

TITLE

PROCESS OF MAKING HFO-1252ZC FROM PYROLYSIS OF
CHLORODIFLUOROMETHANE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application 63/527,100 filed July 17, 2023, the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention is directed to processes for producing difluoroolefins, compositions and uses thereof.

BACKGROUND

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

[0004] This regulatory landscape is continuously evolving, taking into consideration properties beyond just ODP and GWP. More particularly, there is a need for refrigerant compositions that not only meet low ODP standards and have low global warming potentials, but that also exhibit low or no flammability, provide

superior performance in a variety of applications and which meet the standards of evolving regulations.

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

[0006] Some fluoropropenes, particularly difluoropropenes such as 1,1-difluoropropene (HFO-1252zc, $\text{CH}_3\text{CH}=\text{CF}_2$), are such potential new refrigerants. Therefore, there is a need for efficient and effective methods of preparing difluoropropenes such as such as HFO-1252zc, as well as intermediates and compositions thereof.

SUMMARY

[0007] The present invention relates to processes of making a difluoroolefin by pyrolysis of a hydrochlorofluorocarbon and hydrocarbon or hydrocarbon derivative. In some embodiments, the difluoroolefin is a difluoropropene. In some embodiments, the difluoroolefin is HFO-1252zc.

[0008] In one aspect, the invention relates to a process for producing HFO-1252zc. The process comprises contacting chlorodifluoromethane (HCFC-22) and one of a hydrocarbon and a hydrocarbon derivative in a heated reaction zone to form HFO-1252zc.

[0009] In one aspect, the invention relates to a composition comprising HFO-1252zc and one or more additional compounds selected from chlorodifluoromethane (HCFC-22), ethylene (HC-1150), 2-fluoropropene (HFO-1261yf), 1,1-difluorocyclopropane (HFC-C252), 1,1,1-trifluoropropane (HFC-263fb), 3,3,3-trifluoropropene (HFO-1243zf), octafluorocyclobutane (FC-C318), hexafluorocyclobutane (HFC-C336), hexafluorobutane (HFC-374) isomers and chlorofluoropropene (HCFO-1251).

[0010] In one aspect, the invention relates to a composition comprising HFO-1252zc and one or more additional compounds selected from chlorodifluoromethane (HCFC-22), ethane, ethanal, chloroethane, ethanol, and 3,3,4,4-tetrafluoro-1-butene.

[0011] 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. In case of conflict, the present specification, including definitions, will control. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, suitable methods and materials are described below. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

DETAILED DESCRIPTION

[0012] 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.

[0013] In one aspect, the present invention relates to processes of making HFO-1252zc by pyrolysis of a mixed feed containing HCFC-22 and a hydrocarbon (such as ethylene) or a hydrocarbon derivative (such as ethanol), in the absence of added catalyst, by pyrolysis at temperatures ranging from 450°C to 800°C. Residence time in the reactor may span from about 5 seconds to about 180 seconds.

[0014] Before addressing details of embodiments described herein, certain terms are defined or clarified as follows.

[0015] 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 is true (or present).

[0016] The transitional phrase “consisting essentially of” is used to define a composition, method that includes materials, steps, features, components, or elements, in addition to those literally disclosed provided that these additional included materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention, especially the mode of action to achieve the desired result of any of the processes of the present invention. The term ‘consisting essentially of’ occupies a middle ground between “comprising” and “consisting of.”

[0017] 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.

[0018] Where applicants have defined an invention or a portion thereof with an open-ended term such as “comprising,” it should be readily understood that (unless otherwise stated) the description should be interpreted to also include such an invention using the terms “consisting essentially of” or “consisting of.”

[0019] 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.

[0020] 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/or 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.

[0021] As used herein GC/FID peak area correlates to the amount of a compound present as a proportion of the total area of all detected peaks. FID area% can be converted to mol% using response factors either calculated or measured.

[0022] As used herein, the term “about” is meant to account for variations due to experimental error (e.g., plus or minus approximately 10% of the indicated value. $\pm 1\%$, $\pm 2\%$, ± 3 , ... $\pm 10\%$). All measurements reported herein are understood to be modified by the term “about,” whether or not the term is explicitly used, unless explicitly stated otherwise.

[0023] Certain embodiments disclosed herein relate to a process of making HFO-1252zc by contacting a hydrochlorofluorocarbon, such as chlorodifluoromethane, with a halogen-free compound, including but not limited to ethanol or ethylene, at an elevated temperature.

[0024] One embodiment disclosed herein relates to the pyrolysis of a mixed feed containing a hydrochlorofluorocarbon and a hydrocarbon or hydrocarbon derivative, in the absence of added catalyst, to produce a difluoropropene, and more preferably HFO-1252zc.

[0025] In one embodiment, the pyrolysis which accomplishes the production of HFO-1252zc from the hydrochlorofluorocarbon and hydrocarbon or hydrocarbon derivative is suitably conducted at a temperature between about 470°C to about 750°C. In another embodiment, the pyrolysis is conducted at a temperature of from about 500°C to about 700°C. In another embodiment, the pyrolysis is conducted at a temperature of from about 550°C to about 650°C. The pyrolysis temperature is the temperature of the gases inside the reaction zone at about the mid-point.

[0026] In one embodiment, the residence time of gases in the reaction zone is from about 5 second to about 180 seconds. In other embodiments, the residence time is one of about 5 seconds, about 10 seconds, about 15 seconds, about 20 seconds, about 25 seconds, about 30 seconds, about 35 seconds, about 40 seconds, about 45 seconds, about 50 seconds, about 55 seconds, about 60 seconds, about 65 seconds, about 70 seconds, about 75 seconds, about 80 seconds, about 85 seconds, about 90 seconds, about 95 seconds, or about 100 seconds to one of less than about 150 seconds, less than about 155 seconds, less

than about 160 seconds, less than about 165 seconds, less than about 170 seconds, less than about 175 seconds or less than or equal to about 180 seconds.

[0027] In some embodiments, the hydrofluorocarbon is chlorodifluoromethane (HCFC-22, CHF_2Cl). In some embodiments, the hydrocarbon is ethylene. In some embodiments, the hydrocarbon derivative is an alcohol hydrocarbon derivative, and more preferably ethanol. In some embodiments, the hydrofluorocarbon is HCFC-22 and the hydrocarbon is ethylene. In some embodiments, the hydrofluorocarbon is HCFC-22 and the hydrocarbon derivative is ethanol.

[0028] Certain embodiments of the invention disclosed herein relate to processes of making HFO-1252zc by thermolytic treatment of HCFC-22 in the presence of one of ethanol or ethylene at a temperature of between about 470°C to about 750°C, preferably at a temperature of at least about 500°C.

[0029] The pyrolysis can be conducted in the presence of one or more unreactive diluent gases, which diluent gases do not react under the pyrolysis conditions. Such unreactive diluent gases include the inert gases nitrogen, argon, and/or helium. Of note are processes where the amount of inert gas, such as nitrogen, makes up about 20-80% (by volume or mol) of the feed stream to the pyrolysis reactor. Nitrogen is a preferred inert gas because of its comparatively low cost.

[0030] Certain embodiments of the invention disclosed herein relate to processes of making HFO-1252zc by exposing a mixture of HCFC-22, one of ethanol or ethylene, and optionally nitrogen to pyrolytic temperatures.

[0031] Embodiments of the invention disclosed herein relate to processes of making HFO-1252zc by contacting HCFC-22 and one of ethanol or ethylene in the presence of heat at a temperature between about 470°C to about 750°C, preferably at a temperature between about 500°C and about 700°C, preferably at a temperature of about 500°C, about 550°C, about 600°C, about 650°C or about 700°C, and all values and ranges therebetween.

[0032] Embodiments of the invention disclosed herein relate to processes of making HFO-1252zc by contacting HCFC-22 and one of ethanol or ethylene in the presence of heat at a temperature between about 470°C to about 750°C and with a residence time of gases in the reaction zone of from about 5 to about 180 seconds.

[0033] Certain embodiments of the invention disclosed herein relate to processes of making HFO-1252zc by heating a mixture of HCFC-22 and one of ethanol or ethylene to a temperature between about 470°C to about 750°C, preferably at a temperature between about 500°C and about 700°C, preferably at a temperature of about 500°C, about 550°C, about 600°C, about 650°C or about 700°C, and all values and ranges therebetween.

[0034] Certain embodiments of the invention disclosed herein relate to processes of making HFO-1252zc by heating a mixture of HCFC-22 and one of ethanol or ethylene to a temperature between about 470°C to about 750°C in a reaction zone with a residence time of gases in the reaction zone of from about 5 to about 180 seconds.

[0035] Embodiments of the invention disclosed herein relate to processes of making HFO-1252zc with HCFC-22 in the presence of one of ethanol or ethylene, at a mole ratio of HCFC-22:ethylene or HCFC-22:ethanol of about 0.3:1 to about 2:1, optionally in the presence of nitrogen. Nitrogen can be present in an amount of 20-80% based on the total amount of the reactant stream. The reaction is preferably carried out in the absence of a catalyst.

[0036] Embodiments of the invention disclosed herein relate to processes of making HFO-1252zc by contacting HCFC-22 in the presence of one of ethanol or ethylene, optionally in the presence of nitrogen, at mole ratio of HCFC-22:ethylene or HCFC-22:ethanol of about 0.3:1 to about 2:1 at a temperature between about 500°C and about 750°C. Nitrogen can be present in an amount of 20-80% based on the total amount of the reactant stream. The reaction is preferably carried out in the absence of a catalyst.

[0037] Embodiments of the invention disclosed herein relate to processes of making HFO-1252zc by contacting HCFC-22 in the presence of one of ethanol or ethylene, optionally in the presence of nitrogen, at mole ratio of HCFC-22:ethylene or HCFC-22:ethanol of about 0.3:1 to about 2:1 at temperature between about 500°C and about 750°C with a residence time of about 5 seconds to about 180 seconds. Nitrogen can be present in an amount of 20-80% based on the total amount of the reactant stream. The reaction is preferably carried out in the absence of a catalyst.

[0038] One embodiment disclosed herein relate to a process of making HFO-1252zc by subjecting HCFC-22 and ethanol to pyrolysis.

[0039] One embodiment disclosed herein relate to a process of making HFO-1252zc by subjecting HCFC-22 and ethanol in the presence of a nitrogen diluent to pyrolysis, preferably wherein the amount of nitrogen is between 20 and 80% of the feed stream comprising HCFC-22, ethanol, and N₂.

[0040] One embodiment disclosed herein relate to a process of making HFO-1252zc by subjecting HCFC-22 and ethanol, in the presence of a diluent such as nitrogen, to pyrolysis, wherein the ratio of HCFC-22:ethanol is between about 0.3:1 to about 2:1.

[0041] In some embodiments, the pyrolysis reaction of HCFC-22 and ethanol to form HFO-1252zc is carried out at a pressure of between about 0 psig and about 300 psig, including but not limited to 1 psig, 2 psig, 3 psig, 4 psig, 5 psig, 10 psig, 15 psig, 20 psig, 25 psig, 30 psig, 40 psig, 50 psig, 60 psig, 70 psig, 80 psig, 90 psig, 100 psig, 125 psig, 150 psig, 175 psig, 200 psig, 250 psig or 300 psig, and all values and ranges therebetween, including between 0, 1 psig, 2 psig, 3 psig, 4 psig, 5 psig, 10 psig, 15 psig, 20 psig, 25 psig, 30 psig, 40 psig, 50 psig, 60 psig, 70 psig, 80 psig, 90 psig, 100 psig, 125 psig, or 150 psig and 175 psig, 200 psig, 250 psig or 300 psig, or between about 0.5 psig and about 5 psig, or between about 0.5 psig and about 2.5 psig, or between about 0.5 and about 1.5 psig, inclusive of all values and ranges therebetween.

[0042] One embodiment disclosed herein relates to a process of making HFO-1252zc by subjecting HCFC-22 and ethanol, at a mole ratio of about 0.3:1 to about 2:1, in the presence of a diluent such as nitrogen, to pyrolysis, wherein the amount of nitrogen is between 20 and 80% of the feed stream comprising HCFC-22, ethanol, and N₂, and wherein the pressure of the reaction is between about 0 psig and about 300 psig, including but not limited to 1 psig, 2 psig, 3 psig, 4 psig, 5 psig, 10 psig, 15 psig, 20 psig, 25 psig, 30 psig, 40 psig, 50 psig, 60 psig, 70 psig, 80 psig, 90 psig, 100 psig, 125 psig, 150 psig, 175 psig, 200 psig, 250 psig or 300 psig, and all values and ranges therebetween, including between 0, 1 psig, 2 psig, 3 psig, 4 psig, 5 psig, 10 psig, 15 psig, 20 psig, 25 psig, 30 psig, 40 psig, 50 psig, 60 psig, 70 psig, 80 psig, 90 psig, 100 psig, 125 psig, or 150 psig and 175 psig, 200 psig, 250 psig or 300 psig,

or between about 0.5 psig and about 5 psig, or between about 0.5 psig and about 2.5 psig, or between about 0.5 and about 1.5 psig, inclusive of all values and ranges therebetween.

[0043] One embodiment disclosed herein relate to a process of making HFO-1252zc by subjecting HCFC-22 and ethylene to pyrolysis.

[0044] One embodiment disclosed herein relate to a process of making HFO-1252zc by subjecting HCFC-22 and ethylene in the presence of a nitrogen diluent to pyrolysis, preferably wherein the amount of nitrogen is between 20 and 80% of the feed stream comprising HCFC-22, ethylene, and N₂.

[0045] One embodiment disclosed herein relate to a process of making HFO-1252zc by subjecting HCFC-22 and ethylene, in the presence of a diluent such as nitrogen, to pyrolysis, wherein the ratio of HCFC-22:ethylene is between about 0.3:1 to about 2:1.

[0046] In some embodiments, the pyrolysis reaction of HCFC-22 and ethylene to form HFO-1252zc is carried out at a pressure of between about 0 psig and about 300 psig, including but not limited to 1 psig, 2 psig, 3 psig, 4 psig, 5 psig, 10 psig, 15 psig, 20 psig, 25 psig, 30 psig, 40 psig, 50 psig, 60 psig, 70 psig, 80 psig, 90 psig, 100 psig, 125 psig, 150 psig, 175 psig, 200 psig, 250 psig or 300 psig, and all values and ranges therebetween, including between 0, 1 psig, 2 psig, 3 psig, 4 psig, 5 psig, 10 psig, 15 psig, 20 psig, 25 psig, 30 psig, 40 psig, 50 psig, 60 psig, 70 psig, 80 psig, 90 psig, 100 psig, 125 psig, or 150 psig and 175 psig, 200 psig, 250 psig or 300 psig, or between about 0.5 psig and about 5 psig, or between about 0.5 psig and about 2.5 psig, or between about 0.5 and about 1.5 psig, inclusive of all values and ranges therebetween.

[0047] One embodiment disclosed herein relates to a process of making HFO-1252zc by subjecting HCFC-22 and ethylene at a mole ratio of about 0.3:1 to about 2:1, in the presence of a diluent such as nitrogen, to pyrolysis, wherein the amount of nitrogen is between 20 and 80% of the feed stream comprising HCFC-22, ethylene, and N₂, and wherein the pressure of the reaction is between about 0 psig and about 300 psig.

[0048] Any of the processes described herein further comprise recovering HFO-1252zc. In some embodiments, any of the processes disclosed herein may further comprise separating, recovering and recycling unconverted feeds selected from one of chlorodifluoromethane, ethanol, and ethene (e.g., to the heated reaction zone).

[0049] Certain embodiments of the invention disclosed herein are compositions comprising, consisting essentially of, or consisting of HFO-1252zc and one or more additional compounds identified in Table 1 other than HFO-1252zc.

Table 1

Ashrae Ref.	Chemical Name	Structure
HC-1150	ethylene (HC-1150)	$\text{CH}_2=\text{CH}_2$
HFC-22	chlorodifluoromethane (HFC-22)	CHClF_2
HFO-1261yf	2-fluoro-1-propene (HFO-1261yf)	$\text{CH}_2=\text{CF}-\text{CH}_3$
C252	1,1-difluorocyclopropane (C252)	Cyclic $\text{CF}_2-\text{CH}_2\text{CH}_2$
HFO-1252zc	1,1-difluoropropene (HFO-1252zc)	$\text{CF}_2=\text{CHCH}_3$
HFC-263fb	1,1,1-trifluoropropane (HFC-263fb)	$\text{CF}_3\text{CH}_2\text{CH}_3$
C318	1,1,2,2,3,3,4,4-octafluorobutane (FC-318)	cyclic $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2$
C336	1,1,2,2,3,3-hexafluoro-cyclobutane (HFC-336)	cyclic $\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2$
HFC-374	hexafluorobutane (HFC-374) isomers	$\text{C}_4\text{H}_6\text{F}_4$
HCFO-1251	chlorofluoropropene (HCFO-1251)	$\text{C}_3\text{H}_4\text{ClF}$
HFO-1243zf	3,3,3-trifluoropropene (HFO-1243zf)	CF_3CHCH_3
	Ethane	C_2H_6
	Ethanal	CH_3CHO
	ethanol	$\text{C}_2\text{H}_5\text{OH}$
HCC-160	chloroethane	$\text{CH}_3\text{CH}_2\text{Cl}$
HFO-1354fzc	3,3,4,4-tetrafluoro-1-butene	$\text{CH}_2=\text{CHCF}_2\text{CHF}_2$

[0050] Embodiments disclosed herein relate to compositions comprising, consisting of or consisting essentially of HFO-1252zc and one or more additional compounds selected from HCFC-22, ethylene (HC-1150, $\text{CH}_2=\text{CH}_2$), 2-fluoropropene (HFO-1261yf, $\text{CH}_2=\text{CF}-\text{CH}_3$), 1,1-difluorocyclopropane (HFC-C252, cyclic $\text{CF}_2-\text{CH}_2\text{CH}_2$), 1,1,1-trifluoropropane (HFC-263fb, $\text{CF}_3\text{CH}_2\text{CH}_3$), 3,3,3-trifluoropropene (HFO-1243zf, $\text{CF}_3\text{CH}=\text{CH}_2$), octafluorocyclobutane (FC-C318, cyclic $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2$), hexafluorocyclobutane (HFC-C336, cyclic $\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2$), $\text{C}_4\text{H}_6\text{F}_4$ (HFC-374) isomers and $\text{C}_3\text{H}_4\text{ClF}$ (HCFO-1251).

[0051] Embodiments disclosed herein relate to compositions comprising, consisting of or consisting essentially of HFO-1252zc and one or more additional

compounds selected from HCFC-22, HC-1150, HFO-1261yf, HFC-C252, HFC-263fb, FC-C318, HFC-C336, HFC-374 isomers and HCFO-1251.

[0052] Embodiments disclosed herein relate to compositions comprising, consisting of or consisting essentially of HFO-1252zc and one or more additional compounds selected from HC-22, HC-1150, HFC-263fb, HFC-C252, FC-C318, HFC-C336, and HFC-374 isomers.

[0053] Embodiments disclosed herein relate to compositions comprising, consisting of or consisting essentially of HFO-1252zc and one or more additional compounds selected from HC-1150, HCFC-22, HFO-1243zf, HFC-263fb, FC-C318, HFC-C336, and HFC-374 isomers.

[0054] Embodiments disclosed herein relate to compositions comprising, consisting of or consisting essentially of HFO-1252zc and one or more additional compounds selected from HCFC-22, ethane, ethanal, chloroethane, ethanol, and 3,3,4,4-tetrafluoro-1-butene.

[0055] Embodiments disclosed herein relate to compositions comprising, consisting of or consisting essentially of HFO-1252zc and one or more additional compounds selected from chloroethane, ethanol and 3,3,4,4-tetrafluoro-1-butene.

[0056] In a preferred embodiment, compositions according to the present invention are free of or substantially free of Group A Fluorinated Substances. In one embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that (i) contains at least one fully fluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) carbon atom (without any H/Cl/Br/I attached to it); and (ii) meets the criterion for persistence in soil/sediment and water established in Annex XIII (Section 1.1.1) of the European Union's REACH Regulation (<https://reachonline.eu/reach/en/annex-xiii-1-1.1-1.1.1.html> as accessed on May 2, 2023) and referenced in the Annex XV Restriction Report dated March 22, 2023, the disclosure of which is hereby incorporated by reference (<https://echa.europa.eu/documents/10162/f605d4b5-7c17-7414-8823-b49b9fd43aea> as accessed on May 2, 2023).

[0057] In another embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that has a Henry's Law constant ≤ 250

$\text{Pa}\cdot\text{m}^3/\text{mol}$ and contains at least one fully fluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) carbon atom (without any H/Cl/Br/I attached to it).

[0058] In embodiments, Group A Fluorinated Substances include, but are not limited to, TFA.

[0059] The phrase "free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by gas chromatography with a flame ionization detector, gas chromatography with a mass detector by analysis of a gas sample or liquid sample, and/or ion chromatography by analysis of a water sample after bubbling the thermal fluid through water. Such methodologies are well known to those skilled in the art. The phrase "substantially free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is > 0 wt.% and ≤ 5 wt.%, or > 0 wt.% and ≤ 4 wt.%, or > 0 wt.% and ≤ 3 wt.%, or > 0 wt.% and ≤ 2 wt.%, or > 0 wt.% and ≤ 1 wt.%, and all values and ranges therebetween, when measured by gas chromatographic (GC) techniques, for example gas chromatography (GC) with a flame ionization or electron-capture detector, or GC coupled with a mass detector (gas chromatography/mass spectral (GC/MS) method), by ion chromatograph(IC) or ion chromatography mass spectrometry (IC-MS) techniques, or by high-performance liquid chromatography (HPLC) or high-performance liquid chromatography mass spectrometry (HPLC-MS) techniques. The TFA analytical standard may be used in either gas chromatography or ion chromatography and is available from, for example, Sigma Aldrich.

[0060] In a preferred embodiment, degradation products of compositions according to the present invention are free of or substantially free of Group A Fluorinated Substances. The phrase "free of" as used herein with respect to the formation of Group A Fluorinated Substances as degradation products of the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during tropospheric degradation of the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by GC techniques, for

example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques. The phrase "substantially free of" as used herein with respect to the formation of Group A Fluorinated Substances by the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during tropospheric degradation of the compositions is $> 0\%$ and $\leq 5\%$, or $> 0\%$ and $\leq 4\%$, or $> 0\%$ and $\leq 3\%$, or $> 0\%$ and $\leq 2\%$, or $> 0\%$ and $\leq 1\%$, and all values and ranges therebetween, when measured by GC techniques, for example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques.

[0061] Certain embodiments of the invention disclosed herein relate to compositions comprising, consisting essentially of, or consisting of HFO-1252zc, and are free of or substantially free of Group A Fluorinated Substances. In some embodiments, compositions of the present invention comprise, consist essentially of, or consist of HFO-1252zc, and degradation products of such compositions are free of or substantially free of Group A Fluorinated Substances, as defined herein.

[0062] Certain embodiments of the invention disclosed herein relate to compositions comprising, consisting essentially of, or consisting of HFO-1252zc and one or more of the additional compounds, and are free of or substantially free of Group A Fluorinated Substances. In some embodiments, compositions of the present invention comprise, consist essentially of, or consist of HFO-1252zc and one or more of the additional compounds, and degradation products of such compositions are free of or substantially free of Group A Fluorinated Substances, as defined herein.

[0063] As disclosed herein, conversion of HCFC-22 is conducted at temperatures above about 500°C , i.e., under pyrolytic conditions. Pyrolysis, as the term is used herein, means a chemical change produced by heating in the absence of catalyst. Pyrolysis reactors generally comprise three zones: a) a preheat zone, in which reactants are brought close to the reaction temperature; b) a reaction zone, in which reactants reach reaction temperature and are at least partially pyrolyzed, and products and any byproducts form; and c) a quench zone, in which the stream exiting the reaction zone is cooled to stop the pyrolysis reaction. Laboratory-scale

reactors have a reaction zone, but the preheating and quenching zones may be omitted.

[0064] The reactor for carrying out the pyrolysis may be of any shape consistent with the process, but is preferably a cylindrical tube, either straight or coiled. Although not critical, such reactors typically have an inner diameter of from about 1.3 to about 5.1 cm (about 0.5 to about 2 inches). Heat is applied to the outside of the tube, with the chemical reaction taking place on the inside of the tube. The reactor and its associated feed lines, effluent lines and associated units should be constructed, at least as regards the surfaces exposed to the reactants and products, of materials resistant to hydrogen fluoride. Typical materials of construction include stainless steels, in particular of the austenitic type, the well-known high nickel alloys, such as nickel-copper alloys commercially available from Special Metals Corp. (New Hartford, N.Y.) under the trademark Monel®, nickel-based alloys commercially available from Haynes International (Kokomo, Ind.) under the trademark Hastelloy® (hereinafter referred to as “Hastelloy®”) and nickel-chromium alloys commercially available from Special Metals Corp. under the trademark Inconel®, and copper-clad steel.

[0065] Where the reactor is exposed to high temperatures, the reactor may be constructed of more than one material. For example, the outer surface layer of the reactor should be chosen for the ability to maintain structural integrity and resist corrosion at the pyrolysis temperature, while the inner surface layer of the reactor should be chosen of materials resistant to attack by, that is, inert to, the reactant and products. In the case of the present process, the product hydrogen fluoride is corrosive to certain materials. Thus, the reactor may be constructed of an outer material chosen for physical strength at high temperatures and an inner material chosen for resistance to corrosion by the reactants and products under the temperature of the pyrolysis.

[0066] In some embodiments, the free volume of the reaction zone is at least about 80%, preferably at least about 90%, and more preferably about 95%. The free volume is the volume of the reaction zone minus the volume of the material that makes up the reactor packing.

[0067] A number of reactor configurations are possible, including but not limited to, packed bed tube or column reactors, operated in batch, semi-batch or continuous modes. In addition to the reactors disclosed herein, preheaters and vaporizers, heat exchangers, feed and effluent lines, units associated with mass transfer, contacting vessels (pre-mixers), distillation columns, and valving associated with reactors, heat exchangers, vessels, columns, and units that are used in the processes of various embodiments disclosed herein should be constructed of materials resistant to corrosion.

[0068] Aspects of the present invention will now be described with reference to the following Examples.

EXAMPLES

Example 1: Pyrolysis of HCFC-22 with ethylene to make HFO-1252zc

[0069] In a 12-inches long ½" OD Inconel 600 reactor, under N₂ purge, the reactor was heated up to 550°C, 600°C and 650°C. HCFC-22, ethylene and N₂ were fed through mass flow controllers into the reactor. The reaction test conditions are listed on Table 2 below. The reactor effluent was analyzed by online GC-MS-FID. The results of the analysis are listed in Tables 3-5 below.

Table 2

Furnace Temp C	Pressure psig	Ethylene Sccm	N2 sccm	HCFC-22 sccm
550	0.9	4.00	0.00	7.00
600	0.9	4.00	0.00	7.00
650	0.9	4.00	0.00	7.00

Table 3: Product GC analysis result at 550°C

550°C		
Compounds		GC-FID area%
Ethylene	HC-1150	73.9303%
CHClF ₂	HFC-22	13.5100%
CH ₂ =CF-CH ₃	HFO-1261yf	0.1643%
Cyclic CF ₂ -CH ₂ CH ₂	C252	1.9468%
CF ₂ =CHCH ₃	HFO-1252zc	1.2804%
CF ₃ CH ₂ CH ₃	HFC-263fb	5.1732%
cyclic CF ₂ CF ₂ CF ₂ CF ₂	C318	0.1743%

550°C		
Compounds		GC-FID area%
cyclic CF ₂ CF ₂ CF ₂ CH ₂	C336	2.0607%
C ₄ H ₆ F ₄	374	0.2664%
C ₃ H ₄ ClF	1251	0.2494%
C ₄ H ₆ F ₄	HFC-374 isomer	0.8446%
Others		0.3997%

Table 4: Product GC analysis result at 600°C

600°C		
Compounds		GC-FID area%
Ethylene	HC-1150	46.5384%
CHClF ₂	HFC-22	13.8354%
cyclic CF ₂ -CH ₂ CH ₂	C252	3.3681%
CF ₂ =CHCH ₃	1252zc	1.8730%
CF ₃ CH ₂ CH ₃	HFC-263fb	1.7093%
cyclic CF ₂ CF ₂ CF ₂ CF ₂	C318	1.5625%
cyclic CF ₂ CF ₂ CF ₂ CH ₂	C336	13.9225%
C ₄ H ₆ F ₄	HFC-374 isomer	1.7960%
C ₄ H ₆ F ₄	HFC-374 isomer	3.8475%
Others		11.5474%

Table 5: Product GC analysis result at 650°C

650°C		
Compounds		GC-FID area%
Ethylene	HC-1150	38.6495%
CHClF ₂	HFC-22	9.7556%
CF ₃ CH=CH ₂	HFO-1243zf	2.0331%
CF ₂ =CHCH ₃	HFO-1252zc	0.6747%
CF ₃ CH ₂ CH ₃	HFC-263fb	2.5294%
cyclic CF ₂ CF ₂ CF ₂ CF ₂	C318	2.8430%
cyclic CF ₂ CF ₂ CF ₂ CH ₂	C336	8.7902%
C ₄ H ₆ F ₄	374 isomer	1.8292%
C ₄ H ₆ F ₄	374 isomer	1.8524%
Others		31.0429%

Example 2: Pyrolysis of HCFC-22 with ethanol to make HFO-1252zc

[0070] In a 12-inches long ½" OD Inconel 600 reactor. Under N₂ purge, the reactor was heated up to 550°C. HCFC-22 and N₂ were fed through mass flow controllers into the reactor. Ethanol was fed by a pump. The reaction test conditions

are listed on Table 6 below. The reactor effluent was analyzed by online GC-MS-FID. The results of the analysis are listed in Table 6 below.

Table 6

Temp	Press	Feed			Mole Percent%			
		C ₂ H ₅ OH	R22	N ₂	others	ethane	R22	CH ₃ CHO
C	psi	ml/hr	sccm	sccm				
550	0.9	1.50	5.04	24.98	37.31%	26.23%	8.14%	4.10%
600	0.9	1.50	5.04	24.97	8.42%	59.78%	4.60%	6.50%
650	1.0	1.50	5.07	25.11	1.43%	87.31%	0.00%	0.00%
550	0.8	1.30	5.03	14.97	35.33%	28.82%	15.01%	2.72%
575	1.2	1.30	5.05	15.09	13.34%	46.28%	10.53%	0.00%
600	1.1	1.30	5.07	15.12	17.87%	62.30%	5.03%	0.00%

Table 6 (Cont'd.)

Temp	Press	Feed			Mole Percent%			
		C ₂ H ₅ OH	R22	N ₂				
C	psi	ml/hr	sccm	sccm	1252zc	CH ₃ CH ₂ Cl	C ₂ H ₅ OH	1-Butene, 3,3,4,4-tetrafluoro-
550	0.9	1.50	5.04	24.98	5.02%	2.35%	6.79%	10.06%
600	0.9	1.50	5.04	24.97	8.08%	4.08%	7.16%	1.38%
650	1.0	1.50	5.07	25.11	6.62%	2.93%	0.00%	1.71%
550	0.8	1.30	5.03	14.97	7.97%	3.77%	6.37%	0.00%
575	1.2	1.30	5.05	15.09	9.40%	4.70%	14.21%	1.54%
600	1.1	1.30	5.07	15.12	7.54%	3.19%	3.67%	0.40%

Other Embodiments

[0071] Embodiment 1. A process for producing 1,1-difluoropropene (HFO-1252zc) comprising contacting chlorodifluoromethane (HCFC-22) and one of a hydrocarbon and a hydrocarbon derivative in a heated reaction zone to form HFO-1252zc.

[0072] Embodiment 2. The process of Embodiment 1, wherein the contacting of HCFC-22 and the hydrocarbon or hydrocarbon derivative occurs in the absence of an added catalyst.

[0073] Embodiment 3. The process of any of Embodiments 1 to 2, wherein the reaction zone is heated to a temperature of between 500°C and 750°C, preferably a temperature selected from one of 550°C, 575°C, 600°C, 625°C and 650°C.

[0074] Embodiment 4. The process of any of Embodiments 1 to 3, wherein HCFC-22 and the hydrocarbon or hydrocarbon derivative are vaporized prior to contact in the reaction zone.

[0075] Embodiment 5. The process of any of Embodiments 1 to 4, wherein HCFC-22 is fed to the heated reaction zone at a molar excess.

[0076] Embodiment 6. The process of any of Embodiments 1 to 5, wherein a diluent is optionally fed to the reaction zone.

[0077] Embodiment 7. The process of any of 1 to Embodiments 6, wherein the heated reaction zone subjects the HCFC-22 and hydrocarbon or hydrocarbon derivative, in the presence of a diluent, to pyrolysis.

[0078] Embodiment 8. The process of any of Embodiments 1 to 7, wherein the heated reaction zone subjects the HCFC-22 and the hydrocarbon or hydrocarbon derivative, in the presence of a diluent, to pyrolysis, the ratio of HCFC-22:hydrocarbon or HCFC-22:hydrocarbon derivative is between about 0.3:1 to 2:1.

[0079] Embodiment 9. The process of any of Embodiments 1-8, wherein the hydrocarbon comprises ethylene, or wherein the hydrocarbon derivative comprises ethanol.

[0080] Embodiment 10. The process of Embodiment 9, wherein the hydrocarbon is ethylene and a diluent is fed to the heated reaction zone, and wherein the heated reaction zone is at a temperature sufficient to pyrolysis HFC-22 and ethylene.

[0081] Embodiment 11. The process of Embodiment 10, where the contacting occurs at a pressure in the range of 0 to 300 psig.

[0082] Embodiment 12. The process of Embodiment 9, wherein the hydrocarbon derivative is ethanol and a diluent is fed to the heated reaction zone, and and

wherein the heated reaction zone is at a temperature sufficient to pyrolysis HFC-22 and ethanol.

[0083] Embodiment 13. The process of Embodiment 12, where the contacting occurs at a pressure in the range of 0 to 300 psig.

[0084] Embodiment 14. The process of Embodiment 10, wherein the heated reaction zone subjects the HCFC-22 and ethylene, in the presence of a diluent, at a pressure in the range of 0 to 300 psig.

[0085] Embodiment 15. The process of Embodiment 12, wherein the heated reaction zone subjects the HCFC-22 and ethanol, in the presence of a diluent, at a pressure in the range of 0 to 300 psig.

[0086] Embodiment 16. The process of any of Embodiments 1 to 15, wherein the heated reaction zone is defined by a pyrolysis reactor.

[0087] Embodiment 17. The process of any of Embodiments 1 to 16, wherein the heated reaction zone is free of added catalyst.

[0088] Embodiment 18. The process of any of Embodiments 1 to 17, wherein the heated reaction zone is empty and free of added catalyst.

[0089] Embodiment 19. The process of any of Embodiments 1 to 18 wherein the heated reaction zone contains an inert support and is free of added catalyst.

[0090] Embodiment 20. The process of any of Embodiments 1 to 19, further comprising recovering HFO-1252zc.

[0091] Embodiment 21. The process of any of Embodiments 1 to 20, further comprising separating, recovering and recycling unconverted feeds selected from one of chlorodifluoromethane, ethanol, and ethene.

[0092] Embodiment 22. A system for carrying out the process of any of Embodiments 1 to 21, the system comprising a defined source of HCFC-22, a defined source of a hydrocarbon such as ethylene or a hydrocarbon derivative such as ethanol, a vaporizer connected to one of said defined sources, a flow through pyrolysis reactor configured for a contact time of HCFC-22 and the hydrocarbon or

hydrocarbon derivative, and optionally nitrogen, between 5 to 180 second and at a temperature of between 500°C and 700°C to make HFO-1252zc.

[0093] Embodiment 23. A composition produced by processes of any of Embodiments 1-21 or the system of Embodiment 22.

[0094] Embodiment 24. A composition comprising 1,1-difluoropropene (HFO-1252zc) and one or more additional compounds selected from the group consisting of chlorodifluoromethane (HCFC-22), ethylene (HC-1150), 2-fluoropropene (HFO-1261yf), 1,1-difluorocyclopropane (HFC-C252), 1,1,1-trifluoropropane (HFC-263fb), 3,3,3-trifluoropropene (HFO-1243zf), octafluorocyclobutane (FC-C318), hexafluorocyclobutane (HFC-C336), hexafluorobutane (HFC-374) isomers and chlorofluoropropene (HCFO-1251).

[0095] Embodiment 25. The composition of Embodiment 24, wherein the one or more additional compounds are selected from the group consisting of HCFC-22, HC-1150, HFO-1261yf, HFC-C252, HFC-263fb, FC-C318, HFC-C336, HFC-374 isomers and HCFO-1251.

[0096] Embodiment 26. The composition of Embodiment 24, wherein the one or more additional compounds are selected from the group consisting of HC-22, HC-1150, HFC-263fb, HFC-C252, FC-C318, HFC-C336, and HFC-374 isomers.

[0097] Embodiment 27. The composition of Embodiment 24, wherein the one or more additional compounds are selected from the group consisting of HC-1150, HCFC-22, HFO-1243zf, HFC-263fb, FC-C318, HFC-C336, and HFC-374 isomers.

[0098] Embodiment 28. The composition of any of Embodiments 24 to 27, wherein at least one of the additional compounds is a fluorocyclopropane or fluorocyclobutane, preferably at least one of hexafluorocyclobutane and octafluorocyclobutane.

[0099] Embodiment 29. A composition comprising 1,1-difluoropropene (HFO-1252zc) and one or more additional compounds selected from the group consisting of chlorodifluoromethane (HCFC-22), ethane, ethanal, chloroethane, ethanol, and 3,3,4,4-tetrafluoro-1-butene.

[0100] Embodiment 30. The composition of Embodiment 29, wherein the one or more additional compounds are selected from the group consisting of chloroethane, ethanol and 3,3,4,4-tetrafluoro-1-butene.

[0101] Embodiment 31. The composition of any of Embodiments 23 to 30, wherein the composition is free of or substantially free of Group A Fluorinated Substances.

[0102] Embodiment 32. The composition of any of Embodiments 23 to 31, wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.

[0103] 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. A process for producing 1,1-difluoropropene (HFO-1252zc) comprising contacting chlorodifluoromethane (HCFC-22) and one of a hydrocarbon and a hydrocarbon derivative in a heated reaction zone to form HFO-1252zc.
2. The process of claim 1, wherein the contacting of HCFC-22 and the hydrocarbon or hydrocarbon derivative occurs in the absence of an added catalyst.
3. The process of any of claims 1 to 2, wherein the reaction zone is heated to a temperature of between 500°C and 750°C, preferably a temperature selected from one of 550°C, 575°C, 600°C, 625°C and 650°C.
4. The process of any of claims 1 to 3, wherein HCFC-22 and the hydrocarbon or hydrocarbon derivative are vaporized prior to contact in the reaction zone.
5. The process of any of claims 1 to 4, wherein HCFC-22 is fed to the heated reaction zone at a molar excess.
6. The process of any of claims 1 to 5, wherein a diluent is optionally fed to the reaction zone.
7. The process of any of 1 to claims 6, wherein the heated reaction zone subjects the HCFC-22 and hydrocarbon or hydrocarbon derivative, in the presence of a diluent, to pyrolysis.
8. The process of any of claims 1 to 7, wherein the heated reaction zone subjects the HCFC-22 and the hydrocarbon or hydrocarbon derivative, in the presence of a diluent, to pyrolysis, the ratio of HCFC-22:hydrocarbon or HCFC-22:hydrocarbon derivative is between about 0.3:1 to 2:1.
9. The process of any of claims 1-8, wherein the hydrocarbon comprises ethylene, or wherein the hydrocarbon derivative comprises ethanol.
10. The process of claim 9, wherein the hydrocarbon is ethylene and a diluent is fed to the heated reaction zone, and wherein the heated reaction zone is at a temperature sufficient to pyrolysis HFC-22 and ethylene.

11. The process of claim 10, where the contacting occurs at a pressure in the range of 0 to 300 psig.
12. The process of claim 9, wherein the hydrocarbon derivative is ethanol and a diluent is fed to the heated reaction zone, and wherein the heated reaction zone is at a temperature sufficient to pyrolysis HFC-22 and ethanol.
13. The process of claim 12, where the contacting occurs at a pressure in the range of 0 to 300 psig.
14. The process of claim 10, wherein the heated reaction zone subjects the HCFC-22 and ethylene, in the presence of a diluent, at a pressure in the range of 0 to 300 psig.
15. The process of claim 12, wherein the heated reaction zone subjects the HCFC-22 and ethanol, in the presence of a diluent, at a pressure in the range of 0 to 300 psig.
16. The process of any of claims 1 to 15, wherein the heated reaction zone is defined by a pyrolysis reactor.
17. The process of any of claims 1 to 16, wherein the heated reaction zone is free of added catalyst.
18. The process of any of claims 1 to 17, wherein the heated reaction zone is empty and free of added catalyst.
19. The process of any of claims 1 to 18 wherein the heated reaction zone contains an inert support and is free of added catalyst.
20. The process of any of claims 1 to 19, further comprising recovering HFO-1252zc.
21. The process of any of claims 1 to 20, further comprising separating, recovering and recycling unconverted feeds selected from one of chlorodifluoromethane, ethanol, and ethene.
22. A system for carrying out the process of any of claims 1 to 21, the system comprising a defined source of HCFC-22, a defined source of a hydrocarbon such as ethylene or a hydrocarbon derivative such as ethanol, a vaporizer

connected to one of said defined sources, a flow through pyrolysis reactor configured for a contact time of HCFC-22 and the hydrocarbon or hydrocarbon derivative, and optionally nitrogen, between 5 to 180 second and at a temperature of between 500°C and 700°C to make HFO-1252zc.

23. A composition produced by processes of any of claims 1-21 or the system of claim 22.
24. A composition comprising 1,1-difluoropropene (HFO-1252zc) and one or more additional compounds selected from the group consisting of chlorodifluoromethane (HCFC-22), ethylene (HC-1150), 2-fluoropropene (HFO-1261yf), 1,1-difluorocyclopropane (HFC-C252), 1,1,1-trifluoropropane (HFC-263fb), 3,3,3-trifluoropropene (HFO-1243zf), octafluorocyclobutane (FC-C318), hexafluorocyclobutane (HFC-C336), hexafluorobutane (HFC-374) isomers and chlorofluoropropene (HCFO-1251).
25. The composition of claim 24, wherein the one or more additional compounds are selected from the group consisting of HCFC-22, HC-1150, HFO-1261yf, HFC-C252, HFC-263fb, FC-C318, HFC-C336, HFC-374 isomers and HCFO-1251.
26. The composition of claim 24, wherein the one or more additional compounds are selected from the group consisting of HC-22, HC-1150, HFC-263fb, HFC-C252, FC-C318, HFC-C336, and HFC-374 isomers.
27. The composition of claim 24, wherein the one or more additional compounds are selected from the group consisting of HC-1150, HCFC-22, HFO-1243zf, HFC-263fb, FC-C318, HFC-C336, and HFC-374 isomers.
28. The composition of any of claims 24 to 27, wherein at least one of the additional compounds is a fluorocyclopropane or fluorocyclobutane, preferably at least one of hexafluorocyclobutane and octafluorocyclobutane.
29. A composition comprising 1,1-difluoropropene (HFO-1252zc) and one or more additional compounds selected from the group consisting of chlorodifluoromethane (HCFC-22), ethane, ethanal, chloroethane, ethanol, and 3,3,4,4-tetrafluoro-1-butene.

30. The composition of claim 29, wherein the one or more additional compounds are selected from the group consisting of chloroethane, ethanol and 3,3,4,4-tetrafluoro-1-butene.
31. The composition of any of claims 23 to 30, wherein the composition is free of or substantially free of Group A Fluorinated Substances.
32. The composition of any of claims 23 to 31, wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.