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(54) Title: SYSTEMS AND PROCESSES FOR THE PRODUCTION OF Z-1,1,1,4,4,4-HEXAFLUORO-2-BUTENE

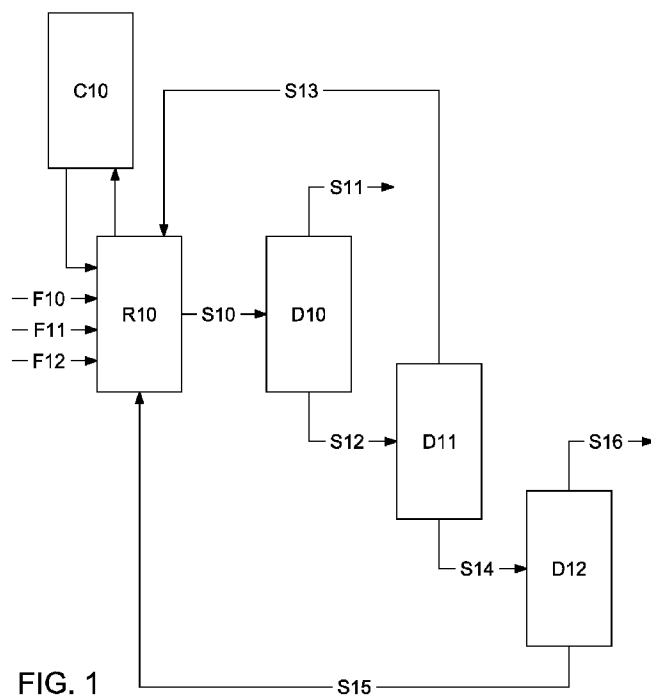


FIG. 1

(57) Abstract: Systems and processes for preparing (Z)-1,1,1,4,4,4-hexafluoro-2-butene are provided. Compositions prepared according to one or more of the systems and processes described herein and methods of using the compositions are also provided.

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TITLE OF THE INVENTION

SYSTEMS AND PROCESSES FOR THE PRODUCTION OF Z-1,1,1,4,4,4-
HEXAFLUORO-2-BUTENE

FIELD

[0001] This disclosure relates in general to methods of synthesis of fluorinated olefins. More particularly, this invention relates to processes and intermediates for preparing (Z)-1,1,1,4,4,4-hexafluoro-2-butene and compositions which may be useful in applications including refrigerants, high-temperature heat pumps, organic Rankine cycles, as fire extinguishing/fire suppression agents, propellants, foam blowing agents, solvents, cleaning fluids, and/or immersion cooling fluids.

BACKGROUND

[0002] The fluorocarbon industry has been working for the past few decades to find replacement refrigerants for the ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) being phased out as a result of the Montreal Protocol. The solution for many applications has been the commercialization of hydrofluorocarbon (HFC) compounds for use as refrigerants, solvents, fire extinguishing agents, blowing agents and propellants. These new compounds, such as HFC refrigerants, HFC-134a and HFC-125 being the most widely used at this time, have zero ozone depletion potential and thus are not affected by the current regulatory phase-out as a result of the Montreal Protocol.

[0003] In addition to ozone depleting concerns, global warming is another environmental concern in many of these applications. Thus, there is a need for compositions that meet both low ozone depletion standards as well as having low global warming potentials. Certain hydrofluoroolefins are believed to meet both goals. Thus, there is a need for manufacturing processes that provide hydrofluoroolefins that have a low global warming potential.

[0004] (Z)-1,1,1,4,4,4-hexafluoro-2-butene (Z-HFO-1336mzz) is an example of such a hydrofluoroolefin. The present invention provides economical systems and processes for manufacturing Z-HFO-1336mzz from hexachlorobutadiene (HCBD).

[0005] HCBD is primarily produced in chlorinolysis plants as a by-product in the production of carbon tetrachloride and tetrachloroethene. Chlorinolysis is a radical chain reaction that occurs when hydrocarbons are exposed to chlorine gas under pyrolytic conditions. The hydrocarbon is chlorinated and the resulting chlorocarbons are broken down. This process is analogous to combustion, but with chlorine instead of oxygen.

[0006] Carbon tetrachloride and tetrachloroethene are two commodities which are manufactured on such a large scale, that enough HCBD can generally be obtained to meet industrial demand. Thus, HCBD may constitute a low cost and obtainable starting material for manufacturing processes that provides halogenated hydrocarbons and fluoroolefins.

[0007] Further, as a by-product in the production of carbon tetrachloride and tetrachloroethene, HCBD constitutes a waste that must be disposed of to prevent environmental pollution. Thus, the manufacturing processes of the present invention, which utilize HCBD as a starting material for producing hydrofluoroolefins convert a potential environmental pollutant waste into environmentally friendly product.

SUMMARY

[0008] Any of the embodiments of the invention discussed herein can be used alone or in combination with each other. It will be understood by those skilled in the art that different embodiments discussed herein can be combined and form part of the invention. It will also be understood by those skilled in the art that certain aspects of different embodiments discussed herein can be combined and form part of the invention.

[0009] In one embodiment, the present invention is related to a system for purification of E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz). The system comprises: a reactor configured to react hexachlorobutadiene (HCBD) with hydrofluoric acid (HF) in the presence of a fluorination catalyst to form a composition comprising HCFO-1326mxz, HCl, unreacted HCBD, and unreacted HF; a first distillation column configured to receive the composition from the reactor and configured to separate the first composition into

a first fraction $F1_{D10}$ comprising HCl, and a second fraction $F2_{D10}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz; a second distillation column configured to receive the second fraction $F2_{D10}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the first distillation column and configured to separate the second fraction into a third fraction $F3_{D11}$ comprising an azeotrope of unreacted HF and HCFO-1326mxz, and a fourth fraction $F4_{D11}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz, the second distillation column being configured to optionally return the third fraction $F3_{D11}$ to the reactor; and a third distillation column configured to receive the fourth fraction $F4_{D11}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the second distillation column and configured to separate the fourth fraction $F4_{D11}$ into a fifth fraction $F5_{D12}$ comprising unreacted HF and unreacted HCBd, and a sixth fraction $F6_{D12}$ comprising HCFO-1326mxz, the third distillation column being configured to optionally return the fifth fraction $F5_{D12}$ to the reactor.

[0010] In one embodiment, the present invention is related to a system for purification of E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz). The system comprises: a reactor configured to react hexachlorobutadiene (HCBd) with hydrofluoric acid (HF) in the presence of a fluorination catalyst to form a composition comprising HCFO-1326mxz, HCl, unreacted HCBd, and unreacted HF; a first distillation column configured to receive the composition from the reactor and configured to separate the first composition into a first fraction $F1_{D20}$ comprising HCl, and a second fraction $F2_{D20}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz; a second distillation column configured to receive the second fraction $F2_{D20}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the first distillation column and configured to separate the second fraction $F2_{D20}$ into a third fraction $F3_{D21}$ comprising unreacted HF and unreacted HCBd, and a fourth fraction $F4_{D21}$ comprising an azeotrope of HF and HCFO-1326mxz, the second distillation column being configured to optionally return the third fraction $F3_{D21}$ to the reactor; and an acid neutralizer configured to receive the fourth fraction $F4_{D21}$ comprising an azeotrope of HF and HCFO-1326mxz from the second distillation column and configured to separate the fourth fraction $F4_{D21}$ into a fifth fraction $F5_{A20}$ comprising neutralized HF and a sixth fraction $F6_{A20}$ comprising HCFO-1326mxz.

[0011] In one embodiment, the present invention is related to a system for purification of hexafluoro-2-butyne (HFB). The system comprises: a reactor configured to react E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz) with a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst to form a composition comprising a vapor portion and a liquid portion, the vapor portion comprising HFB and HCFO-1326mxz, the liquid portion comprising water, HCFO-1326mxz, excess phase transfer catalyst and an alkali metal halide salt, the liquid portion being comprised of an aqueous liquid phase and an organic liquid phase; and a distillation column configured to receive the vapor portion of the composition from the reactor and configured to separate the vapor portion into a fraction F5_{D31} comprising HFB, and a fraction F6_{D31} comprising HCFO-1326mxz, the distillation column being configured to return the fraction F6_{D31} comprising HCFO-1326mxz to the reactor, the distillation column optionally being configured to provide the fraction F5_{D31} comprising HFB to one or more additional distillation columns.

[0012] In one embodiment, the present invention is related to a system for purification of cis-1,1,1,4,4,4-hexafluoro-2-butene (Z-HFO-1336mzz). The system comprises: a reactor configured to react hexafluoro-2-butyne (HFB) with hydrogen in the presence of a hydrogenation catalyst to form a composition comprising HFO-1336mzz(Z) and HFB; and a first distillation column configured to receive the composition from the reactor and configured to separate the composition into a first fraction F1_{D40} comprising HFB and a second fraction F2_{D40} comprising HFO-1336mzz(Z), the first distillation column being configured to return the first fraction F1_{D40} to the reactor.

[0013] In one embodiment, the present invention is related to a process for purification of E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz). The process comprises: reacting hexachlorobutadiene (HCBd) with hydrofluoric acid (HF) in the presence of a fluorination catalyst in a reactor to form a composition comprising HCFO-1326mxz, HCl, unreacted HCBd, and unreacted HF; providing the composition to a first distillation column and separating the composition into a first fraction F1_{D10} comprising HCl, and a second fraction F2_{D10} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz; providing the second fraction F2_{D10} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the first

distillation column to a second distillation column and separating the second fraction into a third fraction F_{3D11} comprising an azeotrope of unreacted HF and HCFO-1326mxz, and a fourth fraction F_{4D11} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz; optionally returning the third fraction F_{3D11} from the second distillation column to the reactor; providing the fourth fraction F_{4D11} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the second distillation column to a third distillation column and separating the fourth fraction F_{4D11} into a fifth fraction F_{5D12} comprising unreacted HF and unreacted HCBd, and a sixth fraction F_{6D12} comprising HCFO-1326mxz; and optionally returning the fifth fraction F_{5D12} from the third distillation column to the reactor.

[0014] In one embodiment, the present invention is related to a process for purification of E- and/or Z--chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz). The process comprises: reacting hexachlorobutadiene (HCBd) with hydrofluoric acid (HF) in the presence of a fluorination catalyst in a reactor to form a composition comprising HCFO-1326mxz, HCl, unreacted HCBd, and unreacted HF; providing the composition from the reactor to a first distillation column and separating the first composition into a first fraction F_{1D20} comprising HCl, and a second fraction F_{2D20} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz; providing the second fraction F_{2D20} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the first distillation column to a second distillation column and separating the second fraction F_{2D20} into a third fraction F_{3D21} comprising unreacted HF and unreacted HCBd, and a fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz; optionally returning the third fraction F_{3D21} from the second distillation column to the reactor; and providing the fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz from the second distillation column to an acid neutralizer configured and separating the fourth fraction F_{4D21} into a fifth fraction F_{5A20} comprising neutralized HF and a sixth fraction F_{6A20} comprising HCFO-1326mxz.

[0015] In one embodiment, the present invention is related to a process for purification of hexafluoro-2-butyne (HFB). The process comprises: reacting E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz) with a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst in a reactor to form a composition comprising a vapor portion and a liquid portion, the

vapor portion comprising HFB and unreacted HCFO-1326mxz, the liquid portion comprising water, unreacted HCFO-1326mxz, excess phase transfer catalyst and an alkali metal halide salt, the liquid portion being comprised of an aqueous liquid phase and an organic liquid phase; providing the vapor portion of the composition from the reactor to one or more distillation columns and separating the vapor portion into a fraction F5_{D31} comprising HFB, and a fraction F6_{D31} comprising unreacted HCFO-1326mxz; and optionally returning the fraction F6_{D31} comprising unreacted HCFO-1326mxz from the distillation column to the reactor.

[0016] Embodiment 1: A system for purification of E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz), the system comprising:

a reactor configured to react hexachlorobutadiene (HCBD) with hydrofluoric acid (HF) in the presence of a fluorination catalyst to form a composition comprising HCFO-1326mxz, HCl, unreacted HCBD, and unreacted HF;

a first distillation column configured to receive the composition from the reactor and configured to separate the first composition into a first fraction F1_{D10} comprising HCl, and a second fraction F2_{D10} comprising unreacted HCBD, unreacted HF and HCFO-1326mxz;

a second distillation column configured to receive the second fraction F2_{D10} comprising unreacted HCBD, unreacted HF and HCFO-1326mxz from the first distillation column and configured to separate the second fraction into a third fraction F3_{D11} comprising an azeotrope of unreacted HF and HCFO-1326mxz, and a fourth fraction F4_{D11} comprising unreacted HCBD, unreacted HF and HCFO-1326mxz, the second distillation column being configured to optionally return the third fraction F3_{D11} to the reactor; and

a third distillation column configured to receive the fourth fraction F4_{D11} comprising unreacted HCBD, unreacted HF and HCFO-1326mxz from the second distillation column and configured to separate the fourth fraction F4_{D11} into a fifth fraction F5_{D12} comprising unreacted HF and unreacted HCBD, and a sixth fraction F6_{D12} comprising HCFO-1326mxz, the third distillation column being configured to optionally return the fifth fraction F5_{D12} to the reactor.

[0017] Embodiment 2: The system of Embodiment 1, wherein the first fraction F_{1D10} comprises HCl, HF, and one or more additional compounds selected from the group consisting of (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz); (E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E-HCFO-1326mxz); (E)-(2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) (E-CFO-1317mx); (Z)-(2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) (Z-CFO-1317mx); 2-chloro-1,1-difluoroethylene (HCFC-1122); 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); pentachlorofluoroethane (CFC-111); 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113); 2-chloro-1,1,1-trifluoroethane (CFC-133a); 2,2-dichloro-1,1,1-trifluoroethane (CFC-123); 1,2-dichloro-1,1,2-trifluoroethane (CFC-123a); 1,2,2-trichloro-1,1-difluoroethane (CFC-122); 1,1,1,2-tetrachloro-2,2-difluoroethane (CFC-112a); 1,1,1,3-tetrafluoro-2,3,3-trichloropropane (HCFC-224db); 1,2-dichloro-1,1,3,3,3-pentafluoropropane (HCFC-225da); 2,3-dichloro-1,1,1,3-tetrafluoropropane (HCFC-234da); 2-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235da); 1-chloro-1,1,3,3,3-pentafluoropropane (CFC-235fa); 1,1,1,3,3,3-hexafluoropropane (HFC-236fa) and 1,1,1,2,4,4,4-heptafluoro-2-butene (HFO-1327mz).

[0018] Embodiment 3: The system of Embodiment 2, wherein the HF comprises about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the first fraction F_{1D10}.

[0019] Embodiment 4: The system of Embodiment 2, wherein each of the additional compounds present in the first fraction F_{1D10} are present in amount of about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the first fraction F_{1D10}.

[0020] Embodiment 5: The system of Embodiment 2, wherein a total amount of the additional compounds of the first fraction F_{1D10} is about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the first fraction F_{1D10}.

[0021] Embodiment 6: The system of Embodiment 1, wherein the sixth fraction F_{6D12} comprises:

- (i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz);
- (ii) optionally HF; and
- (iii) one or more additional compounds selected from the group consisting of:

E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
 E-HFO-1316mxx (E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 Z-HFO-1316mxx (Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 HFO-1327mz (1,1,1,2,4,4,4-heptafluoro-2-butene),
 HFO-1325lxz (1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene),
 HFO-1325dx (1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene),
 HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane),
 HFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane),
 HFC-336lbf (1,2-dichloro-1,1,2,4,4,4-hexafluorobutane),
 HFC-337mbf (2-chloro-1,1,1,2,4,4,4-heptafluorobutane),
 HFC-337mde (2-chloro-1,1,1,3,4,4,4-heptafluorobutane),
 HFC-356mff (1,1,1,4,4,4-hexafluorobutane),
 HFC-346mdf (2-chloro-1,1,1,4,4,4-hexafluorobutane),
 HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane),
 HCFC-1122 (2-chloro-1,1-difluoroethylene),
 HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane),
 CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane),
 CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane),
 CFC-133a (2-chloro-1,1,1-trifluoroethane),
 CFC-123 (2,2-dichloro-1,1,1-trifluoroethane),
 CFC-123a (1,2-dichloro-1,1,2-trifluoroethane),
 CFC-122 (1,2,2-trichloro-1,1-difluoroethane),
 CFC-112a (1,1,1,2-tetrachloro-2,2-difluoroethane),
 HCFC-224db (1,1,1,3-tetrafluoro-2,3,3-trichloropropane),
 HFC-225da (1,2-dichloro-1,1,3,3,3-pentafluoropropane),
 HFC-235da (2-chloro-1,1,1,3,3-pentafluoropropane),

HFC-235fa (1-chloro-1,1,3,3,3-pentafluoropropane),
HFC-236fa (1,1,1,3,3,3-hexafluoropropane), and
E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

[0022] Embodiment 7: The system of Embodiment 1, wherein the sixth fraction F_{6D12} comprises (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz); optionally HF; and one or more additional compounds selected from the group consisting of E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene, HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), E- Z-CFO-1317mx (E-2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) and Z-CFO-1317mx (Z-2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

[0023] Embodiment 8: The system of any of Embodiments 6 and 7, alone or in any combination thereof, wherein the HF comprises about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the sixth fraction F_{6D12} .

[0024] Embodiment 9: A system for purification of E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz), the system comprising:

a reactor configured to react hexachlorobutadiene (HCBD) with hydrofluoric acid (HF) in the presence of a fluorination catalyst to form a composition comprising HCFO-1326mxz, HCl, unreacted HCBD, and unreacted HF;

a first distillation column configured to receive the composition from the reactor and configured to separate the first composition into a first fraction F_{1D20} comprising HCl, and a second fraction F_{2D20} comprising unreacted HCBD, unreacted HF and HCFO-1326mxz;

a second distillation column configured to receive the second fraction F_{2D20} comprising unreacted HCBD, unreacted HF and HCFO-1326mxz from the first distillation column and configured to separate the second fraction F_{2D20} into a third fraction F_{3D21} comprising unreacted HF and unreacted HCBD, and a fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz, the second distillation column being configured to optionally return the third fraction F_{3D21} to the reactor; and

an acid neutralizer configured to receive the fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz from the second distillation column and configured to separate the fourth fraction F_{4D21} into a fifth fraction F_{5A20} comprising neutralized HF and a sixth fraction F_{6A20} comprising HCFO-1326mxz.

[0025] Embodiment 10: The system of Embodiment 9, wherein the first fraction F_{1D20} comprises HCl, HF, and one or more additional compounds selected from the group consisting of (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz); (E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E-HCFO-1326mxz); (E)-(2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) (E-CFO-1317mx); (Z)-(2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) (Z-CFO-1317mx); 2-chloro-1,1-difluoroethylene (HCFC-1122); 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); pentachlorofluoroethane (CFC-111); 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113); 2-chloro-1,1,1-trifluoroethane (CFC-133a); 2,2-dichloro-1,1,1-trifluoroethane (CFC-123); 1,2-dichloro-1,1,2-trifluoroethane (CFC-123a); 1,2,2-trichloro-1,1-difluoroethane (CFC-122); 1,1,1,2-tetrachloro-2,2-difluoroethane (CFC-112a); 1,1,1,3-tetrafluoro-2,3,3-trichloropropane (HCFC-224db); 1,2-dichloro-1,1,3,3,3-pentafluoropropane (HCFC-225da); 2,3-dichloro-1,1,1,3-tetrafluoropropane (HCFC-234da); 2-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235da); 1-chloro-1,1,3,3,3-pentafluoropropane (CFC-235fa); 1,1,1,3,3,3-hexafluoropropane (HFC-236fa) and 1,1,1,2,4,4,4-heptafluoro-2-butene (HFO-1327mz).

[0026] Embodiment 11: The system of Embodiment 10, wherein the HF comprises about 1 wt. % or less, or about 0.5 wt. % or less, or about 0.1 wt. % or less, based on the total weight of the first fraction F_{1D20} .

[0027] Embodiment 12: The system of Embodiment 10, wherein each of the additional compounds present in the first fraction F_{1D20} are present in amount of about 1 wt. % or less, or about 0.5 wt. % or less, or about 0.1 wt. % or less, based on the total weight of the first fraction F_{1D20} .

[0028] Embodiment 13: The system of Embodiment 10, wherein a total amount of the additional compounds of the first fraction F_{1D20} is about 1 wt. % or less, or about

0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the first fraction F1_{D20}.

[0029] Embodiment 14: The system of Embodiment 9, wherein the sixth fraction F6_{A20} comprises

- (i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz);
- (ii) optionally HF; and
- (iii) one or more additional compounds selected from the group consisting of:

E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
 E-HFO-1316mxx (E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 Z-HFO-1316mxx (Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 HFO-1327mz (1,1,1,2,4,4,4-heptafluoro-2-butene),
 HFO-1325lxz (1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene),
 HFO-1325dx (1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene),
 HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane),
 HFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane),
 HFC-336lbf (1,2-dichloro-1,1,2,4,4,4-hexafluorobutane),
 HFC-337mbf (2-chloro-1,1,1,2,4,4,4-heptafluorobutane),
 HFC-337mde (2-chloro-1,1,1,3,4,4,4-heptafluorobutane),
 HFC-356mff (1,1,1,4,4,4-hexafluorobutane),
 HFC-346mdf (2-chloro-1,1,1,4,4,4-hexafluorobutane),
 HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane),
 HCFC-1122 (2-chloro-1,1-difluoroethylene),
 HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane),
 CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane),
 CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane),
 CFC-133a (2-chloro-1,1,1-trifluoroethane),

CFC-123 (2,2-dichloro-1,1,1-trifluoroethane),
CFC-123a (1,2-dichloro-1,1,2-trifluoroethane),
CFC-122 (1,2,2-trichloro-1,1-difluoroethane),
CFC-112a (1,1,1,2-tetrachloro-2,2-difluoroethane),
HCFC-224db (1,1,1,3-tetrafluoro-2,3,3-trichloropropane),
HFC-225da (1,2-dichloro-1,1,3,3,3-pentafluoropropane),
HFC-235da (2-chloro-1,1,1,3,3-pentafluoropropane),
HFC-235fa (1-chloro-1,1,3,3,3-pentafluoropropane),
HFC-236fa (1,1,1,3,3,3-hexafluoropropane), and
E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

[0030] Embodiment 15: The system of Embodiment 9, wherein the sixth fraction F_{6A20} comprises

- (i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz);
- (ii) optionally HF; and
- (iii) one or more additional compounds selected from the group consisting of E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene, HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), E- Z-CFO-1317mx (E-2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) and Z-CFO-1317mx (Z-2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

[0031] Embodiment 16: The system of Embodiment 15, wherein the HF comprises about 1 wt. % or less, or about 0.5 wt. % or less, or about 0.1 wt. % or less, based on the total weight of the sixth fraction F_{6A20}.

[0032] Embodiment 17: The system of any of Embodiments 1 to 16, alone or in any combination thereof, wherein the system further comprises a partial condenser coupled to the reactor.

[0033] Embodiment 18: A system for purification of hexafluoro-2-butyne (HFB), the system comprising:

a reactor configured to react E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz) with a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst to form a composition comprising a vapor portion and a liquid portion, the vapor portion comprising HFB and HCFO-1326mxz, the liquid portion comprising water, HCFO-1326mxz, excess phase transfer catalyst and an alkali metal halide salt, the liquid portion being comprised of an aqueous liquid phase and an organic liquid phase;

a distillation column configured to receive the vapor portion of the composition from the reactor and configured to separate the vapor portion into a fraction F_{5D31} comprising HFB, and a fraction F_{6D31} comprising HCFO-1326mxz, the distillation column being configured to return the fraction F_{6D31} comprising HCFO-1326mxz to the reactor, the distillation column optionally being configured to provide the fraction F_{5D31} comprising HFB to one or more additional distillation columns.

[0034] Embodiment 19: The system according to Embodiment 18, wherein the system further comprises a partial condenser coupled to the reactor.

[0035] Embodiment 20: The system according to any of Embodiments 17-18, alone or in any combination thereof, wherein the fraction F_{6D31} comprises:

- (i) HCFO-1326mxz,
- (ii) one or more compounds selected from the group consisting of trifluoroacetone, trifluoropropyne, and hexafluoro-2-butyne, and
- (iii) one or more of the additional compounds selected from the group consisting of:

E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,

E-HFO-1316mxx (E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),

Z-HFO-1316mxx (Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),

HFO-1327mz (1,1,1,2,4,4,4-heptafluoro-2-butene),

HFO-1325lxz (1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene),

HFO-1325dx (1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene),

HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane),

HFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane),
HFC-336lbf (1,2-dichloro-1,1,2,4,4,4-hexafluorobutane),
HFC-337mbf (2-chloro-1,1,1,2,4,4,4-heptafluorobutane),
HFC-337mde (2-chloro-1,1,1,3,4,4,4-heptafluorobutane),
HFC-356mff (1,1,1,4,4,4-hexafluorobutane),
HFC-346mdf (2-chloro-1,1,1,4,4,4-hexafluorobutane),
HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane),
HCFC-1122 (2-chloro-1,1-difluoroethylene),
HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane),
CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane),
CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane),
CFC-133a (2-chloro-1,1,1-trifluoroethane),
CFC-123 (2,2-dichloro-1,1,1-trifluoroethane),
CFC-123a (1,2-dichloro-1,1,2-trifluoroethane),
CFC-122 (1,2,2-trichloro-1,1-difluoroethane),
CFC-112a (1,1,1,2-tetrachloro-2,2-difluoroethane),
HCFC-224db (1,1,1,3-tetrafluoro-2,3,3-trichloropropane),
HFC-225da (1,2-dichloro-1,1,3,3,3-pentafluoropropane),
HFC-235da (2-chloro-1,1,1,3,3-pentafluoropropane),
HFC-235fa (1-chloro-1,1,3,3,3-pentafluoropropane),
HFC-236fa (1,1,1,3,3,3-hexafluoropropane), and
E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

[0036] Embodiment 21: The system according to any of Embodiments 18-20, alone or in any combination thereof, wherein a water content of the fraction F6_{D31} is about 5000 ppm or less, or about 4000 ppm or less, or about 3000 ppm or less, or about 1000 ppm or less.

[0037] Embodiment 22: The system according to any of Embodiments 18-22, alone or in any combination thereof, the system further comprising:

a decanter configured to receive the liquid portion of the composition from the reactor and configured to separate the aqueous liquid phase into a first fraction $F1_{E30}$ comprising water and the alkali metal halide salt and to separate the organic liquid phase into a second fraction $F2_{E30}$ comprising the unreacted HCFO-1326mxz and excess phase transfer catalyst, the decanter being configured to return a first portion of the second fraction $F2_{E30}$ to the reactor; and

an additional distillation column configured to receive a second portion of the second fraction $F2_{E30}$ from the decanter and configured to separate the second portion of the second fraction $F2_{E30}$ into a third fraction $F3_{D30}$ comprising unreacted HCFO-1326mxz, and a fourth fraction $F4_{D30}$ comprising unreacted HCFO-1326mxz and excess PTC, the additional distillation column being configured to return the third fraction $F3_{D30}$ comprising unreacted HCFO-1326mxz to the reactor.

[0038] Embodiment 23: The system of Embodiment 22, wherein the third fraction $F3_{D30}$ comprises:

- (i) HCFO-1326mxz,
- (ii) (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and
- (iii) one or more of the additional compounds selected from the group consisting of:

E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
 E-HFO-1316mxx (E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 Z-HFO-1316mxx (Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 HFO-1327mz (1,1,1,2,4,4,4-heptafluoro-2-butene),
 HFO-1325lxz (1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene),
 HFO-1325dx (1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene),
 HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane),
 HFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane),
 HFC-336lbf (1,2-dichloro-1,1,2,4,4,4-hexafluorobutane),
 HFC-337mbf (2-chloro-1,1,1,2,4,4,4-heptafluorobutane),

HFC-337mde (2-chloro-1,1,1,3,4,4,4-heptafluorobutane),
HFC-356mff (1,1,1,4,4,4-hexafluorobutane),
HFC-346mdf (2-chloro-1,1,1,4,4,4-hexafluorobutane),
HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane,
HCFC-1122 (2-chloro-1,1-difluoroethylene),
HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane),
CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane),
CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane),
CFC-133a (2-chloro-1,1,1-trifluoroethane),
CFC-123 (2,2-dichloro-1,1,1-trifluoroethane),
CFC-123a (1,2-dichloro-1,1,2-trifluoroethane),
CFC-122 (1,2,2-trichloro-1,1-difluoroethane),
CFC-112a (1,1,1,2-tetrachloro-2,2-difluoroethane),
HCFC-224db (1,1,1,3-tetrafluoro-2,3,3-trichloropropane),
HFC-225da (1,2-dichloro-1,1,3,3,3-pentafluoropropane),
HFC-235da (2-chloro-1,1,1,3,3,3-pentafluoropropane),
HFC-235fa (1-chloro-1,1,3,3,3-pentafluoropropane),
HFC-236fa (1,1,1,3,3,3-hexafluoropropane), and
E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

[0039] Embodiment 24: The system according to any of Embodiments 22-23, alone or in any combination thereof, wherein the third fraction F3_{D30} comprises about 100 ppm or less of the base.

[0040] Embodiment 25: The system according to any of Embodiments 22-24, alone or in any combination thereof, wherein the third fraction F3_{D30} comprises about 500 ppm or less of the phase transfer catalyst.

[0041] Embodiment 26: A system for purification of cis-1,1,1,4,4,4-hexafluoro-2-butene (Z-HFO-1336mzz), the system comprising:

a reactor configured to react hexafluoro-2-butyne (HFB) with hydrogen in the presence of a hydrogenation catalyst to form a composition comprising HFO-1336mzz(Z) and HFB; and

a first distillation column configured to receive the composition from the reactor and configured to separate the composition into a first fraction F1_{D40} comprising HFB and a second fraction F2_{D40} comprising HFO-1336mzz(Z), the first distillation column being configured to return the first fraction F1_{D40} to the reactor.

[0042] Embodiment 27: The system of Embodiment 26, wherein the reactor contains a heat diluent, preferably selected from the group consisting of HFC-32, HFC-143a, HFC-134a and HFC-134.

[0043] Embodiment 28: The system of any of Embodiments 26-27, alone or in any combination thereof, the system further comprising a second distillation column configured to receive the second fraction F2_{D40} from the first distillation column and configured to separate the second fraction F2_{D40} into a third fraction F3_{D41} comprising HFO-1336mzz(Z), HFO-1336mzz(E), 1,1,4,4,4-hexafluorobutane (HCFC-356mff), and lower boiling organic byproducts from the hydrogenation reaction, and a fourth fraction F4_{D41} comprising HFO-1336mzz(Z) and higher boiling organic byproducts from the hydrogenation reaction, the system optionally further comprising a third distillation column configured to receive the fourth fraction F4_{D41} from the second distillation column and configured to separate the fourth fraction F4_{D41} into a first fraction F5_{D42} comprising Z-HFO-1336mzz, and a second fraction F6_{D42} comprising Z-HFO-1336mzz and higher boiling organic byproducts from the hydrogenation reaction.

[0044] Embodiment 29: An integrated system for preparing Z-HFO-1336mzz from HCBD, the integrated system comprising the system of Embodiments 1-8 or the system of Embodiment 9-17 and the system of Embodiments 18-25 and the system of Embodiments 26-28, alone or in any combination thereof.

[0045] Embodiment 30: The integrated system according to Embodiment 29, wherein the third distillation column of the system according to Embodiments 1-8 is configured to supply the sixth fraction $F6_{D12}$ comprising HCFO-1326mxz to the dehydrochlorination reactor of the system according to Embodiments 18-25, and wherein the distillation column of the system according to Embodiments 18-5 is configured to supply the seventh fraction $F7_{D32}$ comprising HFB to the hydrogenation reactor of the system according to Embodiments 26-28, alone or in any combination thereof.

[0046] Embodiment 31: The integrated system according to Embodiment 29 wherein the acid neutralizer A20 of the system according to Embodiments 9-17 is configured to supply the sixth fraction $F6_{A20}$ comprising HCFO-1326mxz to the dehydrochlorination reactor of the system according to Embodiments 18-25, and wherein the distillation column of the system according to Embodiments 18-25 is configured to supply the seventh fraction $F7_{D32}$ comprising HFB to the hydrogenation reactor of the system according to Embodiments 2-28, alone or in any combination thereof.

[0047] Embodiment 32: A process for purification of E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz), the process comprising:

reacting hexachlorobutadiene (HCBd) with hydrofluoric acid (HF) in the presence of a fluorination catalyst in a reactor to form a composition comprising HCFO-1326mxz, HCl, unreacted HCBd, and unreacted HF;

providing the composition to a first distillation column and separating the composition into a first fraction $F1_{D10}$ comprising HCl, and a second fraction $F2_{D10}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz;

providing the second fraction $F2_{D10}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the first distillation column to a second distillation column and separating the second fraction into a third fraction $F3_{D11}$ comprising an azeotrope of unreacted HF and HCFO-1326mxz, and a fourth fraction $F4_{D11}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz,

optionally returning the third fraction $F3_{D11}$ from the second distillation column to the reactor;

providing the fourth fraction F_{4D11} comprising unreacted HCB D , unreacted HF and HCFO-1326mxz from the second distillation column to a third distillation column and separating the fourth fraction F_{4D11} into a fifth fraction F_{5D12} comprising unreacted HF and unreacted HCB D , and a sixth fraction F_{6D12} comprising HCFO-1326mxz; and

optionally returning the fifth fraction F_{5D12} from the third distillation column to the reactor.

[0048] Embodiment 33: A process for purification of E- and/or Z--chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz), the process comprising:

reacting hexachlorobutadiene (HCB D) with hydrofluoric acid (HF) in the presence of a fluorination catalyst in a reactor to form a composition comprising HCFO-1326mxz, HCl, unreacted HCB D , and unreacted HF;

providing the composition from the reactor to a first distillation column and separating the first composition into a first fraction F_{1D20} comprising HCl, and a second fraction F_{2D20} comprising unreacted HCB D , unreacted HF and HCFO-1326mxz;

providing the second fraction F_{2D20} comprising unreacted HCB D , unreacted HF and HCFO-1326mxz from the first distillation column to a second distillation column and separating the second fraction F_{2D20} into a third fraction F_{3D21} comprising unreacted HF and unreacted HCB D , and a fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz;

optionally returning the third fraction F_{3D21} from the second distillation column to the reactor; and

providing the fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz from the second distillation column to an acid neutralizer configured and separating the fourth fraction F_{4D21} into a fifth fraction F_{5A20} comprising neutralized HF and a sixth fraction F_{6A20} comprising HCFO-1326mxz.

[0049] Embodiment 34: A process for purification of hexafluoro-2-butyne (HFB), the process comprising:

reacting E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz) with a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst in a reactor to form a composition comprising a vapor portion and a liquid portion, the vapor portion comprising HFB and unreacted HCFO-1326mxz, the liquid portion comprising water, unreacted HCFO-1326mxz, excess phase transfer catalyst and an alkali metal halide salt, the liquid portion being comprised of an aqueous liquid phase and an organic liquid phase;

providing the vapor portion of the composition from the reactor to one or more distillation columns and separating the vapor portion into a fraction F5_{D31} comprising HFB, and a fraction F6_{D31} comprising unreacted HCFO-1326mxz; and

optionally returning the fraction F6_{D31} comprising unreacted HCFO-1326mxz from the distillation column to the reactor.

[0050] Embodiment 35: The process according to Embodiment 34, the process further comprising:

providing the liquid portion of the composition from the reactor to a decanter and separating the aqueous liquid phase into a first fraction F1_{E30} comprising water and the alkali metal halide salt and separating the organic liquid phase into a second fraction F2_{E30} comprising the unreacted HCFO-1326mxz and excess phase transfer catalyst;

optionally returning a first portion of the second fraction F2_{E30} from the decanter to the reactor;

providing a second portion of the second fraction F2_{E30} from the decanter to an additional distillation column and separating the second portion of the second fraction F2_{E30} into a third fraction F3_{D30} comprising unreacted HCFO-1326mxz, and a fourth fraction F4_{D30} comprising unreacted HCFO-1326mxz and excess PTC; and

optionally returning the third fraction F3_{D30} comprising unreacted HCFO-1326mxz from the additional distillation column to the reactor.

[0051] Embodiment 36: A process for purification of cis-1,1,1,4,4,4-hexafluoro-2-butene (Z-HFO-1336mzz), the process comprising:

reacting hexafluoro-2-butyne (HFB) with hydrogen in the presence of a hydrogenation catalyst in a reactor to form a composition comprising HFO-1336mzz(Z) and unreacted HFB;

providing the composition from the reactor to a first distillation column and separating the composition into a first fraction F1_{D40} comprising unreacted HFB and a second fraction F2_{D40} comprising HFO-1336mzz(Z); and

optionally returning the first fraction F1_{D40} from the first distillation column to the reactor.

[0052] Embodiment 37: The process of Embodiment 36, the process further comprising providing the second fraction F2_{D40} from the first distillation column to a second distillation column and separating the second fraction F2_{D40} into a third fraction F3_{D41} comprising HFO-1336mzz(Z), HFO-1336mzz(E), 1,1,4,4,4-hexafluorobutane (HCFC-356mff), and lower boiling organic byproducts from the hydrogenation reaction and a fourth fraction F4_{D41} comprising HFO-1336mzz(Z) and higher boiling organic byproducts from the hydrogenation reaction.

[0053] Embodiment 38: An integrated process for purification of Z-HFO-1336mzz from HCBd, the integrated process comprising the processes of Embodiments 32 and 34-37, alone or in any combination thereof, wherein the integrated process comprises providing the sixth fraction F6_{D12} comprising HCFO-1326mxz from the third distillation column of the process according to Embodiment 32 to the dehydrochlorination reactor of the process according to Embodiment 34, and providing the seventh fraction F7_{D32} comprising HFB from the distillation column of the process according to Embodiment 34 to the hydrogenation reactor of the process according to Embodiment 36.

[0054] Embodiment 39: An integrated process for purification of Z-HFO-1336mzz from HCBd, the integrated process comprising the processes of Embodiments 33-37, alone or in any combination thereof, the integrated process comprising providing the sixth fraction F6_{A20} comprising HCFO-1326mxz from the acid neutralizer A20 of the process according to Embodiment 33 to the dehydrochlorination reactor of the

process according to Embodiment 34, and providing the seventh fraction F7_{D32} comprising HFB from the distillation column of the process according to Embodiment 34 to the hydrogenation reactor of the process according to Embodiment 36.

[0055] Embodiment 40: A composition prepared by the system of any of Embodiments 1-17 or the process of any of Embodiments 32-33, alone or in any combination thereof, the composition comprising:

i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene; and

ii) one or more additional compounds selected from:

- 1,1,1,3,3,3-hexafluoropropane;
- 1,1,1,2,2,4,4,4-octafluorobutane;
- 1,1,1,4,4,4-hexafluorobutane;
- 1,2-dichloro-1,1,2,2-tetrafluoroethane;
- 2-chloro-1,1,1-trifluoroethane;
- 2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
- 2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
- 2-chloro-1,1,1,3,3,3-pentafluoropropane;
- 1-chloro-1,1,3,3,3-pentafluoropropane;
- (E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
- 1,2-dichloro-3,3,4,4-tetrafluorocyclobut-1-ene;
- 2-chloro-1,1,1,4,4,4-hexafluorobutane;
- 2,2-dichloro-1,1,1-trifluoroethane;
- 1,2-dichloro-1,1,2-trifluoroethane;
- 1,2-dichloro-1,1,3,3,3-pentafluoropropane;
- (E)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
- 1,1,2-trichloro-1,2,2-trifluoroethane;
- (Z)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
- 1,2-dichloro-3,3,3-trifluoroprop-1-ene;
- (Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;

2,2-dichloro-1,1,1,4,4,4-hexafluorobutane;
dl-2,3-dichloro-1,1,1,4,4,4-hexafluorobutane;
meso-2,3-dichloro-1,1,1,4,4,4-hexafluorobutane;
1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene;
2,3-dichloro-1,1,1,3-tetrafluoropropane;
1,2-dichloro-1,1,2,4,4,4-hexafluorobutane;
1,2,2-trichloro-1,1-difluoroethane;
1,1,1-trichloro-2,2-difluoroethane;
1,1,2,2-tetrachloro-1,2-difluoroethane;
1,1,1,2-tetrachloro-2,2-difluoroethane;
1,2,3-trichloro-1,1,4,4,4-pentafluorobutane; and
1,1,2,3-tetrachloro-4,4,4-trifluorobut-1-ene,

wherein the composition comprises greater than about 95 mole percent Z-HCFO-1326mxz.

[0056] Embodiment 41: A composition prepared by the system of any of Embodiments 18-25 or the process of any of Embodiments 34-35, alone or in any combination thereof, the composition comprising:

- i) hexafluorobutyne (HFB); and
- ii) one or more additional compounds selected from the group consisting of:
 - 1,1,1,3,3,3-hexafluoropropane;
 - 1,1,1,2,4,4,4-heptafluoro-2-butene;
 - (E)-1,1,1,4,4,4-hexafluorobutene;
 - 1,1,1,2,2,4,4,4-octafluorobutane;
 - 1,1,1,4,4,4-hexafluorobutane;
 - 1,2-dichloro-1,1,2,2-tetrafluoroethane;
 - 2-chloro-1,1,1-trifluoroethane;
 - (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;

1-chloro-3,3,4,4,4-pentafluorobut-1-yne;
1-chloro-3,3,4,4,4-pentafluorobut-2-yne;
(Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;
1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene
2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
2-chloro-1,1,1,3,3-pentafluoropropane;
1-chloro-1,1,3,3,3-pentafluoropropane;
(E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
2-chloro-1,1,1,4,4,4-hexafluorobutane;
2,2-dichloro-1,1,1-trifluoroethane;
1,2-dichloro-1,1,2-trifluoroethane;
1,2-dichloro-1,1,3,3,3-pentafluoropropane;
(E)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
1,1,2-trichloro-1,2,2-trifluoroethane;
(Z)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
1-chloro-3,3,3-trifluoroprop-1-yne;
1,2-dichloro-3,3,3-trifluoroprop-1-ene;
(Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;
1-chloro-1,1,2,4,4,4-hexafluoro-2-butene;
2-chloro-1,3,3,3-tetrafluoroprop-1-ene;
1,1,3,3,3-pentafluoroprop-1-ene; and
2-chloro-1,1,3,3,3-pentafluoroprop-1-ene,

wherein the composition comprises greater than about 95 mole percent HFB.

[0057] Embodiment 42: A composition prepared by the system of any of Embodiments 26-31 or the process of any of Embodiments 36-39, alone or in any combination thereof, the composition comprising:

- i) (Z)-1,1,1,4,4,4-hexafluoro-2-butene (Z-HFO-1336mzz); and
- ii) one or more additional compounds selected from the group consisting of:

1,1,1,3,3,3-hexafluoropropane;
(E)-1,1,1,4,4,4-hexafluorobutene;
1,1,1,2,2,4,4,4-octafluorobutane;
1,2-dichloro-1,1,2,2-tetrafluoroethane;
3-chloro-1,1,1-trifluoropropane;
4-chloro-1,1,1,2,2-pentafluorobutane;
2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
2-chloro-1,1,1,3,3-pentafluoropropane;
1-chloro-1,1,3,3,3-pentafluoropropane;
2-chloro-1,1,1,4,4,4-hexafluorobutane;
1,2-dichloro-1,1,3,3,3-pentafluoropropane;
1,2-dichloro-3,3,3-trifluoroprop-1-ene;
1-chloro-3,3,3-trifluoro-propene;
1-chloro-1,1,2,4,4,4-hexafluoro-2-butene;
1-chloro-1,1,4,4,4-pentafluorobutane;
2-chloro-1,1,1,3-tetrafluoropropane; and
1,1,1,3,3-pentafluoropropane,

wherein the composition comprises greater than about 99 mole percent Z-HFO-1336mzz.

BRIEF DESCRIPTION OF THE DRAWINGS

[0058] The following detailed description of preferred embodiments of the present invention will be better understood when read in conjunction with the appended drawings. For the purposes of illustrating the invention, there is shown in the drawings embodiments which are presently preferred. It is understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown. In the drawings:

[0059] Fig. 1 is a schematic illustration of a system and process for producing 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene from hexachlorobutadiene, according to one embodiment of the present invention;

[0060] Fig. 2 is a schematic illustration of a system and process for producing 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene from hexachlorobutadiene, according to another embodiment of the present invention;

[0061] Fig. 3 is a schematic illustration of a system and process for producing hexafluoro-2-butyne from 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene, according to an embodiment of the present invention; and

[0062] Fig. 4 is a schematic illustration of a system and process for producing (Z)-1,1,1,4,4,4-hexafluoro-2-butene from hexafluoro-2-butyne, according to an embodiment of the present invention.

DETAILED DESCRIPTION

[0063] The present invention generally relates to processes and intermediates for preparing (Z)-1,1,1,4,4,4-hexafluoro-2-butene and compositions.

[0064] As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a composition, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, process, method, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not

present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0065] 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.

[0066] 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".

[0067] 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."

[0068] 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.

[0069] 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). 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.

[0070] 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

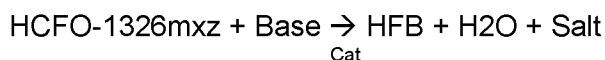
preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

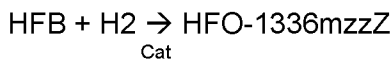
[0071] The term “compound” as used herein is meant to include all stereoisomers, geometric isomers, tautomers, and isotopes of the structures or chemical described. Compounds herein identified by name or structure as one particular tautomeric form are intended to include other tautomeric forms unless otherwise specified.

[0072] As used herein, the term “catalyst”, refers to a substance that speeds up the chemical reaction, but is not consumed by the reaction; thus it can be recovered chemically unchanged at the end of the reaction.

[0073] Disclosed is a process for the preparation of cis-1,1,1,4,4,4-hexafluoro-2-butene comprising fluorinating hexachlorobutadiene (HCBD) in the presence of a catalyst to obtain a first product mixture comprising E- or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E- or Z-HCFO-1326mxz), recovering the E- or Z-HCFO-1326mxz such as by subjecting the first product mixture to one or more separation steps to provide E- or Z-HCFO-1326mxz, dehydrochlorination of the E- or Z-HCFO-1326mxz in a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst to produce a second product mixture comprising hexafluoro-2-butyne (HFB), recovering the HFB such as by subjecting the second product mixture to one or more separation steps to provide hexafluoro-2-butyne, hydrogenation of the HFB in the presence of a hydrogenation catalyst to produce a third reaction mixture comprising Z-HFO-1336mzz, and recovering the Z-HFO-1336mzz such as by subjecting the third product mixture to one or more separation steps to provide Z-HFO-1336mzz.

[0074] Reactions for this process are as follows:





[0075] Also disclosed is a system for the preparation of Z-HFO-1336mzz comprising a first reactor for fluorination of HCBd to produce E- or Z-HCFO-1326mxz, a second reactor for dehydrochlorination of E- or Z-HCFO-1326mxz to produce HFB, and a third reactor for hydrogenation of HFB to produce Z-HFO-1336mzz.

[0076] It will be understood by those skilled in the art that for each reaction or process step, the system may comprise more than one reactor. For example, the system may comprise a first plurality of reactors for fluorination of HCBd to produce E- or Z-HCFO-1326mxz, a second plurality of reactors for dehydrochlorination of E- or Z-HCFO-1326mxz to produce HFB, and/or a third plurality of reactors for hydrogenation of HFB to produce Z-HFO-1336mzz. Each reactor of the first, second and third pluralities may be used in parallel or may be used alternately, for example when one reactor is offline, the other reactor may be online for production.

[0077] Also disclosed is a system for the preparation of Z-HFO-1336mzz comprising a first reactor for fluorination of HCBd to produce E- or Z-HCFO-1326mxz, a first set of one or more distillation columns for isolation and recovery of the E- or Z-HCFO-1326mxz, a second reactor for dehydrochlorination of E- or Z-HCFO-1326mxz to produce HFB, a second set of one or more distillation columns for isolation and recovery of the HFB, a third reactor for hydrogenation of HFB to produce Z-HFO-1336mzz, and a third set of one or more distillation columns for isolation and recovery of the Z-HFO-1336mzz.

[0078] Also disclosed herein is a process comprising fluorinating HCBd in the presence of a catalyst to produce E- or Z-HCFO-1326mxz. The present invention is also directed to a system for fluorination of HCBd to produce E- or Z-HCFO-1326mxz, the system comprising a reactor for the fluorination reaction and one or more distillation columns for isolation and recovery of the E- or Z-HCFO-1326mxz, wherein optionally a stream recovered from one or more of the distillation columns is returned to the fluorination reactor. In one embodiment, the system may also include an acid neutralizer and one or more dryers.

[0079] Also disclosed herein is a process comprising dehydrochlorination of E- or Z-HCFO-1326mxz in a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst to produce HFB. The present invention is also directed to a system for dehydrochlorination of E- or Z-HCFO-1326mxz to produce HFB, the system comprising a reactor for the dehydrochlorination reaction, one or more decanters, and one or more distillation columns for isolation and recovery of the HFB, wherein optionally a stream recovered from one or more of the distillation columns is returned to the dehydrochlorination reactor. In one embodiment, the system for dehydrochlorination of E- or Z-HCFO-1326mxz to produce HFB further comprises one or more dryers. For example, the system may comprise an aluminum containing adsorbent, such as a molecular sieve, preferably an aluminosilicate molecular sieve (zeolite) such as a zeolite A and more particularly a molecular sieve selected from zeolite 3A, zeolite 4A and zeolite 5A.

[0080] Also disclosed herein is a process comprising hydrogenation of HFB in the presence of a hydrogenation catalyst to produce Z-HFO-1336mzz. The present invention is also directed to a system for hydrogenation of HFB to produce Z-HFO-1336mzz, the system comprising a reactor for the hydrogenation reaction and one or more distillation columns for isolation and recovery of the Z-HFO-1336mzz, wherein optionally a stream recovered from one or more of the distillation columns is returned to the hydrogenation reactor.

[0081] In some embodiments, the system further comprises one or more driers or adsorbents, such as adsorbent beds. In one embodiment, the adsorbent bed may be in the form of a solid, porous core comprising a zeolite, a binder and any auxiliary desiccants or adsorbents such as silica gel, calcium sulfate, alumina or activated carbon. In use, the core is contained within a cartridge and the circulating refrigeration fluid is caused to pass through the cartridge and the method comprises passing a composition, either in a liquid or vapor state, through the cartridge in contact with the core (i.e., the molecular sieve) for removal of acids, trace impurities, and the like.

SYSTEMS AND PROCESSES

System A and Process 1, Embodiment 1

[0082] Fig. 1 shows a schematic diagram of a system and process for producing 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz) from HCBd, according to one embodiment of the present invention. As shown in Fig. 1, a preferred embodiment of the system includes reactor R10, a first distillation column D10 in flow communication with reactor R10, a second distillation column D11 in flow communication with the first distillation column D10 and reactor R10, and a third distillation column D12 in flow communication with the second distillation column D11 and reactor R10.

[0083] Referring to Fig. 1, HCBd is introduced into reactor R10 in stream F10. Anhydrous hydrogen fluoride (HF) is introduced into reactor R10 in stream F11. In some embodiments, an oxidizing agent may be fed to reactor R10 in stream F12. It will be understood by those skilled in the art that the oxidizing agent need not be utilized in all circumstances. In R10, the HCBd is subjected to fluorination in the presence of a catalyst comprising a catalytically effective amount to produce a product mixture comprising E- and Z-HCFO-1326mxz. This reaction is shown below:



[0084] In some embodiments, the fluorination process is conducted by flowing HF, HCBd, and optionally an oxidizing agent into reactor R10 at a specified temperature. In some embodiments the process is conducted by flowing HF, HCBd, optionally an oxidizing agent for example Cl₂, and a carrier gas into the reactor. Examples of carrier gases include inert gases such as nitrogen, argon and helium.

[0085] The desired reaction results may be achieved through proper selection of operating conditions such as temperature, contact time and HF to HCBd ratios.

[0086] The reaction temperature for the catalytic fluorination of HCBd is in the range of from about 80°C to about 150°C, or about 80°C to about 140°C. In some embodiments, the process is performed at a temperature of from about 90°C to about 135°C. The formation of byproducts can be reduced, and the deactivation of the catalyst can be suppressed by maintaining the reaction temperature within these

ranges. However, it will be understood by those skilled in the art that catalytic fluorination of HCBF is an exothermic reaction and temperatures higher than the range of from about 150°C may occur locally within the reactor R10 or catalyst.

[0087] The contact time (CT) of the reactants and catalyst within reactor R10 is determined by the following equation:

$$CT = VR/VF,$$

[0088] where VR is the volume (m³) of the reactor R10 in cubic meters and VF is the total liquid volumetric flow rate (m³/hr) of the reactor feeds. In one embodiment, the contact time is in the range of from about 0.1 to about 10 hours, inclusive of all values and ranges therebetween. It will be understood by those skilled in the art that the contact time may impact selectivity and conversion of the HCBF, and thus adjustment of the contact time, either to a target time within the range of about 0.1 to about 10 hours or to a target time shorter or longer than this range, may be carried out as needed to achieve the desired reaction results.

[0089] The reactions in reactor R10 are typically conducted at atmospheric pressure, or at a pressure lower than atmospheric pressure, or at a pressure higher than atmospheric pressure. That is, the reaction pressure in reactor R10 for the fluorination reaction is not critical and may be adjusted as needed to achieve the desired reaction results. In one embodiment, the catalytic fluorination reaction in reactor R10 is carried out at pressures greater than atmospheric pressure, for example, because increased pressure reduces the size of equipment proceeding the reaction. In one embodiment, the pressure within reactor R10 is in a range from about 0 to 2.0 MPaG (gauge pressure).

[0090] The reaction mixture obtained in reactor R10 exits reactor R10 as a first stream S10 and is supplied to a first distillation column D10 to remove unreacted materials and impurities. The reaction mixture (i.e., first stream S10) comprises, consists essentially, or consists of unreacted HCBF (normal boiling point 213°C to 215°C), HCFO-1326mxz (normal boiling point 35 to 43°C), unreacted HF (normal boiling point 20°C) and hydrogen chloride (HCl) (normal boiling point -85°C). The HCl is formed as a product of the fluorination reaction of HCBF with HF in reactor R10.

[0091] In some embodiments, the first distillation column D10 operates at a pressure of about 300 psig or less, or about 200 psig or less.

[0092] The first distillation column D10 separates, by distillation, the first stream S10 into a first fraction comprising, consisting essentially of, or consisting of HCl and impurities, and a second fraction comprising, consisting essentially of, or consisting of HCBD, HF and HCFO-1326mxz. The first fraction is removed from the first distillation column D10 in a second stream S11. The second fraction is removed from the first distillation column D10 in a third stream S12.

[0093] More particularly, the second stream S11 (i.e., the first fraction) comprises, consists essentially of or consists of HCl, optionally trace amounts of HF, and optionally one or more additional compounds selected from (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz); (E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E-HCFO-1326mxz); (E)-(2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) (E-CFO-1317mx); (Z)-(2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) (Z-CFO-1317mx); 2-chloro-1,1-difluoroethylene (HCFC-1122); 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); pentachlorofluoroethane (CFC-111); 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113); 2-chloro-1,1,1-trifluoroethane (CFC-133a); 2,2-dichloro-1,1,1-trifluoroethane (CFC-123); 1,2-dichloro-1,1,2-trifluoroethane (CFC-123a); 1,2,2-trichloro-1,1-difluoroethane (CFC-122); 1,1,1,2-tetrachloro-2,2-difluoroethane (CFC-112a); 1,1,1,3-tetrafluoro-2,3,3-trichloropropane (HCFC-224db); 1,2-dichloro-1,1,3,3,3-pentafluoropropane (HCFC-225da); 2,3-dichloro-1,1,1,3-tetrafluoropropane (HCFC-234da); 2-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235da); 1-chloro-1,1,3,3,3-pentafluoropropane (CFC-235fa); 1,1,1,3,3,3-hexafluoropropane (HFC-236fa) and 1,1,1,2,4,4,4-heptafluoro-2-butene (HFO-1327mz).

[0094] In some embodiments, trace amounts of HF comprise about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the first fraction.

[0095] In some embodiments, each additional compound of the first fraction (stream S11) may be present in an amount of about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the first fraction.

[0096] In some embodiments, the total amount of the additional compounds of the first fraction (stream S11) is about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the first fraction.

[0097] In some embodiments, the second fraction of the third stream S12 comprising, consisting essentially of, or consisting of HCBD, HF, HCFO-1326mxz and optionally trace amounts of HCl. In some embodiments, trace amounts of HCl comprise about 0.1 wt.% or less, or about 0.05 wt.% or less, or about 0.02 wt.% or less, based on the total weight of the first fraction.

[0098] The third stream S12 is then supplied from the first distillation column D10 to a second distillation column D11 to remove unreacted materials and impurities. In some embodiments, the second distillation column D11 operates at a pressure of about 200 psig or less, or about 150 psig or less, or about 100 psig or less. The second distillation column D11 separates, by distillation, the third stream S12 into a first fraction comprising, consisting essentially of, or consisting of an azeotrope of HF and HCFO-1326mxz, and a second fraction comprising, consisting essentially of, or consisting of HCBD, HF and HCFO-1326mxz. The first fraction is removed from the second distillation column D11 in a fourth stream S13, and the second fraction is removed from the second distillation column D11 in a fifth stream S14.

[0099] The fourth stream S13 comprising, consisting essentially of, or consisting of an azeotrope of HF and HCFO-1326mxz is returned or recycled from the second distillation column D11 to reactor R10 for further conversion of the HF.

[0100] The fifth stream S14 comprising, consisting essentially of, or consisting of HCBD, HF and HCFO-1326mxz is supplied to a third distillation column D12 to remove unreacted materials and impurities. In some embodiments, the third distillation column D12 operates at a pressure of about 200 psig or less, or about 150 psig or less, or about 100 psig or less. The third distillation column D12 separates, by distillation, the fifth stream S14 into a first fraction comprising, consisting essentially of, or consisting of HF and HCBD, and a second fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz. The first fraction is removed from the third distillation column D12 in a sixth stream S15, and the second fraction is removed from the third distillation column D12 in a seventh stream S16.

[0101] The seventh stream S16 comprises, consists essentially of, or consists of HCFO-1326mxz. In some embodiments, the seventh stream S16 comprises, consists essentially of, or consists of:

- i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz);
- ii) optionally trace amounts of HF; and
- iii) one or more additional compounds selected from:
 - E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
 - E-HFO-1316mxx (E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 - Z-HFO-1316mxx (Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 - HFO-1327mz (1,1,1,2,4,4,4-heptafluoro-2-butene),
 - HFO-1325lxz (1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene),
 - HFO-1325dx (1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene),
 - HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane),
 - HFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane),
 - HFC-336lbf (1,2-dichloro-1,1,2,4,4,4-hexafluorobutane),
 - HFC-337mbf (2-chloro-1,1,1,2,4,4,4-heptafluorobutane),
 - HFC-337mde (2-chloro-1,1,1,3,4,4,4-heptafluorobutane),
 - HFC-356mff (1,1,1,4,4,4-hexafluorobutane),
 - HFC-346mdf (2-chloro-1,1,1,4,4,4-hexafluorobutane),
 - HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane),
 - HCFC-1122 (2-chloro-1,1-difluoroethylene),
 - HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane),
 - CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane),
 - CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane),
 - CFC-133a (2-chloro-1,1,1-trifluoroethane),
 - CFC-123 (2,2-dichloro-1,1,1-trifluoroethane),
 - CFC-123a (1,2-dichloro-1,1,2-trifluoroethane),
 - CFC-122 (1,2,2-trichloro-1,1-difluoroethane),
 - CFC-112a (1,1,1,2-tetrachloro-2,2-difluoroethane),
 - HCFC-224db (1,1,1,3-tetrafluoro-2,3,3-trichloropropane),

HFC-225da (1,2-dichloro-1,1,3,3,3-pentafluoropropane),
HFC-235da (2-chloro-1,1,1,3,3-pentafluoropropane),
HFC-235fa (1-chloro-1,1,3,3,3-pentafluoropropane),
HFC-236fa (1,1,1,3,3,3-hexafluoropropane), and
E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

In some embodiments, the composition comprises greater than about 95 mole percent Z-HCFO-1326mxz.

[0102] The one or more additional compounds of the composition comprising Z-HCFO-1326mxz are selected from and listed in Table 1.

TABLE 1: COMPOUNDS OF Z-HCFO-1326MXZ COMPOSITION

Name	Code	Structure
Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene	Z-1326mxz	CF ₃ -CCl=CH-CF ₃
E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene	E-1326mxz	CF ₃ -CCl=CH-CF ₃
E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene	E-1316mxx	CF ₃ -CCl=CCl-CF ₃
Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene	Z-1316mxx	CF ₃ -CCl=CCl-CF ₃
1,1,1,2,4,4,4-heptafluoro-2-butene	E/Z-1327mz	CF ₃ -CF=CH-CF ₃
1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene	E/Z-1325lxz	CClF ₂ -CCl=CH-CF ₃
1,2-dichloro-3,3,4,4,4-pentafluoro-1butene	E/Z-1325dx	CHCl=CCl-CF ₂ -CF ₃
2,3-dichloro-1,1,1,4,4,4-hexafluorobutane	336mdd	CF ₃ -CHCl-CHCl-CF ₃
2,2-dichloro-1,1,1,4,4,4-hexafluorobutane	336maf	CF ₃ -CCl ₂ -CH ₂ -CF ₃
1,2-dichloro-1,1,2,4,4,4-hexafluorobutane	336lbf	CClF ₂ -CClF-CH ₂ -CF ₃
2-chloro-1,1,1,2,4,4,4-heptafluorobutane	337mbf	CF ₃ -CClF-CH ₂ -CF ₃
2-chloro-1,1,1,3,4,4,4-heptafluorobutane	337mde	CF ₃ -CHCl-CHF-CF ₃
1,1,1,4,4,4-hexafluorobutane	356mff	CF ₃ -CH ₂ -CH ₂ -CF ₃
2-chloro-1,1,1,4,4,4-hexafluorobutane	346mdf	CF ₃ -CHCl-CH ₂ -CF ₃
1,1,1,2,2,4,4,4-octafluorobutane	338mf	CF ₃ -CH ₂ -CF ₂ -CF ₃
2-chloro-1,1-difluoroethylene	1122	CHCl=CF ₂
2-chloro-1,1,1,2-tetrafluoroethane	124	CHClF-CF ₃
1,2-dichloro-1,1,2,2-tetrafluoroethane	114	CClF ₂ -CClF ₂
1,1,2-trichloro-1,2,2-trifluoroethane	113	CCl ₂ F-CClF ₂
2-chloro-1,1,1-trifluoroethane	133a	CH ₂ Cl-CF ₃
2,2-dichloro-1,1,1-trifluoroethane	123	CHCl ₂ -CF ₃
1,2-dichloro-1,1,2-trifluoroethane	123a	CClF ₂ -CHClF
1,2,2-trichloro-1,1-difluoroethane	122	CClF ₂ -CHCl ₂
1,1,1,2-tetrachloro-2,2-difluoroethane	112a	CCl ₃ -CClF ₂
1,1,2-trichloro-1,3,3,3-tetrafluoropropane	224db	CCl ₂ F-CHCl-CF ₃
1,2-dichloro-1,1,3,3,3-pentafluoropropane	225da	CClF ₂ -CHCl-CF ₃
2-chloro-1,1,1,3,3-pentafluoropropane	235da	CF ₃ -CHCl-CHF ₂
1-chloro-1,1,3,3,3-pentafluoropropane	235fa	CClF ₂ -CH ₂ -CF ₃

Name	Code	Structure
1,1,1,3,3,3-hexafluoropropane	236fa	CF ₃ -CH ₂ -CF ₃
2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene	1317mx	CF ₃ -CCl-CFCF ₃

[0103] In some embodiments, the seventh stream S16 comprises, consists essentially of, or consists of: Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene; optionally trace amounts of HF, and one or more additional compounds selected from: E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene and HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene). In some embodiments, the composition comprises greater than about 95 mole percent Z-HCFO-1326mxz.

[0104] In some embodiments, the seventh stream S16 comprises, consists essentially of, or consists of: Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene, HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane) and optionally trace amounts of HF, wherein the composition comprises greater than about 95 mole percent Z-HCFO-1326mxz, or greater than about 96 mole percent Z-HCFO-1326mxz, greater than about 97 mole percent Z-HCFO-1326mxz, greater than about 98 mole percent Z-HCFO-1326mxz, greater than about 99 mole percent Z-HCFO-1326mxz, greater than about 99.2 mole percent Z-HCFO-1326mxz, greater than about 99.5 mole percent Z-HCFO-1326mxz, greater than about 99.7 mole percent Z-HCFO-1326mxz, or greater than about 99.9 mole percent Z-HCFO-1326mxz, with the balance being HCFC-336mdd and optionally HF.

[0105] In some embodiments, the seventh stream S16 comprises, consists essentially of, or consists of:

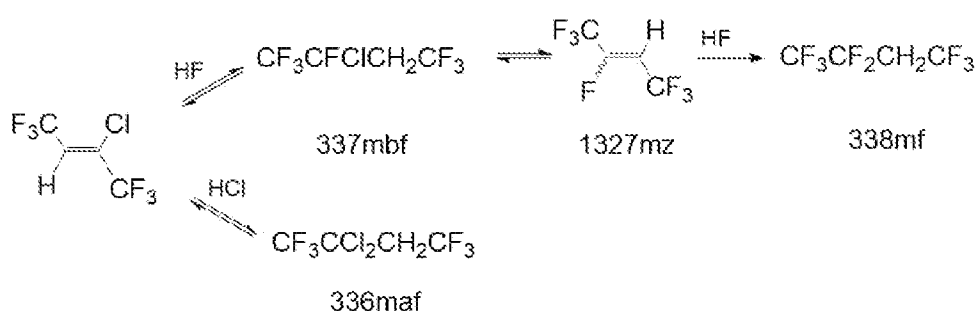
- i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
- ii) optionally trace amounts of HF; and
- iii) one or more additional compounds selected from:
 - 1,1,1,3,3,3-hexafluoropropane;
 - 1,1,1,2,2,4,4,4-octafluorobutane;
 - 1,1,1,4,4,4-hexafluorobutane;
 - 1,2-dichloro-1,1,2,2-tetrafluoroethane;
 - 2-chloro-1,1,1-trifluoroethane;
 - 2-chloro-1,1,1,2,4,4,4-heptafluorobutane;

2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
2-chloro-1,1,1,3,3-pentafluoropropane;
1-chloro-1,1,3,3,3-pentafluoropropane;
(E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
1,2-dichloro-3,3,4,4-tetrafluorocyclobut-1-ene;
2-chloro-1,1,1,4,4,4-hexafluorobutane;
2,2-dichloro-1,1,1-trifluoroethane;
1,2-dichloro-1,1,2-trifluoroethane;
1,2-dichloro-1,1,3,3,3-pentafluoropropane;
(E)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
1,1,2-trichloro-1,2,2-trifluoroethane;
(Z)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
1,2-dichloro-3,3,3-trifluoroprop-1-ene;
(Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;
2,2-dichloro-1,1,1,4,4,4-hexafluorobutane;
dl-2,3-dichloro-1,1,1,4,4,4-hexafluorobutane;
meso-2,3-dichloro-1,1,1,4,4,4-hexafluorobutane;
1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene;
2,3-dichloro-1,1,1,3-tetrafluoropropane;
1,2-dichloro-1,1,2,4,4,4-hexafluorobutane;
1,2,2-trichloro-1,1,1-difluoroethane;
1,1,1-trichloro-2,2,2-difluoroethane;
1,1,2,2-tetrachloro-1,2-difluoroethane;
1,1,1,2-tetrachloro-2,2-difluoroethane;
1,2,3-trichloro-1,1,4,4,4-pentafluorobutane; and
1,1,2,3-tetrachloro-4,4,4-trifluorobut-1-ene.

[0106] In some embodiments, the seventh stream S16 comprises greater than about 95 mole percent Z-HCFO-1326mxz.

[0107] In some embodiments, trace amounts of HF in the seventh stream S16 comprise about 500 ppm or less, about 250 ppm or less, or about 100 ppm or less, based on the total weight of the first fraction.

[0108] In one embodiment, the sixth stream S15 comprising, consisting essentially of, or consisting of HF and HCBD, and more particularly unreacted HCBD and unreacted HF, is returned or recycled from the third distillation column D12 to reactor R10 for further participation in the conversion of the HCBD and HF. In one embodiment, reactor R10 may be provided with a condenser C10 (e.g., a partial condenser), in order to enhance the removal of hydrogen chloride gas and HCFO-1326mxz, as shown in the following reaction scheme:



[0109] In the above reaction scheme, R-337mbf, R-1327mz and R-338mf are over-fluorinated products of HCFO-1326mxz, and R-336maf is an HCl adduct to HCFO-1326mxz. The partial condenser C10 enables the HCFO-1326mxz, HF, HCl to escape from reactor R10 to prevent the formation of these over-fluorinated products.

[0110] As shown in Fig. 1, a preferred embodiment of the system for producing HCFO-1326mxz from HCBD includes reactor R10 for producing a composition comprising, consisting of or consisting essentially of HCBD and a series of distillation columns D10, D11, D12 for isolation, purification and recovery of the HCBD. The system may further comprise a condenser C10 (e.g., a partial condenser), to enhance the removal of hydrogen chloride gas and HCFO-1326mxz.

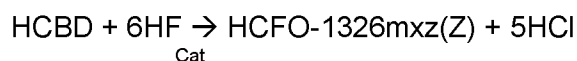
[0111] As shown in Fig. 1, a preferred embodiment of the present invention provides a process for purification of a mixture comprising HCFO-1326mxz. The process comprises providing the mixture to a series of distillation columns D10, D11, D12 for purification and recovery of a composition comprising, consisting of or consisting essentially of HCFO-1326mxz, and recycling of unreacted HCBD and HF

from the series of distillation columns for reacting HCBF with HF to produce the mixture.

System B and Process 1, Embodiment 2

[0112] Fig. 2 shows a schematic diagram of a system and process for producing HCFO-1326mxz from HCBF, according to one embodiment of the present invention. As shown in Fig. 2, a preferred embodiment of the system includes reactor R20, a first distillation column D20 in flow communication with reactor R20, a second distillation column D21 in flow communication with the first distillation column D20 and reactor R20, and an acid neutralizer A20 in flow communication with the second distillation column D21.

[0113] Referring to Fig. 2, HCBF is introduced into reactor R20 in stream F20. Anhydrous hydrogen fluoride (HF) is introduced into reactor R20 in stream F21. In some embodiments, an oxidizing agent may be fed to reactor R20 in stream F22. It will be understood by those skilled in the art that the oxidizing agent need not be utilized in all circumstances. In reactor R20, the HCBF is subjected to fluorination in the presence of a catalyst to produce a product mixture comprising E- and Z-HCFO-1326mxz. This reaction is shown below:



[0114] In some embodiments, the fluorination process is conducted simply by flowing HF, HCBF, and optionally an oxidizing agent into a catalyst bed in reactor R20 at a specified temperature. In some embodiments the process is conducted by flowing HF, HCBF, optionally an oxidizing agent, and a carrier gas into the catalyst bed in the reactor. Examples of carrier gases include inert gases such as nitrogen, argon and helium.

[0115] The desired reaction results may be achieved through proper selection of operating conditions such as temperature, contact time and HF to HCBF ratios.

[0116] The reaction temperature for the catalytic fluorination of HCBF is in the range of from about 80°C to about 150°C, or about 80°C to about 140°C. In some embodiments, the process is performed a temperature of from about 90°C to about 135°C. The formation of byproducts can be reduced, and the deactivation of the

catalyst can be suppressed by maintaining the reaction temperature within these ranges. However, it will be understood by those skilled in the art that catalytic fluorination of HCBF is an exothermic reaction and temperatures higher than the range of from about 150°C may occur locally within the reactor R20 or catalyst.

[0117] The contact time (CT) of the reactants and catalyst within reactor R20 is determined by the following equation:

$$CT = VR/VF,$$

where VR is the volume (m³) of the reactor R20 in cubic meters and VF is the total liquid volumetric flow rate (m³/hr) of the reactor feeds. In one embodiment, the contact time is in the range of from about 0.1 to about 10 hours, inclusive of all values and ranges therebetween. It will be understood by those skilled in the art that the contact time may impact selectivity and conversion of the HCBF, and thus adjustment of the contact time, either to a target time within the range of about 0.1 to about 10 hours or to a target time shorter or longer than this range, may be carried out as needed to achieve the desired reaction results.

[0118] The reactions in reactor R20 are typically conducted at atmospheric pressure, or at a pressure lower than atmospheric pressure, or at a pressure higher than atmospheric pressure. That is, the reaction pressure in reactor R20 for the fluorination reaction is not critical and may be adjusted as needed to achieve the desired reaction results. In one embodiment, the catalytic fluorination reaction reactor R20 is carried out at pressures greater than atmospheric pressure, for example, because increased pressure reduces the size of equipment proceeding the reaction. In one embodiment, the pressure within reactor R20 is in a range from about 0 to 2.0 MPaG (gauge pressure).

[0119] The reaction mixture obtained in reactor R20 exits reactor R20 as a first stream S20 and is supplied to a first distillation column D20 to remove unreacted materials and impurities. The reaction mixture (i.e., first stream S20) comprises, consists essentially, or consists of unreacted HCBF (normal boiling point 213°C), HCFO-1326mxz (normal boiling point 35 to 43°C), unreacted HF (normal boiling point 20°C) and HCl (normal boiling point -85°C), where the HCl is formed as a product of the fluorination reaction of HCBF with HF in reactor R20.

[0120] In some embodiments, the first distillation column D20 operates at a pressure of about 300 psig or less, or about 200 psig or less.

[0121] The first distillation column D20 separates, by distillation, the first stream S20 into a first fraction comprising, consisting essentially of, or consisting of HCl and impurities, and a second fraction comprising, consisting essentially of, or consisting of HCBd, HF and HCFO-1326mxz. The first fraction is removed from the first distillation column D20 in a second stream S21. In some embodiments, the composition of the second stream S21 of this second embodiment is the same as that of the second stream S11 of the first embodiment.

[0122] The second fraction is removed from the first distillation column D20 in a third stream S22. In some embodiments, the composition of the third stream S22 of this second embodiment is the same as that of the third stream S12 of the first embodiment.

[0123] The third stream S22 is then supplied from the first distillation column D20 to a second distillation column D21 to remove unreacted materials and impurities. In some embodiments, the second distillation column D21 operates at a pressure of about 200 psig or less, or about 150 psig or less, or about 100 psig or less. The second distillation column D21 separates, by distillation, the third stream S22 into a first fraction comprising, consisting essentially of, or consisting of HCBd and HF, and a second fraction comprising, consisting essentially of, or consisting of azeotrope of HF and HCFO-1326mxz. The first fraction is removed from the second distillation column D21 in a fourth stream S23, and the second fraction is removed from the second distillation column D21 in a fifth stream S24.

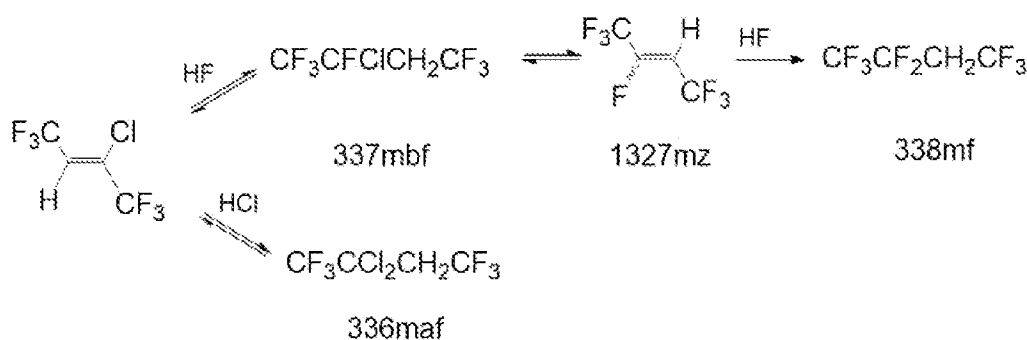
[0124] The fourth stream S23 comprising, consisting essentially of, or consisting of HCBd and HF is returned or recycled from the second distillation column D21 to reactor R20 for further conversion of the HCBd and HF.

[0125] The fifth stream S24 comprising, consisting essentially of, or consisting of an azeotrope of HF and HCFO-1326mxz is supplied to an acid neutralizer A20. A stream F23 comprising, consisting essentially of, or consisting of either water or a neutralizing agent, such as potassium hydroxide, is co-fed to the acid neutralizer A20 along with the fifth stream S24. In some embodiments, the acid neutralizer A20 operates at atmospheric pressure, or a pressure of about 300 psig or less, or about

150 psig or less, or about 100 psig or less, or about 50 psig or less. The acid neutralizer A20 removes any acid present in the fifth stream S24, thereby separating the fifth stream S24 into a first fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz, and a second fraction comprising, consisting essentially of, or consisting of neutralized HF. The first fraction exits the acid neutralizer A20 as a sixth stream S25, and the second fraction exits the acid neutralizer A20 as a seventh stream S26.

[0126] In some embodiments, the composition of the seventh stream S25 of this second embodiment is the same as that of the seventh stream S16 of the first embodiment, namely (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz), optionally trace amounts of HF, and one or more additional compounds selected from and listed in Table 1. In some embodiments, the seventh stream S25 further comprises moisture in an amount of about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less.

[0127] In one embodiment, reactor R20 may be provided with a condenser (e.g., a partial condenser) in order to enhance the removal of hydrogen chloride gas and 1326mxz, as shown in the following reaction scheme:



[0128] In the above reaction scheme, R-337mbf, R-1327mz and R-338mf are over-fluorinated products of HCFO-1326mxz, and R-336maf is an HCl adduct to HCFO-1326mxz. Condenser C20 enables the HCFO-1326mxz, HF, HCl to escape from reactor R20 to prevent the formation of these over-fluorinated products.

[0129] As shown in Fig. 2, a preferred embodiment of the system for producing HCFO-1326mxz from HCBd includes reactor R20 for producing a composition comprising, consisting of or consisting essentially of HCBd and a series of distillation columns D20, D21 for isolation, purification and recovery of the HCBd, and an acid neutralizer A20 for further isolation, purification and recovery of the HCBd. The system may further include a partial condenser to facilitate escape of HCFO-1326mxz, HF, HCl to escape from reactor R20.

[0130] As shown in Fig. 2, a preferred embodiment of the present invention provides a process for purification of a mixture comprising HCFO-1326mxz. The process comprises providing the mixture to a series of distillation columns D20, D21 and an acid neutralizer for purification and recovery of a composition comprising, consisting of or consisting essentially of HCFO-1326mxz, and recycling of unreacted HCBd and HF from the series of distillation columns for reacting HCBd with HF to produce the mixture.

Additional Details of Process 1

[0131] In any of the above-disclosed embodiments of Process 1, greater than about 90 mole percent, or greater than about 95 mole percent, greater than about 97 mole percent, greater than about 99 mole percent, greater than about 99.5 mole percent, or greater than about 99.9 mole percent of the hexachlorobutadiene is converted to the 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene.

[0132] In any of the above-disclosed embodiments of Process 1, greater than about 99 mole percent, greater than about 99.5 mole percent, or greater than about 99.7 mole percent, or greater than about 99.9 mole percent, of the 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene produced by the processes provided herein is (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene.

[0133] In any of the above-disclosed embodiments of Process 1, the composition produced by the system and process comprises:

- i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz); and
- ii) one or more additional compounds selected from:
E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,

E-HFO-1316mxx (E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
Z-HFO-1316mxx (Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
HFO-1327mz (1,1,1,2,4,4,4-heptafluoro-2-butene),
HFO-1325lxz (1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene),
HFO-1325dx (1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene),
HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane),
HFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane),
HFC-336lbf (1,2-dichloro-1,1,2,4,4,4-hexafluorobutane),
HFC-337mbf (2-chloro-1,1,1,2,4,4,4-heptafluorobutane),
HFC-337mde (2-chloro-1,1,1,3,4,4,4-heptafluorobutane),
HFC-356mff (1,1,1,4,4,4-hexafluorobutane),
HFC-346mdf (2-chloro-1,1,1,4,4,4-hexafluorobutane),
HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane),
HCFC-1122 (2-chloro-1,1-difluoroethylene),
HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane),
CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane),
CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane),
CFC-133a (2-chloro-1,1,1-trifluoroethane),
CFC-123 (2,2-dichloro-1,1,1-trifluoroethane),
CFC-123a (1,2-dichloro-1,1,2-trifluoroethane),
CFC-122 (1,2,2-trichloro-1,1-difluoroethane),
CFC-112a (1,1,1,2-tetrachloro-2,2-difluoroethane),
HCFC-224db (1,1,1,3-tetrafluoro-2,3,3-trichloropropane),
HFC-225da (1,2-dichloro-1,1,3,3,3-pentafluoropropane),
HFC-235da (2-chloro-1,1,1,3,3,3-pentafluoropropane),
HFC-235fa (1-chloro-1,1,3,3,3-pentafluoropropane),
HFC-236fa (1,1,1,3,3,3-hexafluoropropane), and
E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

[0134] In some embodiments, the composition comprises greater than about 95 mole percent Z-HCFO-1326mxz.

[0135] In any of the above-disclosed embodiments of Process 1, the process may be conducted in a batchwise process or a continuous process.

[0136] In one embodiment, upon completion of a batchwise or continuous fluorination process, the HCFO-1326mxz is of sufficient purity to not require further purification steps.

[0137] In another embodiment, upon completion of a batchwise or continuous fluorination process, the HCFO-1326mxz can be recovered through any conventional process, including for example, fractional distillation as described above.

[0138] In any of the above-disclosed embodiments of Process 1, greater than about 90 mole percent, or greater than about 95, or greater than about 97, or greater than about 99, or greater than about 99.5, or greater than about 99.9 mole percent, of the hexachlorobutadiene is converted to the 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene in less than about 10 hours of reacting (e.g., less than about 8 hours, less than about 6 hours, less than about 5 hours of reacting).

[0139] In any of the above-disclosed embodiments of Process 1, the catalyst in reactor R10, R20 is a fluorination catalyst. In some embodiments, the catalyst for the fluorination of the HCBd is a transition metal catalyst, and more preferably a Group V transition metal catalyst. In some embodiments, the Group V transition metal is niobium or tantalum. In some embodiments, the transition metal catalyst is selected from a tantalum catalyst, a niobium catalyst, or a tantalum-niobium catalyst.

[0140] In some embodiments, the transition metal catalyst is a tantalum catalyst. In some embodiments, the transition metal catalyst is a tantalum halide catalyst. In some embodiments, the transition metal catalyst is tantalum (V) chloride. In some embodiments, the transition metal catalyst is a niobium catalyst. In some embodiments, the transition metal catalyst is a niobium halide catalyst. In some embodiments, the transition metal catalyst is selected from niobium (IV) chloride, niobium (V) chloride, or a mixture thereof. In some embodiments, the transition metal catalyst is tantalum (V) chloride, niobium (IV) chloride, niobium (V) chloride, or any mixture thereof.

[0141] In some embodiments, the transition metal catalyst is a mixture of a tantalum catalyst and a niobium catalyst. In some embodiments, the transition metal catalyst is a mixture of a tantalum halide catalyst and a niobium halide catalyst. In some embodiments, the transition metal catalyst is a mixture of tantalum chloride and niobium chloride.

[0142] In some embodiments, the transition metal catalyst is a mixture of tantalum (V) chloride and niobium (IV) chloride. In some embodiments, the transition metal catalyst is a mixture of tantalum (V) chloride and niobium (V) chloride. In some embodiments, the transition metal catalyst is a mixture of tantalum (V) chloride, niobium (IV) chloride, and niobium (V) chloride.

[0143] In some embodiments, the catalyst for the fluorination of the HCBF is a Lewis acid catalyst, such as a metal halide catalyst, including but not limited to antimony halides, tin halides, thallium halides, iron halides and combinations of two or more. In certain embodiments, metal chlorides and metal fluorides are employed, including but not limited to SbCl_5 , SbCl_3 , SbF_5 , SnCl_4 , TiCl_4 , NiF_5 , FeCl_3 , and combinations of two or more of these.

[0144] In some embodiments, examples of liquid phase fluorination catalysts include but are not limited to antimony halide, tin halide, tantalum halide, titanium halide, niobium halide, molybdenum halide, iron halide, fluorinated chrome halide, fluorinated chrome oxide or combinations thereof. In some embodiments, examples of liquid phase fluorination catalysts include but are not limited to SbCl_5 , SbCl_3 , SbF_5 , SnCl_4 , TaCl_5 , TiCl_4 , NbCl_5 , MoCl_6 , FeCl_3 , fluorinated species of SbCl_5 , fluorinated species of SbCl_3 , fluorinated species of SnCl_4 , fluorinated species of TaCl_5 , fluorinated species of TiCl_4 , fluorinated species of NbCl_5 , fluorinated species of MoCl_6 , fluorinated species of FeCl_3 , or combinations thereof. These catalysts can be readily regenerated by any means known in the art if they become deactivated.

[0145] In one embodiment, the liquid phase fluorination catalyst is selected from SbF_5 , SnCl_4 , TaCl_5 , TiCl_4 , NbCl_5 , and fluorinated species thereof. In another embodiment, the liquid phase fluorination catalyst is selected from SbF_5 , SnCl_4 , TaCl_5 , TiCl_4 and/or fluorinated species thereof. In another embodiment the liquid phase fluorination catalyst is SbF_5 or SbCl_5 .

[0146] In some embodiments, the process of preparing 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene provided herein is performed as a liquid phase process. In some embodiments, the process of preparing 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (e.g., the liquid phase process) is performed in the absence of an additional solvent component.

[0147] In some embodiments, the reaction zone temperature for the liquid-phase catalytic fluorination of HCBF is in the range of from about 30°C to about 150°C, or about 50°C to about 150°C, about 50°C to about 140°C, about 70°C to about 140°C, about 90°C to about 130°C. In some embodiments, the process is performed at a temperature of from about 80°C to about 150°C. The formation of byproducts can be reduced, and the deactivation of the catalyst can be suppressed by maintaining the reaction temperature within these ranges. However, it will be understood by those skilled in the art that catalytic fluorination of HCBF is an exothermic reaction and temperatures higher than the range of from about 30°C to about 150°C may occur locally within the reactor or catalyst.

[0148] In some embodiments, the contact time (CT) of the reactants and catalyst within the reactor is in the range of from about 0.1 to about 10 hours, inclusive of all values and ranges therebetween. It will be understood by those skilled in the art that the contact time may impact selectivity and conversion of the HCBF, and thus adjustment of the contact time, either to a target time within the range of about 0.1 to about 10 hours or to a target time shorter or longer than this range, may be carried out as needed to achieve the desired reaction results.

[0149] In some embodiments, the reactions in the reactor are typically conducted at atmospheric pressure, or at a pressure lower than atmospheric pressure, or at a pressure higher than atmospheric pressure. That is, the reaction pressure in the reactor for the fluorination reaction is not critical and may be adjusted as needed to achieve the desired reaction results. In one embodiment, the catalytic fluorination reaction in the reactor is carried out at pressures greater than atmospheric pressure, for example, because increased pressure reduces the size of equipment proceeding the reaction. In one embodiment, the pressure within the reactor is in a range from about 0 to 2.0 MPaG (gauge pressure).

[0150] In some embodiments, the catalytic fluorination processes of this disclosure produce desired products with high selectivity. In some embodiments of this invention, the product selectivity to the compound of formula $\text{CF}_3\text{CR}=\text{CClCF}_3$, such as HCFO-1326mxz, is at least 90 mol% (Z to E ratio 1:1), preferably at least 95 mol%, more preferably at least 99 mol%.

[0151] In some embodiments, the process may be conducted in a batchwise process or a continuous process.

[0152] In some embodiments, a molar excess of HF is used based on 1 molar equivalent of hexachlorobutadiene, for example, greater than 1 molar equivalent, greater than 2 molar equivalents, greater than 5 molar equivalents, greater than 10 molar equivalents, greater than 20 molar equivalents, greater than 50 molar equivalents, or greater than 100 molar equivalents of HF is used based on 1 molar equivalent of hexachlorobutadiene.

[0153] In some embodiments, about 10 to about 50 molar equivalents of HF is used based on 1 molar equivalent of hexachlorobutadiene, for example about 10 to about 40, about 10 to about 30, about 10 to about 20, about 20 to about 50, about 20 to about 40, about 20 to about 30, about 30 to about 50, about 30 to about 40, or about 40 to about 50 molar equivalents of HF. In some embodiments, about 15 to about 20 molar equivalents of HF is used based on 1 molar equivalent of hexachlorobutadiene.

[0154] In some embodiments, a catalytic amount of the transition metal catalyst is used based on 1 molar equivalent of hexachlorobutadiene, for example, less than 0.85 molar equivalent, less than 0.6 molar equivalents, less than 0.4 molar equivalents, less than 0.2 molar equivalents, of transition metal catalyst is used based on 1 molar equivalent of hexachlorobutadiene.

[0155] In some embodiments, about 0.05 to about 0.5 molar equivalents of the metal halide catalyst is used based on 1 molar equivalent of hexachlorobutadiene, for example, about 0.05 to about 0.3, about 0.05 to about 0.2, about 0.05 to about 0.1, about 0.1 to about 0.5, about 0.1 to about 0.3, about 0.1 to about 0.2, about 0.2 to about 0.5, about 0.2 to about 0.3, or about 0.3 to about 0.5 molar equivalents of metal halide catalyst is used based on 1 molar equivalent of hexachlorobutadiene. In some embodiments, about 0.1 to about 0.3 molar equivalents of the metal halide catalyst is used based on 1 molar equivalent of hexachlorobutadiene.

[0156] In some embodiments, the process may comprise adding the fluorination catalyst to the HF to form a first mixture, and adding the hexachlorobutadiene to the first mixture to form a second mixture, and then introducing the second mixture into the reactor for the fluorination of the HCBD.

[0157] In an embodiment, the fluorination reaction is conducted in the absence of water. In some embodiments, if water is present, it is present in less than 1000 ppm in an embodiment, or in another embodiment, less than 500 by weight. In some embodiments, if water is present, it is present in less than about 50 ppm, or less than about 25 ppm, or preferably less than about 15 ppm.

System C and Process 2

[0158] Fig. 3 shows a schematic diagram for a system and process for producing hexafluoro-2-butyne (HFB) from the 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz) produced according to the process of Process 1, according to an embodiment of the present invention.

[0159] As shown in Fig. 3, a preferred embodiment of the system includes a reactor R30 for producing a reaction mixture comprising HFB, a decanter E30 in flow communication with the reactor R30 and configured to receive a liquid portion of the reaction mixture formed in the reactor R30, a first distillation column D30 in flow communication with the decanter E30 and the reactor R30, and a second distillation column D31 in flow communication with the reactor R30 and configured to receive a vapor portion of the reaction mixture formed in the reactor R30.

[0160] Referring to Fig. 3, the seventh stream S16 of Fig. 1 or the seventh stream S26 of Fig. 2 comprising, consisting essentially of, or consisting of HCFO-1326mxz is fed to a reactor R30 via a feed stream F30. In the reactor R30, the HCFO-1326mxz is subjected to dehydrochlorination to form HFB. More particularly, in the reactor R30, the HCFO-1326mxz is reacted with a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst to form hexafluorobutyne (HFB) (also sometimes referred to herein as perfluorobut-2-yne, PFBY). In addition to HFB, the product mixture produced from the dehydrochlorination of HCFO-1326mxz also comprises water and byproduct salts, particularly an alkali metal halide salt. This reaction is shown below:



[0161] The base (e.g., a solution such as potassium hydroxide or sodium hydroxide) is fed to the reactor R30 in stream F31.

[0162] In one embodiment, the phase transfer catalyst (PTC) is fed to the reactor R30 in stream F32. In another embodiment, the dehydrochlorination process is conducted by flowing HCFO-1326mxz and the base solution into a catalyst bed in the reactor R30 at a specified temperature. In some embodiments the process is conducted by flowing HCFO-1326mxz, the base solution and a carrier gas into the phase transfer catalyst bed in the reactor. Examples of carrier gases include inert gases such as nitrogen, argon and helium.

[0163] In one embodiment, the phase transfer catalyst is a quaternary alkylammonium salt wherein the alkyl groups are alkyl chains having from four to twelve carbon atoms, or four to ten carbon atoms. In one embodiment, the quaternary alkyl ammonium salt is a tetrabutylammonium salt. The anions of the salt can be halides such as chloride or bromide, hydrogen sulfate, or any other commonly used anion.

[0164] In another embodiment, the quaternary alkylammonium salt is trioctylmethylammonium chloride (Aliquat 336). In another embodiment, the quaternary alkylammonium salt is tetraoctylammonium chloride. In yet another embodiment, the quaternary alkylammonium salt is tetraoctylammonium hydrogen sulfate.

[0165] Other compounds commonly thought of as phase transfer catalysts in other applications, including crown ethers, cryptands or non-ionic surfactants alone, do not have a significant effect on conversion or the rate of the dehydrochlorination reaction in the same fashion.

[0166] In another embodiment, the HCFO-1326mxz(Z) can be twice dehydrochlorinated at temperatures well below 100°C using an aqueous basic solution in combination with quaternary alkylammonium salts wherein the alkyl groups are alkyl chains of at least four or more carbon atoms and further in combination with a non-ionic surfactant. One example of such a quaternary alkylammonium salt is tetrabutylammonium chloride.

[0167] In yet another embodiment, dehydrochlorination of the HCFO-1326mxz(Z) can be effected with quaternary alkylammonium salts, wherein the alkyl groups are alkyl chains having from four to twelve carbon atoms, and in the presence of a non-ionic surfactant. In one embodiment, the non-ionic surfactant is an ethoxylated

nonylphenol or an ethoxylated C12-C15 linear aliphatic alcohol. Suitable non-ionic surfactants include Bio-soft® N25-9 and Makon® 10 are from Stepan Company.

[0168] In one embodiment, the quaternary alkylammonium salt is selected from tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium hydrogen sulfate, tetraoctylammonium chloride, tetraoctylammonium bromide, tetraoctylammonium hydrogen sulfate, methytrioctylammonium chloride, methyltrioctylammonium bromide, tetradecylammonium chloride, tetradecylammonium bromide, and tetradodecylammonium chloride.

[0169] In one embodiment, the quaternary alkyl ammonium salt is a tetrabutylammonium salt. In another embodiment, the quaternary alkylammonium salt is a tetrahexylammonium salt. In another embodiment, the quaternary alkylammonium salt is a tetraoctylammonium salt. In yet another embodiment, the quaternary alkylammonium salt is a trioctylmethylammonium salt.

[0170] Dehydrochlorination of HCFO-1326mxz(Z) can be effected with quaternary alkylammonium salts, wherein the alkyl groups are alkyl chains having at least one alkyl chain of 8 carbons or more. In another embodiment, the quaternary alkylammonium salt has three alkyl chains of 8 carbons or more, such as trioctylmethylammonium salt. In yet another embodiment, the quaternary alkylammonium salt is a tetraoctylammonium salt. In yet another embodiment, the quaternary ammonium salt is a tetradecylammonium salt. In yet another embodiment, the quaternary alkylammonium salt is a tetradodecylammonium salt. The anions of the salt can be halides such as chloride or bromide, hydrogen sulfate, or any other commonly used anion.

[0171] In one embodiment, the quaternary alkylammonium salts is added in an amount of from 0.5 mole percent to 2.0 mole percent of the HCFO-1326mxz(Z). In another embodiment, the quaternary alkylammonium salts is added in an amount of from 1 mole percent to 2 mole percent of the HCFO-1326mxz(Z). In yet another embodiment, the quaternary alkylammonium salts is added in an amount of from 1 mole percent to 1.5 mole percent of the HCFO-1326mxz(Z). In one embodiment, the quaternary alkylammonium salt is added in an amount of from 1 mole percent to 1.5 mole percent of the HCFO-1326mxz(Z) and the weight of non-ionic surfactant added is from 1.0 to 2.0 times the weight of the quaternary alkylammonium salt.

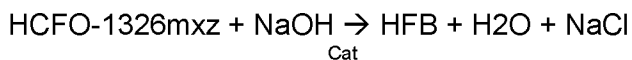
[0172] Exemplary bases include, but are not limited to, lithium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium oxide, calcium oxide, sodium carbonate, potassium carbonate, sodium phosphate, potassium phosphate, and mixtures thereof. Some example strong bases include, but are not limited to, hydroxides, alkoxides, metal amides, metal hydrides, metal dialkylamides and arylamines, wherein; alkoxides include lithium, sodium and potassium salts of methyl, ethyl and t-butyl oxides; metal amides include sodium amide, potassium amide and lithium amide; metal hydrides include sodium hydride, potassium hydride and lithium hydride; and metal dialkylamides include lithium, sodium, and potassium salts of methyl, ethyl, n-propyl, iso-propyl, n-butyl, tert-butyl, trimethylsilyl and cyclohexyl substituted amides.

[0173] In some embodiments, the base is selected from the group consisting of lithium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium oxide, calcium oxide, sodium carbonate, potassium carbonate, sodium phosphate, potassium phosphate, and mixtures thereof.

[0174] In some embodiments, the base is an aqueous basic solution. As used herein, the "basic aqueous solution" is a liquid (e.g., a solution, dispersion, emulsion, or suspension, and the like) that is primarily an aqueous liquid having a pH of over 7.

[0175] In some embodiments, the basic aqueous solution contains small amounts of organic liquids which may be miscible or immiscible with water. In some embodiments, the liquid medium in the basic aqueous solution is at least 90% water, for example, at least 95%, at least 97%, at least 98%, at least 99%, at least 99.5%, or at least 99.9%. In some embodiments, the water used in the aqueous basic solution is tap water. In some embodiments, the water is used in the aqueous basic solution deionized water or distilled water.

[0176] In a preferred embodiment, the base used for the dehydrochlorination reaction is an aqueous solution of sodium hydroxide and the alkali metal halide salt produced as a byproduct is sodium chloride. This reaction is shown below:



[0177] In some embodiments, about 1 to about 5 molar equivalents of base is used based on one molar equivalent of the HCFO-1326mxz, for example, about 1 to about 3, about 1 to about 2, about 1 to about 1.5, about 1.5 to about 5, about 1.5 to about 3, about 1.5 to about 2, about 2 to about 5, about 2 to about 3, or about 3 to about 5 molar equivalents. In some embodiments, about 1 to about 1.5 molar equivalents of base is used based on one molar equivalent of the HCFO-1326mxz. In some embodiments, a molar excess of base is used based on one molar equivalent of the HCFO-1326mxz.

[0178] In one embodiment, the conversion of HCFO-1326mxz to HFB is at least 50% per hour.

[0179] The desired reaction results may be achieved through proper selection of operating conditions such as temperature, contact time and feed stream and/or catalyst ratios.

[0180] The reaction zone temperature for the dehydrochlorination of HCFO-1326mxz is in the range of from about 0°C to about 150°C, or about 30°C to about 60°C, for example, about 30° to about 50°C, about 30° to about 40°C, about 40° to about 60°C, about 40° to about 50°C, or about 50°C to about 60°C. The formation of byproducts can be reduced, and the deactivation of the catalyst can be suppressed by maintaining the reaction temperature within these ranges.

[0181] The contact time (CT) of the reactants and catalyst within the dehydrochlorination reactor R30 is determined by the following equation:

$$CT = VR/VF,$$

where VR is the volume (m³) of the dehydrochlorination reactor R30 in cubic meters and VF is the total liquid volumetric flow rate (m³/hr) of the reactor feeds. In one embodiment, the contact time is in the range of from about 0.1 to about 20 hours, preferably about 0.5 to about 5 hours, inclusive of all values and ranges therebetween. It will be understood by those skilled in the art that the contact time may impact selectivity and conversion of the HCFO-1326mxz to HFB, and thus adjustment of the contact time, either to a target time within the range of about 0.1 to about 20 hours or to a target time shorter or longer than this range, may be carried out as needed to achieve the desired reaction results.

[0182] The reactions in the dehydrochlorination reactor R30 are typically conducted at atmospheric pressure, or at a pressure lower than atmospheric pressure, or at a pressure higher than atmospheric pressure. That is, the reaction pressure in the dehydrochlorination reactor R30 for the dehydrochlorination reaction is not critical and may be adjusted as needed to achieve the desired reaction results. In one embodiment, the dehydrochlorination of HCFO-1326mxz reaction in the dehydrochlorination reactor R30 is carried out at a pressure in a range from about -0.05 to 1.8 MPaG (gauge pressure) to achieve improved reaction selectivity.

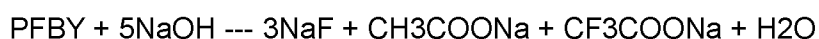
[0183] In some embodiments, the process of preparing the HFB in the dehydrochlorination reactor R30 is performed as a liquid phase process. In some embodiments, the process of preparing the HFB is performed in the absence of an additional solvent component.

[0184] The process of preparing the HFB may be conducted in a batchwise process or a continuous process.

[0185] In one embodiment, upon completion of a batchwise or continuous dehydrochlorination process, the HFB is of sufficient purity to not require further purification steps.

[0186] In another embodiment, upon completion of a batchwise or continuous dehydrochlorination process, the HFB can be recovered through any conventional process, including for example, fractional distillation.

[0187] The boiling point of the HCFO-1326mxz starting material is about 35°C and the boiling point of HFB is about -25°C. Thus, in one embodiment, the dehydrochlorination reactor R30 may be provided with a condenser (e.g., a partial condenser) in order to enhance the removal of the HFB and also prevent HFB decomposition in contact with the base, as shown in the following reaction scheme:



[0188] In one embodiment, the reaction mixture obtained in the dehydrochlorination reactor R30 from the dehydrochlorination of HCFO-1326mxz comprises both vapor and liquid portions. A first stream S30 comprises the liquid portion of the reaction mixture and comprises, consists essentially of, or consists of water, unreacted HCFO-1326mxz, excess PTC and byproducts, such as salts (e.g.,

sodium chloride) formed in the reaction forming the HFB. The first stream S30 is comprised of separate aqueous and organic liquid phases.

[0189] The first stream S30 is supplied from reactor R30 to a decanter E30. In some embodiments, the decanter E30 operates at atmospheric pressure, or a pressure of about 500 psig or less, or about 300 psig or less, or about 100 psig or less, or about 50 psig or less. The temperature of the decanter E30 is not specifically limited and may proceed at reduced, preferred and increased temperature. In one embodiment, the operating temperature of the decanter E30 is from about 0°C to about 50°C.

[0190] The decanter E30 separates the aqueous liquid and organic liquid phases contained in stream S30 into a lower density, aqueous first fraction comprising, consisting essentially of, or consisting of water and salts formed in the dehydrochlorination of HCFO-1326mxz, and a higher density, organic second fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz, excess PTC and other organic byproducts from the dehydrochlorination reaction. The first fraction is removed from the decanter E30 in a second stream S31, and the second stream S31 is removed from the process.

[0191] The second fraction is removed from the decanter E30 as a third stream S32. A first portion of the third stream S32 returns to reactor R30 (optionally passing through one or more filters) via a fourth stream S33 for further participation in the reaction to produce HFB. The remaining (second) portion of the third stream S32 is supplied to a first distillation column D30 as a fifth stream S34. The proportion of the split of the first and second portions of the third stream S32 may vary between 0% direct return to reactor R30 in fourth stream S33 to 100% direct return to reactor R30 in fourth stream S33. The ratio of the split may be adjusted as needed to achieve the desired reaction results and to control the concentration of impurities and PTC in the reaction system.

[0192] In some embodiments, the first distillation column D30 operates at a pressure of about 300 psig or less, or about 150 psig or less, or about 75 psig or less. In one embodiment, the operating pressure of the first distillation column D30 is slightly lower than the operating pressure of the decanter E30 to allow for flow from the decanter E30 to the first distillation column D30.

[0193] In the first distillation column D30, the fifth stream S34 is separated, by distillation, into a lower boiling, first fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz and optionally other organic byproducts from the dehydrochlorination reaction, and a higher boiling, second fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz, excess PTC and other organic byproducts from the dehydrochlorination reaction. The majority of the HCFO-1326mxz supplied to the first distillation column D30 is removed from the column in the lower boiling, first fraction. The first fraction is removed from the first distillation column D30 via a sixth stream S35 which is returned to the dehydrochlorination reactor R30 for further participation in the reaction to produce HFB. The second fraction is removed from the first distillation column D30 via a seventh stream S36, which is ultimately removed from the process.

[0194] In some embodiments, the sixth stream S35 (first fraction) comprises (i) HCFO-1326mxz, (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and (iii) one or more of the additional compounds listed in Table 1. In some embodiments, the composition of the sixth stream S35 comprises greater than about 95 mole percent Z-HCFO-1326mxz, or greater than 96 mole percent Z-HCFO-1326mxz, or greater than 97 mole percent Z-HCFO-1326mxz, or greater than 98 mole percent Z-HCFO-1326mxz, or greater than 99 mole percent Z-HCFO-1326mxz.

[0195] In some embodiments, the water content of the composition of the sixth stream S35 is about 10000 ppm or less or 5000 ppm or less, or about 4000 ppm or less, or about 3000 ppm or less, or about 1000 ppm or less. In some embodiments, the composition of the sixth stream S35 comprises about 100 ppm or less of the base, and about 500 ppm or less of the phase transfer catalyst.

[0196] Referring back to reactor R30, an eighth stream S37 comprises the vapor portion of the reaction mixture and comprises, consists essentially of, or consists of HFB (normal boiling point -24°C), HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction. The eighth stream S37 is supplied from the dehydrochlorination reactor R30 to a second distillation column D31. In some embodiments, the second distillation column D31 operates at a pressure of about 300 psig or less, or about 150 psig or less, or about 75 psig or less. In one embodiment, the operating pressure of the second distillation column

D31 is slightly lower than the operating pressure of the reactor R30 to allow for flow from the reactor R30 to the second distillation column D31.

[0197] The second distillation column D31 separates, by distillation, the eighth stream S37 into a lower boiling, first fraction comprising, consisting essentially of, or consisting of HFB, and a higher boiling, second fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction. The second fraction is removed from the second distillation column D31 via a ninth stream S38, which is comprised mostly of HCFO-1326mxz. The ninth stream S38 is returned to reactor R30 for further participation in the reaction to produce HFB.

[0198] In some embodiments, the ninth stream S38 (second fraction) comprises (i) HCFO-1326mxz, (ii) one or more of trifluoroacetone, trifluoropropyne, and hexafluoro-2-butyne, and (iii) one or more of the additional compounds listed in Table 1. In some embodiments, the composition of the ninth stream S38 comprises greater than about 95 mole percent Z-HCFO-1326mxz, or greater than 96 mole percent Z-HCFO-1326mxz, or greater than 97 mole percent Z-HCFO-1326mxz, or greater than 98 mole percent Z-HCFO-1326mxz, or greater than 99 mole percent Z-HCFO-1326mxz.

[0199] In some embodiments, the water content of the composition of the ninth stream S38 is about 5000 ppm or less, or about 4000 ppm or less, or about 3000 ppm or less, or about 1000 ppm or less.

[0200] The majority of the HFB supplied to the second distillation column D31 is removed from the column in the lower boiling fraction stream S39.

[0201] In one embodiment, the lower boiling, first fraction is removed from the second distillation column D31 via a tenth stream S39 which is comprised mostly of HFB, as well as HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction, and the lower boiling fraction (stream S39) from the second distillation column D31 may then be supplied to a third distillation column D32. The pressure of the third distillation column D32 is not specifically limited and may proceed at reduced, preferred and increased pressure. In one embodiment, the operating pressure of the third distillation column D32 is about 0.1 to about 0.5 MPaG.

[0202] In another embodiment, the lower boiling, first fraction is optionally removed from the second distillation column D31 via a tenth stream S39 which is comprised mostly of HFB. The desired product HFB may then be recovered from the tenth stream S39 and utilized, for example, to produce HCFO-1336mzz(Z).

[0203] The third distillation column D32 separates the components into lower boiling and higher boiling fractions. The lower boiling fraction comprises the desired product from this process step, namely HFB, and is removed from the third distillation column D32 in stream S3-10. The majority of the HFB supplied to the third distillation column D32 is removed from the column in an eleventh stream S3-10 comprising the lower boiling fraction. The eleventh stream S3-10 is removed from the process. The higher boiling fraction is removed from the third distillation column D32 in a twelfth stream S3-11. The twelfth stream S3-11 comprises, consists of or consists essentially of HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction.

[0204] The higher boiling fraction from the third distillation column D32 may optionally be supplied to a fourth distillation column D33 in the twelfth stream S3-11. The fourth distillation column D33 separates the components into lower boiling and higher boiling fractions. The lower boiling fraction comprises, consists of or consists essentially of HCFO-1326mxz; 1,1,1,4,4,4-hexafluoro-but-2-ene (HCFO-1336mzz); water and other lower boiling organic byproducts from the dehydrochlorination reaction. The lower boiling fraction exits the fourth distillation column D33 in a thirteenth stream S3-12. The thirteenth stream S3-12 is removed from the process. The higher boiling fraction is removed from the fourth distillation column D33 in a fourteenth stream S3-13. The fourteenth stream S3-13 comprises, consists of or consists essentially of HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction.

[0205] The fourteenth stream S3-13 comprising HCFO-1326mxz, water and other organic byproducts is returned to the reactor R30 for further participation in the dehydrochlorination reaction to produce HFB.

[0206] In one embodiment, the operating pressure of the fourth distillation column D33 is slightly lower than the operating pressure of the third distillation column D32

to allow for flow from the third distillation column D32 to the fourth distillation column D33.

[0207] As shown in Fig. 3, a preferred embodiment of the system for producing HFB from HCFO-1326mxz includes a reactor R30 for producing a composition comprising, consisting of or consisting essentially of HFB, a decanter for removing water and salts from the composition, and a series of distillation columns D30, D31, D32 and D33 for isolation, purification and recovery of the HFB. The system may further comprise a partial condenser to facilitate recovery of HFB product from the reactor R30.

[0208] As shown in Fig. 3, a preferred embodiment of the present invention provides a process for purification of a mixture comprising HFB. The process comprises providing the mixture to a series of distillation columns D30, D31, D32 and D33 for purification and recovery of a composition comprising, consisting of or consisting essentially of HFB, and recycling of unreacted HCFO-1326mxz from the series of distillation columns for dehydrochlorination to produce the mixture comprising HFB.

[0209] In one embodiment, the above-described system and process of dehydrochlorination of HCFO-1326mxz produces a composition comprising:

- i) hexafluorobutylene; and
- ii) one or more additional compounds selected from:
 - 1,1,1,3,3,3-hexafluoropropane;
 - 1,1,1,2,4,4,4-heptafluoro-2-butene;
 - (E)-1,1,1,4,4,4-hexafluorobutene;
 - 1,1,1,2,2,4,4,4-octafluorobutane;
 - 1,1,1,4,4,4-hexafluorobutane;
 - 1,2-dichloro-1,1,2,2-tetrafluoroethane;
 - 2-chloro-1,1,1-trifluoroethane;
 - (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
 - 1-chloro-3,3,4,4,4-pentafluorobut-1-yne;
 - 1-chloro-3,3,4,4,4-pentafluorobut-2-yne;
 - (Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;
 - 1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene

2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
2-chloro-1,1,1,3,3-pentafluoropropane;
1-chloro-1,1,3,3,3-pentafluoropropane;
(E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
2-chloro-1,1,1,4,4,4-hexafluorobutane;
2,2-dichloro-1,1,1-trifluoroethane;
1,2-dichloro-1,1,2-trifluoroethane;
1,2-dichloro-1,1,3,3,3-pentafluoropropane;
(E)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
1,1,2-trichloro-1,2,2-trifluoroethane;
(Z)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
1-chloro-3,3,3-trifluoroprop-1-yne;
1,2-dichloro-3,3,3-trifluoroprop-1-ene;
(Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;
1-chloro-1,1,2,4,4,4-hexafluoro-2-butene;
2-chloro-1,3,3,3-tetrafluoroprop-1-ene;
1,1,3,3,3-pentafluoroprop-1-ene; and
2-chloro-1,1,3,3,3-pentafluoroprop-1-ene;

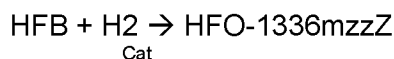
[0210] In some embodiments, the composition comprises greater than about 95 mole percent HFB.

System D and Process 3

[0211] Fig. 4 shows a schematic diagram for a system and process for producing (Z)-1,1,1,4,4,4-hexafluoro-2-butene ((Z)-HFO-1336mzz) from the HFB produced according to the process of Process 2, according to an embodiment of the present invention. As shown in Fig. 4, a preferred embodiment of the system includes a reactor R40, a first distillation column D40 in flow communication with the reactor R40, and a second distillation column D41 in flow communication with the first distillation column D40. In one embodiment, the reactor R40 is a continuous vapor phase reactor containing solid catalyst. In one embodiment, the reactor configuration for producing Z-HFO-1336mzz could be a single reactor or multiple reactors in series.

[0212] Referring to Fig. 4, the eleventh stream S3-10 comprising, consisting essentially of, or consisting of HFB is fed to a reactor R40 via a first feed stream F40. In the reactor R40, the HFB is subjected to hydrogenation in the presence of a catalyst to form HFO-1336mzz(Z) (normal boiling point 33°C). More particularly, in the hydrogenation reactor R40, along with the feed stream F40 comprising HFB, hydrogen is co-fed to the reactor R40 in a second feed stream F41.

[0213] The hydrogenation reaction is shown below:



[0214] In some embodiments, the hydrogenation process is conducted simply by flowing HFB and hydrogen into a catalyst bed in the reactor R40 at a specified temperature. In some embodiments, the process is conducted by flowing HFB, hydrogen, and a carrier gas into the catalyst bed in the reactor R40. Examples of carrier gases include inert gases such as nitrogen, argon and helium.

[0215] The desired reaction results may be achieved through proper selection of operating conditions such as temperature, contact time and HFB to hydrogen ratios.

[0216] The reaction zone temperature for the hydrogenation of HFB is in the range of from about 20°C to about 200°C, or about room temperature, about 40°C to about 90°C, about 60°C to about 90°C, about 60°C to about 150°C. In some embodiments, the process is performed a temperature of from about 60°C to about 120°C. The formation of byproducts can be reduced, and the deactivation of the catalyst can be suppressed by maintaining the reaction temperature within these ranges. However, it will be understood by those skilled in the art that hydrogenation of HFB is an exothermic reaction and temperatures higher than the range of from about 30°C to about 200°C may occur locally within the hydrogenation reactor R40 or catalyst. The pressure of the reactor is from 1 psig to 300 psig, 20 psig to 200 psig, 40 psig to 100 psig

[0217] In one embodiment, a heat diluent may be used to reduce any temperature increase generated by the exothermic reaction. For example, the heat diluent may be an inert material which is compatible with the process and is injected into reactor R40.

[0218] In some embodiments, the process of preparing the HFO-1336mzzZ is performed as a liquid phase process. In some embodiments, the process of preparing the HFO-1336mzzZ is performed in the absence of an additional solvent component. In one embodiment, a controlled feed of the hydrogen is introduced to reactor R40 as a heat diluent or mitigation component.

[0219] In another embodiment, the hydrogen is hydrogen gas and the process of preparing the HFO-1336mzzZ is performed as a vapor phase process. In one embodiment, to enhance heat mitigation due to the exothermic nature of the reaction for preparing the HFO-1336mzzZ, a plurality of gas phase reactors, such as multiple reactors R40, are arranged for carrying out the hydrogenation reaction to prepare HFO-1336mzzZ.

[0220] The contact time (CT) of the reactants and catalyst within the hydrogenation reactor R40 is determined by the following equation:

$$CT = VR/VF,$$

where VR is the volume (m³) of the hydrogenation reactor R40 in cubic meters and VF is the total liquid volumetric flow rate (m³/hr) of the reactor feeds. In one embodiment, the contact time is in the range of from about 1 to about 120 seconds, or about 1 to about 60 seconds, or about 5 to about 120 seconds, inclusive of all values and ranges therebetween. It will be understood by those skilled in the art that the contact time may impact selectivity and conversion of the HFB, and thus adjustment of the contact time, either to a target time within the range of about 1 to about 60 seconds or to a target time shorter or longer than this range, may be carried out as needed to achieve the desired reaction results.

[0221] The reactions in the hydrogenation reactor R40 are typically conducted at atmospheric pressure, or at a pressure lower than atmospheric pressure, or at a pressure higher than atmospheric pressure. That is, the reaction pressure in the hydrogenation reactor R40 for the hydrogenation reaction is not critical and may be adjusted as needed to achieve the desired reaction results. In one embodiment, the hydrogenation reaction in the hydrogenation reactor R40 is carried out at pressures greater than atmospheric pressure, for example, because increased pressure reduces the size of equipment proceeding the reaction. In one embodiment, the

pressure within the hydrogenation reactor R40 is in a range from about 0 to 2.0 MPaG (gauge pressure).

[0222] Preferably, the process of preparing the HFO-1336mzzZ is performed as a vapor phase process.

[0223] The process of preparing the HFO-1336mzzZ may be conducted in a batchwise process or a continuous process.

[0224] In some embodiments, about 1 molar equivalent of hydrogen is used based on 1 molar equivalent of the HFB. In some embodiments, about 0.5 to about 1 molar equivalents of hydrogen is used based on 1 molar equivalent of the hydrogenation of HFB. In some embodiments, about 0.67 to about 1 molar equivalents of hydrogen is used based on 1 molar equivalent of the hydrogenation of HFB.

[0225] In some embodiments, the hydrogenation catalyst is a palladium catalyst. In one embodiment, the catalyst is a palladium catalyst dispersed on aluminum oxide or titanium silicate, doped with silver and/or a lanthanide, with a low loading of palladium. In one embodiment, the palladium loading is from 100 ppm to 5000 ppm. In another embodiment, the palladium loading is from 200 ppm to 5000 ppm. In one embodiment, the catalyst is doped with at least one of silver, cerium or lanthanum. In one embodiment, the mole ratio of cerium or lanthanum to palladium is from 2:1 to 3:1. In one embodiment the mole ratio of silver to palladium is about 0.5:1.0.

[0226] In some embodiments, the hydrogenation catalyst is Lindlar's catalyst. As used herein, the term "Lindlar's catalyst" refers to a heterogeneous palladium catalyst on a calcium carbonate support, which has been deactivated or conditioned with a lead compound. The lead compound can be, for example, lead acetate, lead oxide, or any other suitable lead compound. In some embodiments, the Lindlar's catalyst is prepared by reduction of a palladium salt in the presence of a slurry of calcium carbonate, followed by the addition of the lead compound. In some embodiments, the palladium salt is palladium chloride. In some embodiments, the catalyst is deactivated or conditioned with quinoline. In some embodiments, the hydrogenation catalyst is a palladium catalyst dispersed on aluminum oxide or titanium silicate, doped with silver and/or a lanthanide. In some embodiments, the palladium loading on the aluminum oxide or titanium silicate is from 100 ppm to 5000

ppm. In some embodiments, the palladium loading on the aluminum oxide or titanium silicate is from 200 ppm to 5000 ppm.

[0227] In some embodiments, the hydrogenation catalyst is doped with at least one of silver, cerium, or lanthanum. In some embodiments, the hydrogenation catalyst is doped with silver. In some embodiments, the molar ratio of silver to palladium is about 0.5:1.0. In some embodiments, the hydrogenation catalyst is doped with cerium or lanthanum. In some embodiments, the molar ratio of cerium or lanthanum to palladium is from about 2:1 to about 3:1.

[0228] In some embodiments, a catalytic amount (i.e., less than 1 molar equivalent) of the hydrogenation catalyst is used based on 1 molar equivalent of the hydrogenation of HFB.

[0229] In one embodiment of a continuous process, the mixture of HFB and hydrogen further comprises an inert carrier gas. In one embodiment, the inert carrier gas is selected from the group consisting of nitrogen, helium, or argon. In one embodiment, the inert carrier gas is from about 10% to about 80% of the gas fed to the continuous process. In another embodiment, the inert carrier gas is from about 20% to about 50% of the gas fed to the continuous process.

[0230] In one embodiment of a continuous process, the amount of palladium on the support in the Lindlar catalyst is 5% by weight. In another embodiment, the amount of palladium on the support in the Lindlar catalyst is greater than 5% by weight. In yet another embodiment, the amount of palladium on the support can be from about 5% by weight to about 1% by weight.

[0231] In some embodiments, about 0.5 to about 4 percent by weight of the hydrogenation catalyst is used based on the weight of hydrogenation of HFB. In some embodiments, about 1 to about 3 percent by weight of the hydrogenation catalyst is used based on the weight of hydrogenation of HFB. In some embodiments, about 1 to about 2 percent by weight of the hydrogenation catalyst is used based on the weight of hydrogenation of HFB.

[0232] In some embodiments, greater than about 95 mole percent of the HFO-1336mzz produced by the process provided herein is Z-HFO-1336mzz, for example, greater than about 97 mole percent, greater than about 98 mole percent, greater

than about 99 mole percent, greater than about 99.5 mole percent, greater than about 99.9 mole percent. In some embodiments, greater than about 99 mole percent of the HFO-1336mzz produced by the process provided herein is Z-HFO-1336mzz.

[0233] In one embodiment, upon completion of a batch-wise or continuous hydrogenation process, the Z-HFO-1336mzz is of sufficient purity to not require further purification steps.

[0234] In another embodiment, upon completion of a batch-wise or continuous hydrogenation process, the Z-HFO-1336mzz can be recovered through any conventional process, including for example, fractional distillation.

[0235] The reaction mixture obtained in the hydrogenation reactor R40 exits the hydrogenation reactor R40 as a first stream S40. The first stream S40 (i.e., the reaction mixture) comprises, consists essentially of, or consists of unreacted HFB and HFO-1336mzz(Z). A heat diluent, if used for the hydrogenation reaction, may also be present in the first stream S40. Example of the heat diluent include, but are not limited to, HFC-32, HFC-143a, HFC-134a and HFC-134.

[0236] The first stream S40 is supplied from the hydrogenation reactor R40 to a first distillation column D40. In some embodiments, the first distillation column D40 operates at a pressure of about 300 psig or less, or about 200 psig or less, or about 100 psig or less. In one embodiment, the operating pressure of the first distillation column D40 is slightly higher than the operating pressure of the hydrogenation reactor R40 to allow for flow from the first distillation column D40 to the reactor R40.

[0237] The first distillation column D40 separates the first stream S40 into a lower boiling, first fraction comprising, consisting essentially of or consisting of unreacted HFB, other lower boiling organic byproducts from the hydrogenation reaction, and a heat diluent if used, and a higher boiling, second fraction comprising, consisting essentially of or consisting of Z-HFO-1336mzz and other higher boiling organic byproducts from the hydrogenation reaction. The majority of the HFB supplied to the first distillation column D40 leaves the column in the lower boiling first fraction. The first fraction is removed from the first distillation column D40 in a second stream S41. Preferably, the second stream S41 is returned to the hydrogenation reactor R40 for continued participation in the reaction to produce HFB. The second fraction is removed from the first distillation column D40 in a third stream S42.

[0238] The third stream S42 comprising, consisting essentially of or consisting of Z-HFO-1336mzz and other higher boiling organic byproducts from the hydrogenation reaction is supplied from the first distillation column D40 to a second distillation column D41. In some embodiments, the second distillation column D41 operates at a pressure of about 150 psig or less, or about 100 psig or less, or about 50 psig or less. In one embodiment, the operating pressure of the second distillation column D41 is slightly lower than the operating pressure of the first distillation column D40 to allow for flow from the first distillation column D40 to the second distillation column D41.

[0239] The second distillation column D41 separates the third stream S42 into a lower boiling, first fraction comprising, consisting essentially of or consisting of mostly Z-HFO-1336mzz, 1,1,1,4,4,4-hexafluorobutane (HCFC-356mff), and other lower boiling organic byproducts from the hydrogenation reaction, and a higher boiling, second fraction comprising, consisting essentially of or consisting of Z-HFO-1336mzz and other higher boiling organic byproducts from the hydrogenation reaction. The first fraction is removed from the second distillation column D41 in a fourth stream S43. The second fraction comprising mostly (Z)-HFO-1336mzz and other higher boiling organic byproducts from the hydrogenation reaction is removed from the second distillation column D41 in a fifth stream S44. The majority of the (Z)-HFO-1336mzz supplied to the second distillation column D41 is removed from the column in the higher boiling fraction stream S44.

[0240] In one embodiment, the high boiling fraction of the second distillation column D41 in stream S44 may optionally be supplied to a third distillation column D42. In one embodiment, the operating pressure of the third distillation column D42 is slightly lower than the operating pressure of the second distillation column D41 to allow for flow from the third distillation column D41 to the second distillation column D40.

[0241] The third distillation column D42 separates the components of the fifth stream S44 into a lower boiling, first fraction comprising, consisting of or consisting essentially of Z-HFO-1336mzz, and a higher boiling, second fraction comprising, consisting of or consisting essentially of Z-HFO-1336mzz and higher boiling organic byproducts from the hydrogenation reaction. The lower boiling fraction is the desired

product from this process step, i.e., Z-HFO-1336mzz, and is removed from the process in a sixth stream S45. The majority of the Z-HFO-1336mzz supplied to the third distillation column D42 is removed from the column in the lower boiling fraction stream S45. The higher boiling fraction is removed from the third distillation column D42 in a seventh stream S46.

[0242] As shown in Fig. 4, a preferred embodiment of the system for producing Z-HFO-1336mzz from HFB includes a reactor R40 for producing a composition comprising, consisting of or consisting essentially of Z-HFO-1336mzz and a series of distillation columns D40, D41, D42 for isolation, purification and recovery of the Z-HFO-1336mzz.

[0243] As shown in Fig. 4, a preferred embodiment of the present invention provides a process for purification of a mixture comprising Z-HFO-1336mzz. The process comprises providing the mixture to a series of distillation columns D40, D41, D42 for purification and recovery of a composition comprising, consisting of or consisting essentially of Z-HFO-1336mzz, and recycling of unreacted HFB from the series of distillation columns for hydrogenation to produce the mixture comprising Z-HFO-1336mzz.

[0244] In one embodiment, the above-described system and process of hydrogenation of HFB produces a composition comprising:

- i) (Z)-1,1,1,4,4,4-hexafluoro-2-butene; and
- ii) one or more additional compounds selected from:
 - 1,1,1,3,3,3-hexafluoropropane;
 - (E)-1,1,1,4,4,4-hexafluorobutene;
 - 1,1,1,2,2,4,4,4-octafluorobutane;
 - 1,2-dichloro-1,1,2,2-tetrafluoroethane;
 - 3-chloro-1,1,1-trifluoropropane;
 - 4-chloro-1,1,1,2,2-pentafluorobutane;
 - 2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,3-pentafluoropropane;
 - 1-chloro-1,1,3,3,3-pentafluoropropane;
 - 2-chloro-1,1,1,4,4,4-hexafluorobutane;

1,2-dichloro-1,1,3,3,3-pentafluoropropane;
1,2-dichloro-3,3,3-trifluoroprop-1-ene;
1-chloro-3,3,3-trifluoro-propene;
1-chloro-1,1,2,4,4,4-hexafluoro-2-butene;
1-chloro-1,1,4,4,4-pentafluorobutane;
2-chloro-1,1,1,3-tetrafluoropropane; and
1,1,1,3,3-pentafluoropropane;

wherein the composition comprises greater than about 99 mole percent Z-HFO-1336mzz.

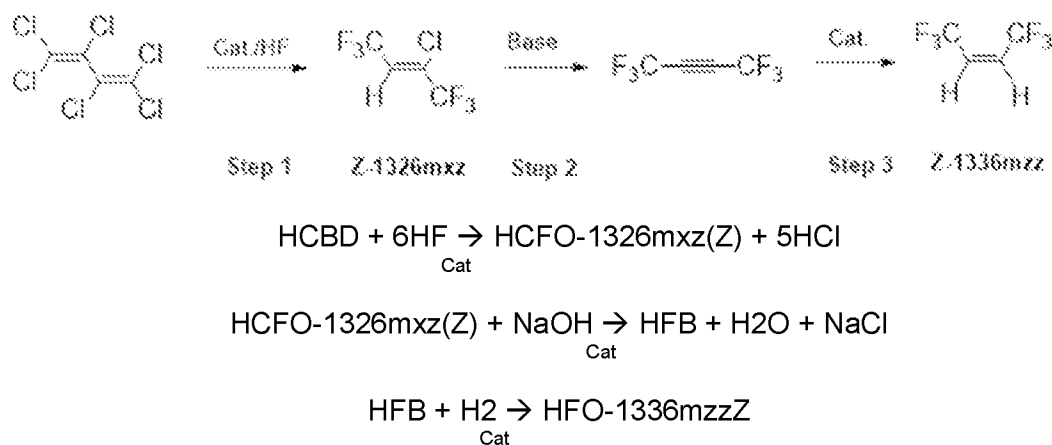
Integrated System and Process

[0245] The present application further provides a process of preparing Z-HFO-1336mzz comprising: i) reacting HCBD with HF in the presence of a fluorination catalyst to form a first composition comprising, consisting of or consisting essentially of HCFO-1326mxz (both isomers); ii) reacting the HCFO-1326mxz with a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst to form a second composition comprising, consisting of or consisting essentially of HFB; and iii) reacting the HFB with hydrogen in the presence of a hydrogenation catalyst to form a third composition comprising, consisting of or consisting essentially of Z-HFO-1336mzz. The catalysts, reagents, process parameters, conversions, and the like of this integrated process embodiment may be selected from any of the respective disclosures provided above with respect to the individual process embodiments.

[0246] The present application further provides a process of preparing Z-HFO-1336mzz comprising: i) reacting HCBD with HF in the presence of a fluorination catalyst to form a first composition comprising, consisting of or consisting essentially of HCFO-1326mxz (both isomers); ii) recovering the HCFO-1326mxz; iii) reacting the HCFO-1326mxz with a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst to form a second composition comprising, consisting of or consisting essentially of HFB; iv) recovering the HFB; v) reacting the HFB with hydrogen in the presence of a hydrogenation catalyst to form a third composition comprising, consisting of or consisting essentially of Z-HFO-1336mzz; and vi) recovering the Z-HFO-1336mzz. The catalysts, reagents, process parameters,

conversions, and the like of this integrated process embodiment may be selected from any of the respective disclosures provided above with respect to the individual process embodiments.

[0247] The present application further provides a process of preparing Z-HFO-1336mzz comprising: i) reacting HCBD with HF in the presence of a fluorination catalyst to form a first composition comprising, consisting of or consisting essentially of HCFO-1326mxz (both isomers); ii) reacting the HCFO-1326mxz with an aqueous basis solution comprising sodium hydroxide in the presence of a phase transfer catalyst to form a second composition comprising, consisting of or consisting essentially of HFB; and iii) reacting the HFB with hydrogen in the presence of a hydrogenation catalyst to form a third composition comprising, consisting of or consisting essentially of Z-HFO-1336mzz. The catalysts, reagents, process parameters, conversions, and the like of this integrated process embodiment may be selected from any of the respective disclosures provided above with respect to the individual process embodiments. These reactions are as follows:



[0248] In some embodiments, the present invention provides a system (System A) for preparing HCFO-1326mxz comprising:

- i) a reactor configured to react HCBD with HF in the presence of a catalyst to form a composition comprising HCFO-1326mxz (both isomers), HCl, unreacted HCBD, unreacted HF and optionally impurities;

- ii) a first distillation column configured to receive the composition from the reactor and configured to separate the first composition into a first fraction F_{1D10} comprising HCl and impurities, and a second fraction F_{2D10} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz;
- iii) a second distillation column configured to receive the second fraction F_{2D10} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the first distillation column and configured to separate the second fraction into a third fraction F_{3D11} comprising an azeotrope of unreacted HF and HCFO-1326mxz, and a fourth fraction F_{4D11} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz, the second distillation column being configured to return the third fraction F_{3D11} to the reactor; and
- iv) a third distillation column configured to receive the fourth fraction F_{4D11} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the second distillation column and configured to separate the fourth fraction F_{4D11} into a fifth fraction F_{5D12} comprising unreacted HF and unreacted HCBd, and a sixth fraction F_{6D12} comprising HCFO-1326mxz, the third distillation column being configured to return the fifth fraction F_{5D12} to the reactor.

[0249] In some embodiments, the present invention provides a process for preparation and purification of HCFO-1326mxz comprising:

- i) reacting HCBd with HF in the presence of a catalyst in a reactor to form a first composition comprising HCFO-1326mxz (both isomers), HCl, unreacted HCBd, unreacted HF and optionally impurities;
- ii) providing the first composition to a first distillation column and separating the first composition into a first fraction F_{1D10} comprising HCl and impurities, and a second fraction F_{2D10} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz;
- iii) providing the second fraction F_{2D10} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the first distillation column

to a second distillation column and separating the second fraction into a third fraction F_{3D11} comprising an azeotrope of unreacted HF and HCFO-1326mxz, and a fourth fraction F_{4D11} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz; and

- iv) providing the fourth fraction F_{4D11} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the second distillation column to a third distillation column and separating the fourth fraction F_{4D11} into a fifth fraction F_{5D12} comprising unreacted HF and unreacted HCBd, and a sixth fraction F_{6D12} comprising HCFO-1326mxz,

wherein optionally, the third fraction F_{3D11} is recycled from the second distillation column to the reactor, and wherein optionally the fifth fraction F_{5D12} is recycled from the third distillation column to the reactor.

[0250] In some embodiments, the present invention provides a system (System B) for preparing HCFO-1326mxz comprising:

- i) a reactor configured to react HCBd with HF in the presence of a catalyst to form a composition comprising HCFO-1326mxz (both isomers), HCl, unreacted HCBd, unreacted HF and optionally impurities;
- ii) a first distillation column configured to receive the composition from the reactor and configured to separate the first composition into a first fraction F_{1D20} comprising HCl and impurities, and a second fraction F_{2D20} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz;
- iii) a second distillation column configured to receive the second fraction F_{2D20} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the first distillation column and configured to separate the second fraction F_{2D20} into a third fraction F_{3D21} comprising unreacted HF and unreacted HCBd, and a fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz, the

second distillation column being configured to return the third fraction F_{3D21} to the reactor; and

- iv) an acid neutralizer configured to receive the fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz from the second distillation column and configured to separate the fourth fraction F_{4D21} into a fifth fraction F_{5A20} comprising neutralized HF and a sixth fraction F_{6A20} comprising HCFO-1326mxz.

[0251] In some embodiments, the present invention provides a process for preparation and purification of HCFO-1326mxz comprising:

- i) react HCBd with HF in the presence of a catalyst in a reactor to form a composition comprising HCFO-1326mxz (both isomers), HCl, unreacted HCBd, unreacted HF and optionally impurities;
- ii) providing the composition to a first distillation column and separating the first composition into a first fraction F_{1D20} comprising HCl and impurities, and a second fraction F_{2D20} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz;
- iii) providing the second fraction F_{2D20} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the first distillation column to a second distillation column and separating the second fraction F_{2D20} into a third fraction F_{3D21} comprising unreacted HF and unreacted HCBd, and a fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz; and
- iv) providing the fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz from the second distillation column to an acid neutralizer and separating the fourth fraction F_{4D21} into a fifth fraction F_{5A20} comprising neutralized HF and a sixth fraction F_{6A20} comprising HCFO-1326mxz,

wherein optionally the third fraction F_{3D21} is returned from the second distillation column to the reactor.

[0252] In some embodiments, the present invention provides a system (System C) for preparing HFB comprising:

- i) a reactor configured to react HCFO-1326mxz with a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst to form a composition comprising a vapor portion and a liquid portion, the vapor portion comprising HFB and unreacted HCFO-1326mxz, the liquid portion comprising water, unreacted HCFO-1326mxz, excess phase transfer catalyst and an alkali metal halide salt, the liquid portion being comprised of an aqueous liquid phase and an organic liquid phase;
- ii) a decanter configured to receive the liquid portion of the composition from the reactor and configured to separate the aqueous liquid phase into a first fraction $F1_{E30}$ comprising water and the alkali metal halide salt and to separate the organic liquid phase into a second fraction $F2_{E30}$ comprising the unreacted HCFO-1326mxz and excess phase transfer catalyst, the decanter being configured to return a first portion of the second fraction $F2_{E30}$ to the reactor;
- iii) a first distillation column configured to receive a second portion of the second fraction $F2_{E30}$ from the decanter and configured to separate the second portion of the second fraction $F2_{E30}$ into a third fraction $F3_{D30}$ comprising unreacted HCFO-1326mxz, and a fourth fraction $F4_{D30}$ comprising unreacted HCFO-1326mxz, excess PTC and optionally impurities, the first distillation column being configured to return the third fraction $F3_{D30}$ to the reactor; and
- iv) a second distillation column configured to receive the vapor portion of the composition from the reactor and configured to separate the vapor portion into a fifth fraction $F5_{D31}$ comprising HFB, and a sixth fraction $F6_{D31}$ comprising unreacted HCFO-1326mxz, the second distillation column being configured to return the sixth fraction $F6_{D31}$ to the reactor.

[0253] In some embodiments, the present invention provides a process for preparing HFB comprising:

- i) react HCFO-1326mxz with a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst in a reactor to form a composition comprising a vapor portion and a liquid portion, the vapor portion comprising HFB and unreacted HCFO-1326mxz, the liquid portion comprising water, unreacted HCFO-1326mxz, excess phase transfer catalyst and an alkali metal halide salt, the liquid portion being comprised of an aqueous liquid phase and an organic liquid phase;
- ii) providing the liquid portion of the composition from the reactor to a decanter configured and separating the aqueous liquid phase of the liquid portion into a first fraction $F1_{E30}$ comprising water and the alkali metal halide salt and separating the organic liquid phase of the liquid portion into a second fraction $F2_{E30}$ comprising the unreacted HCFO-1326mxz and excess phase transfer catalyst, wherein optionally a first portion of the second fraction $F2_{E30}$ is returned from the decanter to the reactor;
- iii) providing a second portion of the second fraction $F2_{E30}$ from the decanter to a first distillation column and separating the second portion of the second fraction $F2_{E30}$ into a third fraction $F3_{D30}$ comprising unreacted HCFO-1326mxz, and a fourth fraction $F4_{D30}$ comprising unreacted HCFO-1326mxz, excess PTC and optionally impurities, wherein optionally the third fraction $F3_{D30}$ is recycled from the first distillation column to the reactor; and
- iv) providing the vapor portion of the composition from the reactor to a second distillation column and separating the vapor portion into a fifth fraction $F5_{D31}$ comprising HFB, and a sixth fraction $F6_{D31}$ comprising unreacted HCFO-1326mxz, wherein optionally the sixth fraction $F6_{D31}$ is recycled from the second distillation column to the reactor.

[0254] In some embodiments, the present invention provides a process (System D) for preparing Z-HFO-1336mzz comprising:

- i) a reactor configured to react HFB with hydrogen in the presence of a hydrogenation catalyst to form a composition comprising HFO-1336mzz(Z) and unreacted HFB; and
- ii) a first distillation column configured to receive the composition from the reactor and configured to separate the composition into a first fraction $F1_{D40}$ comprising unreacted HFB and a second fraction $F2_{D40}$ comprising HFO-1336mzz(Z), the first distillation column being configured to return the $F1_{D40}$ to the reactor.

[0255] In one embodiment of the system for preparing Z-HFO-1336mzz, where the second fraction $F2_{D40}$ of the composition may comprise some impurities in addition to HFO-1336mzz(Z), the system further comprises a second distillation column configured to receive the second fraction $F2_{D40}$ from the first distillation column and configured to separate the second fraction $F2_{D40}$ into a third fraction $F3_{D41}$ comprising HFO-1336mzz(Z), HFO-1336mzz(E), 1,1,4,4,4-hexafluorobutane (HCFC-356mff), and lower boiling organic byproducts from the hydrogenation reaction and a fourth fraction $F4_{D41}$ comprising HFO-1336mzz(Z) and higher boiling organic byproducts from the hydrogenation reaction.

[0256] In some embodiments, the present invention provides a process for preparation and purification of Z-HFO-1336mzz comprising:

- iii) react HFB with hydrogen in the presence of a hydrogenation catalyst in a reactor to form a composition comprising HFO-1336mzz(Z) and unreacted HFB; and
- iv) providing the composition from the reactor to a first distillation column and separating the composition into a first fraction $F1_{D40}$ comprising unreacted HFB and a second fraction $F2_{D40}$ comprising HFO-1336mzz(Z), wherein optionally the first $F1_{D40}$ is returned from first distillation column to the reactor.

[0257] In one embodiment of the process for preparing and purifying Z-HFO-1336mzz, where the second fraction F_{D40} of the composition may comprise some impurities in addition to HFO-1336mzz(Z), the process further comprises providing the second fraction F_{D40} from the first distillation column to a second distillation column and separating the second fraction F_{D40} into a third fraction F_{D41} comprising HFO-1336mzz(Z), HFO-1336mzz(E), 1,1,4,4,4-hexafluorobutane (HCFC-356mff), and lower boiling organic byproducts from the hydrogenation reaction and a fourth fraction F_{D41} comprising HFO-1336mzz(Z) and higher boiling organic byproducts from the hydrogenation reaction.

[0258] In some embodiments, the above-described systems and/or process are integrated together to form a collective system and/or process for preparing HFO-1336mzz(Z) from HCBD.

[0259] As such, in one embodiment, an integrated system according to the present invention comprises the third distillation column D12 of System A being configured to supply the sixth fraction F_{D12} comprising HCFO-1326mxz to the dehydrochlorination reactor R30 of System C, and the second distillation column D31 of System C being configured to supply the seventh fraction F_{D32} ~~fifth fraction F_{D34}~~ comprising HFB to the hydrogenation reactor R40 of System D. In another embodiment, an integrated system according to the present invention comprises the acid neutralizer A20 of System B being configured to supply the sixth fraction F_{A20} comprising HCFO-1326mxz to the dehydrochlorination reactor R30 of System C, and the second distillation column D31 of System C being configured to supply the seventh fraction F_{D32} comprising HFB to the hydrogenation reactor R40 of System D.

[0260] In another embodiment, an integrated purification process according to the present invention comprises: providing the sixth fraction F_{D12} comprising HCFO-1326mxz from the third distillation column D12 of System A to the dehydrochlorination reactor R30 of Process 2 to produce HFB, and providing the seventh fraction F_{D32} comprising HFB from the second distillation column D31 of Process 2 to the hydrogenation reactor R40 of Process 3 to produce Z-HFO-1336mzz. In another embodiment, an integrated process according to the present invention comprises providing the sixth fraction F_{A20} comprising HCFO-1326mxz from the acid neutralizer A20 of System B to the dehydrochlorination reactor R30 of

Process 2, and providing the seventh fraction F7_{D32} comprising HFB from the second distillation column D31 of Process 2 to the hydrogenation reactor R40 of Process 3.

[0261] In some embodiments, the first composition comprises greater than about 95 mole percent, greater than about 97 mole percent, greater than about 98 mole percent, greater than about 99 mole percent, greater than about 99.5 mole percent, or greater than about 99.9 mole percent Z-HCFO-1326mxz. In some embodiments, the first composition comprises greater than about 97 mole percent Z-HCFO-1326mxz.

[0262] In some embodiments, the second composition comprises greater than about 95 mole percent, greater than about 97 mole percent, greater than about 98 mole percent, greater than about 99 mole percent, greater than about 99.5 mole percent, or greater than about 99.9 mole percent HFB.

[0263] In some embodiments, the third composition comprises greater than about 95 mole percent, greater than about 97 mole percent, greater than about 98 mole percent, greater than about 99 mole percent, greater than about 99.5 mole percent, or greater than about 99.9 mole percent Z-HFO-1336mzz.

[0264] In some embodiments, the above-described integrated systems and processes produce a composition comprising:

- i) (Z)-1,1,1,4,4,4-hexafluoro-2-butene; and
- ii) one or more additional compounds selected from:
 - 1,1,1,3,3,3-hexafluoropropane;
 - (E)-1,1,1,4,4,4-hexafluorobutene;
 - 1,1,1,2,2,4,4,4-octafluorobutane;
 - 1,2-dichloro-1,1,2,2-tetrafluoroethane;
 - 3-chloro-1,1,1-trifluoropropane;
 - 4-chloro-1,1,1,2,2-pentafluorobutane;
 - 2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,3-pentafluoropropane;
 - 1-chloro-1,1,3,3,3-pentafluoropropane;
 - 2-chloro-1,1,1,4,4,4-hexafluorobutane;

1,2-dichloro-1,1,3,3,3-pentafluoropropane;
1,2-dichloro-3,3,3-trifluoroprop-1-ene;
1-chloro-3,3,3-trifluoro-propene;
1-chloro-1,1,2,4,4,4-hexafluoro-2-butene;
1-chloro-1,1,4,4,4-pentafluorobutane;
2-chloro-1,1,1,3-tetrafluoropropane; and
1,1,1,3,3-pentafluoropropane;

wherein the composition comprises greater than about 99 mole percent Z-HFO-1336mzz.

Compositions

[0265] The present application further provides compositions comprising a major component (e.g., Z-HCFO-1326mxz, HFB, or Z-HFO-1336mzz) in combination with one or more additional compounds. In some embodiments, the compositions are prepared according to one or more of the processes described herein.

[0266] The additional compounds of the compositions described herein may provide improved solubility for active ingredients in an aerosol or polymer constituents of a foam. Additionally, for refrigerant applications, such as use in air conditioning, heat pumps, refrigeration, and power cycles (e.g., organic Rankine cycles), the additional compounds may provide improved solubility with refrigeration lubricants, such as mineral oils, alkylbenzenes, synthetic paraffins, synthetic naphthenes, poly(alpha)olefins, polyol esters (POE), polyalkylene glycols (PAG), polyvinyl ethers (PVE), or perfluoropolyethers (PFPE), or mixtures thereof.

[0267] Further, the presence of the additional compounds in a sample of Z-HCFO-1326mxz, HFB, or Z-HFO-1336mzz may be used to identify the process by which the compound was manufactured.

Z-HCFO-1326mxz Compositions

[0268] The present application further provides a composition, comprising:

- i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz); and
- ii) one or more additional compounds selected from:
E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,

E-HFO-1316mxx (E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
Z-HFO-1316mxx (Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
HFO-1327mz (1,1,1,2,4,4,4-heptafluoro-2-butene),
HFO-1325lxz (1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene),
HFO-1325dx (1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene),
HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane),
HFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane),
HFC-336lbf (1,2-dichloro-1,1,2,4,4,4-hexafluorobutane),
HFC-337mbf (2-chloro-1,1,1,2,4,4,4-heptafluorobutane),
HFC-337mde (2-chloro-1,1,1,3,4,4,4-heptafluorobutane),
HFC-356mff (1,1,1,4,4,4-hexafluorobutane),
HFC-346mdf (2-chloro-1,1,1,4,4,4-hexafluorobutane),
HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane),
HCFC-1122 (2-chloro-1,1-difluoroethylene),
HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane),
CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane),
CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane),
CFC-133a (2-chloro-1,1,1-trifluoroethane),
CFC-123 (2,2-dichloro-1,1,1-trifluoroethane),
CFC-123a (1,2-dichloro-1,1,2-trifluoroethane),
CFC-122 (1,2,2-trichloro-1,1-difluoroethane),
CFC-112a (1,1,1,2-tetrachloro-2,2-difluoroethane),
HCFC-224db (1,1,1,3-tetrafluoro-2,3,3-trichloropropane),
HFC-225da (1,2-dichloro-1,1,3,3,3-pentafluoropropane),
HFC-235da (2-chloro-1,1,1,3,3,3-pentafluoropropane),
HFC-235fa (1-chloro-1,1,3,3,3-pentafluoropropane),
HFC-236fa (1,1,1,3,3,3-hexafluoropropane), and
E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

[0269] In some embodiments, the composition comprises greater than about 95 mole percent Z-HCFO-1326mxz.

[0270] In some embodiments, the composition comprises Z-HCFO-1326mxz and one of the additional compounds. In some embodiments, the composition comprises Z-HCFO-1326mxz and more than one of the additional compounds (e.g., two or

more; three or more; five or more; ten or more; and the like). In some embodiments, the composition comprises Z-HCFO-1326mxz and each of the additional compounds. In some embodiments, the composition comprises Z-HCFO-1326mxz and from one to twenty-five of the additional compounds. In some embodiments, the composition comprises Z-HCFO-1326mxz and from one to twenty of the additional compounds. In some embodiments, the composition comprises Z-HCFO-1326mxz and from one to ten of the additional compounds. In some embodiments, the composition comprises Z-HCFO-1326mxz and from one to five of the additional compounds. In some embodiments, the composition comprises Z-HCFO-1326mxz and from one to four of the additional compounds. In some embodiments, the composition comprises Z-HCFO-1326mxz and from one to three of the additional compounds. In some embodiments, the composition comprises Z-HCFO-1326mxz and from one to two of the additional compounds.

[0271] In some embodiments, the composition comprises:

- i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene; and
- ii) one or more additional compounds selected from:
 - 2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
 - (E)-2-chloro-1,1,1,4,4,4-hexafluoro-but2ene;
 - 1,2-dichloro-3,3,4,4-tetrafluorocyclobut-1-ene;
 - 1,2-dichloro-1,1,3,3,3-pentafluoropropane; and
 - 1,1,2-trichloro-1,2,2-trifluoroethane;

wherein the composition comprises greater than about 95 mole percent (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene.

[0272] In some embodiments, the composition comprises greater than about 97 mole percent Z-HCFO-1326mxz. In some embodiments, the composition comprises greater than about 98 mole percent Z-HCFO-1326mxz. In some embodiments, the composition comprises greater than about 99 mole percent Z-HCFO-1326mxz. In some embodiments, the composition comprises greater than about 99.5 mole percent Z-HCFO-1326mxz. In some embodiments, the composition comprises greater than about 99.9 mole percent Z-HCFO-1326mxz.

[0273] In some embodiments, the composition consists essentially of the Z-HCFO-1326mxz and the one or more additional compounds.

Hexafluorobutyne (Perfluorobut-2-yne) Compositions

[0274] The present application further provides a composition comprising:

- i) hexafluorobutyne; and
- ii) one or more additional compounds selected from:
 - 1,1,1,3,3,3-hexafluoropropane;
 - 1,1,1,2,4,4,4-heptafluoro-2-butene;
 - (E)-1,1,1,4,4,4-hexafluorobutene;
 - 1,1,1,2,2,4,4,4-octafluorobutane;
 - 1,1,1,4,4,4-hexafluorobutane;
 - 1,2-dichloro-1,1,2,2-tetrafluoroethane;
 - 2-chloro-1,1,1-trifluoroethane;
 - (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
 - 1-chloro-3,3,4,4,4-pentafluorobut-1-yne;
 - 1-chloro-3,3,4,4,4-pentafluorobut-2-yne;
 - (Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;
 - 1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene
 - 2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,3-pentafluoropropane;
 - 1-chloro-1,1,3,3,3-pentafluoropropane;
 - (E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
 - 2-chloro-1,1,1,4,4,4-hexafluorobutane;
 - 2,2-dichloro-1,1,1-trifluoroethane;
 - 1,2-dichloro-1,1,2-trifluoroethane;
 - 1,2-dichloro-1,1,3,3,3-pentafluoropropane;
 - (E)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
 - 1,1,2-trichloro-1,2,2-trifluoroethane;
 - (Z)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
 - 1-chloro-3,3,3-trifluoroprop-1-yne;
 - 1,2-dichloro-3,3,3-trifluoroprop-1-ene;

(Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;
1-chloro-1,1,2,4,4,4-hexafluoro-2-butene;
2-chloro-1,3,3,3-tetrafluoroprop-1-ene;
1,1,3,3,3-pentafluoroprop-1-ene; and
2-chloro-1,1,3,3,3-pentafluoroprop-1-ene;
trifluoroacetone;
trifluoropropyne; and
1,1,4,4,4-pentafluoro-1-butene

wherein the composition comprises greater than about 95 mole percent HFB.

[0275] In some embodiments, the composition comprises HFB and one of the additional compounds. In some embodiments, the composition comprises HFB and more than one of the additional compounds (e.g., two or more; three or more; five or more; ten or more; and the like). In some embodiments, the composition comprises HFB and each of the additional compounds. In some embodiments, the composition comprises HFB and from one to twenty-five of the additional compounds. In some embodiments, the composition comprises HFB and from one to twenty of the additional compounds. In some embodiments, the composition comprises HFB and from one to ten of the additional compounds. In some embodiments, the composition comprises HFB and from one to five of the additional compounds. In some embodiments, the composition comprises HFB and from one to four of the additional compounds. In some embodiments, the composition comprises HFB and from one to three of the additional compounds. In some embodiments, the composition comprises HFB and from one to two of the additional compounds.

[0276] In some embodiments, the composition comprises:

- i) hexafluorobutyne; and
- ii) one or more additional compounds selected from:
(Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
(E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene; and
trifluoroacetone; trifluoropropyne;
1,1,4,4,4-pentafluoro-1-butene,

wherein the composition comprises greater than about 95 mole percent HFB.

[0277] In some embodiments, the composition comprises greater than about 97 mole percent HFB. In some embodiments, the composition comprises greater than about 98 mole percent HFB. In some embodiments, the composition comprises greater than about 99 mole percent HFB. In some embodiments, the composition comprises greater than about 99.5 mole percent HFB. In some embodiments, the composition comprises greater than about 99.9 mole percent HFB.

[0278] In some embodiments, the composition consists essentially of the HFB and the one or more additional compounds.

(Z)-1,1,1,4,4,4-hexafluoro-2-butene Compositions

[0279] The present application further provides a composition comprising:

- i) (Z)-1,1,1,4,4,4-hexafluoro-2-butene; and
- ii) one or more additional compounds selected from:
 - 1,1,1,3,3,3-hexafluoropropane;
 - (E)-1,1,1,4,4,4-hexafluorobutene;
 - 1,1,1,2,2,4,4,4-octafluorobutane;
 - 1,2-dichloro-1,1,2,2-tetrafluoroethane;
 - 3-chloro-1,1,1-trifluoropropane;
 - 4-chloro-1,1,1,2,2-pentafluorobutane;
 - 2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,3-pentafluoropropane;
 - 1-chloro-1,1,3,3,3-pentafluoropropane;
 - 2-chloro-1,1,1,4,4,4-hexafluorobutane;
 - 1,2-dichloro-1,1,3,3,3-pentafluoropropane;
 - 1,2-dichloro-3,3,3-trifluoroprop-1-ene;
 - 1-chloro-3,3,3-trifluoro-propene;
 - 1-chloro-1,1,2,4,4,4-hexafluoro-2-butene;
 - 1-chloro-1,1,4,4,4-pentafluorobutane;
 - 2-chloro-1,1,1,3-tetrafluoropropane; and

1,1,1,3,3-pentafluoropropane;
(Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene; and
(E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,

wherein the composition comprises greater than about 99 mole percent Z-HFO-1336mzz.

[0280] In some embodiments, the composition comprises Z-HFO-1336mzz and one of the additional compounds. In some embodiments, the composition comprises Z-HFO-1336mzz and more than one of the additional compounds (e.g., two or more; three or more; five or more; ten or more; and the like). In some embodiments, the composition comprises Z-HFO-1336mzz and each of the additional compounds. In some embodiments, the composition comprises Z-HFO-1336mzz and from one to ten of the additional compounds. In some embodiments, the composition comprises Z-HFO-1336mzz and from one to five of the additional compounds. In some embodiments, the composition comprises Z-HFO-1336mzz and from one to four of the additional compounds. In some embodiments, the composition comprises Z-HFO-1336mzz and from one to three of the additional compounds. In some embodiments, the composition comprises Z-HFO-1336mzz and from one to two of the additional compounds.

[0281] In some embodiments, the composition comprises:

- i) (Z)-1,1,1,4,4,4-hexafluoro-2-butene; and
- ii) one or more additional compounds selected from:
(Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
(E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene; and
2-chloro-1,1,1,4,4,4-hexafluorobutane,

wherein the composition comprises greater than about 99 mole percent Z-HFO-1336mzz.

[0282] In some embodiments, the composition comprises greater than about 97 mole percent Z-HFO-1336mzz. In some embodiments, the composition comprises greater than about 98 mole percent Z-HFO-1336mzz. In some embodiments, the composition comprises greater than about 99 mole percent Z-HFO-1336mzz. In some embodiments, the composition comprises greater than about 99.5 mole

percent Z-HFO-1336mzz. In some embodiments, the composition comprises greater than about 99.9 mole percent Z-HFO-1336mzz.

[0283] In some embodiments, the composition consists essentially of the Z-HFO-1336mzz and the one or more additional compounds.

Methods of Use

[0284] The compositions provided herein (*i.e.*, the compositions of the invention) may be useful, for example, in a wide range of applications, including their use as refrigerants, uses in high-temperature heat pumps, organic Rankine cycles, as fire extinguishing/fire suppression agents, propellants, foam blowing agents, solvents, and/or cleaning fluids.

[0285] In some embodiments, the additional compounds of the compositions containing at least one chlorine atom may provide improved solubility for the major component of the composition (*e.g.*, (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene, or hexafluorobutylene, or (Z)-1,1,1,4,4,4-hexafluoro-2-butene) in an aerosol or polymer constituents of a foam.

[0286] For example, unsaturated fluorocarbons, such as (Z)-1,1,1,4,4,4-hexafluoro-2-butene, exhibit different solubility than other fluorocarbon propellants. This reduced solubility can make it difficult to prepare single phase aqueous homogenous aerosol formulations. The presence of low-level chlorinated impurities can improve mixing and ease formulations and use of aerosol products.

[0287] Unsaturated fluorocarbons, such as (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene, also exhibit different solubility than other common blowing agents. The reduced solubility can assist in seeding small cell growth during a foaming reaction, but the compounds can be difficult to mix. The presence of low-level chlorinated impurities can improve mixing and foam processing performance without sacrificing the benefits from the lower HFO solubility. Also, the chlorinated compounds typically have lower vapor thermal conductivities and so will impart improved insulating performance to a foam insulation product.

[0288] Additionally, for refrigerant applications, such as use in air conditioning, heat pumps, refrigeration, and power cycles (*e.g.*, organic Rankine cycles), additional compounds containing at least one chlorine atom may provide improved

solubility with refrigeration lubricants, such as mineral oils, alkylbenzenes, synthetic paraffins, synthetic naphthenes, poly(alpha)olefins, polyol esters (POE), polyalkylene glycols (PAG), polyvinyl ethers (PVE), or perfluoropolyethers (PFPE) or mixtures thereof.

[0289] Further, the additional compounds of the compositions provided herein may assist in improving leak detection ability. Leakage of refrigerants may lead to loss of refrigerant from a system, thus increasing cost of operation due to the need to top-off refrigerant charge, and even minor loss of refrigerant from a system may impact proper operation. Finally, leakage of refrigerant may lead to excessive environmental contamination. In particular, chlorinated compounds, even at low levels can increase the detectability of refrigerant at the point of a leak. Thus, the system may be repaired or redesigned to prevent refrigerant leakage.

[0290] The levels of additional compounds (e.g., additional chlorinated compounds) must be kept low, however, because higher levels of the additional compounds may create compatibility problems with materials of construction. In aerosols, these compatibility problems may be with the aerosol container (e.g., cans) or with plastic valve parts. In foams, these compatibility problems may be with equipment seals and gaskets. Additionally, in aerosol products interaction of higher levels of additional compounds (e.g., chlorinated compounds) may cause instability of the formulation. For example, in foam products, higher levels of chlorinated compounds may soften the foam resulting in dimensional instability and poor strength of the foam.

[0291] The compositions described herein may also useful as low global warming potential (GWP) heat transfer compositions, refrigerants, power cycle working fluids, aerosol propellants, foaming agents, blowing agents, solvents, cleaning agents, carrier fluids, displacement drying agents, buffing abrasion agents, polymerization media, expansion agents for poly-olefins and polyurethane, gaseous dielectrics, fire extinguishing agents, and fire suppression agents, in liquid or gaseous form. In some embodiments, the compositions provided herein may be useful as a working fluid used to carry heat from a heat source to a heat sink. Such heat transfer compositions may also be useful as a refrigerant in a cycle wherein the fluid undergoes a phase change (e.g., from a liquid to a gas and back or vice versa).

[0292] Examples of heat transfer systems include but are not limited to air conditioners, freezers, refrigerators, heat pumps, water chillers, flooded evaporator chillers, direct expansion chillers, walk-in coolers, heat pumps, mobile refrigerators, mobile air conditioning units and combinations thereof.

[0293] In some embodiments, the compositions provided herein may be useful in mobile heat transfer systems, including refrigeration, air conditioning, or heat pump systems or apparatus. In some embodiments, the compositions may be useful in stationary heat transfer systems, including refrigeration, air conditioning, or heat pump systems or apparatus.

[0294] As used herein, mobile heat transfer systems refers to any refrigeration, air conditioner, or heating apparatus incorporated into a transportation unit for the road, rail, sea or air. In addition, mobile refrigeration, or air conditioner units, include those apparatus that are independent of any moving carrier and are known as “intermodal” systems. Such intermodal systems include “containers” (combined sea/land transport) as well as “swap bodies” (combined road/rail transport).

[0295] As used herein, stationary heat transfer systems are systems that are fixed in place during operation. A stationary heat transfer system may be associated within or attached to buildings of any variety or may be stand-alone devices located out of doors, such as a soft drink vending machine. These stationary applications may be stationary air conditioning and heat pumps (including but not limited to chillers, high temperature heat pumps, including trans-critical heat pumps (e.g., with condenser temperatures above 50°C, above 70°C, above 80°C, above 100°C, above 120°C, above 140°C, above 160°C, above 180°C, or above 200°C), residential, commercial or industrial air conditioning systems, and including window, ductless, ducted, packaged terminal, chillers, and those exterior but connected to the building such as rooftop systems). In stationary refrigeration applications, the compositions provided herein may be useful in high temperature, medium temperature, and/or low temperature refrigeration equipment including commercial, industrial or residential refrigerators and freezers, ice machines, self-contained coolers and freezers, flooded evaporator chillers, direct expansion chillers, walk-in and reach-in coolers and freezers, and combination systems. In some embodiments, the disclosed compositions may be used in supermarket refrigerator systems.

[0296] Therefore, in accordance with the present invention, the compositions provided herein may be useful in methods for producing cooling, producing heating, and transferring heat.

[0297] In some embodiments, the present application provides a method for producing cooling comprising evaporating a composition provided herein in the vicinity of a body to be cooled, and thereafter condensing said composition.

[0298] In some embodiments, the present application provides a method for producing heating comprising condensing a composition provided herein in the vicinity of a body to be heated, and thereafter evaporating said compositions.

[0299] In some embodiments, the present application provides a method of using compositions provided herein as heat transfer fluid compositions. In some embodiments, the method comprises transporting said composition from a heat source to a heat sink.

[0300] The compositions provided herein may also be useful as low global warming potential (GWP) replacements for currently used refrigerants, including but not limited to, R-123 (*i.e.*, HFC-123, 2,2-dichloro-1,1,1-trifluoroethane), R-11 (*i.e.*, CFC-11, trichlorofluoromethane), R-245fa (*i.e.* HFC-245fa, 1,1,1,3,3-pentafluoropropane), R-114 (*i.e.*, CFC-114, 1,2-dichloro-1,1,2,2-tetrafluoroethane), R-236fa (*i.e.*, HFC-236a, 1,1,1,3,3,3-hexafluoropropane), R-236ea (*i.e.*, HFC-236ea, 1,1,1,2,3,3-hexafluoropropane), R-124 (*i.e.*, HCFC-124, 2-chloro-1,1,1,2-tetrafluoroethane), among others.

[0301] In some embodiments, the composition provided herein may be useful as refrigerants and provide at least comparable cooling performance (*i.e.*, cooling capacity and energy efficiency) as the refrigerant for which a replacement is being sought. Additionally, the compositions of the present invention may provide heating performance (*i.e.*, heating capacity and energy efficiency) comparable to a refrigerant being replaced.

[0302] In some embodiments the present application provides a method for recharging a heat transfer system that contains a refrigerant to be replaced and a lubricant, said method comprising removing the refrigerant to be replaced from the heat transfer system while retaining a substantial portion of the lubricant in said

system and introducing one of compositions of the present invention to the heat transfer system. In some embodiments, the lubricant in the system is partially replaced (e.g., replace a portion of the mineral oil lubricant used with HCFO-123 with a POE lubricant).

[0303] In some embodiments, the compositions of the present invention may be used to top-off a refrigerant charge in a chiller. For example, if a chiller using HCFO-123 has diminished performance due to leakage of refrigerant, the compositions provided herein may be added to bring performance back up to specification.

[0304] The present application further provides a heat exchange system containing any of the compositions provided herein, wherein said system is selected from the group consisting of air conditioners, freezers, refrigerators, heat pumps, water chillers, flooded evaporator chillers, direct expansion chillers, walk-in coolers, heat pumps, mobile refrigerators, mobile air conditioning units, and systems having combinations thereof. Additionally, the compositions of the invention may be useful in secondary loop systems wherein these compositions serve as the primary refrigerant thus providing cooling to a secondary heat transfer fluid that thereby cools a remote location.

[0305] Vapor-compression refrigeration, air-conditioning, or heat pump systems include an evaporator, a compressor, a condenser, and an expansion device. A vapor-compression cycle re-uses refrigerant in multiple steps producing a cooling effect in one step and a heating effect in a different step. The cycle can be described simply as follows: Liquid refrigerant enters an evaporator through an expansion device, and the liquid refrigerant boils in the evaporator, by withdrawing heat from the environment, at a low temperature to form a vapor and produce cooling. The low-pressure vapor enters a compressor where the vapor is compressed to raise its pressure and temperature. The higher-pressure (compressed) vapor refrigerant then enters the condenser in which the refrigerant condenses and discharges its heat to the environment. The refrigerant returns to the expansion device through which the liquid expands from the higher-pressure level in the condenser to the low-pressure level in the evaporator, thus repeating the cycle.

[0306] The present application further provides foam expansion agent compositions comprising a composition of the invention for use in preparing foams. In some embodiments, the present application provides foamable compositions, including but not limited to, thermoset (e.g., polyurethane, polyisocyanurate, or phenolic) foam compositions, thermoplastic (e.g., polystyrene, polyethylene, or polypropylene) foam compositions and methods of preparing foams. In some embodiments, one or more of the present compositions may be included as a foam expansion agent in the foamable compositions, wherein foamable composition may include one or more additional components capable of reacting and/or mixing and foaming under the proper conditions to form a foam or cellular structure.

[0307] The present application further provides a method of forming a foam comprising: (a) adding to a foamable composition a composition of the present invention; and (b) processing the foamable composition under conditions effective to form a foam.

[0308] The present application further provides the use of the compositions of the present invention as propellants in sprayable compositions. Additionally, the present application provides sprayable compositions of the invention. The active ingredient to be sprayed together with inert ingredients, solvents, and other materials may also be present in a sprayable composition. In some embodiments, the sprayable composition is an aerosol. The compositions of the invention can also be used to formulate a variety of industrial aerosols or other sprayable compositions such as contact cleaners, dusters, lubricant sprays, mold release sprays, insecticides, and the like, and consumer aerosols such as personal care products (e.g., hair sprays, deodorants, and perfumes), household products (e.g., waxes, polishes, pan sprays, room fresheners, and household insecticides), and automotive products (e.g., cleaners and polishers), as well as medicinal materials such as anti-asthma and anti-halitosis medications. Examples include, but are not limited to, metered dose inhalers (MDIs) for the treatment of asthma and other chronic obstructive pulmonary diseases and for delivery of medicaments to accessible mucous membranes or intranasally.

[0309] The present invention further provides a process for producing aerosol products comprising the step of adding a composition of the invention to a formulation to an aerosol container, wherein said composition of the invention functions as a propellant. Additionally, the present application further provides a process for producing aerosol products comprising the step of adding a composition of the invention to a barrier type aerosol package (e.g., a bag-in-a-can or piston can) wherein said composition of the invention is kept separated from other formulation ingredients in an aerosol container, and wherein said composition of the invention functions as a propellant. Additionally, the present application further provides a process for producing aerosol products comprising the step of adding only a composition of the invention to an aerosol package, wherein said composition functions as the active ingredient (e.g., a duster, or a cooling or freezing spray).

[0310] The present application further provides a process for converting heat from a heat source to mechanical energy, comprising heating a working fluid comprising a composition of the invention and thereafter expanding the heated working fluid. In the process, heating of the working fluid uses heat supplied from the heat source; and expanding of the heated working fluid generates mechanical energy as the pressure of the working fluid is lowered.

[0311] The process for converting heat may be a subcritical cycle, a trans-critical cycle, or a supercritical cycle. In a transcritical cycle, the working fluid is compressed to a pressure above its critical pressure prior to being heated, and then during expansion the working fluid pressure is reduced to below its critical pressure. In a super critical cycle, the working fluid remains above its critical pressure for the complete cycle (e.g., compression, heating, expansion and cooling).

[0312] Heat sources may include, for example, low pressure steam, industrial waste heat, solar energy, geothermal hot water, low-pressure geothermal steam (primary or secondary arrangements), or distributed power generation equipment utilizing fuel cells or prime movers such as turbines, microturbines, or internal combustion engines. One source of low-pressure steam could be the process known as a binary geothermal Rankine cycle. Large quantities of low-pressure steam can be found in numerous locations, such as in fossil fuel powered electrical generating power plants. Other sources of heat include waste heat recovered from gases

exhausted from mobile internal combustion engines (*e.g.*, truck or rail diesel engines or ships), waste heat from exhaust gases from stationary internal combustion engines (*e.g.*, stationary diesel engine power generators), waste heat from fuel cells, heat available at combined heating, cooling and power or district heating and cooling plants, waste heat from biomass fueled engines, heat from natural gas or methane gas burners or methane-fired boilers or methane fuel cells (*e.g.*, at distributed power generation facilities) operated with methane from various sources including biogas, landfill gas and coal-bed methane, heat from combustion of bark and lignin at paper/pulp mills, heat from incinerators, heat from low pressure steam at conventional steam power plants (to drive "bottoming" Rankine cycles), and geothermal heat.

[0313] In some embodiments, the process of converting heat is performed using an organic Rankine power cycle. Heat available at relatively low temperatures compared to steam (inorganic) power cycles can be used to generate mechanical power through Rankine cycles using working fluids as described herein. In some embodiments, the working fluid is compressed prior to being heated. Compression may be provided by a pump which pumps working fluid to a heat transfer unit (*e.g.*, a heat exchanger or an evaporator) where heat from the heat source is used to heat the working fluid. The heated working fluid is then expanded, lowering its pressure. Mechanical energy is generated during the working fluid expansion using an expander. Examples of expanders include, but are not limited to, turbo or dynamic expanders, such as turbines, and positive displacement expanders, such as screw expanders, scroll expanders, and piston expanders. Examples of expanders also include rotary vane expanders.

[0314] Mechanical power can be used directly (*e.g.*, to drive a compressor) or be converted to electrical power through the use of electrical power generators. In a power cycle where the working fluid is re-used, the expanded working fluid is cooled. Cooling may be accomplished in a working fluid cooling unit (*e.g.*, a heat exchanger or a condenser). The cooled working fluid can then be used for repeated cycles (*i.e.*, compression, heating, expansion, etc.). The same pump used for compression may be used for transferring the working fluid from the cooling stage.

[0315] The present application further provides a method for detecting a leak from a container comprising sampling the air in the vicinity of the container and detecting at least one additional compound of a composition provided herein with means for detecting the leak, wherein a composition of the present invention is contained inside the container. The term “in the vicinity of” refers to within 12 inches of the outside surface of the container. Alternatively, in the vicinity may be within 6 inches, within 3 inches or within one inch of the outside surface of the container.

[0316] A container may be any known container or system or apparatus that is filled with a composition of the inventor. A container may include, but is not limited to, a storage container, a transport container, an aerosol can, a fire extinguishing system, a chiller apparatus, a heat pump apparatus, heat transfer container, and a power cycle apparatus (e.g., an organic Rankine cycle system).

[0317] Means for detecting a leak may be performed using any known sensor designed to detect leaks. In particular, means for detecting the leak includes, but is not limited to, electrochemical, corona discharge, and mass spectroscopic leak detectors.

[0318] Many aspects and embodiments have been described above and are merely exemplary and not limiting. After reading this specification, skilled artisans appreciate that other aspects and embodiments are possible without departing from the scope of the invention.

EXAMPLES

[0319] The invention will be described in greater detail by way of specific examples. The following examples are offered for illustrative purposes and are not intended to limit the invention in any manner.

Example 1: System A and Process 1 (Embodiment 1) for making high purity Z-HCFO-1326mxz

[0320] NbCl₅ (220 g) is added to a 5-gallon autoclave with a partial condenser, followed by HF activation at 100°C. HF and hexachlorobutadiene (HCBD) are co-fed to the autoclave continuously. The total feed of HF is 700 g, and the total feed of HCBD is 600 g. HCFO-1326mxz is formed. The formed HCFO-1326mxz is removed

continuously and purified based on the system shown in Fig. 1 and as described above with respect to Fig. 1. The final purity of (Z)-HCFO-1326mxz is greater than 98% by mol .

Example 2: System C and Process 2 for making high purity hexafluoro-2 butyne

[0321] KOH aqueous solution (1200 mL, 12 mol), Z-HCFO-1326mxz made in accordance with Example 1 (purity >98%) (2000 g, 10 mol), Aliquat® 336 (53 g, 0.1325 mol), and KCl (5 wt% aqueous solution) are co-fed to a dehydrochlorination reactor. The system and process utilized for this example are the same as the system shown in Fig. 3 and as described above with respect to Fig. 3. The reaction temperature is controlled to be between 35°C – 40°C. Hexafluoro-2 butyne is formed. The formed hexafluoro-2 butyne is purified based on the system shown in Fig. 3 and as described above with respect to Fig. 3. The final purity of the hexafluoro-2 butyne is greater than 99.5% by mol.

Example 3: System D and Process 3 for making high purity Z-HFO-1336mzz

[0322] A Hastelloy tube reactor 80" long with a 1" O.D. (outside diameter) and 0.074" wall thickness is filled with 30 g of catalyst. The catalyst is conditioned at 70°C with a flow of nitrogen (1000 sccm) and hydrogen (1000 sccm) for one hour at 200°C. The reactor is cooled to 74°C. A mixture of hexafluoro-2-butyne (1090 sccm) generated in accordance with Example 2, hydrogen (218 sccm) and N₂ (1090.6 sccm) are then flowed into the reactor with a back pressure of 50 psig continuously. Z-HFO-1336mzz is formed. The product is purified based on the system shown in Fig. 4 and as described above with respect to Fig. 4. The final purity of the Z-HFO-1336mzz is greater than 99.5% by weight.

[0323] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety, unless a particular passage is

cited. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

CLAIMS

What is claimed is:

1. A system for purification of E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz), the system comprising:
 - a reactor configured to react hexachlorobutadiene (HCBD) with hydrofluoric acid (HF) in the presence of a fluorination catalyst to form a composition comprising HCFO-1326mxz, HCl, unreacted HCBD, and unreacted HF;
 - a first distillation column configured to receive the composition from the reactor and configured to separate the first composition into a first fraction F_{1D10} comprising HCl, and a second fraction F_{2D10} comprising unreacted HCBD, unreacted HF and HCFO-1326mxz;
 - a second distillation column configured to receive the second fraction F_{2D10} comprising unreacted HCBD, unreacted HF and HCFO-1326mxz from the first distillation column and configured to separate the second fraction into a third fraction F_{3D11} comprising an azeotrope of unreacted HF and HCFO-1326mxz, and a fourth fraction F_{4D11} comprising unreacted HCBD, unreacted HF and HCFO-1326mxz, the second distillation column being configured to optionally return the third fraction F_{3D11} to the reactor; and
 - a third distillation column configured to receive the fourth fraction F_{4D11} comprising unreacted HCBD, unreacted HF and HCFO-1326mxz from the second distillation column and configured to separate the fourth fraction F_{4D11} into a fifth fraction F_{5D12} comprising unreacted HF and unreacted HCBD, and a sixth fraction F_{6D12} comprising HCFO-1326mxz, the third distillation column being configured to optionally return the fifth fraction F_{5D12} to the reactor.
2. The system of claim 1, wherein the first fraction F_{1D10} comprises HCl, HF, and one or more additional compounds selected from the group consisting of (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz); (E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E-HCFO-1326mxz); (E)-(2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) (E-CFO-1317mx); (Z)-(2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) (Z-CFO-1317mx); 2-chloro-1,1-difluoroethylene (HCFC-1122); 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); pentachlorofluoroethane (CFC-111); 1,2-dichloro-1,1,2,2-

tetrafluoroethane (CFC-114); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113); 2-chloro-1,1,1-trifluoroethane (CFC-133a); 2,2-dichloro-1,1,1-trifluoroethane (CFC-123); 1,2-dichloro-1,1,2-trifluoroethane (CFC-123a); 1,2,2-trichloro-1,1-difluoroethane (CFC-122); 1,1,1,2-tetrachloro-2,2-difluoroethane (CFC-112a); 1,1,1,3-tetrafluoro-2,3,3-trichloropropane (HCFC-224db); 1,2-dichloro-1,1,3,3,3-pentafluoropropane (HCFC-225da); 2,3-dichloro-1,1,1,3-tetrafluoropropane (HCFC-234da); 2-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235da); 1-chloro-1,1,3,3,3-pentafluoropropane (CFC-235fa); 1,1,1,3,3,3-hexafluoropropane (HFC-236fa) and 1,1,1,2,4,4,4-heptafluoro-2-butene (HFO-1327mz).

3. The system of claim 2, wherein the HF comprises about 1 wt. % or less, or about 0.5 wt. % or less, or about 0.1 wt. % or less, based on the total weight of the first fraction F_{1D10}.
4. The system of claim 2, wherein each of the additional compounds present in the first fraction F_{1D10} are present in amount of about 1 wt. % or less, or about 0.5 wt. % or less, or about 0.1 wt. % or less, based on the total weight of the first fraction F_{1D10}.
5. The system of claim 2, wherein a total amount of the additional compounds of the first fraction F_{1D10} is about 1 wt. % or less, or about 0.5 wt. % or less, or about 0.1 wt. % or less, based on the total weight of the first fraction F_{1D10}.
6. The system of claim 1, wherein the sixth fraction F_{6D12} comprises
 - (iv) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz);
 - (v) optionally HF; and
 - (vi) one or more additional compounds selected from the group consisting of:

E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
 E-HFO-1316mxx (E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 Z-HFO-1316mxx (Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 HFO-1327mz (1,1,1,2,4,4,4-heptafluoro-2-butene),
 HFO-1325lxz (1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene),

HFO-1325dx (1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene),
 HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane),
 HFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane),
 HFC-336lbf (1,2-dichloro-1,1,2,4,4,4-hexafluorobutane),
 HFC-337mbf (2-chloro-1,1,1,2,4,4,4-heptafluorobutane),
 HFC-337mde (2-chloro-1,1,1,3,4,4,4-heptafluorobutane),
 HFC-356mff (1,1,1,4,4,4-hexafluorobutane),
 HFC-346mdf (2-chloro-1,1,1,4,4,4-hexafluorobutane),
 HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane),
 HCFC-1122 (2-chloro-1,1-difluoroethylene),
 HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane),
 CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane),
 CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane),
 CFC-133a (2-chloro-1,1,1-trifluoroethane),
 CFC-123 (2,2-dichloro-1,1,1-trifluoroethane),
 CFC-123a (1,2-dichloro-1,1,2-trifluoroethane),
 CFC-122 (1,2,2-trichloro-1,1-difluoroethane),
 CFC-112a (1,1,1,2-tetrachloro-2,2-difluoroethane),
 HCFC-224db (1,1,1,3-tetrafluoro-2,3,3-trichloropropane),
 HFC-225da (1,2-dichloro-1,1,3,3,3-pentafluoropropane),
 HFC-235da (2-chloro-1,1,1,3,3-pentafluoropropane),
 HFC-235fa (1-chloro-1,1,3,3,3-pentafluoropropane),
 HFC-236fa (1,1,1,3,3,3-hexafluoropropane), and
 E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

7. The system of claim 1, wherein the sixth fraction F_{6D12} comprises
- (i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz);
 - (ii) optionally HF; and

- (iii) one or more additional compounds selected from the group consisting of E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene, HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), E- Z-CFO-1317mx (E-2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) and Z-CFO-1317mx (Z-2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).
8. The system of any of claims 6 and 7, wherein the HF comprises about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the sixth fraction F_{6D12}.
9. A system for purification of E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz), the system comprising:
- a reactor configured to react hexachlorobutadiene (HCBd) with hydrofluoric acid (HF) in the presence of a fluorination catalyst to form a composition comprising HCFO-1326mxz, HCl, unreacted HCBd, and unreacted HF;
 - a first distillation column configured to receive the composition from the reactor and configured to separate the first composition into a first fraction F_{1D20} comprising HCl, and a second fraction F_{2D20} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz;
 - a second distillation column configured to receive the second fraction F_{2D20} comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the first distillation column and configured to separate the second fraction F_{2D20} into a third fraction F_{3D21} comprising unreacted HF and unreacted HCBd, and a fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz, the second distillation column being configured to optionally return the third fraction F_{3D21} to the reactor; and
 - an acid neutralizer configured to receive the fourth fraction F_{4D21} comprising an azeotrope of HF and HCFO-1326mxz from the second distillation column and configured to separate the fourth fraction F_{4D21} into a fifth fraction F_{5A20} comprising neutralized HF and a sixth fraction F_{6A20} comprising HCFO-1326mxz.

10. The system of claim 9, wherein the first fraction $F1_{D20}$ comprises HCl, HF, and one or more additional compounds selected from the group consisting of (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz); (E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E-HCFO-1326mxz); (E)-(2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) (E-CFO-1317mx); (Z)-(2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) (Z-CFO-1317mx); 2-chloro-1,1-difluoroethylene (HCFC-1122); 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); pentachlorofluoroethane (CFC-111); 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113); 2-chloro-1,1,1-trifluoroethane (CFC-133a); 2,2-dichloro-1,1,1-trifluoroethane (CFC-123); 1,2-dichloro-1,1,2-trifluoroethane (CFC-123a); 1,2,2-trichloro-1,1,1-difluoroethane (CFC-122); 1,1,1,2-tetrachloro-2,2-difluoroethane (CFC-112a); 1,1,1,3-tetrafluoro-2,3,3-trichloropropane (HCFC-224db); 1,2-dichloro-1,1,3,3,3-pentafluoropropane (HCFC-225da); 2,3-dichloro-1,1,1,3-tetrafluoropropane (HCFC-234da); 2-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235da); 1-chloro-1,1,3,3,3-pentafluoropropane (CFC-235fa); 1,1,1,3,3,3-hexafluoropropane (HFC-236fa) and 1,1,1,2,4,4,4-heptafluoro-2-butene (HFO-1327mz).
11. The system of claim 10, wherein the HF comprises about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the first fraction $F1_{D20}$.
12. The system of claim 10, wherein each of the additional compounds present in the first fraction $F1_{D20}$ are present in amount of about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the first fraction $F1_{D20}$.
13. The system of claim 10, wherein a total amount of the additional compounds of the first fraction $F1_{D20}$ is about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the first fraction $F1_{D20}$.
14. The system of claim 9, wherein the sixth fraction $F6_{A20}$ comprises
 - (iv) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz);
 - (v) optionally HF; and

- (vi) one or more additional compounds selected from the group consisting of:

E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
E-HFO-1316mxx (E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
Z-HFO-1316mxx (Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
HFO-1327mz (1,1,1,2,4,4,4-heptafluoro-2-butene),
HFO-1325lxz (1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene),
HFO-1325dx (1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene),
HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane),
HFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane),
HFC-336lbf (1,2-dichloro-1,1,2,4,4,4-hexafluorobutane),
HFC-337mbf (2-chloro-1,1,1,2,4,4,4-heptafluorobutane),
HFC-337mde (2-chloro-1,1,1,3,4,4,4-heptafluorobutane),
HFC-356mff (1,1,1,4,4,4-hexafluorobutane),
HFC-346mdf (2-chloro-1,1,1,4,4,4-hexafluorobutane),
HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane),
HCFC-1122 (2-chloro-1,1-difluoroethylene),
HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane),
CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane),
CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane),
CFC-133a (2-chloro-1,1,1-trifluoroethane),
CFC-123 (2,2-dichloro-1,1,1-trifluoroethane),
CFC-123a (1,2-dichloro-1,1,2-trifluoroethane),
CFC-122 (1,2,2-trichloro-1,1-difluoroethane),
CFC-112a (1,1,1,2-tetrachloro-2,2-difluoroethane),
HCFC-224db (1,1,1,3-tetrafluoro-2,3,3-trichloropropane),
HFC-225da (1,2-dichloro-1,1,3,3,3-pentafluoropropane),
HFC-235da (2-chloro-1,1,1,3,3,3-pentafluoropropane),
HFC-235fa (1-chloro-1,1,3,3,3-pentafluoropropane),
HFC-236fa (1,1,1,3,3,3-hexafluoropropane), and
E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

15. The system of claim 9, wherein the sixth fraction F_{6A20} comprises
- (iv) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz);
 - (v) optionally HF; and
 - (vi) one or more additional compounds selected from the group consisting of E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene, HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), E- Z-CFO-1317mx (E-2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene) and Z-CFO-1317mx (Z-2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).
16. The system of claim 15, wherein the HF comprises about 1 wt.% or less, or about 0.5 wt.% or less, or about 0.1 wt.% or less, based on the total weight of the sixth fraction F_{6A20} .
17. The system of any of claims 1 to 16, wherein the system further comprises a partial condenser coupled to the reactor.
18. A system for purification of hexafluoro-2-butyne (HFB), the system comprising:
- a reactor configured to react E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz) with a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst to form a composition comprising a vapor portion and a liquid portion, the vapor portion comprising HFB and HCFO-1326mxz, the liquid portion comprising water, HCFO-1326mxz, excess phase transfer catalyst and an alkali metal halide salt, the liquid portion being comprised of an aqueous liquid phase and an organic liquid phase;
 - a distillation column configured to receive the vapor portion of the composition from the reactor and configured to separate the vapor portion into a fraction F_{5D31} comprising HFB, and a fraction F_{6D31} comprising HCFO-1326mxz, the distillation column being configured to return the fraction F_{6D31} comprising HCFO-1326mxz to the reactor, the distillation column optionally being configured to provide the fraction F_{5D31} comprising HFB to one or more additional distillation columns.

19. The system according to claim 18, wherein the system further comprises a partial condenser coupled to the reactor.
20. The system according to any of claims 17-18, wherein the fraction F6_{D31} comprises:
 - (iv) HCFO-1326mxz,
 - (v) (ii) one or more compounds selected from the group consisting of trifluoroacetone, trifluoropropyne, and hexafluoro-2-butyne, and
 - (vi) one or more of the additional compounds selected from the group consisting of:
 - E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
 - E-HFO-1316mxx (E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 - Z-HFO-1316mxx (Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
 - HFO-1327mz (1,1,1,2,4,4,4-heptafluoro-2-butene),
 - HFO-1325lxz (1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene),
 - HFO-1325dx (1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene),
 - HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane),
 - HFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane),
 - HFC-336lbf (1,2-dichloro-1,1,2,4,4,4-hexafluorobutane),
 - HFC-337mbf (2-chloro-1,1,1,2,4,4,4-heptafluorobutane),
 - HFC-337mde (2-chloro-1,1,1,3,4,4,4-heptafluorobutane),
 - HFC-356mff (1,1,1,4,4,4-hexafluorobutane),
 - HFC-346mdf (2-chloro-1,1,1,4,4,4-hexafluorobutane),
 - HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane),
 - HCFC-1122 (2-chloro-1,1-difluoroethylene),
 - HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane),
 - CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane),
 - CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane),
 - CFC-133a (2-chloro-1,1,1-trifluoroethane),
 - CFC-123 (2,2-dichloro-1,1,1-trifluoroethane),
 - CFC-123a (1,2-dichloro-1,1,2-trifluoroethane),
 - CFC-122 (1,2,2-trichloro-1,1-difluoroethane),
 - CFC-112a (1,1,1,2-tetrachloro-2,2-difluoroethane),

HCFC-224db (1,1,1,3-tetrafluoro-2,3,3-trichloropropane),
HFC-225da (1,2-dichloro-1,1,3,3,3-pentafluoropropane),
HFC-235da (2-chloro-1,1,1,3,3-pentafluoropropane),
HFC-235fa (1-chloro-1,1,3,3,3-pentafluoropropane),
HFC-236fa (1,1,1,3,3,3-hexafluoropropane), and
E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

21. The system according to any of claims 18-20, wherein a water content of the fraction F_{6D31} is about 5000 ppm or less, or about 4000 ppm or less, or about 3000 ppm or less, or about 1000 ppm or less.
22. The system according to any of claims 18-21, the system further comprising:
- a decanter configured to receive the liquid portion of the composition from the reactor and configured to separate the aqueous liquid phase into a first fraction F_{1E30} comprising water and the alkali metal halide salt and to separate the organic liquid phase into a second fraction F_{2E30} comprising the unreacted HCFO-1326mxz and excess phase transfer catalyst, the decanter being configured to return a first portion of the second fraction F_{2E30} to the reactor; and
 - an additional distillation column configured to receive a second portion of the second fraction F_{2E30} from the decanter and configured to separate the second portion of the second fraction F_{2E30} into a third fraction F_{3D30} comprising unreacted HCFO-1326mxz, and a fourth fraction F_{4D30} comprising unreacted HCFO-1326mxz and excess PTC, the additional distillation column being configured to return the third fraction F_{3D30} comprising unreacted HCFO-1326mxz to the reactor.
23. The system of claim 22, wherein the third fraction F_{3D30} comprises:
- (iv) HCFO-1326mxz,
 - (v) (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and
 - (vi) one or more of the additional compounds selected from the group consisting of:
 - E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
 - E-HFO-1316mxx (E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),

Z-HFO-1316mxx (Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene),
HFO-1327mz (1,1,1,2,4,4,4-heptafluoro-2-butene),
HFO-1325lxz (1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene),
HFO-1325dx (1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene),
HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane),
HFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane),
HFC-336lbf (1,2-dichloro-1,1,2,4,4,4-hexafluorobutane),
HFC-337mbf (2-chloro-1,1,1,2,4,4,4-heptafluorobutane),
HFC-337mde (2-chloro-1,1,1,3,4,4,4-heptafluorobutane),
HFC-356mff (1,1,1,4,4,4-hexafluorobutane),
HFC-346mdf (2-chloro-1,1,1,4,4,4-hexafluorobutane),
HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane),
HCFC-1122 (2-chloro-1,1-difluoroethylene),
HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane),
CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane),
CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane),
CFC-133a (2-chloro-1,1,1-trifluoroethane),
CFC-123 (2,2-dichloro-1,1,1-trifluoroethane),
CFC-123a (1,2-dichloro-1,1,2-trifluoroethane),
CFC-122 (1,2,2-trichloro-1,1-difluoroethane),
CFC-112a (1,1,1,2-tetrachloro-2,2-difluoroethane),
HCFC-224db (1,1,1,3-tetrafluoro-2,3,3-trichloropropane),
HFC-225da (1,2-dichloro-1,1,3,3,3-pentafluoropropane),
HFC-235da (2-chloro-1,1,1,3,3,3-pentafluoropropane),
HFC-235fa (1-chloro-1,1,3,3,3-pentafluoropropane),
HFC-236fa (1,1,1,3,3,3-hexafluoropropane), and
E- and Z-CFO-1317mx (2-chloro-1,1,1,3,4,4,4-heptafluoro-2-butene).

24. The system according to any of claims 22-23, wherein the third fraction F_{3D30} comprises about 100 ppm or less of the base.
25. The system according to any of claims 22-24, wherein the third fraction F_{3D30} comprises about 500 ppm or less of the phase transfer catalyst.

26. A system for purification of cis-1,1,1,4,4,4-hexafluoro-2-butene (Z-HFO-1336mzz), the system comprising:
- a reactor configured to react hexafluoro-2-butyne (HFB) with hydrogen in the presence of a hydrogenation catalyst to form a composition comprising HFO-1336mzz(Z) and HFB; and
 - a first distillation column configured to receive the composition from the reactor and configured to separate the composition into a first fraction $F1_{D40}$ comprising HFB and a second fraction $F2_{D40}$ comprising HFO-1336mzz(Z), the first distillation column being configured to return the first fraction $F1_{D40}$ to the reactor.
27. The system of claim 26, wherein the reactor contains a heat diluent, preferably selected from the group consisting of HFC-32, HFC-143a, HFC-134a and HFC-134.
28. The system of any of claims 26-27, the system further comprising a second distillation column configured to receive the second fraction $F2_{D40}$ from the first distillation column and configured to separate the second fraction $F2_{D40}$ into a third fraction $F3_{D41}$ comprising HFO-1336mzz(Z), HFO-1336mzz(E), 1,1,4,4,4-hexafluorobutane (HCFC-356mff), and lower boiling organic byproducts from the hydrogenation reaction, and a fourth fraction $F4_{D41}$ comprising HFO-1336mzz(Z) and higher boiling organic byproducts from the hydrogenation reaction, the system optionally further comprising a third distillation column configured to receive the fourth fraction $F4_{D41}$ from the second distillation column and configured to separate the fourth fraction $F4_{D41}$ into a sixth fraction $F6_{D42}$ comprising Z-HFO-1336mzz, and a fifth fraction $F5_{D42}$ comprising Z-HFO-1336mzz and higher boiling organic byproducts from the hydrogenation reaction.
29. An integrated system for preparing Z-HFO-1336mzz from HCBF, the integrated system comprising the system of claims 1-8 or the system of claim 9-17 and the system of claims 18-25 and the system of claims 26-28.
30. The integrated system according to claim 29, wherein the third distillation column of the system according to claims 1-8 is configured to supply the sixth fraction $F6_{D12}$ comprising HCFO-1326mxz to the dehydrochlorination reactor of

the system according to claims 18-25, and wherein the distillation column of the system according to claims 18-25 is configured to supply the seventh fraction $F7_{D32}$ comprising HFB to the hydrogenation reactor of the system according to claims 26-28.

31. The integrated system according to claim 29 wherein the acid neutralizer A20 of the system according to claims 9-17 is configured to supply the sixth fraction $F6_{A20}$ comprising HCFO-1326mxz to the dehydrochlorination reactor of the system according to claims 18-25, and wherein the distillation column of the system according to claims 18-25 is configured to supply the seventh fraction $F7_{D32}$ comprising HFB to the hydrogenation reactor of the system according to claims 2-28.

32. A process for purification of E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz), the process comprising:

reacting hexachlorobutadiene (HCBd) with hydrofluoric acid (HF) in the presence of a fluorination catalyst in a reactor to form a composition comprising HCFO-1326mxz, HCl, unreacted HCBd, and unreacted HF;

providing the composition to a first distillation column and separating the composition into a first fraction $F1_{D10}$ comprising HCl, and a second fraction $F2_{D10}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz;

providing the second fraction $F2_{D10}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the first distillation column to a second distillation column and separating the second fraction into a third fraction $F3_{D11}$ comprising an azeotrope of unreacted HF and HCFO-1326mxz, and a fourth fraction $F4_{D11}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz,

optionally returning the third fraction $F3_{D11}$ from the second distillation column to the reactor;

providing the fourth fraction $F4_{D11}$ comprising unreacted HCBd, unreacted HF and HCFO-1326mxz from the second distillation column to a third distillation column and separating the fourth fraction $F4_{D11}$ into a fifth

fraction F5_{D12} comprising unreacted HF and unreacted HCB_D, and a sixth fraction F6_{D12} comprising HCFO-1326mxz; and

optionally returning the fifth fraction F5_{D12} from the third distillation column to the reactor.

33. A process for purification of E- and/or Z--chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz), the process comprising:

reacting hexachlorobutadiene (HCB_D) with hydrofluoric acid (HF) in the presence of a fluorination catalyst in a reactor to form a composition comprising HCFO-1326mxz, HCl, unreacted HCB_D, and unreacted HF;

providing the composition from the reactor to a first distillation column and separating the first composition into a first fraction F1_{D20} comprising HCl, and a second fraction F2_{D20} comprising unreacted HCB_D, unreacted HF and HCFO-1326mxz;

providing the second fraction F2_{D20} comprising unreacted HCB_D, unreacted HF and HCFO-1326mxz from the first distillation column to a second distillation column and separating the second fraction F2_{D20} into a third fraction F3_{D21} comprising unreacted HF and unreacted HCB_D, and a fourth fraction F4_{D21} comprising an azeotrope of HF and HCFO-1326mxz;

optionally returning the third fraction F3_{D21} from the second distillation column to the reactor; and

providing the fourth fraction F4_{D21} comprising an azeotrope of HF and HCFO-1326mxz from the second distillation column to an acid neutralizer configured and separating the fourth fraction F4_{D21} into a fifth fraction F5_{A20} comprising neutralized HF and a sixth fraction F6_{A20} comprising HCFO-1326mxz.

34. A process for purification of hexafluoro-2-butyne (HFB), the process comprising:

reacting E- and/or Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz) with a base comprising an alkali metal hydroxide in the presence of a phase transfer catalyst in a reactor to form a composition comprising a vapor portion and a liquid portion, the vapor portion comprising HFB and unreacted HCFO-1326mxz, the liquid portion comprising water, unreacted

HCFO-1326mxz, excess phase transfer catalyst and an alkali metal halide salt, the liquid portion being comprised of an aqueous liquid phase and an organic liquid phase;

providing the vapor portion of the composition from the reactor to one or more distillation columns and separating the vapor portion into a fraction F_{5D31} comprising HFB, and a fraction F_{6D31} comprising unreacted HCFO-1326mxz; and

optionally returning the fraction F_{6D31} comprising unreacted HCFO-1326mxz from the distillation column to the reactor.

35. The process according to claim 34, the process further comprising:

providing the liquid portion of the composition from the reactor to a decanter and separating the aqueous liquid phase into a first fraction F_{1E30} comprising water and the alkali metal halide salt and separating the organic liquid phase into a second fraction F_{2E30} comprising the unreacted HCFO-1326mxz and excess phase transfer catalyst;

optionally returning a first portion of the second fraction F_{2E30} from the decanter to the reactor;

providing a second portion of the second fraction F_{2E30} from the decanter to an additional distillation column and separating the second portion of the second fraction F_{2E30} into a third fraction F_{3D30} comprising unreacted HCFO-1326mxz, and a fourth fraction F_{4D30} comprising unreacted HCFO-1326mxz and excess PTC; and

optionally returning the third fraction F_{3D30} comprising unreacted HCFO-1326mxz from the additional distillation column to the reactor.

36. A process for purification of cis-1,1,1,4,4,4-hexafluoro-2-butene (Z-HFO-1336mzz), the process comprising:

reacting hexafluoro-2-butyne (HFB) with hydrogen in the presence of a hydrogenation catalyst in a reactor to form a composition comprising HFO-1336mzz(Z) and unreacted HFB;

providing the composition from the reactor to a first distillation column and separating the composition into a first fraction F_{1D40} comprising unreacted HFB and a second fraction F_{2D40} comprising HFO-1336mzz(Z); and

optionally returning the first fraction F_{1D40} from the first distillation column to the reactor.

37. The process of claim 36, the process further comprising providing the second fraction F_{2D40} from the first distillation column to a second distillation column and separating the second fraction F_{2D40} into a third fraction comprising HFO-1336mzz(Z), HFO-1336mzz(E), 1,1,4,4,4-hexafluorobutane (HCFC-356mff), and lower boiling organic byproducts from the hydrogenation reaction and a fourth fraction F_{4D41} comprising HFO-1336mzz(Z) and impurities.
38. An integrated process for purification of Z-HFO-1336mzz from HCBd, the integrated process comprising the processes of claims 32 and 34-37, wherein the integrated process comprises providing the sixth fraction F_{6D12} comprising HCFO-1326mxz from the third distillation column of the process according to claim 32 to the dehydrochlorination reactor of the process according to claim 34, and providing the seventh fraction F_{7D32} ~~fifth fraction F_{5D34}~~ comprising HFB from the distillation column of the process according to claim 34 to the hydrogenation reactor of the process according to claim 36.
39. An integrated process for purification of Z-HFO-1336mzz from HCBd, the integrated process comprising the processes of claims 33-37, the integrated process comprising providing the sixth fraction F_{6A20} comprising HCFO-1326mxz from the acid neutralizer A20 of the process according to claim 33 to the dehydrochlorination reactor of the process according to claim 34, and providing the seventh fraction F_{7D32} comprising HFB from the distillation column of the process according to claim 34 to the hydrogenation reactor of the process according to claim 36.
40. A composition prepared by the system of any of claims 1-17 or the process of any of claims 32-33, the composition comprising:
- (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene; and
 - one or more additional compounds selected from:

1,1,1,3,3,3-hexafluoropropane;
1,1,1,2,2,4,4,4-octafluorobutane;
1,1,1,4,4,4-hexafluorobutane;
1,2-dichloro-1,1,2,2-tetrafluoroethane;
2-chloro-1,1,1-trifluoroethane;
2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
2-chloro-1,1,1,3,3-pentafluoropropane;
1-chloro-1,1,3,3,3-pentafluoropropane;
(E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
1,2-dichloro-3,3,4,4-tetrafluorocyclobut-1-ene;
2-chloro-1,1,1,4,4,4-hexafluorobutane;
2,2-dichloro-1,1,1-trifluoroethane;
1,2-dichloro-1,1,2-trifluoroethane;
1,2-dichloro-1,1,3,3,3-pentafluoropropane;
(E)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
1,1,2-trichloro-1,2,2-trifluoroethane;
(Z)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
1,2-dichloro-3,3,3-trifluoroprop-1-ene;
(Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;
2,2-dichloro-1,1,1,4,4,4-hexafluorobutane;
dl-2,3-dichloro-1,1,1,4,4,4-hexafluorobutane;
meso-2,3-dichloro-1,1,1,4,4,4-hexafluorobutane;
1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene;
2,3-dichloro-1,1,1,3-tetrafluoropropane;
1,2-dichloro-1,1,2,4,4,4-hexafluorobutane;
1,2,2-trichloro-1,1-difluoroethane;
1,1,1-trichloro-2,2-difluoroethane;

1,1,2,2-tetrachloro-1,2-difluoroethane;
1,1,1,2-tetrachloro-2,2-difluoroethane;
1,2,3-trichloro-1,1,4,4,4-pentafluorobutane; and
1,1,2,3-tetrachloro-4,4,4-trifluorobut-1-ene,

wherein the composition comprises greater than about 95 mole percent Z-HCFO-1326mxz.

41. A composition prepared by the system of any of claims 18-25 or the process of any of claims 34-35, the composition comprising:

- i) hexafluorobutyne (HFB); and
- ii) one or more additional compounds selected from the group consisting of:
 - 1,1,1,3,3,3-hexafluoropropane;
 - 1,1,1,2,4,4,4-heptafluoro-2-butene;
 - (E)-1,1,1,4,4,4-hexafluorobutene;
 - 1,1,1,2,2,4,4,4-octafluorobutane;
 - 1,1,1,4,4,4-hexafluorobutane;
 - 1,2-dichloro-1,1,2,2-tetrafluoroethane;
 - 2-chloro-1,1,1-trifluoroethane;
 - (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
 - 1-chloro-3,3,4,4,4-pentafluorobut-1-yne;
 - 1-chloro-3,3,4,4,4-pentafluorobut-2-yne;
 - (Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;
 - 1,2-dichloro-3,3,4,4,4-pentafluorobut-1-ene
 - 2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,3-pentafluoropropane;
 - 1-chloro-1,1,3,3,3-pentafluoropropane;
 - (E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene;
 - 2-chloro-1,1,1,4,4,4-hexafluorobutane;
 - 2,2-dichloro-1,1,1-trifluoroethane;
 - 1,2-dichloro-1,1,2-trifluoroethane;

1,2-dichloro-1,1,3,3,3-pentafluoropropane;
(E)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
1,1,2-trichloro-1,2,2-trifluoroethane;
(Z)-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene;
1-chloro-3,3,3-trifluoroprop-1-yne;
1,2-dichloro-3,3,3-trifluoroprop-1-ene;
(Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;
1-chloro-1,1,2,4,4,4-hexafluoro-2-butene;
2-chloro-1,3,3,3-tetrafluoroprop-1-ene;
1,1,3,3,3-pentafluoroprop-1-ene;
2-chloro-1,1,3,3,3-pentafluoroprop-1-ene;
trifluoroacetone;
trifluoropropyne; and
1,1,4,4,4-pentafluoro-1-butene,

wherein the composition comprises greater than about 95 mole percent HFB.

42. A composition prepared by the system of any of claims 26-31 or the process of any of claims 36-39, the composition comprising:

- i) (Z)-1,1,1,4,4,4-hexafluoro-2-butene (Z-HFO-1336mzz); and
- ii) one or more additional compounds selected from the group consisting of:
 - 1,1,1,3,3,3-hexafluoropropane;
 - (E)-1,1,1,4,4,4-hexafluorobutene;
 - 1,1,1,2,2,4,4,4-octafluorobutane;
 - 1,2-dichloro-1,1,2,2-tetrafluoroethane;
 - 3-chloro-1,1,1-trifluoropropane;
 - 4-chloro-1,1,1,2,2-pentafluorobutane;
 - 2-chloro-1,1,1,2,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,4,4,4-heptafluorobutane;
 - 2-chloro-1,1,1,3,3-pentafluoropropane;
 - 1-chloro-1,1,3,3,3-pentafluoropropane;
 - 2-chloro-1,1,1,4,4,4-hexafluorobutane;
 - 1,2-dichloro-1,1,3,3,3-pentafluoropropane;

1,2-dichloro-3,3,3-trifluoroprop-1-ene;
1-chloro-3,3,3-trifluoro-propene;
1-chloro-1,1,2,4,4,4-hexafluoro-2-butene;
1-chloro-1,1,4,4,4-pentafluorobutane;
2-chloro-1,1,1,3-tetrafluoropropane;
1,1,1,3,3-pentafluoropropane;
(Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene; and
(E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene

wherein the composition comprises greater than about 99 mole percent Z-HFO-1336mzz.

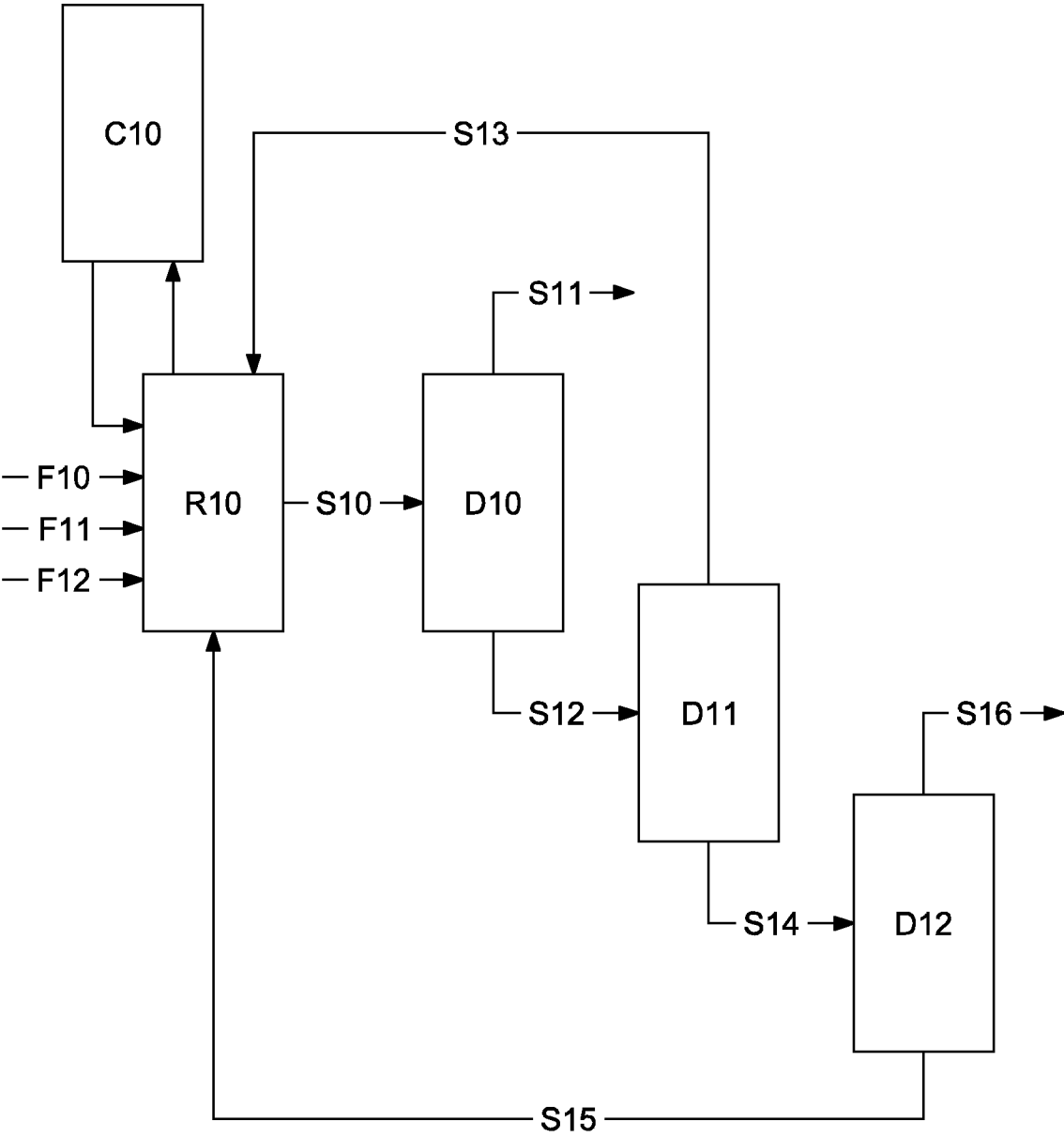


FIG. 1

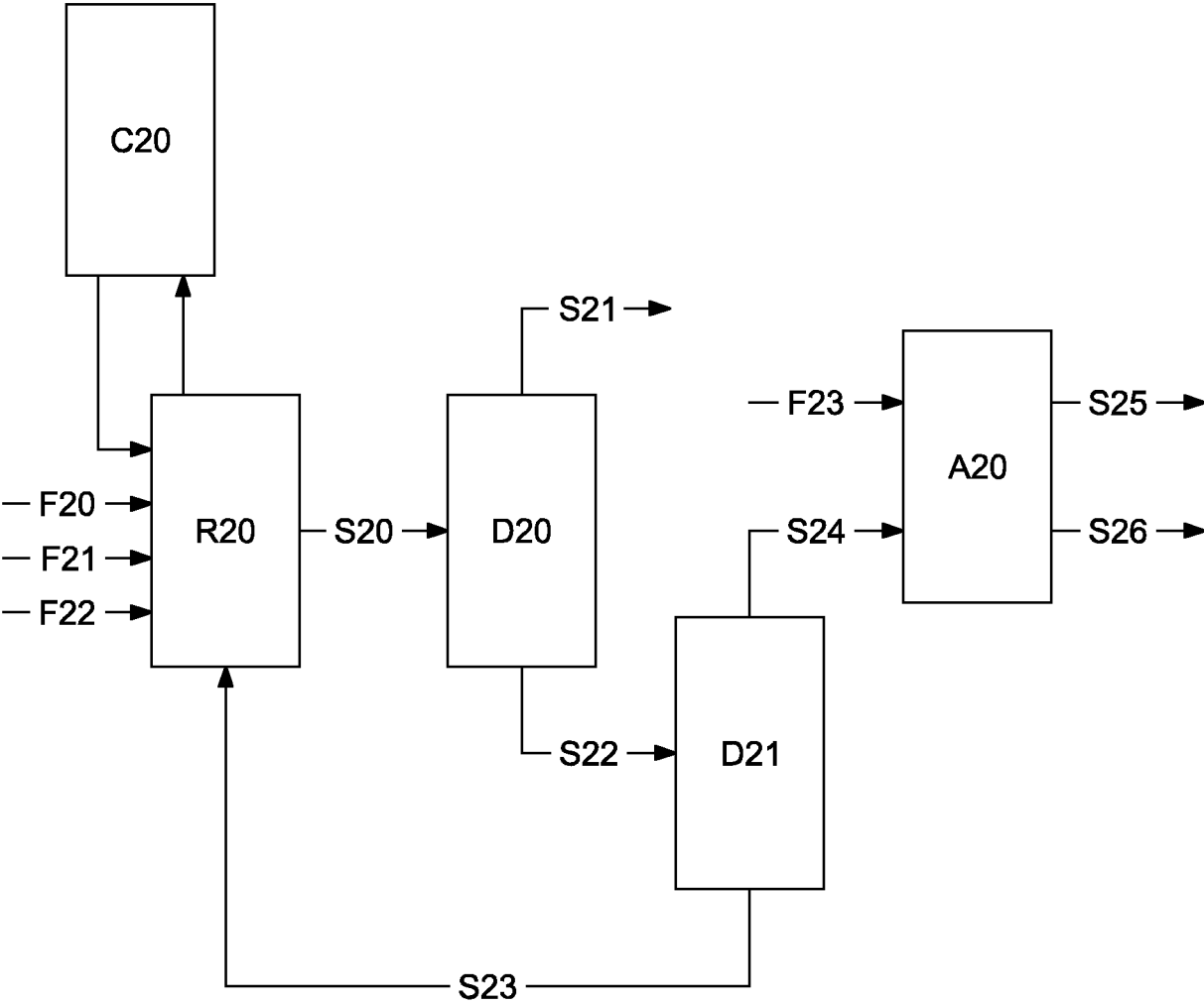


FIG. 2

3/4

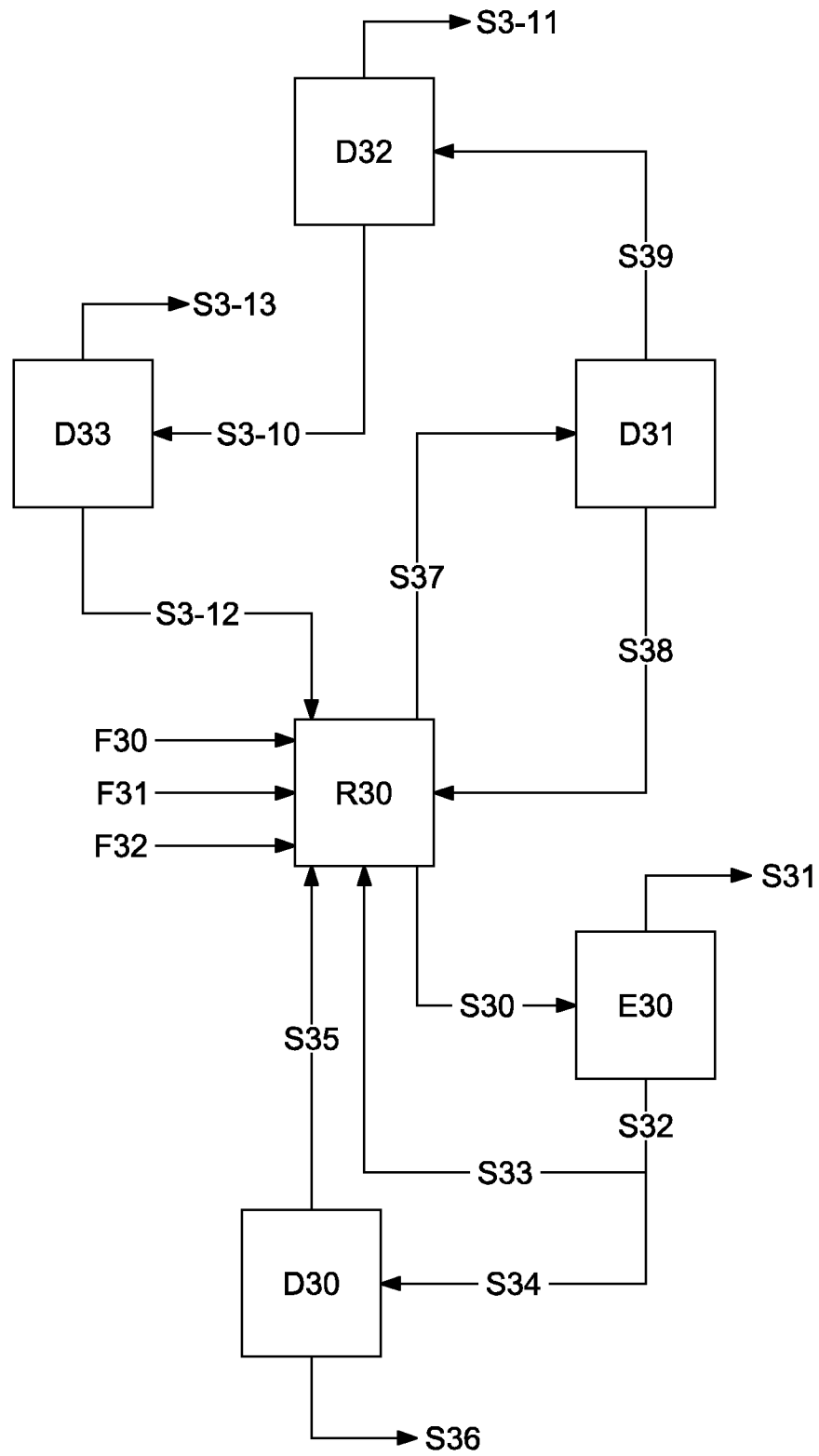


FIG. 3

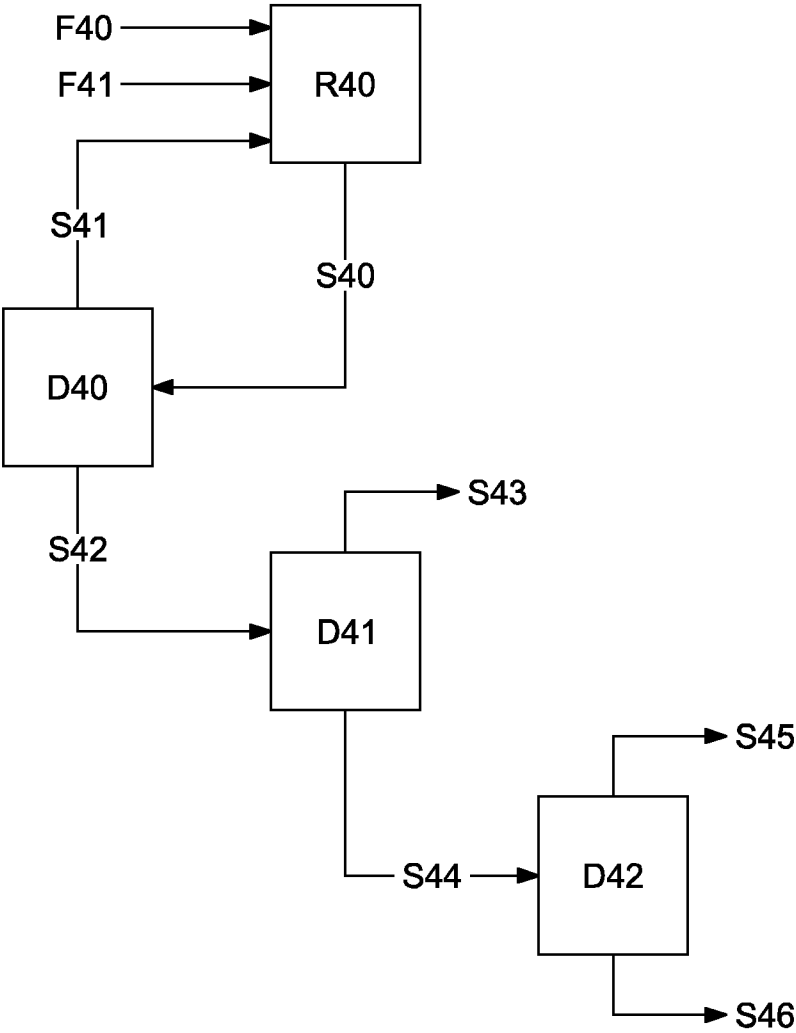


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/038691

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C17/21 C07C17/383
ADD.

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)
C07C

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2019/023572 A1 (CHEMOURS CO FC LLC [US]) 31 January 2019 (2019-01-31)	32,40
Y	Process of: preparing 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene, comprising reacting hexachlorobutadiene with hydrofluoric acid in the presence of a transition metal catalyst, wherein greater than about 99 mole percent of the 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene produced is (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (see claim 1 and example 1, page 35). a composition comprising i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene and ii) one or more additional compounds selected from a list of fluorinated or -/-	1-8,32



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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

25 October 2024

Date of mailing of the international search report

09/01/2025

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/038691

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	chlorinated hydrocarbons such as 1,1,1,3,3,3-hexafluoropropane (see claim 28) -----	
X	CN 106 008 147 A (BEIJING YUJI SCIENCE & TECH CO LTD) 12 October 2016 (2016-10-12) Figure 1 discloses a system for purification of hydrocarbons comprising a reactor (4), a first distillation column (7) and a second distillation column (10), followed by a further reactor (14) and a third distillation column (21) followed by a fourth, fifth and sixth distillation column (23-29). compositions comprising E-2- Chlorohexafluoro-2-butene and at least one further chlorinated/fluorinated hydrocarbon, such as octafluoro-2-butene: see top-components of second distillation column 10 -----	1-8,40
X	US 2 439 299 A (HOVEY ROGER S ET AL) 6 April 1948 (1948-04-06)	1
Y	system for purification of halogenated hydrocarbons comprising a reactor and a first distillation column: see figure 1 ----- -/-	1-8,32

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/038691

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
T	WO 2015/120250 A1 (DU PONT [US]) 13 August 2015 (2015-08-13) process for the preparation of cis-1,1,1,4,4,4-hexafluoro-2-butene (1326 mxz) comprising: a) contacting 1,1,1-trifluoro,2,2,2-trichloroethane with hydrogen in the presence of a catalyst comprising ruthenium to produce a product mixture comprising 2,3-dichloro-1,1,1,4,4,4-trifluoro-but-2-ene (1316mxx) b) recovering said 1316mxx as a mixture of Z- and E- isomers; c) contacting said 1316mxx with hydrogen, in the presence of a catalyst selected from the group consisting of copper on carbon, nickel on carbon, copper and nickel on carbon and copper and palladium on carbon, to produce a second product mixture, comprising 2-chloro-1,1,1,4,4,4-trifluoro-but-2-ene (2-E- or Z-CFC-1326mxz); d) subjecting said second product mixture to a separation step to provide E- or Z-2-chloro-1,1,1,4,4,4-trifluoro-but-2-ene 1(E/Z-326mxz). e) further reacting said E- or Z-1326mxz with an aqueous solution of an alkali metal hydroxide in the presence of an ammonium phase-transfer-catalyst, converting said Z-1326mxz to 1,1,1,4,4,4-hexafluoro-2-butyne, and recovering the 1,1,1,4,4,4-hexafluoro-2-butyne (see claim 2) f) hydrogenating the hexafluorobut-2-yne to give cis- or trans-1,1,1,4,4,4-hexafluoro-2-butene (E- or Z-HFO-1336mzz) (see claim 21) -----	1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/038691

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.:
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:

3. ☐ Claims Nos.:
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:

see additional sheet

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 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.:
1 - 8, 32 (completely) ; 40 (partially)

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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-8, 32 (completely); 40 (partially)

A system for purification of E/Z-2-Chloro-1,1,1,4,4,4-hexafluoro-2-butene (HFO-1326mxz), characterized by the presence of a 3rd distillation column; Processes for purification of E/Z-2-Chloro-1,1,1,4,4,4-hexafluoro-2-butene, characterized by reacting HCBd with HF in a reactor, followed by distillations in at least three distillation columns; compositions comprising E/Z-2-Chloro-1,1,1,4,4,4-hexafluoro-2-butene and at least one further fluoro/chloro-hydrocarbon, prepared by the process of claims 1-8.

2. claims: 9-17, 33 (completely); 40 (partially)

A system for purification of E/Z-2-Chloro-1,1,1,4,4,4-hexafluoro-2-butene (HFO-1326mxz), characterized by the presence of an acid neutralizer after the 2nd distillation column; Processes for purification of E/Z-2-Chloro-1,1,1,4,4,4-hexafluoro-2-butene, characterized by reacting HCBd with HF in a reactor, followed by 2 distillations and an acid neutralizer; compositions comprising E/Z-2-Chloro-1,1,1,4,4,4-hexafluoro-2-butene and at least one further fluoro/chloro-hydrocarbon, prepared by the process of claims 9-17.

3. claims: 18-25, 34, 35, 41

A system for purification of 1,1,1,4,4,4-hexafluoro-2-butyne (HFB). Processes for purification of 1,1,1,4,4,4-hexafluoro-2-butyne. Compositions comprising 1,1,1,4,4,4-hexafluoro-2-butyne and at least one further fluoro/chloro-hydrocarbon, prepared by the process of claims 18-25 or 34-35.

4. claims: 26-28, 36, 37 (completely); 42 (partially)

A system for purification of 1,1,1,4,4,4-hexafluoro-2-butene (E/Z-HFO-1336mzz), characterized in starting from HFB. Processes for purification of 1,1,1,4,4,4-hexafluoro-2-butene. Compositions comprising 1,1,1,4,4,4-hexafluoro-2-butene and at least one further fluoro/chloro-hydrocarbon, prepared by the process of claims 26-28 or claims 36-37.

5. claims: 29-31, 38, 39 (completely); 42 (partially)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Integrated systems for preparing
1,1,1,4,4,4-hexafluoro-2-butene (Z-HFO-1336mzz)
characterized in starting from hexachloro-butadiene (HCBD),
integrated processes for purification of Z-HFO-1336mzz,
characterized in starting from hexafluoro-butadiene (HCBD).
Compositions comprising 1,1,1,4,4,4-hexafluoro-2-butene and
at least one further fluoro/chloro-hydrocarbon, prepared by
the process of claims 29-31 or claims 38-39.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2024/038691

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