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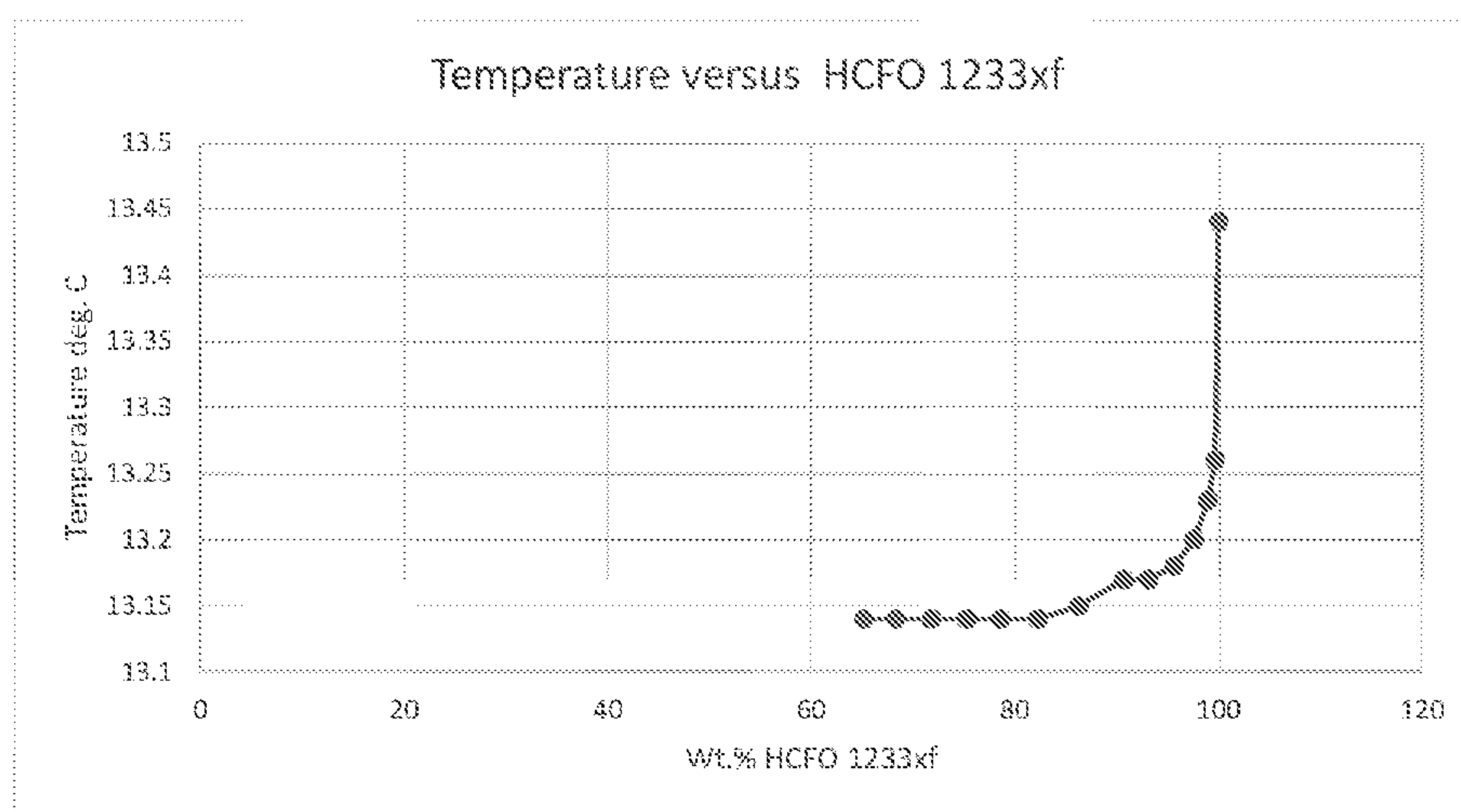


FIGURE 1

(57) Abstract: Heterogenous azeotrope or azeotrope-like compositions comprising 2-chloro-3,3,3- trifluoropropene (HFCO-1233xf) and water which may include from about 0.09 wt.% to about 92.69 wt.% 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and from about 7.31 wt.% to about 99.91 wt.% water and having a boiling point between about 12.0°C and about 13.6°C at a pressure of between about 12.5 psia and about 16.5 psia. The azeotrope or azeotrope-like compositions may be used to separate impurities, including water, from 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf).

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**AZEOTROPE OR AZEOTROPE-LIKE COMPOSITIONS OF 2-CHLORO-3,3,3-TRIFLUOROPROPENE (HCFO-1233XF) AND WATER**

FIELD

**[0001]** The present disclosure pertains to azeotrope or azeotrope-like compositions and, in particular, azeotrope or azeotrope-like compositions comprising effective amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water.

BACKGROUND OF THE DISCLOSURE

**[0002]** Hydrofluoroolefins (HFOs), such as tetrafluoropropenes, including 2,3,3,3-tetrafluoropropene (HFO-1234yf), are known to be effective refrigerants, heat transfer media, propellants, foaming agents, blowing agents, gaseous dielectrics, sterilant carriers, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents, displacement drying agents and power cycle working fluids. Unlike chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), both of which potentially damage the Earth's ozone layer, HFOs pose no threat to the ozone layer. HFO-1234yf has also been shown to be a low global warming compound with low toxicity and, hence, can meet increasingly stringent requirements for refrigerants in mobile air conditioning. Accordingly, compositions containing HFO-1234yf are among the materials being developed for use in many of the aforementioned applications.

**[0003]** One manufacturing process for HFO-1234yf uses 1,1,2,3-tetrachloropropene (HCFC-1230xa) as starting raw material. The process comprises the following three steps:

**Step (1)** 1230xa + 3HF --> 2-chloro-3,3,3-trifluoropropene (1233xf) + 3HCl in a vapor phase reactor charged with a solid catalyst;

**Step (2)** 1233xf + HF --> 2-chloro-1,1,1,2-tetrafluoropropane (244bb) in a liquid phase reactor charged with a liquid catalyst; and

**Step (3)** 244bb --> 1234yf + HCl in a vapor phase reactor or in the liquid phase.

During the foregoing process, by-products may be produced and/or impurities, including water, may be present. It is desirable to have all reactants and intermediate products in a pure a form as possible to limit unwanted side reactions. Therefore, methods of reducing impurities in reactants and intermediate products are desired.

SUMMARY

**[0004]** The present disclosure provides azeotrope or azeotrope-like compositions of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water.

**[0005]** It is well-recognized in the art that it is not possible to predict the formation of azeotropes, and the present inventors have discovered unexpectedly that 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water form azeotrope or azeotrope-like compositions and, in particular, form heterogeneous azeotrope or azeotrope-like compositions.

**[0006]** The present disclosure provides a composition comprising an azeotrope or azeotrope-like composition consisting essentially of effective amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water, preferably wherein the azeotrope or azeotrope-like composition has a boiling point between about 12.0°C and about 13.6°C, preferably about 13.1 to about 13.2, at a pressure of between about 12.5 psia and about 16.5 psia, preferably about 14.5 psia.

**[0007]** The azeotrope or azeotrope-like composition may consist essentially of from about 0.09 wt.% to about 92.69 wt.% 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and from about 7.31 wt.% to about 99.91 wt.% water, preferably wherein the azeotrope or azeotrope-like composition consists essentially of from about 65 wt.% to about 90 wt.% 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and from about 10 wt.% to about 35 wt.% water; preferably the azeotrope or azeotrope-like composition consists essentially of from about 65.14 wt.% to about 86.25 wt.% 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and from about 13.75 wt.% to about 34.86 wt.% water. The azeotrope or azeotrope-like composition preferably has a boiling point between about 12.0°C and about 13.6°C, preferably about 13.1 to about 13.2, at a pressure of between about 12.5 psia and about 16.5 psia, preferably about 14.5 psia.

**[0008]** The present disclosure also provides a method of forming an azeotrope or azeotrope-like composition comprising the step of combining 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water to form an azeotrope or azeotrope-like composition consisting essentially of effective amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water and preferably having a boiling point between about 12.0°C and about 13.6°C at a pressure of between about 12.5 psia and about 16.5 psia.

**[0009]** The present disclosure further provides a method of separating impurities, including water, from a composition which includes 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and at least one impurity, which may include water, comprising the steps of:

providing a composition including 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and at least one impurity; modifying the relative amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water, and subjecting the composition to conditions effective to form an azeotrope or azeotrope-like composition consisting essentially of, or consisting of, effective amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water; and separating the azeotrope or azeotrope-like composition from the composition including 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), wherein the separation step may comprise at least one of phase separation, distillation, drying, and fractionation.

**[0010]** In the foregoing method, the step of modifying the relative amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water may involve adding 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) to the composition, adding water to the composition, or adding both 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water to the composition.

**[0011]** The present disclosure also provides a method of producing 2,3,3,3-tetrafluoropropene (HFO-1234yf) comprising:

converting at least some of the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) present in the azeotrope or azeotrope-like composition into 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb); and

converting at least some of the 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) into 2,3,3,3-tetrafluoropropene (HFO-1234yf).

**[0012]** The 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) present in the azeotrope or azeotrope-like composition can be separated from the water before being converted into 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb), which is beneficial because it means that 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) can be converted into 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) in the presence of a catalyst that is sensitive to the presence of water. Converting at least some of the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) into 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) can comprise reacting the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) with HF, preferably anhydrous HF, in the presence of a catalyst. The catalyst can comprise metal halide catalyst, preferably selected from  $\text{SbCl}_5$ ,  $\text{SbF}_5$ ,  $\text{TiCl}_4$  or a combination thereof, or is a fluorosulfonic acid; and/or converting at least some of the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) into 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) can be carried out at a temperature of 5-100°C, preferably 50-100°C. Converting at least some of the 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) into 2,3,3,3-tetrafluoropropene (HFO-1234yf) can

comprise reacting the 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) with a base, a caustic base, preferably an alkali metal hydroxide, preferably KOH or NaOH. The reaction is preferably conducted in an aqueous environment, preferably in the presence of a phase transfer catalyst, preferably an ammonium halide, preferably a trialkylammonium halide of a tetraalkylammonium halide, preferably a trialkylammonium chloride of a tetraalkylammonium chloride. The reaction can preferably be conducted at a temperature of from about 0 °C to about 100 °C, preferably from about 20 °C to about 90 °C, preferably from about 50 °C to about 90 °C, preferably from about 60 °C to about 80 °C. Converting the 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) into 2,3,3,3-tetrafluoropropene (HFO-1234yf) may suitably occur at super-atmospheric pressure, atmospheric pressure, or sub-atmospheric pressure.

#### DESCRIPTION OF THE DRAWING

**[0013]** Figure 1 is a plot of boiling point versus percentage of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) in water.

#### DETAILED DESCRIPTION

**[0014]** In the first step (above), starting materials such as 1,1,2,3-tetrachloropropene (“HCO-1230xa” or “1230xa”) and/or 1,1,1,2,3-pentachloropropene (“HCC-240db” or “240db”) and/or 2,3,3,3-tetrachloropropene (HCO-1230xf) are reacted with anhydrous hydrogen fluoride (HF) in a first vapor phase reactor (fluorination reactor) to produce a mixture of at least HCFO-1233xf (2-chloro-3,3,3-trifluoropropene) and HCl. The reaction can be carried out at a temperature of about 200°C to about 400°C and a pressure of about 0 to about 200 psig. The effluent stream exiting the vapor phase reactor may optionally comprise additional components, such as un-reacted hydrogen fluoride (HF), heavy intermediates, 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb), 1,1,1,2,2-pentafluoropropane (HFC-245cb), and the like.

**[0015]** The reaction may be conducted in any reactor suitable for a vapor phase fluorination reaction. The reactor may be constructed from materials which are resistant to the corrosive effects of hydrogen fluoride and catalyst such as Hastelloy®, Inconel®, Monel®, and the like. In case of a vapor phase process, the reactor is filled with a vapor phase fluorination catalyst. Any fluorination catalysts known in the art may be used in this process. Suitable catalysts include, but are not limited to chromium, aluminum, cobalt,

manganese, nickel and iron oxides, hydroxides, halides, oxyhalides, inorganic salts thereof and their mixtures any of which may be optionally halogenated. Combinations of catalysts suitable for the present invention nonexclusively include  $\text{Cr}_2\text{O}_3$ ,  $\text{FeCl}_3/\text{C}$ ,  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3/\text{AlF}_3$ ,  $\text{Cr}_2\text{O}_3/\text{carbon}$ ,  $\text{CoCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{NiCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{CoCl}_2/\text{AlF}_3$ ,  $\text{NiCl}_2/\text{AlF}_3$  and mixtures thereof. Chromium oxide/aluminum oxide catalysts are described in U.S. Pat. No. 5,155,082, the contents of which are incorporated herein by reference. Chromium (III) oxides such as crystalline chromium oxide or amorphous chromium oxide are preferred with amorphous chromium oxide being most preferred. Chromium oxide ( $\text{Cr}_2\text{O}_3$ ) is a commercially available material which may be purchased in a variety of particle sizes. Fluorination catalysts having a purity of at least 98% are preferred. The fluorination catalyst is present in an excess but in at least an amount sufficient to drive the reaction.

**[0016]** In an embodiment, the molar ratio of hydrogen fluoride (HF) to a compound of Formula I, II or III in Step 1 reaction ranges from about 1:1 to about 50:1, in one embodiment; from about 10:1 to about 50:1, in another embodiment; and in a further embodiment, from about 10:1 to about 20:1. In an embodiment, the reaction between HF and the compound of I, II or III is carried out at a temperature from about 200° C to about 600° C; in another embodiment, from about 200° C to about 400°C; in another embodiment, from about 200° C to about 300° C. The reaction pressure, in an embodiment, ranges from about 0 psig to about 500 psig; in another embodiment, from about 20 psig to about 200 psig, and in a further embodiment, from about 50 to about 100 psig.

**[0017]** For example, when the compound of Formula I is 1230xa, the molar ratio of HF to 1230xa in Step 1 of the reaction ranges from about 1:1 to about 50:1 in one embodiment; from about 10:1 to about 50:1, in another embodiment; and in a further embodiment, from about 10:1 to about 20:1. In an embodiment, the reaction between HF and 1230xa is carried out at a temperature from about 200° C to about 600° C; in another embodiment, from about 200° C to about 400°C; in another embodiment, from about 200° C to about 300° C. The reaction pressure, in an embodiment, ranges from about 0 psig to about 500 psig; in another embodiment, from about 20 psig to about 200 psig, and in a further embodiment, from about 50 to about 100 psig.

**[0018]** Similarly, when the compound of Formula II is 2,3,3,3- tetrachloro-1-propene (HCC-1230xf or 1230xf), the molar ratio of HF to 1230xf in step 1 of the reaction, in one embodiment, ranges from about 1:1 to about 50:1; in another embodiment, from about 10:1 to about 50:1, and, in still further embodiment, from about 10:1 to about 20:1. In an

embodiment, the reaction between HF and 1230xf is carried out at a temperature from about 200°C to about 600°C; in another embodiment, from about 200°C to about 400°C; and, in another embodiment, from about 200°C to about 300° C. The reaction pressure, in an embodiment, ranges from about 0 psig to about 500 psig; in another embodiment, from about 20 psig to about 200 psig, and in another embodiment, from about 50 to about 100 psig.

**[0019]** Similarly, when the compound of Formula III is 1,1,1,2,3-pentachloropropane (HCC-240db or 240db), the molar ratio of HF to 240db in step 1 of the reaction ranges from about 1:1 to about 50:1; in another embodiment, from about 10:1 to about 50:1; and in another embodiment, from about 10:1 to about 20:1. The reaction between HF and 240db is carried out, in an embodiment, at a temperature from about 200°C to about 600° C; in another embodiment, from about 200° C. to about 400° C, and in another embodiment, from about 200° C to about 300° C. The reaction pressure, in an embodiment, ranges from about 0 psig to about 500 psig; in another embodiment, from about 20 psig to about 200 psig; and in a further embodiment, from about 50 to about 100 psig.

**[0020]** The first step of the reaction is not necessarily limited to a vapor phase reaction, as described above, but may also be performed using a liquid phase reaction or a combination of liquid and vapor phases, such as that disclosed in U.S. Published Patent Application No. 20070197842, the contents of which are incorporated herein by reference. It is also contemplated that the reaction can be carried out batch wise, continuously, or a combination of these. For embodiments in which the reaction comprises a liquid phase reaction, the reaction can be catalytic or non-catalytic. Lewis acid catalysts, such as metal-halide catalysts, including antimony halides, tin halides, thallium halides, iron halides, and combinations of two or more of these, may be employed. In certain embodiments, metal chlorides and metal fluorides are employed, including, but not limited to,  $\text{SbCl}_5$ ,  $\text{SbCl}_3$ ,  $\text{SbF}_5$ ,  $\text{SnCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{FeCl}_3$  and combinations of two or more of these.

**[0021]** The fluorination reaction may be carried out to attain a single- or multi-pass conversion of at least 1% or higher, 5% or higher, 10% or higher or about 20% or higher. In certain preferred embodiments of the present invention, the starting reagent is converted to 1233xf in a single pass, wherein the reaction conditions achieve a conversion amount greater than 75%; in an embodiment, greater than 85%; in another embodiment, greater than 95%; and in another embodiment, greater than 99%. To this end, the resulting effluent

includes small or trace amounts of unreacted starting material or may be substantially free of such compounds.

**[0022]** The effluents from the fluorination reaction step, Step 1, including any intermediate effluents that may be present in multi-stage reactor arrangements, are processed to achieve desired degrees of separation. For example, in embodiments in which the reactor effluent includes 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), the effluent will generally also include HCl, unreacted HF, and trace amounts, if any, of unreacted starting component (e.g. 1230xa, 1230xf and/or 240db). The effluent may also include one or more by-product organics such as underfluorinated and/or overfluorinated intermediates. Non-limiting examples of underfluorinated intermediates include trichlorofluoropropene (1231) isomers and 2,3-dichloro-3,3-difluoropropene (1232xf), and non-limiting examples of overfluorinated intermediates include 2-chloro-1,1,1,2-tetrafluoropropane (244bb) and 1,1,1,2,2-pentafluoropropane (245cb) and HFO-1234yf and combinations thereof. In further embodiments, the impurity is hydrogen fluoride. Other by-product organics may also include, but are not limited to, dichlorotrifluoropropane (243) isomers, and trichlorodifluoropropane (242) isomers, and dimers derived from one or more of the starting compounds. By way of non-limiting example, dimers derived from 1230xa include, but are not limited to,  $C_6H_3F_6Cl$ ,  $C_6H_3F_7Cl_2$ ,  $C_6F_6Cl_2$ ,  $C_6H_8Cl_2$ ,  $C_6F_5Cl_3$ ,  $C_6H_3F_2Cl_5$ , and the like.

**[0023]** After HCl is removed by distillation and a portion of the HF is removed by phase separation, water is added to the remaining effluent from Step 1 in an effective amount to form an azeotrope or azeotrope-like mixture comprising 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water, which can then be separated from the effluent with its impurities by techniques described herein. The 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) is then separated from the water as described herein then is fed to the hydrofluorination reactor of Step 2, discussed below.

**[0024]** In Step 2 of the aforementioned process for forming 2,3,3,3-tetrafluoroprop-1-ene, the purified 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) is converted to 2-chloro-1,1,1,2-tetrafluoropropane (244bb). In one embodiment, this step may be performed in the liquid phase in a liquid phase reactor, which may be TFE or PFA-lined. Such a process may be performed in a temperature range of about 70° to about 120° C and at a pressure ranging from about 50 to about 120 psig.

**[0025]** Any liquid phase fluorination catalyst may be used in the invention. A non-exhaustive list includes Lewis acids, transition metal halides, transition metal oxides, Group IVb metal halides, Group Vb metal halides, or combinations thereof. Non-exclusive examples of liquid phase fluorination catalysts are an antimony halide, a tin halide, a tantalum halide, a titanium halide, a niobium halide, and molybdenum halide, an iron halide, a fluorinated chrome halide, a fluorinated chrome oxide or combinations thereof. Specific non-exclusive examples of liquid phase fluorination catalysts are  $\text{SbCl}_5$ ,  $\text{SbCl}_3$ ,  $\text{SbF}_5$ ,  $\text{SnCl}_4$ ,  $\text{TaCl}_5$ ,  $\text{TiCl}_4$ ,  $\text{NbCl}_5$ ,  $\text{MoCl}_6$ ,  $\text{FeCl}_3$ , a fluorinated species of  $\text{SbCl}_5$ , a fluorinated species of  $\text{SbCl}_3$ , a fluorinated species of  $\text{SnCl}_4$ , a fluorinated species of  $\text{TaCl}_5$ , a fluorinated species of  $\text{TiCl}_4$ , a fluorinated species of  $\text{NbCl}_5$ , a fluorinated species of  $\text{MoCl}_6$ , a fluorinated species of  $\text{FeCl}_3$ , or combinations thereof. Antimony pentachloride is most preferred.

**[0026]** The catalysts can be readily regenerated by any means known in the art if they become deactivated. One suitable method of regenerating the catalyst involves flowing a stream of chlorine through the catalyst. For example, from about 0.002 to about 0.2 lb per hour of chlorine can be added to the liquid phase reaction for every pound of liquid phase fluorination catalyst. This may be done, for example, for from about 1 to about 2 hours or continuously at a temperature of from about 65°C to about 100°C.

**[0027]** Step 2 of the reaction, in which 244bb product is formed, is not necessarily limited to a liquid phase reaction and may also be performed using a vapor phase reaction or a combination of liquid and vapor phases, such as that disclosed in U.S. Published Patent Application No. 20070197842, the contents of which are incorporated herein by reference. To this end, the feed stream including 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) is preheated to a temperature of from about 50°C to about 400°C, and is contacted with a catalyst and fluorinating agent. Catalysts may include standard vapor phase agents used for such a reaction and fluorinating agents may include those generally known in the art, such as, but not limited to, hydrogen fluoride.

**[0028]** The effluent from the hydrofluorination reaction step (Step 2), which consists mainly of 244bb and HF (plus small amounts of unreacted 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), overfluorinated by-product 245cb, HCl, and  $\text{Cl}_2$ ), is processed to achieve desired degrees of separation and/or other processing. For example, the product stream is fed to a lights removal column where a stream consisting of mainly 245cb, HCl, and  $\text{Cl}_2$  exits the top of the column and is sent to a thermal-oxidizer (T-OX) for destruction. In one embodiment, water is added to the lights removal column bottom stream consisting mainly

of 244bb and HF (plus a small amount of unreacted 1233xf) to form an azeotrope or azeotrope-like mixture comprised of 1233xf and water. In one embodiment, 244bb is not present in this mixture, in which case the 1233xf is separated from the water by techniques known in the art, as described hereinabove, such as by distillation. In another embodiment, the 244bb is also present in the azeotrope or azeotrope-like mixture comprised of 1233xf and water. The 244bb is then separated from the 1233xf by techniques known in the art, such as described in U.S. Patent No. 8,252, 965, the contents of which are incorporated by reference. The 1233xf that is separated may be recycled back to the hydrofluorination reactor of Step 2, as described above.

**[0029]** Step 3 of the process can be conducted in the vapor phase or liquid phase. When producing HFO-1234yf in the vapor phase, the 244bb is fed to a second vapor phase reactor (dehydrochlorination reactor) to be dehydrochlorinated to make the desired product 2,3,3,3-tetrafluoroprop-1-ene (1234yf). This reactor may optionally contain a catalyst that can catalytically dehydrochlorinate HCFC-244bb to make HFO-1234yf; however, in an embodiment, the reactor contains the catalyst.

**[0030]** The catalysts may be metal halides, halogenated metal oxides, neutral (or zero oxidation state) metal or metal alloy, or activated carbon in bulk or supported form. Metal halide or metal oxide catalysts may include, but are not limited to, mono-, bi-, and tri-valent metal halides, oxides and their mixtures/combinations, and more preferably mono-, and bi-valent metal halides and their mixtures/combinations. Component metals include, but are not limited to,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cs}^+$ . Component halogens include, but are not limited to,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ . Examples of useful mono- or bi-valent metals halide include, but are not limited to,  $\text{LiF}$ ,  $\text{NaF}$ ,  $\text{KF}$ ,  $\text{CsF}$ ,  $\text{MgF}_2$ ,  $\text{CaF}_2$ ,  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{CsCl}$ . Halogenation treatments can include any of those known in the prior art, particularly those that employ HF,  $\text{F}_2$ , HCl,  $\text{Cl}_2$ , HBr,  $\text{Br}_2$ , HI, and  $\text{I}_2$  as the halogenation source.

**[0031]** In one aspect, neutral metals, i.e., zero valent, metals, metal alloys and their mixtures, are used. Useful metals include, but are not limited to, Pd, Pt, Rh, Fe, Co, Ni, Cu, Mo, Cr, Mn, and combinations of the foregoing as alloys or mixtures. The catalyst may be supported or unsupported. Useful examples of metal alloys include, but are not limited to, SS 316, Monel<sup>®</sup> 400, Incoloy<sup>®</sup> 825, Inconel<sup>®</sup> 600, and Inconel<sup>®</sup> 625. Such catalysts may be provided as discrete supported or unsupported elements and/or as part of the reactor and/or the reactor walls.

**[0032]** Exemplary, but non-limiting, catalysts include activated carbon, stainless steel (e.g. SS 316), austenitic nickel-based alloys (e.g. Inconel<sup>®</sup> 625), nickel, fluorinated 10% CsCl/MgO, and 10% CsCl/MgF<sub>2</sub> and the like. In an embodiment, the reaction temperature ranges from about 300 to about 550°C, and the reaction pressure may range from about 0 to about 150 psig. The reactor effluent may be fed to a caustic scrubber or to a distillation column to remove the by-product of HCl to produce an acid-free organic product which, optionally, may undergo further purification using one or any combination of purification techniques that are known in the art.

**[0033]** Step 3 can also be conducted in the liquid phase. Converting 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) into 2,3,3,3-tetrafluoropropene (HFO-1234yf) can, for example, be carried out by employing a base to dehydrochlorinate the 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb). The base can be a caustic base, preferably selected from the group consisting of an alkali metal hydroxide, an alkali metal oxide, an alkaline earth metal hydroxide, an alkaline earth metal oxide and combinations thereof. Preferable examples of the caustic base are KOH, NaOH, LiOH, Mg(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, CaO and combinations thereof. Caustic bases can be added to the reaction in solid form or in a solution. When provided in solution, it is preferable that the solvent is water or an alcohol, preferably MeOH or EtOH. KOH is especially preferred, and is preferably provided as an aqueous solution, preferably comprising from about 5% to about 62% by weight of KOH, preferably 5% to 55% by weight. The liquid phase dehydrochlorination is preferably conducted in an aqueous environment. In the context of a liquid phase step 3, an aqueous environment is one in which the liquid phase reaction mixture comprises 5-80 wt.% water, preferably 10-60 wt.% water, more preferably 20-40 wt.% water. It is also preferable to utilize a phase transfer catalyst, especially when conducting the reaction in an aqueous environment because it is believed to aid reactivity by encouraging intimate contact between the base and the 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb). Such phase transfer catalysts may include, but are not limited to, crown ethers (e.g. 18-crown-6), onium salts (e.g. phosphonium salts or ammonium salts with a halide anion), cryptands (e.g. N[CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>N), polyalkylene glycols (e.g. poly(ethylene glycol), derivatives thereof, and combinations thereof. In one embodiment, the phase transfer catalyst is Aliquat 336. Onium salts, especially ammonium salts, are preferred. The ammonium salt is preferably an ammonium halide, preferably a trialkylammonium halide of

a tetraalkylammonium halide, preferably a trialkylammonium chloride or a tetraalkylammonium chloride.

**[0034]** The liquid phase version of step 3 is preferably conducted at a temperature of from about 0 °C to about 100 °C, preferably from about 20 °C to about 90 °C, preferably from about 50 °C to about 90 °C, preferably from about 60 °C to about 80 °C. Converting the 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) into 2,3,3,3-tetrafluoropropene (HFO-1234yf) may suitably occur at super-atmospheric pressure, atmospheric pressure, or subatmospheric pressure. These temperatures and pressures are especially useful when conducting step 3 in the liquid phase with a base, as described above.

**[0035]** WO-2011/139646 discloses further experimental details for converting 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) into 2,3,3,3-tetrafluoropropene (HFO-1234yf) in the liquid phase, the contents of which are incorporated herein.

**[0036]** An alternative process to make HFO-1234yf employs 1,2-dichloro-3,3,3-trifluoropropane (HCFC-243db) as starting raw material and is conducted in the vapor and liquid phase. In this alternative, the process comprises the following three steps (where Steps (2) and (3) are identical to those above):

Step (1):  $243db \rightarrow 1233xf + HCl$  in the vapor phase (with or without catalyst) or  $243db + base \rightarrow 1233xf + H_2O$  in the liquid phase (optionally with phase transfer catalyst, and/or solvent and/or salt).

Step (2):  $1233xf + HF \rightarrow 244bb$  in a liquid phase reactor charged with a liquid hydrofluorination catalyst; and

Step (3):  $244bb \rightarrow 1234yf + HCl$  in a vapor phase reactor (with or without catalyst) or in the liquid phase.

**[0037]** In the alternative process, wherein the starting composition includes 243db, 243db is dehydrohalogenated to produce a product mixture containing 1233xf. The dehydrohalogenation reaction is a dehydrochlorination reaction when the starting composition comprises 243db. The dehydrochlorination reaction is performed in a reaction zone and may occur in the vapor phase with a catalyst or in liquid phase with base and optionally phase transfer catalyst, and/or solvent and/or salt. For example, WO 2012/115934 discloses vapor phase reaction of 243db with a carbon catalyst. WO 2012/115938 discloses vapor phase reaction of 243db with a chromium oxyfluoride catalyst. WO 2017/044719 discloses reaction of 243db with a fluorinated alkane in the

presence of a fluorination catalyst to produce 1233xf, as well as other compounds useful for producing 1234yf. WO 2017/044724 discloses liquid phase reaction of 243db with caustic. If the dehydrochlorination reaction is performed in the vapor phase, HCl is produced, on the other hand, when the dehydrochlorination reaction is conducted in the liquid phase, no HCl is produced. Other methods may be used when starting with a compound having Formula (III) as will be known to those skilled in the art.

**[0038]** For embodiments where it is desired to maintain moisture- and impurity-free conditions during the synthesis of 1234yf, the reactants and intermediate products may be purified. For example, removing impurities, including water from 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) is desirable.

**[0039]** It has been found that 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water form heterogeneous azeotrope and azeotrope-like compositions or mixtures, and the present disclosure provides heterogeneous azeotrope or azeotrope-like compositions comprising 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water. The azeotrope or azeotrope-like compositions may consist essentially of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water, or the azeotrope or azeotrope-like compositions may consist of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water.

**[0040]** The present inventors have found experimentally that 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water form an azeotrope or azeotrope-like composition.

**[0041]** A heterogeneous azeotrope consists of two liquid phases and one vapor phase all in equilibrium. For a heterogeneous azeotrope at a given temperature and pressure, the composition of each of the two liquid phases and the composition of the vapor phase remain constant. If a heterogeneous azeotrope is formed, at a constant pressure the boiling point of the heterogeneous azeotrope will be less than the lower boiling point component (a "minimum boiling azeotrope").

**[0042]** An "azeotrope" (or "azeotropic") composition is a unique combination of two or more components. An azeotrope can be either homogeneous (which has one liquid phase) or heterogeneous (which has two liquid phases). An azeotrope composition can be characterized in various ways. For example, at a given pressure, an azeotrope composition boils at a constant characteristic temperature which is either greater than the higher boiling point component (maximum boiling azeotrope) or less than the lower boiling point component (minimum boiling azeotrope). However, in the case of a heterogeneous

azeotrope the boiling point of the azeotrope will always be below the boiling point of the lower boiling point component. At this characteristic temperature a homogenous azeotrope has the same composition in both the vapor and liquid phases. In the case of a heterogenous azeotrope then at this characteristic temperature the composition of each of the two liquid phases and the vapor phase will remain constant upon boiling. The azeotrope composition does not fractionate upon boiling or evaporation. Therefore, the components of the azeotrope composition cannot be separated during a phase change.

**[0043]** A homogenous azeotrope composition is also characterized in that at the characteristic azeotrope temperature, the bubble point pressure of the liquid phase is identical to the dew point pressure of the vapor phase. The behavior of an azeotrope composition is in contrast with that of a non-azeotrope composition in which during boiling or evaporation, the liquid composition changes to a substantial degree.

**[0044]** One of ordinary skill in the art would understand however that at different pressures, both the composition and the boiling point of the azeotrope composition will vary to some extent. Therefore, depending on the temperature and/or pressure, an azeotrope composition can have a variable composition. The skilled person would therefore understand that composition ranges, rather than fixed compositions, can be used to define azeotrope compositions. In addition, an azeotrope may be defined in terms of exact weight percentages of each component of the compositions characterized by a fixed boiling point at a specified pressure.

**[0045]** An "azeotrope-like" composition is a composition of two or more components which behaves substantially as an azeotrope composition. Thus, for the purposes of this disclosure, an azeotrope-like composition is a combination of two or more different components which, in the case of a homogenous azeotrope when in liquid form under given pressure, will boil at a substantially constant temperature, and which will provide a vapor composition substantially identical to the liquid composition undergoing boiling. In the case of a heterogenous azeotrope two liquid phases form under a given pressure which will be covered by a vapor composition. Each of the two liquid phases and the vapor phase will remain substantially constant on boiling.

**[0046]** For the purposes of this disclosure, an azeotrope-like composition is a composition or range of compositions which preferably boil(s) at a temperature range of between about 12.0°C and 13.6°C at a pressure from about 12.5 psia to about 16.5 psia.

**[0047]** Azeotrope or azeotrope-like compositions can be identified using a number of different methods.

**[0048]** For the purposes of this disclosure the azeotrope or azeotrope-like composition is identified experimentally using an ebulliometer (Walas, Phase Equilibria in Chemical Engineering, Butterworth-Heinemann, 1985, 533-544). An ebulliometer is designed to provide extremely accurate measurements of the boiling points of liquids by measuring the temperature of the vapor-liquid equilibrium.

**[0049]** The boiling points of each of the components alone are measured at a constant pressure. As the skilled person will appreciate, for a binary azeotrope or azeotrope-like composition, the boiling point of one of the components of the composition is initially measured. The second component of the composition is then added in varying amounts and the boiling point of each of the obtained compositions is measured using the ebulliometer at said constant pressure. In the case of a ternary azeotrope the initial composition would comprise of a binary blend and a third component is added in varying amounts. The boiling point of each of the obtained ternary compositions is measured using the ebulliometer at said constant pressure.

**[0050]** The measured boiling points are plotted against the composition of the tested composition, for example, for a binary azeotrope, the amount of the second component added to the composition, (expressed as either weight % or mole %). The presence of an azeotrope composition can be identified by the observation of a maximum or minimum boiling temperature which is greater or less than the boiling points of any of the components alone.

**[0051]** As the skilled person will appreciate, the identification of the azeotrope or azeotrope-like composition is made by the comparison of the change in the boiling point of the composition on addition of the second component to the first component, relative to the boiling point of the first component. Thus, it is not necessary that the system be calibrated to the reported boiling point of the particular components in order to measure the change in boiling point.

**[0052]** As previously discussed, at the maximum or minimum boiling point, the composition of the vapor phase will be identical to the composition of the liquid phases. The azeotrope-like composition is therefore that composition of components which provides a substantially constant minimum or maximum boiling point, that is a boiling point between about 12.0°C and about 13.6°C, preferably about 13.1 to about 13.2, at a pressure of

between about 12.5 psia and about 16.5 psia, preferably about 14.5 psia, at which substantially constant boiling point the composition of the vapor phase will be substantially identical to the composition of the liquid phases.

**[0053]** The present disclosure provides an azeotrope or azeotrope-like composition which comprises effective amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water to form an azeotrope or azeotrope-like composition. As used herein, the term “effective amount” is an amount of each component which, when combined with the other component, results in the formation of an azeotrope or azeotrope-like composition.

**[0054]** The present azeotrope or azeotrope-like compositions may consist essentially of combinations of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water or consist of combinations of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water.

**[0055]** As used herein, the term “consisting essentially of”, with respect to the components of an azeotrope or azeotrope-like composition or mixture, means the composition contains the indicated components in an azeotrope or azeotrope-like ratio, and may contain additional components provided that the additional components do not form new azeotrope or azeotrope-like systems. For example, azeotrope mixtures consisting essentially of two compounds are those that form binary azeotropes, which optionally may include one or more additional components, provided that the additional components do not render the mixture non-azeotropic and do not form an azeotrope with either or both of the compounds (e.g., do not form a ternary or higher azeotrope).

**[0056]** The present disclosure also provides a method of forming an azeotrope or azeotrope-like composition by mixing, combining, or blending, effective amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water. Any of a wide variety of methods known in the art for combining two or more components to form a composition can be used in the present methods. For example, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water can be mixed, blended, or otherwise combined by hand and/or by machine, as part of a batch or continuous reaction and/or process, or via combinations of two or more such steps. The components can be provided in the required amounts, for example by weighing and then combining the amounts.

**[0057]** The azeotrope or azeotrope-like composition having a boiling point between about 12.0°C and about 13.6°C at a pressure of between about 12.5 psia and about 16.5 psia may also consist essentially of, or consist of, from about 0.09 wt.% to about 92.69

wt.% 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and from about 7.31 wt.% to about 99.91 wt.% water.

**[0058]** The present disclosure also provides a composition comprising the azeotrope or azeotrope-like composition. For example, there is provided a composition comprising at least about 14 wt.% of the azeotrope or azeotrope-like compositions, or at least about 21 wt.% of the azeotrope or azeotrope-like compositions, or at least about 25 wt.% of the azeotrope or azeotrope-like compositions, or at least about 70 wt.% of the azeotrope or azeotrope-like compositions, or at least about 90 wt.% of the azeotrope or azeotrope-like compositions, or at least 95 wt.% of the azeotrope or azeotrope-like compositions, 99 wt.% of the azeotrope or azeotrope-like compositions.

**[0059]** The azeotrope or azeotrope-like composition comprising, consisting essentially of, or consisting of effective amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water disclosed herein may be used for separating impurities from 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf).

**[0060]** The preparation of azeotropic or azeotrope-like compositions comprising, consisting essentially of, or consisting of effective amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water allows separation techniques such as azeotropic distillation, for example, to be used to remove impurities, including water, from 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf).

**[0061]** In particular, an azeotrope or azeotrope-like composition comprising, consisting essentially of, or consisting of effective amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water may be formed from a composition including 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), water, and at least one impurity, which may include water. Following the formation of the azeotrope or azeotrope-like composition, the azeotrope or azeotrope-like composition may be separated from the other chemical compounds by a suitable method, such as by distillation, phase separation, drying or fractionation. Drying may be accomplished by the addition of a drying agent, such as molecular sieves.

**[0062]** In one example, the present disclosure provides a method of separating impurities from 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), comprising the steps of providing a primary composition of crude 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), modifying the relative amounts of 2-chloro-3,3,3-trifluoropropene and water, and subjecting the primary composition to conditions effective to form a secondary composition which is an

azeotrope or azeotrope-like composition consisting essentially of, or consisting of, effective amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water, and separating the secondary composition from the primary composition by a separation technique such as phase separation, distillation, or fractionation, for example. Thereafter, the secondary composition may be subjected to further separation, purification, or drying steps to obtain purified 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf). The step of modifying the relative amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water may involve adding 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) to the composition, adding water to the composition, or adding both 2-chloro-3,3,3-trifluoropropene to the composition.

**[0063]** The azeotrope or azeotrope-like composition comprising, consisting essentially of, or consisting of effective amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water can be used in the production of 2,3,3,3-tetrafluoropropene (HFO-1234yf). For example, as explained above, the azeotrope or azeotrope-like composition can be used to purify 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb), prior to step 3 of the process. 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) removed from 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) via formation of the azeotrope can be subsequently converted into further 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb), before being converted into 2,3,3,3-tetrafluoropropene (HFO-1234yf). Similarly, the azeotrope or azeotrope-like composition may be formed after step 3, if 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) is present in the crude product, e.g. by dehydrofluorination of 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) in step 3. It is also possible, though not inevitable, for the azeotrope or azeotrope-like composition to form in a reaction that produces 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) from 1,2-dichloro-3,3,3-trifluoropropane (HCFC-243db). The existence of the azeotrope or azeotrope-like composition will depend on factors such as whether the azeotropy is disrupted by other substances present. Examples of how it is possible, though not inevitable, for the azeotrope or azeotrope-like composition to form include the following:

- When water is present in the reaction as a solvent, e.g. when the reaction is conducted in an aqueous environment, such as when a base is used in an aqueous solution.
- When water is evolved in a reaction. For example, dehydrochlorinating HCFC-243db with hydroxide ions, in the presence or absence of water as a solvent, would evolve water molecules according to the following equation:  $\text{CF}_3\text{CHClCCH}_2\text{Cl} + \text{OH}^-$

→  $\text{CF}_3\text{CCl}=\text{CH}_2 + \text{Cl}^- + \text{H}_2\text{O}$ . The skilled person will appreciate that it is possible for water molecules to be evolved when other types of base, especially caustic bases, are used.

**[0064]** The following non-limiting examples serve to illustrate the invention.

### EXAMPLES

#### Example 1 – Vapor liquid equilibrium (VLE) Study

**[0065]** An ebulliometer consisting of a vacuum-jacketed tube with a dry-ice cooled condenser on top was equipped with a Quartz Thermometer. The ebulliometer was initially charged with 14.11 grams of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf). Water was then added incrementally, and the temperature of the mixture was recorded at each water increment. The mixture temperature reached a minimum value and then remained essentially constant as additional water was added, indicating the formation of a heterogeneous azeotrope. The ambient pressure during the measurements was 14.5 psia. The mixture compositions and measured temperatures are shown in Table 1. The data from Table 1 is presented graphically in Fig. 1.

TABLE 1

<b>Wt. % HCFO-1233xf</b>	<b>Wt. % Water</b>	<b>Temperature (°C)</b>
100	0.00	13.44
99.65	0.35	13.26
98.95	1.05	13.23
97.58	2.42	13.20
95.6	4.40	13.18
93.07	6.93	13.17
90.68	9.32	13.17
86.25	13.75	13.15
82.23	17.77	13.14
78.56	21.44	13.14
75.21	24.79	13.14
71.77	28.23	13.14
68.30	31.70	13.14

Wt. % HCFO-1233xf	Wt. % Water	Temperature (°C)
65.14	34.86	13.14

Example 2 – Vapor-liquid-liquid equilibrium (VLLE) measurements

**[0066]** A 50:50 by weight mixture of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water was made in a Teflon cell at 23°C. Two separate phases were observed in the cell indicating that a heterogeneous azeotrope had been formed. The upper (water-rich) and lower (2-chloro-3,3,3-trifluoropropene (HCFO-1233xf)-rich) phases were separated and analyzed. The composition of the two phases is shown in Table 2, below.

TABLE 2

Component	Upper Phase Wt.%	Lower Phase Wt.%
HCFO-1233xf	0.09	92.69
Water	99.91	7.31

Example 3 – Purification of 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf)

**[0067]** In this Example, a composition is provided which includes 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and an impurity, which may be water. An effective amount of water is added to the composition, and the composition is subjected to conditions effective to form an azeotrope or azeotrope-like composition consisting essentially of, or consisting of, effective amounts of 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and water. Then, the azeotrope or azeotrope-like composition is separated from the composition including the primary compound by a separation technique such as phase separation, distillation, and/or fractionation. Once the 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) has been separated, it may be further dried by the addition of a drying agent.

Example 4 – Separation of water as an impurity

**[0068]** In this Example, a composition is provided which includes a primary compound, such as 2-chloro-3,3,3-trifluoropropene (1233xf), together with water as an impurity. An effective amount of water is added to the composition, and the composition is subjected to conditions effective to form an azeotrope or azeotrope-like composition consisting essentially of, or consisting of, effective amounts of 2-chloro-3,3,3-trifluoropropene (1233xf) and water. Then, the azeotrope or azeotrope-like composition is

separated from the composition including the primary compound by a separation technique such as phase separation, distillation, and/or fractionation. Once the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) has been separated, it may be further dried by the addition of a drying agent.

Example 5 – Separation water as an impurity

**[0069]** In this Example, a composition is provided which includes a primary compound, such as 2-chloro-3,3,3-trifluoropropene (1233xf), together with water as an impurity. An effective amount of 2-chloro-3,3,3-trifluoropropene (1233xf) is added to the composition, and the composition is subjected to conditions effective to form an azeotrope or azeotrope-like composition consisting essentially of, or consisting of, effective amounts of 2-chloro-3,3,3-trifluoropropene (1233xf) and water. Then, the azeotrope or azeotrope-like composition is separated from the composition including the primary compound by a separation technique such as phase separation, distillation, and/or fractionation. Once the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) has been separated, it may be further dried by the addition of a drying agent.

Example 6 - Representative procedure for converting 1,2-dichloro-3,3,3-trifluoropropane (HCFC-243db) into 2-chloro-3,3,3-trifluoropropene (1233xf)

**[0070]** 86g of 12wt% NaOH solution and 36.5g 243db were charged into a shaker tube reactor. The reactor was chilled to -10°C and evacuated briefly. Then it was heated to 55°C without agitation. Once temperature reached 47°C, it was shaken and heated to 55°C. Then it was held at ~55°C for 60 min. The estimated mixing power was 30-40 HP/1000 gallons. During the reaction, the pressure increased continuously from 6.34 psig to 47 psig. Based on temperature and pressure profile, the reaction was estimated to reach the 98% conversion around 25 min. The product was analyzed by GC-MS and analysis shows about 98% of 243db was converted:

Compound	GC Area%
HCFO-1233xf	96.97%
HCFO-1233zd	0.11%

HCFC-243fa	0.43%
HCFC-243db	1.06%
HCFC-233ab	1.00%
Others	0.43%

Example 7 – Representative procedure for converting 2-chloro-3,3,3-trifluoropropene (1233xf) into 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb)

**[0071]** About 327 grams of HF, about 50 grams 1233xf, and about 75 grams SbCl<sub>5</sub> were charged into a 1-L autoclave. The reaction mixture was stirred at a temperature of about 80° C. for about 3 hours under about 620 psig of pressure. After the reaction, the reactor was cooled to about 0° C. and about 300 ml water was then added slowly into the autoclave over a period of about 45 min. After complete addition of water under stirring, the reactor was cooled to room temperature and then the overhead gases were transferred to another collecting cylinder. The yield of CF<sub>3</sub>CFCICH<sub>3</sub> was about 90% at a 1233xf conversion level of about 98%. The other major by-products were CF<sub>3</sub>CF<sub>2</sub>CH<sub>3</sub> (2%), and an unidentified isomer of a C4 compound of the general formula, C<sub>4</sub>H<sub>3</sub>Cl<sub>3</sub>F<sub>4</sub> (8%).

Example 8 – Representative procedure for converting 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) into 2,3,3,3-tetrafluoropropene (HFO-1234yf)

**[0072]** The dehydrochlorination of HCFC-244bb was carried out in one liter Parr reactor equipped with thermocouple and magnetic stirrer. 15 g Aliquat 336™ was added to reactor. Reactor was then closed and pressure tested. Afterwards 294 g of Organic mixture and 270 g of 45% KOH were added into reactor. The analysis of organic mixture using Gas Chromatography (GC) revealed 8.1 GC Area % of 1234yf, 89.5 GC Area % of 244bb, and 1.8 GC Area % of 1233xf. The stirrer was then turned on and the reactor was heated to 55°C. Upon reaching 55 °C (after about 2 hours), pressure in reactor increased from initial 10 psig to 55 psig. Reactor was held at 55 °C for 4 hours and pressure further increased to 78 psig. A GC analysis of the reactor organic content after the reaction was completed revealed 64.2 GC Area % of 1234yf, 33.2 % GC Area of 244bb, 2.2 GC Area% of 1233xf, and 0.4 GC Area% of unknowns.

The synthesis Examples described above are included to illustrate the reactions, and are not a comment on whether the claimed azeotrope of azeotrope-like composition is present in the synthetic procedure.

Example 9 – Representative purification of HCFO-1233xf

**[0073]** A composition including HCFO-1233xf and water is purified to provide a purified stream of HCFO-1233xf.

**[0074]** 1000 kg of a mixture including 926.9 kg of HCFO-1233xf and 73.1 kg of water is charged to the reboiler of a batch distillation system consisting of a reboiler, multistage rectification section packed with random packing such as IMTP<sup>®</sup> packing available from Koch-Glitsch and a condenser. The condenser is cooled with flowing chilled water at about 5°C at the inlet to the condenser. The reboiler has a half-pipe jacket for steam. The reboiler charge could be the organic phase of a mixture of HCFO-1233xf and water subjected to phase separation where the aqueous phase was decanted off the top.

**[0075]** The batch distillation system is used to distill an overhead stream containing essentially an azeotrope of HCFO-1233xf and water, leaving behind in the reboiler substantially HCFO-1233xf containing about 0.039 wt% water. Refer to Table 3 for a summary. The material in the reboiler may be further dried by passing it through a desiccant such as 3A molecular sieves.

Table 3 - Compositions

	<b>Reboiler Charge (kg)</b>	<b>Distillate (kg)</b>	<b>Bottoms (kg)</b>
HCFO-1233xf	926.9	158.0*	768.9
Water	73.1	72.8	0.3

Under these conditions, azeotropic composition is 68 wt% HCFO-1233xf. Slight excess over the azeotrope is recovered in the overhead.

Although this example shows purification in a batch distillation scheme, it can be adapted to a continuous distillation for purification by those skilled in the art.

ASPECTS

**[0076]** Aspect 1 is a composition comprising an azeotrope or azeotrope-like composition consisting essentially of effective amounts of 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and water.

**[0077]** Aspect 2 is the composition of Aspect 1, wherein the azeotrope or azeotrope-like composition has a boiling point between about 12.0°C and about 13.6°C at a pressure of between about 12.5 psia and about 16.5 psia.

**[0078]** Aspect 3 is the composition of Aspect 1 or Aspect 2, wherein the azeotrope or azeotrope-like composition consists essentially of from about 0.09 wt.% to about 92.69 wt.% 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and from about 7.31 wt.% to about 99.91 wt.% water.

**[0079]** Aspect 4 is a method of forming an azeotrope or azeotrope-like composition comprising the step of combining 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and water to form an azeotrope or azeotrope-like composition consisting essentially of effective amounts of 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and water and having a boiling point between about 12.0°C and about 13.6°C at a pressure of between about 12.5 psia and about 16.5 psia.

**[0080]** Aspect 5 is the method of Aspect 4, wherein the combining step comprises combining from about 0.09 wt.% to about 92.69 wt.% 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and from about 7.31 wt.% to about 99.91 wt.% water.

**[0081]** Aspect 6 is a method of separating impurities, including water, from 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) from a composition which 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and at least one impurity, comprising the steps of providing a composition including 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and at least one impurity, modifying the relative amounts of 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and water and subjecting the composition to conditions effective to form an azeotrope or azeotrope-like composition consisting essentially of, or consisting of, effective amounts of 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and water, and separating the azeotrope or azeotrope-like composition from the 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf).

**[0082]** Aspect 7 is the method of Aspect 6, wherein the separation step comprises at least one of phase separation, distillation, and fractionation.

**[0083]** Aspect 8 is the method according to Aspect 6 or Aspect 7, further comprising separating 2-chloro-3,3,3-trifluoropropene from the water.

- [0084]** Aspect 9 is the method of any of Aspects 6-8, wherein 2-chloro-3,3,3-trifluoropropene is separated from water using a liquid-liquid phase separation.
- [0085]** Aspect 10 is the method of any of Aspects 6-9, wherein 2-chloro-3,3,3-trifluoropropene is separated from water using distillation.
- [0086]** Aspect 11 is the method of any of Aspects 6-10, wherein 2-chloro-3,3,3-trifluoropropene is separated from water using at least one drying agent.
- [0087]** Aspect 12 is the method of any of Aspects 6-11, wherein water is removed first by liquid-liquid phase separation, then by a second method selected from the group consisting of distillation, one or more drying agent, and combinations thereof.
- [0088]** Aspect 13 is the method of any of Aspects 6-12, wherein the step of modifying the relative amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water comprises adding 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) to the composition.
- [0089]** Aspect 14 is the method of any of Aspects 6-13, wherein the step of modifying the relative amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water comprises adding water to the composition.
- [0090]** Aspect 15 is the method of any of Aspects 6-14, wherein the step of modifying the relative amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water comprises adding both 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water to the composition.
- [0091]** As used herein, the phrase “within any range defined between any two of the foregoing values” literally means that any range may be selected from any two of the values listed prior to such phrase regardless of whether the values are in the lower part of the listing or in the higher part of the listing. For example, a pair of values may be selected from two lower values, two higher values, or a lower value and a higher value.
- [0092]** As used herein, the singular forms “a”, “an” and “the” include plural unless the context clearly dictates otherwise. Moreover, when an amount, concentration, or other value or parameter is given as either a range, preferred range, or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It

is not intended that the scope of the disclosure be limited to the specific values recited when defining a range.

**[0093]** As used herein, the phrase “within any range defined between any two of the foregoing values” literally means that any range may be selected from any two of the values listed prior to such phrase regardless of whether the values are in the lower part of the listing or in the higher part of the listing. For example, a pair of values may be selected from two lower values, two higher values, or a lower value and a higher value.

**[0094]** It should be understood that the foregoing description is only illustrative of the present disclosure. Various alternatives and modifications can be devised by those skilled in the art without departing from the disclosure. Accordingly, the present disclosure is intended to embrace all such alternatives, modifications and variances that fall within the scope of the appended claims.

## CLAIMS

What is claimed is:

1. A composition comprising an azeotrope or azeotrope-like composition consisting essentially of effective amounts of 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and water.
2. The composition of claim 1, wherein the azeotrope or azeotrope-like composition has a boiling point between about 12.0°C and about 13.6°C, preferably about 13.1 to about 13.2, at a pressure of between about 12.5 psia and about 16.5 psia, preferably about 14.5 psia.
3. The composition of claim 1 or claim 2, wherein the azeotrope or azeotrope-like composition consists essentially of from about 0.09 wt.% to about 92.69 wt.% 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and from about 7.31 wt.% to about 99.91 wt.% water;  
preferably wherein the azeotrope or azeotrope-like composition consists essentially of from about 65 wt.% to about 90 wt.% 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and from about 10 wt.% to about 35 wt.% water;  
preferably the azeotrope or azeotrope-like composition consists essentially of from about 65.14 wt.% to about 86.25 wt.% 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and from about 13.75 wt.% to about 34.86 wt.% water.
4. A method of forming an azeotrope or azeotrope-like composition comprising the step of combining 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and water to form an azeotrope or azeotrope-like composition as defined in any of claims 1 to 3.
5. A method of separating impurities, including water, from 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) from a composition which 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and at least one impurity, comprising the steps of:  
providing a composition including 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and at least one impurity;  
modifying the relative amounts of 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf) and water and subjecting the composition to conditions effective to form an azeotrope or azeotrope-like composition as defined in any of claims 1 to 3; and

separating the azeotrope or azeotrope-like composition from the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf).

6. The method of claim 5, wherein the separation step comprises at least one of phase separation, distillation, and fractionation; and/or

further comprising separating 2-chloro-3,3,3-trifluoropropene from the water, using a liquid-liquid phase separation, distillation or at least one drying agent.

7. The method of claim 5, wherein water is removed first by liquid-liquid phase separation, then by a second method selected from the group consisting of distillation, one or more drying agent, and combinations thereof.

8. The method of claim 6, wherein the step of modifying the relative amounts of 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water comprises:

adding 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) to the composition;

adding water to the composition; or

adding both 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and water to the composition.

9. A method of producing 2,3,3,3-tetrafluoropropene (HFO-1234yf) comprising:

converting at least some of the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) present in the azeotrope or azeotrope-like composition defined in any of claims 1 to 3 into 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb); and

converting at least some of the 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) into 2,3,3,3-tetrafluoropropene (HFO-1234yf).

10. The method of claim 9, wherein the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) is separated from the water before being converted into 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb), preferably by a method as defined in claim 6 or claim 7.

11. The method of claim 9 or claim 10, wherein converting at least some of the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) into 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-

244bb) comprises reacting the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) with HF, preferably anhydrous HF, in the presence of a catalyst.

12. The method of claim 11, wherein:

the catalyst comprises metal halide catalyst, preferably selected from  $\text{SbCl}_5$ ,  $\text{SbF}_5$ ,  $\text{TiCl}_4$  or a combination thereof, or is a fluorosulfonic acid; and/or

converting at least some of the 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) into 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) is carried out at a temperature of 5-100°C, preferably 50-100°C.

13. The method of any of claims 9 to 12, wherein converting at least some of the 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) into 2,3,3,3-tetrafluoropropene (HFO-1234yf) comprises reacting the 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) with a base;

preferably in an aqueous environment, preferably in the presence of a phase transfer catalyst, preferably an ammonium halide, preferably a trialkylammonium halide of a tetraalkylammonium halide, preferably a trialkylammonium chloride of a tetraalkylammonium chloride; and/or

preferably the base is a caustic base, preferably an alkali metal hydroxide, preferably KOH or NaOH; and/or

preferably at a temperature of from about 0°C to about 100°C, preferably from about 20°C to about 90°C, preferably from about 50°C to about 90°C, preferably from about 60°C to about 80°C.

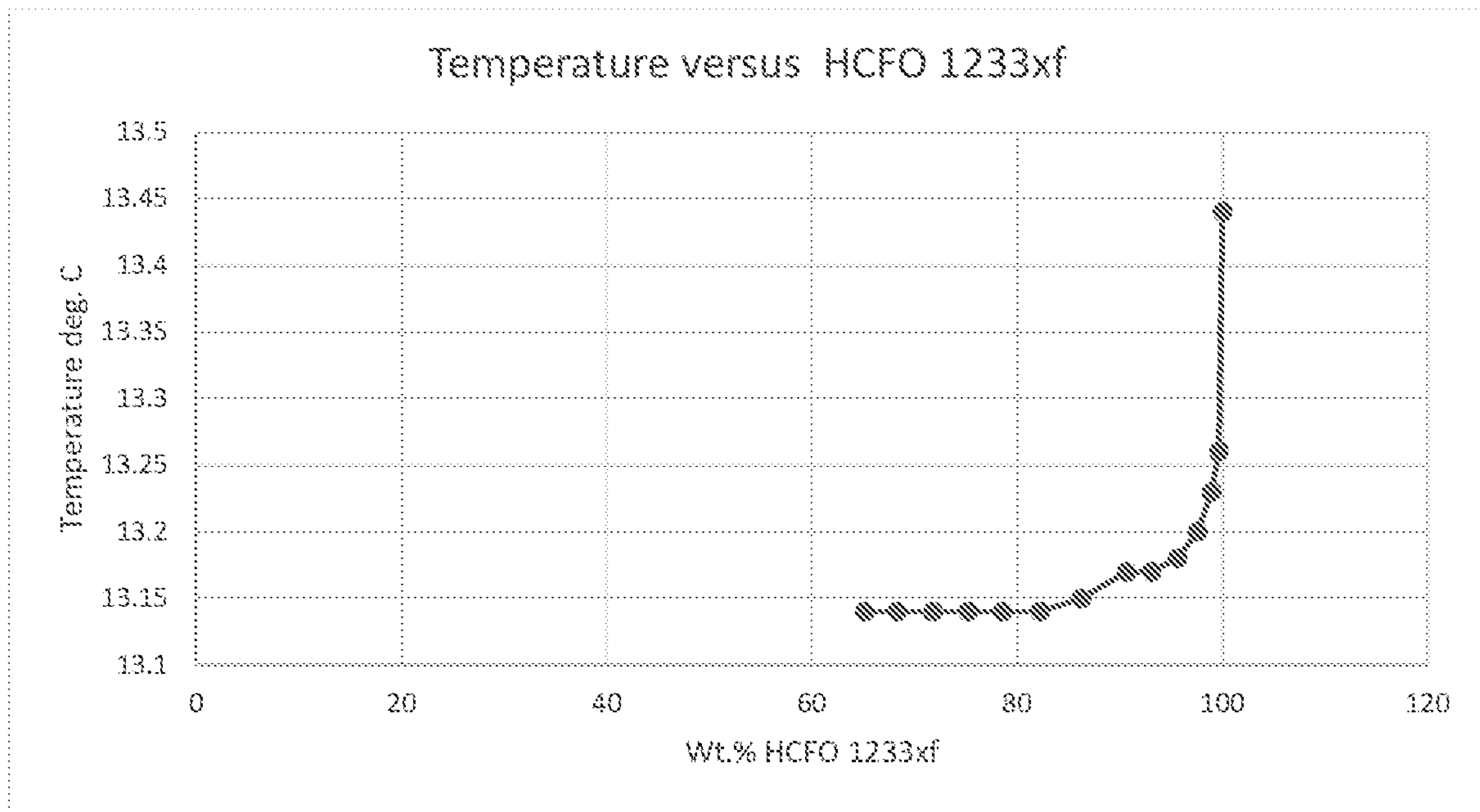


FIGURE 1

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IB2020/020072**A. CLASSIFICATION OF SUBJECT MATTER**

C09K 5/20(2006.01)i, C07C 17/23(2006.01)i, C07C 17/42(2006.01)i, C07C 21/18(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C09K 5/20; A01N 25/02; C07C 17/21; C07C 17/38; C07C 17/42; C07C 19/10; C07C 21/18; C08J 9/00; C09K 3/00; C11D 17/00; C07C 17/23

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models  
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) &amp; Keywords: azeotrope composition, 2-chloro-3,3,3-trifluoropropene (HFCO-1233xf), water, phase separation, producing 2,3,3,3-tetrafluoropropene (HFO-1234yf), 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 3040326 A1 (DAIKIN INDUSTRIES, LTD.) 06 July 2016 See abstract; claim 1.	1-3
X	WO 2008-121776 A1 (ARKEMA INC. et al.) 09 October 2008 See claims 1-12.	1-3
A	US 2016-0152536 A1 (ARKEMA INC.) 02 June 2016 See claims 1-13.	1-3
A	US 2014-0235904 A1 (HONEYWELL INTERNATIONAL INC.) 21 August 2014 See the whole document.	1-3
A	US 2011-0275724 A1 (HULSE, RYAN et al.) 10 November 2011 See the whole document.	1-3
A	EP 2108638 A1 (HONEYWELL INTERNATIONAL INC.) 14 October 2009 See the whole document.	1-3
A	US 2009-0224207 A1 (PHAM, HANG T. et al.) 10 September 2009 See the whole document.	1-3

 Further documents are listed in the continuation of Box C. See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

05 February 2021 (05.02.2021)

Date of mailing of the international search report

09 February 2021 (09.02.2021)

Name and mailing address of the ISA/KR

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**INTERNATIONAL SEARCH REPORT**International application No.  
**PCT/IB2020/020072****Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: 6-8, 12  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
Claims 6-8, 12 refer to multiple dependent claims which do not comply with PCT Rule 6.4(a).
  
3.  Claims Nos.: 4, 5, 9-11, 13  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

- Remark on Protest**
- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
  - The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
  - No protest accompanied the payment of additional search fees.

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/IB2020/020072**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 3040326 A1	06/07/2016	CN 106458802 A	22/02/2017
		CN 111205163 A	29/05/2020
		DK 3040326 T3	30/03/2020
		EP 3040326 A4	05/07/2017
		EP 3040326 B1	08/01/2020
		EP 3130649 A1	15/02/2017
		EP 3130649 A8	29/03/2017
		EP 3549995 A1	09/10/2019
		ES 2774378 T3	20/07/2020
		JP 2016-069634 A	09/05/2016
		JP 2016-190884 A	10/11/2016
		JP 2020-090688 A	11/06/2020
		KR 10-2016-0135263 A	25/11/2016
		KR 10-2018-0130604 A	07/12/2018
		US 10669464 B2	02/06/2020
		US 2016-0230060 A1	11/08/2016
		US 2017-0058170 A1	02/03/2017
		US 2020-0263069 A1	20/08/2020
		WO 2016-047298 A1	31/03/2016
		WO 2008-121776 A1	09/10/2008
CA 2681602 A1	09/10/2008		
CA 2681602 C	28/10/2014		
CA 2681605 A1	09/10/2008		
CA 2681825 A1	09/10/2008		
CA 2681825 C	12/05/2015		
CN 101652411 A	17/02/2010		
CN 101652411 B	23/01/2013		
CN 101652414 A	17/02/2010		
CN 101652414 B	27/06/2012		
CN 101715468 A	26/05/2010		
CN 105001440 A	28/10/2015		
EP 2129710 A1	09/12/2009		
EP 2129710 A4	24/03/2010		
EP 2129710 B1	09/11/2011		
EP 2129711 A1	09/12/2009		
EP 2129711 A4	24/03/2010		
EP 2129711 B1	14/12/2011		
EP 2129711 B2	10/07/2019		
EP 2129712 A1	09/12/2009		
EP 2129712 A4	24/03/2010		
EP 2129712 B1	08/08/2012		
ES 2376290 T3	12/03/2012		
ES 2376290 T5	19/03/2020		
ES 2377420 T3	27/03/2012		
ES 2388457 T3	15/10/2012		
JP 05584114 B2	03/09/2014		
JP 05762737 B2	12/08/2015		
JP 05763338 B2	12/08/2015		

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/IB2020/020072**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		JP 06030710 B2	24/11/2016
		JP 06034335 B2	30/11/2016
		JP 06692734 B2	13/05/2020
		JP 2014-196516 A	16/10/2014
		JP 2015-165032 A	17/09/2015
		JP 2017-071780 A	13/04/2017
		PL 2129710 T3	29/06/2012
		PL 2129711 T3	31/07/2012
		PL 2129711 T5	21/09/2020
		PL 2129712 T3	29/03/2013
		US 08648123 B2	11/02/2014
		US 08772364 B2	08/07/2014
		US 08895635 B2	25/11/2014
		US 09206297 B2	08/12/2015
		US 2010-0105789 A1	29/04/2010
		US 2010-0112328 A1	06/05/2010
		US 2010-0113629 A1	06/05/2010
		US 2012-0101177 A1	26/04/2012
		US 2012-0108688 A1	03/05/2012
		US 2013-0281557 A1	24/10/2013
		US 2014-0031442 A1	30/01/2014
		US 2014-0213678 A1	31/07/2014
		US 2015-0038603 A1	05/02/2015
		US 2015-0299414 A1	22/10/2015
		US 2017-321027 A1	09/11/2017
		US 2019-144629 A1	16/05/2019
		WO 2008-121778 A1	09/10/2008
		WO 2008-121779 A1	09/10/2008
US 2016-0152536 A1	02/06/2016	CN 105358233 A	24/02/2016
		CN 105358233 B	16/02/2018
		EP 3019267 A1	18/05/2016
		EP 3019267 A4	15/03/2017
		EP 3019267 B1	30/10/2019
		JP 2016-523965 A	12/08/2016
		US 9725384 B2	08/08/2017
		WO 2015-006258 A1	15/01/2015
US 2014-0235904 A1	21/08/2014	CN 103946196 A	23/07/2014
		CN 103946196 B	14/12/2016
		EP 2751057 A1	09/07/2014
		EP 2751057 A4	12/08/2015
		JP 2014-534177 A	18/12/2014
		JP 2018-109053 A	12/07/2018
		JP 6613330 B2	27/11/2019
		KR 10-2003550 B1	25/07/2019
		KR 10-2014-0071458 A	11/06/2014
		US 9540295 B2	10/01/2017
		WO 2013-049743 A1	04/04/2013

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0275724 A1	10/11/2011	CN 102939352 A	20/02/2013
		CN 102939352 B	03/08/2016
		EP 2566928 A2	13/03/2013
		EP 2566928 A4	13/01/2016
		EP 2566928 B1	21/03/2018
		EP 3354706 A1	01/08/2018
		JP 2013-529234 A	18/07/2013
		US 8951431 B2	10/02/2015
		WO 2011-139945 A2	10/11/2011
		WO 2011-139945 A3	01/03/2012
EP 2108638 A1	14/10/2009	JP 2009-249632 A	29/10/2009
		JP 5409085 B2	05/02/2014
		KR 10-1655257 B1	07/09/2016
		KR 10-2009-0107931 A	14/10/2009
		US 2009-0256110 A	15/10/2009
		US 8034251 B1	11/10/2011
US 2009-0224207 A1	10/09/2009	CN 101607866 A	23/12/2009
		CN 101607866 B	11/02/2015
		EP 2098499 A1	09/09/2009
		EP 2098499 B1	03/09/2014
		EP 2098499 B2	22/11/2017
		JP 2009-215294 A	24/09/2009
		JP 5430977 B2	05/03/2014
		KR 10-1594018 B1	15/02/2016
		KR 10-2009-0096356 A	10/09/2009
		US 10259760 B2	16/04/2019
		US 2009-0227822 A1	10/09/2009
		US 2014-0012052 A1	09/01/2014
		US 2017-0183278 A1	29/06/2017
		US 8546624 B2	01/10/2013
US 9464013 B2	11/10/2016		