

TITLE OF THE INVENTION

AZEOTROPES OF HF AND WATER WITH 1252ZC AND
KEY INTERMEDIATES AND SEPARATION PROCESSES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application No. 63/527,178 filed July 17, 2023, and U.S. Provisional Application 63/565,032 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 includes azeotrope and azeotrope-like compositions amongst HFO-1252zc, HFC-263fb, HF, and H₂O which are present in the process making HFO-1252zc, processes of forming and using the azeotrope and azeotrope-like compositions.

BACKGROUND OF THE INVENTION

[0003] Many industries have been working for the past few decades to find replacements for the ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). The CFCs and HCFCs have been employed in a wide range of applications, including their use as aerosol propellants, refrigerants, cleaning agents, expansion agents for thermoplastic and thermoset foams, heat transfer media, gaseous dielectrics, power cycle working fluids, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents, and displacement drying agents. In the search for replacements for these versatile compounds, many industries have turned to the use of hydrofluorocarbons (HFCs).

[0004] Although HFCs do not contribute to the destruction of stratospheric ozone, they contribute to the "greenhouse effect", i.e., global warming. As a result of their contribution to global warming, HFCs have come under scrutiny, and their widespread use may also be limited in the future. In view of the environmental impact of CFCs, HCFCs and certain HFCs possess, fluoroolefin and were developed

and used as in a wide range of applications because they possessed both low GWP (Global Warming Potential) and ODP (Ozone Depleting Potential) properties.

[0005] Recently it has been observed that in certain instances some haloolefins undergo decomposition and can pose an environmental concern. Thus there continues to be a need for new refrigerants and methods for their preparation and use which possess low GWP and zero ODP properties and as well as free of decomposition products which are environmentally persistent.

SUMMARY OF THE INVENTION

[0006] The present invention includes azeotrope and azeotrope-like compositions amongst HFO-1252zc, HFC-263fb, HF, and H₂O which are present in the process for making HFO-1252zc, processes of forming and using the azeotrope and azeotrope-like compositions.

[0007] The instant invention relates to low GWP and zero ODP materials which surprisingly offer improved resistance to environmental decomposition, including but not limited to 1,1-difluoro-1-propene (HFO-1252zc, CF₂=CHCH₃), and which unexpectedly form azeotrope and azeotrope-like compositions which are suitable for use in processes for purifying HFO-1252zc.

[0008] Disclosed herein are azeotrope and azeotrope-like compositions that can be formed from product streams containing HFO-1252zc, various intermediates and by-products, and that are useful in processes for separating hydrogen fluoride (HF) and water from a process stream comprising HFO-1252zc and/or 1,1,1-trifluoropropane (HFC-263fb).

[0009] HFO-1252zc unexpectedly formed azeotrope or azeotrope-like compositions with H₂O. Precursor starting materials for the formation of HFO-1252zc, such as HFC-263fb, unexpectedly formed azeotrope or azeotrope-like compositions with HF and H₂O. As it is well-recognized in the art that it is not possible to predict the formation of azeotropes, the present inventors have discovered during the development of processes for producing HFO-1252zc, from various precursor compounds, such as HFC-263fb, that binary azeotrope or azeotrope-like compositions formed, e.g., HFO-1252zc with water and HFC-263fb with one of water and HF. These azeotrope and/or azeotrope-like compositions, which in some cases

may be heterogeneous, and can be used as part of purification process to recover high purity HFO-1252zf and remove or eliminate HF, H₂O and other intermediates from the HFO-1252zc product stream.

[0010] It was also unexpected that intermediates in the production of HFO-1252zc, such as HF-263fb, formed azeotrope or azeotrope-like compositions with HF and H₂O, e.g., heterogeneous azeotrope or azeotrope-like compositions, which can be used as part of purification process to recover high purity HFO-1252zf.

[0011] The present invention discloses azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFO-1252zc and water.

[0012] One embodiment disclosed herein relates to azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFC-263fb and either HF or H₂O.

[0013] In embodiments disclosed herein, the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFO-1252zc and water contain greater than 0 and less than 90 mole percent water.

[0014] In embodiments disclosed herein, the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFO-1252zc and water contain greater than 0 and less than 90 mole percent water at temperatures from about 55°C to about 90°C, and pressures about 212 to about 458 psia.

[0015] In embodiments disclosed herein the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFO-1252zc and about 0.4 to 90% (on a molar basis) water can be present at temperatures from about 55°C to about 90°C, and pressures about 212 to about 458 psia.

[0016] In embodiments disclosed herein the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFO-1252zc and water contain between 0.4 and 90 mole percent water for the azeotrope pressure range of 212.1 to 458.5 psia over the temperature range of 55°C to 90°C.

[0017] In embodiments disclosed herein the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFC-263fb and H₂O at temperatures from 55°C to 80°C.

[0018] In embodiments disclosed herein the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFC-263fb and about 1% to about 90% (on a molar basis) H₂O at pressures between 132.9 psia and 237.6 psia at temperatures from 55°C to 80°C.

[0019] In embodiments disclosed herein the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFC-263fb and about 30% to about 50% (on a molar basis) HF at pressures between 108.0 psia and 293.1 psia.

[0020] Certain embodiments of the invention disclosed herein relate to processes for preparing an azeotrope-like composition comprising, contacting HFO-1252zc and water at temperatures from 55°C to 90°C and at pressures of 212.1 to 458.5 psia to form HFO-1252zc azeotrope-like compositions.

[0021] Certain embodiments of the invention disclosed herein relate to processes for preparing an azeotrope-like composition comprising, contacting HFC-263fb and HF at temperatures from 40°C to 80°C, at sufficient pressure to form HFC-263fb azeotrope-like compositions.

[0022] Certain embodiments of the invention disclosed herein relate to processes for preparing an azeotrope-like composition comprising HFO-1252zc and water, by subjecting the mixture to separation such that at temperatures from 55°C to 90°C C azeotrope-like compositions between HFO-1252zc and water are formed.

[0023] Certain embodiments of the invention disclosed herein relate to processes of subjecting a product mixture comprising HFO-1252zc to a first distillation step in which a composition enriched in either (i) water or (ii) HFO-1252zc is removed as a first distillate composition with a first bottoms composition being enriched in the other of said components (i) or (ii); and b) subjecting said first distillate composition to a second distillation step conducted at a different pressure in which the component enriched as first bottoms composition in (a) is removed in a second distillate composition with a second bottoms composition enriched in the same component which was enriched in the first distillate composition.

[0024] Further process embodiments of the invention disclosed herein relate to processes for the purification of HFO-1252zc from a mixture comprising HFO-

1252zc, HFC-263fb, and water, comprising a) subjecting said mixture to a first distillation step to form a first distillate comprising azeotrope or near-azeotrope compositions containing HFO-1252zc and water.

[0025] Other features and benefits of any one or more of the embodiments described herein will be apparent from the following detailed description, and from the claims.

[0026] The various embodiments of the invention can be used alone or in combinations with each other. The foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as defined in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] Embodiments are illustrated in the accompanying figures to improve understanding of concepts as presented herein.

[0028] Fig. 1 shows a process embodiment to remove water from the fluorochemical HFO-1252zc using the azeotropes disclosed in this application.

[0029] Fig. 2 show another process embodiment to remove water from the fluorochemical HFC-263fb using the azeotropes disclosed in this application.

[0030] Fig. 3 shows a still further process embodiment to remove HF from the fluorochemical HFC-263fb using the azeotropes disclosed in this application.

[0031] Skilled artisans appreciate that objects in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the objects in the figures may be exaggerated relative to other objects to help to improve understanding of embodiments.

DETAILED DESCRIPTION OF THE INVENTION

[0032] The foregoing summary and the following detailed description and drawings are exemplary and explanatory only and are not restrictive of the invention, as defined in the appended claims. Other features and benefits of any one or more of the embodiments will be apparent from the following detailed description, drawings and from the claims.

[0033] As disclosed herein the inventions relates to HFO-1252zc ($\text{CF}_2=\text{CHCH}_3$, 1,1-difluoro-1-propene) and H_2O azeotrope and near azeotrope compositions, HFC-263fb (1,1,1-trifluoropropane, $\text{CF}_3\text{CH}_2\text{CH}_3$) and HF azeotrope and near azeotrope compositions, HFC-263fb and H_2O azeotrope and near azeotrope compositions, and uses thereof.

[0034] Before addressing details of embodiments described below, some terms are defined or clarified. By "azeotrope" composition is meant a constant boiling liquid admixture of two or more substances that behaves as a single substance. One way to characterize an azeotrope composition is that the vapor produced by partial evaporation or distillation of the liquid has the same composition as the liquid from which it was evaporated or distilled, that is, the admixture distills/refluxes without compositional change. Constant boiling compositions are characterized as azeotropic because they exhibit either a maximum or minimum boiling point, as compared with that of the non-azeotropic mixtures of the same components. Azeotrope compositions are also characterized by a minimum or a maximum in the vapor pressure of the mixture relative to the vapor pressure of the neat components at a constant temperature.

[0035] By "azeotropic" composition is meant a constant boiling liquid admixture of two or more substances that behaves as a single substance. In general, azeotropy is the phenomenon where a composition comprising two or more molecular species such that the relative volatility between any binary pair of components is unity. That is, the composition of a boiling liquid mixture exhibiting azeotropy is identical to the vapor phase that is produced.

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j} = 1 \quad \forall \{i, j\},$$

where: α_{ij} is the relative volatility between component i and component j, K_i is the K factor for component i, K_j is the K factor for component j, y_i and x_i are the vapor and liquid molar fractions of component i, y_j and x_j are the vapor and liquid molar fractions of component j.

[0036] Additionally, the temperature of a boiling mixture exhibiting azeotropy is constant at a constant pressure. A system is azeotropic when it can be distilled (or condensed) without change of composition. The notion of a system that is

“azeotrope-like” or exhibiting “near azeotropy” is commonly known as a system close enough to azeotropy such that the compositions of the liquid and vapor phases in phase equilibrium are of very similar compositions such that during a boiling process the boiling temperature only rises to a small degree. Therefore, all relative volatilities for all i-j binary pairs of the system in equation 1 will be very close to unity. Thus, one way to characterize an azeotropic composition is that the vapor produced by partial evaporation or distillation of the liquid has the same composition as the liquid from which it was evaporated or distilled, that is, the admixture distills/refluxes without compositional change. Constant boiling compositions are characterized as azeotropic because they exhibit either a maximum or minimum boiling point, as compared with that of the non-azeotropic mixtures of the same components. Azeotropic compositions are also characterized by a minimum or a maximum in the vapor pressure of the mixture relative to the vapor pressure of the neat components at a constant temperature.

[0037] By “azeotrope-like” composition (sometimes referred to as “near-azeotrope”) is meant a constant boiling, or substantially constant boiling, liquid admixture of two or more substances that behaves as a single substance. One way to characterize an azeotrope-like composition is that the vapor produced by partial evaporation or distillation of the liquid has substantially the same composition as the liquid from which it was evaporated or distilled, that is, the admixture distills/refluxes without substantial composition change. Another way to characterize an azeotrope-like composition is that the bubble point vapor pressure and the dew point vapor pressure of the composition at a particular temperature are substantially the same, for example within 3 percent, as discussed below. Preferably, the terms “azeotrope-like composition” and “near-azeotrope composition” shall be understood to mean a composition wherein the difference between the bubble point pressure (“BP”) and dew point pressure (“DP”) of the composition at a particular temperature is less than or equal to 5 percent based upon the bubble point pressure, i.e., $[(BP- DP)/BP] \times 100 \leq 5$. As used herein, the terms “3 percent azeotrope-like composition” and “3 percent near-azeotrope composition” shall be understood to mean a composition wherein the difference between the bubble point pressure (“BP”) and dew point pressure (“DP”) of the composition at a particular temperature is less than or equal to 3 percent based upon the bubble point pressure, i.e.,

$[(BP- DP)/BP] \times 100$ is 3. An azeotrope-like composition can also be characterized by the area that is adjacent to the maximum or minimum vapor pressure in a plot of composition vapor pressure at a given temperature as a function of mole fraction of components in the composition.

[0038] For compositions that are azeotropic, there is usually some range of compositions around the azeotrope point that, for a maximum boiling azeotrope, have boiling points at a particular pressure higher than the pure components of the composition at that pressure and have vapor pressures at a particular temperature lower than the pure components of the composition at that temperature, and that, for a minimum boiling azeotrope, have boiling points at a particular pressure lower than the pure components of the composition at that pressure and have vapor pressures at a particular temperature higher than the pure components of the composition at that temperature. Boiling temperatures and vapor pressures above or below that of the pure components are caused by unexpected intermolecular forces between and among the molecules of the compositions, which can be a combination of repulsive and attractive forces such as van der Waals forces and hydrogen bonding.

[0039] It is recognized in the art that both the boiling point and the amount of each component of an azeotrope composition can change when the azeotrope liquid composition is subjected to boiling at different pressures. Thus, an azeotrope composition may be defined in terms of the unique relationship that exists among components or in terms of the exact amounts of each component of the composition characterized by a fixed boiling point at a specific pressure. An azeotrope or azeotrope-like composition of two or more compounds can be characterized by defining compositions characterized by a boiling point at a given pressure, thus providing identifying characteristics without unduly limiting the scope of the invention by a specific numerical composition, which is limited by and is only as accurate as the analytical equipment available.

[0040] It is recognized in this field that when the relative volatility of a system approaches 1.0, the system is defined as forming an azeotrope-like composition. Relative volatility is the ratio of the volatility of a first component to the volatility of a second component. The ratio of the mole fraction of a component in vapor to that in liquid is the volatility of the components. To determine the relative volatility of any

two compounds, a method known as the PTx method can be used. In this procedure, the total absolute pressure in a cell of known volume is measured at a constant temperature for various compositions of the two compounds. Use of the PTx Method is described in detail in "Phase Equilibrium in Process Design", Wiley-Interscience Publisher, 1970, written by Harold R. Null, on pages 124 to 126; hereby incorporated by reference. These measurements can be converted into equilibrium vapor and liquid compositions in the PTx cell by using an activity coefficient equation model, such as the Non-Random, Two-Liquid (NRTL) equation, to represent liquid phase nonidealities. Use of an activity coefficient equation, such as the NRTL equation is described in detail in "The Properties of Gases and Liquids," 4th edition, published by McGraw Hill, written by Reid, Prausnitz and Poling, on pages 241 to 387, and in "Phase Equilibria in Chemical Engineering," published by Butterworth Publishers, 1985, written by Stanley M. Walas, pages 165 to 244. Both aforementioned references are hereby incorporated by reference. Without wishing to be bound by any theory or explanation, it is believed that the NRTL equation, together with the PTx cell data, can sufficiently predict the relative volatilities of the binary components and can therefore predict the behavior of these mixtures in multi-stage separation equipment such as distillation columns. See for example, International Publication No. WO2009105517, the disclosure of which is incorporated herein by reference which rely on PTx data to predict mixtures, e.g., 1243zf with HF, as illustrated below.

[0041] The conditions and compositions for HCFO-1243zf/HF azeotropes determined from PTx data (WO2009105517) are provided in Table 1.

Table 1

Temperature °C	Pressure, psia (kPa)	Mole % HF	Mole % HFC-1243zf
-20	19.9	32.8	67.2
-10	29.6	32.4	67.6
0	42.5	31.2	68.8
10	59.2	30.0	70.0
20	80.4	29.0	71.0
29.8	106.6	28.0	72.0
30	107	28.0	72.0
40	140	27.0	73.0
50	181	26.0	74.0

Temperature °C	Pressure, psia (kPa)	Mole % HF	Mole % HFC-1243zf
60	231	25.1	74.9
70	292	24.4	75.6
79.7	363	23.8	76.2
80	366	23.8	76.2
90	458	23.1	76.9
100	578	21.3	78.7
110	817	17.5	82.5

[0042] As used herein, the term “azeotrope” is meant to refer to azeotrope compositions, azeotrope-like compositions, azeotrope composition and/or near-azeotrope composition.

[0043] The process equipment for all the processes disclosed herein and the associated feed lines, effluent lines and associated units may be constructed of materials resistant to hydrogen fluoride. Typical materials of construction, well-known to the art, include carbon steel, stainless steels, in particular of the austenitic type, and the well-known high nickel alloys such as Monel® nickel-copper alloys, Hastelloy® nickel-based alloys and Inconel® nickel-chromium alloys.

[0044] By azeotropic distillation is meant a process in which a distillation column is operated under conditions to cause one or more azeotrope or azeotrope-like compositions to form, and thereby facilitates the separation of the components of the mixture. Azeotrope distillations may occur where only the components of the mixture to be separated are distilled, or where an entrainer is added that forms an azeotrope with one or more of the components of the initial mixture. Entrainers that act in this manner, which is to say, that form an azeotrope with one or more of the components of the mixture to be separated thus facilitating the separation of those components by distillation, are more commonly called azeotroping agents or azeotrope entrainers.

[0045] In conventional or azeotrope distillations, the overhead or distillate stream exiting the column may be condensed using conventional reflux condensers. At least a portion of this condensed stream can be returned to the top of the column as reflux, and the remainder recovered as product or for optional processing. The ratio of the condensed material which is returned to the top of the column as reflux to the

material removed as distillate is commonly referred to as the reflux ratio. The compounds and entrainer exiting the column as distillate or distillation bottoms stream can then be passed to a stripper or second distillation column for separation by using conventional distillation, or may be separated by other methods, such as decantation. If desired, the entrainer may then be recycled back to the first distillation column for reuse. In some embodiments, the composition and the separation process are free of or essentially free of an added entrainer.

[0046] The specific conditions which can be used for practicing the invention depend upon a number of parameters, such as the diameter of the distillation column, feed points, number of separation stages in the column, among others. In some embodiments, the operating pressure of the distillation system may range from about 5 to 500 psia (34 to 3450 kPa), in another embodiment, about 20 to 400 psia (140 to 2760 kPa). Normally, increasing the reflux ratio results in increased distillate stream purity, but generally the reflux ratio ranges between 1/1 to 200/1. The temperature of the condenser, which is located adjacent to the top of the column, is normally sufficient to substantially fully condense the distillate that is exiting from the top of the column or is that temperature required to achieve the desired reflux ratio by partial condensation.

[0047] As used herein, by “essentially free of” is meant that a composition contains less than about 100 ppm (mole basis), less than about 10 ppm or less than about 1 ppm of the specified component. If a composition is essentially free of more than one component, then the total concentration of those components is less than about 100 ppm, less than about 10 ppm, or less than about 1 ppm.

[0048] Hydrogen fluoride (HF, anhydrous) is a commercially available chemical or can be produced by methods known in the art.

[0049] As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one

of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0050] 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.

[0051] 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 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.’

[0052] 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.

[0053] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present disclosure, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety, unless a particular passage is cited. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

[0054] For purposes of this disclosure, "effective amount" is defined as the amount of each component of the inventive compositions which, when combined, results in the formation of an azeotrope or azeotrope-like composition. This definition includes the amounts of each component, which amounts may vary depending on the pressure applied to the composition so long as the azeotrope or azeotrope-like compositions continue to exist at the different pressures, but with possible different boiling points. Therefore, effective amount includes the amounts, such as may be expressed in weight percentages, of each component of the compositions of the instant disclosure which form azeotrope or azeotrope-like compositions at temperatures or pressures other than as described herein.

[0055] For the purposes of this disclosure, azeotrope or constant-boiling is intended to mean also essentially azeotrope or essentially-constant boiling. In other words, included within the meaning of these terms are not only the true azeotropes described above, but also other compositions containing the same components in different proportions, which are true azeotropes at other temperatures and pressures, as well as those equivalent compositions which are part of the same azeotrope system and are azeotrope-like in their properties. As is well recognized in this art, there is a range of compositions which contain the same components as the azeotrope, which will not only exhibit essentially equivalent properties for refrigeration and other applications, but which will also exhibit essentially equivalent properties to the true azeotrope composition in terms of constant boiling characteristics or tendency not to segregate or fractionate on boiling.

[0056] It is possible to characterize, in effect, a constant boiling admixture which may appear under many guises, depending upon the conditions chosen, by any of several criteria: The composition can be defined as an azeotrope of A, B, C (and D . . .) since the very term "azeotrope" is at once both definitive and limitative, and requires that effective amounts of A, B, C (and D . . .) for this unique composition of matter which is a constant boiling composition. It is well known by those skilled in the art, that, at different pressures, the composition of a given azeotrope will vary at least to some degree, and changes in pressure will also change, at least to some degree, the boiling point temperature. Thus, an azeotrope of A, B, C (and D . . .) represents a unique type of relationship but with a variable composition which depends on temperature and/or pressure. Therefore,

compositional ranges, rather than fixed compositions, are often used to define azeotropes. The composition can be defined as a particular weight percent relationship or mole percent relationship of A, B, C (and D . . .), while recognizing that such specific values point out only one particular relationship and that in actuality, a series of such relationships, represented by A, B, C (and D . . .) actually exist for a given azeotrope, varied by the influence of pressure. An azeotrope of A, B, C (and D . . .) can be characterized by defining the compositions as an azeotrope characterized by a boiling point at a given pressure, thus giving identifying characteristics without unduly limiting the scope of the invention by a specific numerical composition, which is limited by and is only as accurate as the analytical equipment available.

[0057] The azeotrope or azeotrope-like compositions of the present disclosure can be prepared by any convenient method including mixing or combining the desired amounts. A preferred method is to weigh the desired component amounts and thereafter combine them in an appropriate container. Another preferred method is to form the azeotrope or azeotrope-like compositions as the distillate stream of a distillation column.

[0058] In certain embodiments disclosed herein, it was surprisingly found that HFO-1252zc and water in an amount of between greater than 0 and up to and including 90 mole percent water forms azeotrope and azeotrope like compositions over a temperature from 55°C to 90°C and pressures of between about 212 to about 458 psia.

[0059] In embodiments disclosed herein the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFO-1252zc and greater than 0 and less than 90 percent water (on a molar basis) can be present at temperatures from about 55°C to about 90°C, and pressures about 212.1 to about 458.5 psia.

[0060] In embodiments disclosed herein the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFO-1252zc and water contain greater than 0 and less than 90 mole percent water for the azeotrope pressure range of 212.1 to 458.5 psia over the temperature range of 55°C to 90°C.

[0061] In embodiments disclosed herein the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFC-263fb and H₂O at temperatures from 55°C to 80°C.

[0062] In embodiments disclosed herein the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFC-263fb and about 1% to about 90% (on a molar basis) H₂O at pressures between 132.7 psia and 237.6 psia at temperatures from 55°C to 80°C.

[0063] In embodiments disclosed herein the azeotrope or azeotrope-like compositions which comprise, consist essentially of, or consist of HFC-263fb and about 30% to about 50% (on a molar basis) HF at pressures between 107.8 psia and 293.1 psia.

[0064] Certain embodiments of the invention disclosed herein relate to processes for preparing an azeotrope-like composition comprising, contacting HFO-1252zc and water at temperatures from 55°C to 90°C and at pressures of 212.1 to 458.5 psia to form HFO-1252zc azeotrope-like compositions.

[0065] Certain embodiments of the invention disclosed herein relate to processes for preparing an azeotrope-like composition comprising, contacting HFC-263fb and HF at temperatures from 40°C to 80°C, at sufficient pressure to form HFC-263fb azeotrope-like compositions.

[0066] Certain embodiments of the invention disclosed herein relate to processes for preparing an azeotrope-like composition comprising HFO-1252zc and water, by subjecting the mixture to separation such that at temperatures from 55°C to 90°C azeotrope-like compositions between HFO-1252zc and water are formed.

[0067] Certain embodiments of the invention disclosed herein relate to processes of subjecting a product mixture comprising HFO-1252zc to a first distillation step in which a composition enriched in either (i) water or (ii) HFO-1252zc is removed as a first distillate composition with a first bottoms composition being enriched in the other of said components (i) or (ii); and b) subjecting said first distillate composition to a second distillation step conducted at a different pressure in which the component enriched as first bottoms composition in (a) is removed in a second distillate

composition with a second bottoms composition enriched in the same component which was enriched in the first distillate composition.

[0068] Further process embodiments of the invention disclosed herein relate to processes for the purification of HFO-1252zc from a mixture comprising HFO-1252zc, HFC-263fb, and water, comprising a) subjecting said mixture to a first distillation step to form a first distillate comprising azeotrope or near-azeotrope compositions containing HFO-1252zc and water.

[0069] In several embodiments, it has been surprisingly found that HFC-263fb and HF form azeotrope and azeotrope like compositions which comprise, consist essentially of, or consist of HFC-263fb and HF under the conditions of pressures between 108.0 and 293.1 at temperatures from 40°C to 80°C.

[0070] In certain embodiments, it has been surprisingly found that HFC-263fb and water (H₂O) form azeotrope and azeotrope like compositions at a psia of 132.9 to 237.6 over a temperature of from 55°C to 80°C.

EXAMPLES

[0071] Examples 1 to 3 demonstrate azeotropic or azeotrope-like behavior of the presently claimed compositions. Examples 4 to 6 describe processes to separate components of a mixture using distillation. Fig. 1 shows a process embodiment to remove water from the fluorochemical HFO-1252zc using the azeotropes disclosed in this application. Fig. 2 show another process embodiment to remove water from the fluorochemical HFC-263fb using the azeotropes disclosed in this application. Fig. 3 shows a still further process embodiment to remove HF from the fluorochemical HFC-263fb using the azeotropes disclosed in this application.

[0072] One skilled in the art will be familiar with other embodiments used in the practice of distillation and separations, including decantation and pressure swing distillation. The column used for examples 4-6 has a feed stream shown by stream F11, the distillate by stream S11, and the bottoms by stream S12. The column operates with a total condenser and a thermosiphon reboiler. The number of theoretical stages and pressure are given in each example. The reflux ratio was 6 on a mass basis in each example.

Example 1: HFO-1252zc/water

[0073] PTx measurements are done with mixtures of 1252zc and water, as shown in Table 2 below.

Table 2

1252zc/Water					
55°C		70°C		90°C	
WATER MOL FR	PRESS PSIA	WATER MOL FR	PRESS PSIA	WATER MOL FR	PRESS PSIA
0	212.012	0	294.422	0	441.118
0.0008	212.043	0.004	295.466	0.006	449.307
0.0016	212.067	0.008	296.083	0.012	454.317
0.0024	212.084	0.012	296.401	0.018	457.261
0.0032	212.094	0.016	296.515	0.024	458.454
0.004	212.098	0.02	296.496	0.03	458.454
0.0048	212.096	0.024	296.463	0.036	458.454
0.0056	212.09	0.028	296.463	0.042	458.454
0.0064	212.079	0.032	296.463	0.048	458.454
0.0072	212.064	0.036	296.463	0.054	458.454
0.008	212.045	0.04	296.463	0.06	458.454
0.1	211.461	0.1	296.463	0.1	458.454
0.5	211.461	0.5	294.463	0.5	458.454
0.9	211.461	0.9	294.463	0.9	458.454
1.0	2.292	1.0	4.531	1.0	10.178

Example 2: HFC-263fb/water

[0074] PTx measurements were done with mixtures of 263fbc and water, as shown in Table 3 below.

Table 3

263fb/water			
	55°C	65°C	80°C
WATER MOL FR	PRESS PSIA	PRESS PSIA	PRESS PSIA
0	132.55	168.22	234.60
0.05	132.80	168.73	235.86

263fb/water			
	55°C	65°C	80°C
WATER MOL FR	PRESS PSIA	PRESS PSIA	PRESS PSIA
0.01	132.90	169.01	236.69
0.02	132.84	169.14	237.49
0.03	132.67	169.00	237.64
0.04	132.67	168.89	237.48
0.05	132.67	168.89	237.31
0.1	132.67	168.89	237.31
0.2	132.67	168.89	237.31
0.3	132.67	168.89	237.31
0.4	132.67	168.89	237.31
0.5	132.67	168.89	237.31
0.6	132.67	168.89	237.31
0.7	132.67	168.89	237.31
0.8	132.67	168.89	237.31
0.9	132.67	168.89	237.31
1	2.29	3.64	6.88

Example 3: HFC-263fb/HF

[0075] PTx measurements are done with mixtures of 263fbc and HF, as shown in Table 4 below.

Table 4

263fb/HF			
	40°C	60°C	80°C
HF MOL FR	PRESS PSIA	PRESS PSIA	PRESS PSIA
0	90.0	149.6	234.6
0.1	103.9	172.8	274.6
0.2	107.1	179.4	287.3
0.3	107.8	181.7	292.1
0.4	108.0	182.1	293.1
0.5	107.7	181.7	292.0
0.6	107.1	180.7	289.5
0.7	106.3	179.2	285.6

263fb/HF			
	40°C	60°C	80°C
HF MOL FR	PRESS PSIA	PRESS PSIA	PRESS PSIA
0.8	104.7	175.4	276.1
0.9	96.0	156.7	239.3
1	29.5	53.8	92.3

Example 4: Removal of water from 1252zc using the azeotrope

[0076] A composition of water and 1252zc comprising 100 ppm water is fed above stage 5 of a distillation column with 70 theoretical stages as shown by stream F11 in Fig. 1. The condenser was operated at a pressure of 275 psia. A bottoms stream S12 essentially free of water (<1 ppmw) was obtained.

Example 5: Removal of water from 263fb using the azeotrope

[0077] A composition of water and 263fb comprising 100 ppm water was fed above stage 5 of a distillation column with 30 theoretical stages as shown by stream F11 in Fig. 2. The condenser was operated at a pressure of 150 psia. A bottoms stream S12 essentially free of water (<1 ppmw) was obtained.

Example 6: Removal of HF from 263fb using the azeotrope

[0078] A composition of HF and 263fb comprising 1000 ppm HF is fed above stage 5 of a distillation column with 30 theoretical stages as shown by stream F11 in Fig. 3. The condenser is operated at a pressure of 150 psia. A bottoms stream S12 essentially free of HF (<1 ppmw) is obtained.

ADDITIONAL EMBODIMENTS

[0079] Embodiment 1. An azeotrope or near-azeotrope composition comprising HFO-1252zc and water, wherein said composition is characterized by a difference between dew point pressure and bubble point pressure that is less than or equal to 3%, based upon bubble point pressure.

[0080] Embodiment 2. The azeotrope or near-azeotrope composition of Embodiment 1, at a pressure range of 212.1 psia to 458.5 psia at a temperature from 55°C to 90°C.

[0081] Embodiment 3. An azeotrope composition of HFO-1252zc and water at a pressure range of about 212 psia to about 458 psia and a temperature of 55°C to 90°C.

[0082] Embodiment 4. The composition of any of Embodiments 1 to 3, wherein the composition contains from about greater than 0 and up to and including 90 mole percent water, preferably from about 0.4 to about 90 mole percent water.

[0083] Embodiment 5. An azeotrope or near-azeotrope composition comprising HFC-263fb and HF, wherein said composition is characterized by a difference between dew point pressure and bubble point pressure that is less than or equal to 3%, based upon bubble point pressure.

[0084] Embodiment 6. The azeotrope or near-azeotrope composition of Embodiment 5, at a pressure range of 107.8 and 293.1 psia at a temperature from 40°C to 80°C.

[0085] Embodiment 7. An azeotrope composition of HFC-263fb and HF at a pressure range of about 108 and 293 psia and a temperature from 40°C to 80°C.

[0086] Embodiment 8. The composition of any of Embodiments 5 to 7, wherein the composition contains from about 30 to about 50 mole percent HF.

[0087] Embodiment 9. An azeotrope or near-azeotrope composition comprising HFC-263fb and water, wherein said composition is characterized by a difference between dew point pressure and bubble point pressure that is less than or equal to 3%, based upon bubble point pressure.

[0088] Embodiment 10. The azeotrope or near-azeotrope composition of Embodiment 9, at a pressure range of 132.7 and 237.6 psia at a temperature from 55°C to 80°C.

[0089] Embodiment 11. An azeotrope composition of HFC-263fb and water at a pressure range of about 133 and 238 psia and a temperature from 55°C to 80°C.

[0090] Embodiment 12. The composition of any of Embodiments 9 to 11, wherein the composition contains from about 1 to about 90 mole percent water.

[0091] Embodiment 13. A process for preparing an azeotrope-like composition, the process comprising contacting HFO-1252zc and water at a temperature from 55°C to

90°C at a sufficient pressure to form an azeotrope-like composition comprising HFO-1252zc and water.

[0092] Embodiment 14. The process of Embodiment 13, wherein the pressure is from 212.1 to 458.5 psia.

[0093] Embodiment 15. A process for preparing an azeotrope-like composition, the process comprising contacting HFC-263fb and HF at a temperature from 40°C to 80°C at a sufficient pressure to form an azeotrope-like composition comprising HFC-263fb and HF.

[0094] Embodiment 16. The process of Embodiment 15, wherein the pressure is from 107.8 to 293.1 psia.

[0095] Embodiment 17. A process for preparing an azeotrope-like composition, the process comprising contacting HFC-263fb and water at a temperature from 55°C to 80°C at a sufficient pressure to form an azeotrope-like composition comprising HFC-263fb and water.

[0096] Embodiment 18. The process of Embodiment 17, wherein the pressure is from 132.7 to 237.6 psia.

[0097] Embodiment 19. A process comprising providing a mixture comprising HFO-1252zc and water, and subjecting the mixture to separation, such that at a temperature from 55°C to 90°C, azeotrope or azeotrope-like compositions comprising HFO-1252zc and water are formed.

[0098] Embodiment 20. A process comprising providing a mixture comprising HFC-263fb and water, and subjecting the mixture to separation, such that at a temperature from 55°C to 80°C, azeotrope or azeotrope-like compositions comprising HFC-263fb and water are formed.

[0099] Embodiment 21. A process comprising providing a mixture comprising HFC-263fb and HF, and subjecting the mixture to separation, such that at a temperature from 40°C to 80°C, azeotrope or azeotrope-like compositions comprising HFC-263fb and HF are formed.

[0100] Although certain aspects, embodiments and principals have been described above, it is understood that this description is made only way of example and not as limitation of the scope of the invention or appended claims. The foregoing various aspects, embodiments and principals can be used alone and in combinations with each other.

CLAIMS

What is claimed is:

1. An azeotrope or near-azeotrope composition comprising HFO-1252zc and water, wherein said composition is characterized by a difference between dew point pressure and bubble point pressure that is less than or equal to 3%, based upon bubble point pressure.
2. The azeotrope or near-azeotrope composition of claim 1, at a pressure range of 212.1 psia to 458.5 psia at a temperature from 55°C to 90°C.
3. An azeotrope composition of HFO-1252zc and water at a pressure range of about 212 psia to about 458 psia and a temperature of 55°C to 90°C.
4. The composition of any of claims 1 to 3, wherein the composition contains from about greater than 0 and up to and including 90 mole percent water, preferably from about 0.4 to about 90 mole percent water.
5. An azeotrope or near-azeotrope composition comprising HFC-263fb and HF, wherein said composition is characterized by a difference between dew point pressure and bubble point pressure that is less than or equal to 3%, based upon bubble point pressure.
6. The azeotrope or near-azeotrope composition of claim 5, at a pressure range of 107.8 and 293.1 psia at a temperature from 40°C to 80°C.
7. An azeotrope composition of HFC-263fb and HF at a pressure range of about 108 and 293 psia and a temperature from 40°C to 80°C.
8. The composition of any of claims 5 to 7, wherein the composition contains from about 30 to about 50 mole percent HF.
9. An azeotrope or near-azeotrope composition comprising HFC-263fb and water, wherein said composition is characterized by a difference between dew point pressure and bubble point pressure that is less than or equal to 3%, based upon bubble point pressure.
10. The azeotrope or near-azeotrope composition of claim 9, at a pressure range of 132.7 and 237.6 psia at a temperature from 55°C to 80°C.

11. An azeotrope composition of HFC-263fb and water at a pressure range of about 133 and 238 psia and a temperature from 55°C to 80°C.
12. The composition of any of claims 9 to 11, wherein the composition contains from about 1 to about 90 mole percent water.
13. A process for preparing an azeotrope-like composition, the process comprising contacting HFO-1252zc and water at a temperature from 55°C to 90°C at a sufficient pressure to form an azeotrope-like composition comprising HFO-1252zc and water.
14. The process of claim 13, wherein the pressure is from 212.1 to 458.5 psia.
15. A process for preparing an azeotrope-like composition, the process comprising contacting HFC-263fb and HF at a temperature from 40°C to 80°C at a sufficient pressure to form an azeotrope-like composition comprising HFC-263fb and HF.
16. The process of claim 15, wherein the pressure is from 107.8 to 293.1 psia.
17. A process for preparing an azeotrope-like composition, the process comprising contacting HFC-263fb and water at a temperature from 55°C to 80°C at a sufficient pressure to form an azeotrope-like composition comprising HFC-263fb and water.
18. The process of claim 17, wherein the pressure is from 132.7 to 237.6 psia.
19. A process comprising providing a mixture comprising HFO-1252zc and water, and subjecting the mixture to separation, such that at a temperature from 55°C to 90°C, azeotrope or azeotrope-like compositions comprising HFO-1252zc and water are formed.
20. A process comprising providing a mixture comprising HFC-263fb and water, and subjecting the mixture to separation, such that at a temperature from 55°C to 80°C, azeotrope or azeotrope-like compositions comprising HFC-263fb and water are formed.

21. A process comprising providing a mixture comprising HFC-263fb and HF, and subjecting the mixture to separation, such that at a temperature from 40°C to 80°C, azeotrope or azeotrope-like compositions comprising HFC-263fb and HF are formed.