. Both the total acidity and fluoride content were reduced significantly after treatment by mol sieve 3A as compared with no mol sieve treatment.

[0271] While the invention has been described with reference to one or more embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims. In addition, all numerical values identified in the detailed description shall be interpreted as though the precise and approximate values are both expressly identified.

CLAIMS

What is claimed is:

1. A method of treating a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting the composition with an aluminum containing adsorbent to remove impurities from the difluoropropene.
2. The method of claim 1, wherein the impurities are one or more impurities selected from the group consisting of water, organic compounds, inorganic compounds, acids, gases, particulates and oils.
3. The method of claim 2, wherein the organic compounds are selected from the group consisting of HFC-152a, HFO-1261ze(E), HFO-1261ze(Z), difluorodimethylsilane, HF, HCl, acetic acid, formic acid, nitric acid, sulfuric acid and trifluoro acetic.
4. The method of any of claims 1 to 3, wherein
 - contacting of the composition with the aluminum containing adsorbent reduces a water content of the composition to about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, about 8 ppmw or less, about 6 ppmw or less, about 4 ppmw or less; and/or
 - contacting of the composition with the aluminum containing adsorbent occurs until an organic impurities content of the composition is reduced by about 5% to about 100% relative to a starting content of the organic impurities; and/or
 - contacting of the composition with the aluminum containing adsorbent reduces an acidity content of the composition.
5. A method of treating a composition comprising HFO-1252zc and one or more additional compounds selected from the group consisting of HFC-152a, HFO-1243zf, difluorodimethylsilane, E-HFO-1261ze, Z-HFO-1261ze, HF, HCl, acetic acid, formic acid, nitric acid, sulfuric acid and trifluoro acetic, the method comprising contacting the composition with an aluminum containing adsorbent

and reducing a content of at least one of the additional compounds from the composition.

6. A method of reducing a water content of a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting the composition with an aluminum containing adsorbent, wherein the reduced water content of the composition is about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, about 8 ppmw or less, about 6 ppmw or less, about 4 ppmw or less.
7. A method of reducing an amount of organic impurities in a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting the composition with an aluminum containing adsorbent until an amount of the organic impurities is reduced by about 5% to about 100% relative to a starting amount of the organic impurities.
8. A method of reducing an acidity content of a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting the composition with an aluminum containing adsorbent.
9. The method of any of claims 1 to 8, wherein the aluminum containing adsorbent is selected from the group consisting of zeolite Y, zeolite X, zeolite beta, zeolite A, zeolite ZK-20, zeolite ZSM-3, faujasite, LZ-10, AW-500, ZSM-5-type zeolites, crystalline silicates such as silicalite, erionite, mordenite, offretite, chabazite, FU-1-type zeolite, NU-type zeolites and LZ-210-type zeolite.
10. The method of any of claims 1 to 9, wherein the aluminum containing adsorbent is a molecular sieve.
11. The method of claim 10,
 - wherein the molecular sieve has openings which have a nominal pore size of about 3 Å to about 10 Å, or
 - wherein the molecular sieve has openings which have a nominal pore size of about 3 Å to about 5 Å, preferably about 3 Å, or

wherein the molecular sieve has openings which have a nominal pore size of about 9 Å to 10 Å, preferably about 10 Å.

12. The method of any of claims 1 to 11, wherein the aluminum containing adsorbent is zeolite 3A or molecular sieve 13X.
13. The method of any of claims 10 to 12, wherein the composition comprises HFO-1252zc and one or more additional compounds selected from the group consisting of HFC-152a, HFO-1243zf, difluorodimethylsilane, E-HFO-1261ze, Z-HFO-1261ze, HF and HCl; and wherein contacting of the composition with the molecular sieve reduces a content of at least one of the additional compounds, preferably reduces a content of at least one of HFC-152a, E-HFO-1261ze and Z-HFO-1261ze.
14. The method according to any of claims 1 to 13, wherein the difluoropropene is HFO-1252zc.
15. The method according to any of claims 1 to 14, wherein the composition comprises at least one other refrigerant component.
16. The method according to any of claims 1 to 15, wherein the composition is in the liquid state.
17. The method according to any of claims 1 to 16, wherein the composition is in the gaseous state.
18. The method according to any of claims 1 to 17, wherein the composition is free of or substantially free of Group A Fluorinated Substances.
19. The method according to any of claims 1 to 18, wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.
20. The method according to any of claims 1 to 19, wherein contacting of the composition with the adsorbent is carried out more than once or for a predetermined duration.
21. The method according to claim 20, wherein the adsorbent is regenerated and reused between one or more contacts.

22. The method according to claim 21, wherein the adsorbent is regenerated by a heated dry nitrogen flow, a water vapor flow, a water vapor in nitrogen flow, an air flow, and/or a heated dry air flow.
23. The method according to any of claims 1 to 22, wherein the water content of the composition is reduced by about 90% to about 100% relative to the starting water content, preferably about 93% to about 100%, or about 93% to about 98%, or about 94% to about 98%, or about 94% to about 97%, or about 94% to about 96%, or about 95% to about 96%, preferably about 96%.
24. The method according to any of claims 1 to 23, wherein the treated composition has a reduced water content of about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, about 8 ppmw or less, about 6 ppmw or less, about 4 ppmw or less.
25. The method according to claim 24, wherein the treated composition has a reduced water content of about 20 ppmw or less.
26. The method according to claim 25, wherein the treated composition has a reduced water content of about 4 ppmw or less.
27. The method of any of claims 1 to 26, wherein a purity of the composition after treatment is at least 99%, preferably at least 99.5%.
28. The method of any of claims 1 to 27, wherein an acidity content of the composition is reduced by about 90% or greater.
29. The method of any of claims 1 to 28, wherein the treated composition has a reduced acid content of about 10 ppm HCl equivalent or less, preferably about 5 ppm HCl equivalent or less.
30. The method according to any of claims 1 to 29, wherein the composition is a reclaimed refrigerant composition.
31. The method according to any of claims 1 to 30, wherein the adsorbent comprises an aluminosilicate.
32. The method according to any of claims 1 to 31, wherein the aluminum containing adsorbent is a molecular sieve having a surface area of from about 600 to about 1000 m²/g.

33. The method according to any of claims 1 to 32, wherein the aluminum containing adsorbent is molecular sieve that is pre-treated by a heated dry nitrogen flow.
34. The method according to any of claims 1 to 33, wherein contacting of the composition with the adsorbent is in the liquid phase or vapor phase, preferably the liquid phase.
35. The method according to any of claims 1 to 34, wherein contacting of the composition in a liquid state with the molecular sieve occurs at a temperature of about -40°C to about 55°C, or about -40°C to about 50°C, or about 5°C to about 55°C, or about -30°C to about 40°C, or about 15°C to about 45°C, or at room temperature.
36. The method according to any of claims 1 to 35, wherein contacting of the composition in a gaseous state with the molecular sieve occurs at a temperature of about -20°C to about 95°C, or about -20°C to about 60°C, or about 5°C to about 95°C, or about -10°C to about 80°C, or about -10°C to about 45°C, or about 15°C to about 80°C, or at room temperature.
37. A method of regenerating a molecular sieve having a nominal pore size of about 3 Å and configured for treating a composition comprising water and a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising:
 - flowing dry nitrogen across the molecular sieve at a first temperature;
 - increasing the temperature to a second temperature of about 150°C to about 350°C; and
 - decreasing the temperature back to the first temperature under a dry nitrogen flow or under vacuum.
38. The method of claim 37, wherein the temperature is maintained at the second temperature until the dewpoint of the nitrogen effluent indicates the water has been removed, such as <-20°C.
39. A method of regenerating a molecular sieve having a nominal pore size of greater than about 3 Å and configured for treating a composition comprising water and a difluoropropene selected from the group consisting of HFO-1252zf,

HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising:

flowing a stream of one of water vapor, wet nitrogen or wet air, across the molecular sieve at a first temperature;

increasing the temperature to a second temperature of about 150°C to about 350°C;

switching to a dry nitrogen flow at the second temperature; and

decreasing the temperature back to the first temperature under a dry nitrogen flow or under vacuum.

40. The method of claim 39, wherein the temperature is maintained at the second temperature under the dry nitrogen flow until the dewpoint of the nitrogen effluent indicates the water has been removed, such as <-20°C.
41. A method of manufacturing a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting a product stream comprising the difluoropropene with an aluminum containing adsorbent to reduce at least one of (i) a water content of the difluoropropene, (ii) an acidity content of the composition, and (iii) an organic impurities content of the composition.
42. A method of reclaiming a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising contacting a stream comprising used difluoropropene with an aluminum containing adsorbent to reduce at least one of (i) a water content of the difluoropropene, (ii) an acidity content of the composition, and (iii) an organic impurities content of the composition.
43. A method of storing a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, the method comprising mixing a composition comprising the difluoropropene with an aluminum containing adsorbent to form a mixture and storing the mixture for a predetermined duration to reduce at least one of (i) a

water content of the difluoropropene, (ii) an acidity content of the composition, and (iii) an organic impurities content of the composition.

44. A container configured to store a composition comprising a difluoropropene selected from the group consisting of HFO-1252zf, HFO-1252yf, HFO-1252ye, HFO-1252ze and HFO-1252zc, wherein the composition has a reduced water content of about 50 ppmw or less, about 40 ppmw or less, about 30 ppmw or less, about 20 ppmw or less, about 10 ppmw or less, or about 8 ppmw or less, or about 6 ppmw or less, preferably about 4 ppmw or less; and/or wherein the difluoropropene has a purity of at least about 99%, preferably at least about 99.55%; and/or wherein the composition has a reduced acids content equivalent to about 10 ppm HCl or less, preferably about 5 ppm HCl or less.
45. The method according to any of claims 37 to 43 or the container according to claim 44, wherein the difluoropropene is HFO-1252zc.
46. The method according to any of claims 37 to 43, wherein the aluminum containing adsorbent is a molecular sieve.
 47. The method of claim 46,
 - wherein the molecular sieve has openings which have a nominal pore size of about 3 Å to about 10 Å, or
 - wherein the molecular sieve has openings which have a nominal pore size of about 3 Å to about 5 Å, preferably about 3 Å, or
 - wherein the molecular sieve has openings which have a nominal pore size of about 9 Å to 10 Å, preferably about 10 Å
48. The method of any of claims 46 to 47, wherein the composition comprises HFO-1252zc and one or more additional compounds selected from the group consisting of HFC-152a, HFO-1243zf, difluorodimethylsilane, E-HFO-1261ze, Z-HFO-1261ze, HF and HCl; and wherein contacting of the composition with the molecular sieve reduces a content of at least one of the additional compounds, preferably reduces a content of at least one of HFC-152a, E-HFO-1261ze and Z-HFO-1261ze.