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(54) Title: PROCESSES FOR THE PRODUCTION OF HEXAFLUORO-2-BUTYNE AND COMPOSITIONS THEREOF

(57) Abstract: Methods of synthesis of intermediates, such as hexafluoro-2-butyne, which can be used in the production fluorinated olefins, such as Z-1,1,1,4,4,4-hexafluoro-2-butene, are provided.

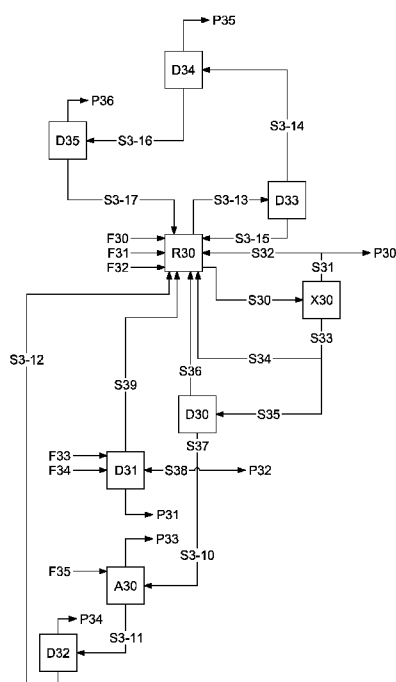


FIG. 1

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TITLE OF THE INVENTION

PROCESSES FOR THE PRODUCTION OF HEXAFLUORO-2-BUTYNE AND
COMPOSITIONS THEREOF

FIELD

[0001] This disclosure relates in general to methods of synthesis of fluorinated olefins and fluorinated alkynes. More particularly, this invention relates to processes and systems for making the intermediate hexafluoro-2-butyne which can be used for the production of fluorinated olefins, such as Z-1,1,1,4,4,4-hexafluoro-2-butene.

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 contain no chlorine that also 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 fluoroolefin. The present invention provides economical and efficient systems and processes for manufacturing intermediate compounds, namely hexafluoro-2-butyne

(HFB), which can then be converted to form the desired Z-HFO-1336mzz hydrofluoroolefin.

SUMMARY

[0005] 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.

[0006] Disclosed herein are processes and systems for producing HFB. The process comprises reacting a chlorinated reactant, and more particularly a chlorofluorocarbon, with a base in the presence of a phase transfer catalyst. In one embodiment, the chlorinated reactant includes a chlorofluorobutane or a chlorofluorobutene. In one embodiment, the chlorinated reactant is HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane) or HCFO-1326mxz (E- or Z-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene).

[0007] In one embodiment, the process comprises first introducing the chlorinated reactant (e.g., HCFC-336mdd, HCFC-336maf or HCFO-1326mxz) to a reactor and subsequently introducing the base to the reactor in the presence of the phase transfer catalyst for dehydrochlorination of the chlorinated reactant to form HFB.

[0008] In one embodiment, the process comprises co-feeding the chlorinated reactant (e.g., HCFC-336mdd, HCFC-336maf or HCFO-1326mxz) and the base to a reactor in the presence of the phase transfer catalyst for dehydrochlorination of the chlorinated reactant to form HFB.

[0009] In one embodiment, the base comprises an alkali metal hydroxide.

[0010] In one embodiment, the process comprises the addition of an alkali metal halide salt to the dehydrochlorination reactor.

[0011] In one embodiment, the alkali metal halide salt is provided as a recycle stream from the product mixture.

[0012] In one embodiment, the present invention relates to a process for producing hexafluoro-2-butyne (HFB). The process comprises reacting a base with a chlorinated organic reactant in a reactor in the presence of a phase transfer catalyst and an alkali metal halide salt to form a product mixture comprising HFB; separating alkali metal halide salt from the product mixture; and returning the separated alkali metal halide salt to the reactor.

[0013] In one embodiment, the present invention relates to a process of preparing hexafluoro-2-butyne (HFB). The process comprises: (i) reacting a base comprising an alkali metal hydroxide with HCFO-1326mxz or HCFC-336 for dehydrochlorination of the HCFO-1326mxz or HCFC-336 in a reactor 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; (ii) providing the vapor portion of the composition from the reactor to a fourth distillation column which separates the vapor portion into a lower boiling fraction $F11_{D33}$ comprising HFB, and a higher boiling fraction $F12_{D33}$ comprising HCFO-1326mxz; and (iii) returning the second fraction $F12_{D33}$ comprising HCFO-1326mxz from the fourth distillation column to the reactor, wherein the higher boiling fraction $F12_{D33}$ further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), trifluoropropyne, R-356mff, R-336maf, R-336mdd and hexafluoro-2-butyne.

[0014] In one embodiment, the present invention relates to a process of preparing hexafluoro-2-butyne (HFB). The process comprises: (i) reacting a base comprising an alkali metal hydroxide with HCFO-1326mxz and/or HCFC-336 in a reactor 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; (ii) providing the liquid portion of the composition from the reactor to a decanter and separating the liquid portion into an aqueous liquid phase fraction $F1_{X30}$ comprising water and the alkali metal halide salt and an organic liquid phase fraction $F2_{X30}$ comprising the HCFO-1326mxz and excess phase transfer catalyst; (iii) providing at least a portion of the organic liquid phase fraction $F2_{X30}$ from the decanter to the first distillation column and separating it into a lower boiling fraction $F3_{D30}$ comprising HCFO-1326mxz, and a higher boiling fraction $F4_{D30}$ comprising HCFO-1326mxz, water, alkali salts, excess PTC and other organic byproducts; and (iv) returning the lower boiling fraction $F3_{D30}$ comprising HCFO-1326mxz from the first distillation column to the reactor, wherein the lower boiling fraction $F3_{D30}$ further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z), R-336mdd, R-336maf and R-346mdf; or from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z) and R-346mdf.

[0015] In one embodiment, the present invention relates to a system for producing hexafluoro-2-butyne (HFB). The system comprises a reactor for reacting a base with a chlorinated organic reactant in the presence of a phase transfer catalyst and an alkali metal halide salt to form a product mixture comprising HFB. The system further comprises a recycle stream for returning alkali metal halide salt separated from the product mixture to the reactor.

[0016] Embodiment 1: A process of preparing hexafluoro-2-butyne (HFB), the process comprising adding a base to a chlorinated organic reactant for dehydrochlorination of the chlorinated organic reactant in a reactor in the presence of a phase transfer catalyst to form a composition comprising HFB.

[0017] Embodiment 2: A process of preparing hexafluoro-2-butyne (HFB), the process comprising co-feeding a base and a chlorinated organic reactant to a reactor

for dehydrochlorination of the chlorinated organic reactant in the presence of a phase transfer catalyst to form a composition comprising HFB.

[0018] Embodiment 3: A process for producing hexafluoro-2-butyne (HFB), the process comprising: reacting a base with a chlorinated organic reactant in a reactor in the presence of a phase transfer catalyst and an alkali metal halide salt to form a product mixture comprising HFB; separating alkali metal halide salt from the product mixture; and returning the separated alkali metal halide salt to the reactor.

[0019] Embodiment 4: The process of any of Embodiments 1, 2 or 3, wherein the chlorinated organic reactant comprises a chlororfluorobutane, a chlorofluorobutene, or a mixture thereof.

[0020] Embodiment 5: The process of any of Embodiments 1 to 4, alone or any combination thereof, wherein the chlorinated organic reactant comprises one or more compounds selected from the group consisting of HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane), E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E-HCFO-1326mxz) and Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz).

[0021] Embodiment 6: The process of any of Embodiments 1 to 5, alone or any combination thereof, wherein the chlorinated organic reactant comprises 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz).

[0022] Embodiment 7: The process of any of Embodiments 1 to 6, alone or any combination thereof, wherein the chlorinated organic reactant comprises Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz) and 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-1325lxx (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).

[0023] Embodiment 8: The process of any of Embodiments 1 to 6, alone or any combination thereof, wherein the chlorinated organic reactant comprises Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz) and one or more additional compounds selected from the group consisting of 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).

[0024] Embodiment 9: The process of any of Embodiments 1 to 6, alone or any combination thereof, wherein the chlorinated reactant comprises Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene and HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane).

[0025] Embodiment 10: The process of any of Embodiments 1 to 6, alone or any combination thereof, wherein the chlorinated reactant comprises (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene and one or more additional compounds selected from the group consisting of:

- 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.

[0026] Embodiment 11: The process of any of Embodiments 5 to 10, alone or any combination thereof, wherein the chlorinated organic reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz.

[0027] Embodiment 12: The process of any of Embodiments 7 to 11, alone or any combination thereof, wherein the composition comprising HFB further comprises 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-heptafluorobut-2-ene;
(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-hexafluorobut-2-ene;
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-pentafluorobut-2-ene;
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-hexafluorobut-2-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-hexafluorobut-2-ene;
1,1,2-trichloro-1,2,2-trifluoroethane;
(Z)-2,3-dichloro-1,1,1,4,4,4-hexafluorobut-2-ene;
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-pentafluorobut-2-ene;
1-chloro-1,1,2,4,4,4-hexafluorobut-2-ene;
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.

[0028] Embodiment 13: The process of any of Embodiments 1 to 6, alone or any combination thereof, wherein the chlorinated organic reactant comprises 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) and one or more additional compounds selected from the group consisting of:

(E)-1,1,1,4,4,4-hexafluoro-2-butene;
1,1,1,4,4,4-hexafluorobutane;
1-chloro-1,1-difluoroethane;
2-chloro-1,1-difluoroethylene;
1,1,4,4,4-Pentafluoro-1-butene;
2-chloro-1,1,1,4,4,4-hexafluorobutane;
1,1,1-trichloro-2,2,2-trifluoroethane;
2,2-dichloro-1,1,1-trifluoroethane; and
1,2-dichloro-2,2-difluoroethane).

[0029] Embodiment 14: The process of Embodiment 13, wherein the chlorinated organic reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz and E-HCFO-1326mxz.

[0030] Embodiment 15: The process of any of Embodiments 13 to 14, alone or any combination thereof, wherein the composition comprising HFB further comprises one or more additional compounds selected from the group consisting of:

1,1,1,2,2,5,5,6,6,7,7,7-dodecafluorosept-3-ene,
1,1,1,4,4,4-hexafluorobut-2-ene,
1,1,1,2,4,4,4-septafluorobut-2-ene,
1,1,1,4,4,4-hexafluorobutane,
1,1,1-trifluoroethane,
Trifluoropropyne,
1,1-difluoroethane,
1,1,1-trifluoropropane,
1-Chloro-1,1-difluoroethane,
Fluoromethane,
1,2-dichloro-1,2-difluoroethylene,
Z-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene,
E-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene,
1,2-dichloro-1,1-difluoroethane, and
Trifluoroacetone.

[0031] Embodiment 16: The process of any of Embodiments 1 to 5, alone or any combination thereof, wherein the chlorinated organic reactant comprises 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane (HCFC-336mdd).

[0032] Embodiment 17: The process of any of Embodiments 1 to 5 and 16, alone or any combination thereof, wherein the chlorinated organic compound comprises 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane (HCFC-336mdd) and one or more additional compounds selected from the group consisting of:

Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene,
Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene,
2,2-dichloro-1,1,1,4,4,4-hexafluorobutane,
1,1,1,4,4,4-hexafluorobutane, and
2-chloro-1,1,1,4,4,4-hexafluorobutane.

[0033] Embodiment 18: The process of any of Embodiments 1 to 5 and 16 to 17, alone or any combination thereof, wherein the chlorinated organic reactant comprises greater than about 95 mole percent HCFC-336mdd.

[0034] Embodiment 19: The process of any of Embodiments 1 to 18, alone or any combination thereof, wherein the phase transfer catalyst is a quaternary alkylammonium salt wherein the alkyl groups are alkyl chains having from four to twelve carbon atoms

[0035] Embodiment 20: The process of any of Embodiments 1 to 19, alone or any combination thereof, wherein the base is selected from the group consisting of hydroxides, alkoxides, metal amides, metal hydrides and metal dialkylamides and arylamines.

[0036] Embodiment 21: The process of Embodiment 20, wherein the base is selected from the group consisting of alkali metal hydroxides, calcium hydroxide, magnesium oxide, calcium oxide, sodium carbonate, potassium carbonate, sodium phosphate, potassium phosphate, and mixtures thereof.

[0037] Embodiment 22: The process of Embodiment 21, wherein the base comprises an alkali metal hydroxide, preferably sodium hydroxide or potassium hydroxide.

[0038] Embodiment 23: The process of any of Embodiments 1 to 22, alone or any combination thereof, further comprising feeding an alkali metal halide salt to the reactor, preferably by co-feeding the alkali metal halide salt with the base.

[0039] Embodiment 24: The process of any of Embodiments 1 to 23, alone or any combination thereof, wherein the dehydrochlorination reaction produces an alkali metal halide salt.

[0040] Embodiment 25: The process of Embodiment 24, wherein the alkali metal halide salt is recycled to the reactor.

[0041] Embodiment 26: The process of Embodiment 25, wherein the recycled alkali metal halide salt has a purity of 90% or greater, preferably a purity of 95% or greater, most preferably a purity of 98% or greater.

[0042] Embodiment 27: The process of Embodiment 25, wherein the recycled alkali metal halide salt comprises less than about 5 mole percent, preferably less than about 3 mole percent, most preferably less than about 1 mole percent, of chlorine, fluorine and/or hydroxides.

[0043] Embodiment 28: The process of any of Embodiments 23 to 27, alone or any combination thereof, wherein the base comprises potassium hydroxide and the salt is potassium chloride.

[0044] Embodiment 29: The process of any of Embodiments 23 to 27, alone or any combination thereof, wherein the base comprises sodium hydroxide and the salt is sodium chloride.

[0045] Embodiment 30: A process of preparing hexafluoro-2-butyne (HFB), the process comprising:

reacting a base comprising an alkali metal hydroxide with HCFO-1326mxz or HCFC-336 for dehydrochlorination of the HCFO-1326mxz or HCFC-336 in a reactor 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;

providing the vapor portion of the composition from the reactor to a fourth distillation column which separates the vapor portion into a lower boiling fraction F11_{D33} comprising HFB, and a higher boiling fraction F12_{D33} comprising HCFO-1326mxz; and

returning the higher boiling fraction F12_{D33} comprising HCFO-1326mxz from the fourth distillation column to the reactor, wherein the higher boiling fraction F12_{D33} further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), trifluoropropyne, R-356mff, R-336maf, R-336mdd and hexafluoro-2-butyne.

[0046] Embodiment 31: The process of Embodiment 30, wherein the lower boiling fraction F11_{D33} comprises HFB, HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction, and wherein the lower boiling fraction F11_{D33} is sent to one or more additional distillation columns.

[0047] Embodiment 32: The process of any of Embodiments 30 to 31, alone or any combination thereof, wherein the one or more additional compounds are selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), trifluoropropyne, R-356mff and hexafluoro-2-butyne.

[0048] Embodiment 33: The process of any of Embodiments 30 to 32, alone or any combination thereof, wherein the base is added to the HCFO-1326mxz.

[0049] Embodiment 34: The process of any of Embodiments 30 to 32, alone or any combination thereof, wherein the base and the HCFO-1326mxz are co-fed to the reactor.

[0050] Embodiment 35: The process of any of Embodiments 30 to 34, alone or any combination thereof, wherein the higher boiling fraction F12_{D33} comprises greater than about 95 mole percent Z-HCFO-1326mxz, preferably greater than 97 mole percent Z-HCFO-1326mxz, most preferably greater than 99 mole percent Z-HCFO-1326mxz.

[0051] Embodiment 36: The process of any of Embodiments any of Embodiments 30 to 35, alone or any combination thereof, wherein a water content of the higher boiling fraction F_{12D33} is about 5000 ppm or less, preferably about 3000 ppm or less, most preferably about 1000 ppm or less

[0052] Embodiment 37: The process according to any of Embodiments 30 to 36, alone or any combination thereof, the process further comprising:

providing the liquid portion of the composition from the reactor to a decanter and separating the liquid portion into an aqueous liquid phase fraction F_{1X30} comprising water and the alkali metal halide salt and an organic liquid phase fraction F_{2X30} comprising HCFO-1326mxz and excess phase transfer catalyst;

optionally returning a first portion of the organic liquid phase fraction F_{2X30} from the decanter to the reactor;

providing a second portion of the organic liquid phase fraction F_{2X30} from the decanter to the first distillation column and separating the second portion of the organic liquid phase fraction F_{2X30} into a lower boiling fraction F_{3D30} comprising HCFO-1326mxz, and a higher boiling fraction F_{4D30} comprising HCFO-1326mxz, water, alkali salts, excess PTC and other organic byproducts; and

returning the lower boiling fraction F_{3D30} comprising HCFO-1326mxz from the first distillation column to the reactor, wherein the lower boiling fraction F_{3D30} further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z), R-336mdd, R-336maf and R-346mdf.

[0053] Embodiment 38: The process of Embodiment 37, wherein the one or more additional compounds are selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z) and R-346mdf.

[0054] Embodiment 39: A process of preparing hexafluoro-2-butyne (HFB), the process comprising:

reacting a base comprising an alkali metal hydroxide with HCFO-1326mxz and/or HCFC-336 in a reactor 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;

providing the liquid portion of the composition from the reactor to a decanter and separating the liquid portion into an aqueous liquid phase fraction $F1_{X30}$ comprising water and the alkali metal halide salt and an organic liquid phase fraction $F2_{X30}$ comprising the HCFO-1326mxz and excess phase transfer catalyst;

providing at least a portion of the organic liquid phase fraction $F2_{X30}$ from the decanter to the first distillation column and separating it into a lower boiling fraction $F3_{D30}$ comprising HCFO-1326mxz, and a higher boiling fraction $F4_{D30}$ comprising HCFO-1326mxz, water, alkali salts, excess PTC and other organic byproducts; and

returning the lower boiling fraction $F3_{D30}$ comprising HCFO-1326mxz from the first distillation column to the reactor, wherein the lower boiling fraction $F3_{D30}$ further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z), R-336mdd, R-336maf and R-346mdf; or from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z) and R-346mdf.

[0055] Embodiment 40: The process of Embodiment 39, wherein the base is added to the HCFO-1326mxz and/or HCFC-336.

[0056] Embodiment 41: The process of Embodiment 39, wherein the base is co-fed with the HCFO-1326mxz and/or HCFC-336 to the reactor.

[0057] Embodiment 42: The process of any of Embodiments 39 to 41, alone or any combination thereof, wherein the lower boiling fraction F_{3D30} comprises greater than about 95 mole percent Z-HCFO-1326mxz, preferably greater than 97 mole percent Z-HCFO-1326mxz, most preferably greater than 99 mole percent Z-HCFO-1326mxz.

[0058] Embodiment 43: The process of any of Embodiments 30 to 42, alone or any combination thereof, the process further comprising separating the alkali metal halide salt from the liquid portion and returning the alkali metal halide salt to the reactor.

[0059] Embodiment 44: The process of Embodiment 43, wherein the recycled alkali metal halide salt has a purity of 90% or greater, preferably a purity of 95% or greater, most preferably a purity of 98% or greater.

[0060] Embodiment 45: The process of Embodiment 43, wherein the recycled alkali metal halide salt comprises less than about 5 mole percent, preferably less than about 3 mole percent, most preferably less than about 1 mole percent, of chlorine, fluorine and/or hydroxides.

[0061] Embodiment 46: The process of any of Embodiments 39 to 45, alone or any combination thereof, further comprising providing the vapor portion of the composition from the reactor to the fourth distillation column or partial condenser configured and separating the vapor portion into a lower boiling fraction F_{11D33} comprising HFB, and a higher boiling fraction F_{12D33} comprising unreacted HCFO-1326mxz; and returning the higher boiling fraction F_{12D33} comprising unreacted HCFO-1326mxz from the fourth distillation column to the reactor, wherein the higher boiling fraction F_{12D33} further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), trifluoropropyne, R-356mff and hexafluoro-2-butyne, or from the group consisting of trifluoroacetone, R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), trifluoropropyne, R-356mff and hexafluoro-2-butyne; and optionally, where the lower boiling fraction F_{11D33} comprises HFB, HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction, sending the lower boiling fraction F_{11D33} is sent to one or more additional distillation columns.

[0062] Embodiment 47: The process of any of Embodiments 39 to 46, alone or any combination thereof, wherein a water content of the lower boiling fraction F_{3D30} is about 5000 ppm or less, preferably about 3000 ppm or less, most preferably about 1000 ppm or less.

[0063] Embodiment 48: The process of any of Embodiments 39 to 46, alone or any combination thereof, wherein the lower boiling fraction F_{3D30} comprises about 100 ppm or less of the base.

[0064] Embodiment 49: The process of any of Embodiments 39 to 48, alone or any combination thereof, wherein the lower boiling fraction F_{3D30} comprises about 500 ppm or less of the phase transfer catalyst.

[0065] Embodiment 50: A system for producing hexafluoro-2-butyne (HFB), the system comprising:

a reactor for reacting a base with a chlorinated organic reactant in the presence of a phase transfer catalyst and an alkali metal halide salt to form a product mixture comprising HFB, and

a recycle stream for returning alkali metal halide salt separated from the product mixture to the reactor.

[0066] Embodiment 51: The system of Embodiment 50, wherein the chlorinated organic reactant comprises a chlororfluorobutane, a chlorofluorobutene, or a mixture thereof.

[0067] Embodiment 52: The system of any of Embodiments 50 to 51, alone or any combination thereof, wherein the chlorinated organic reactant comprises one or more compounds selected from the group consisting of HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane), E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E-HCFO-1326mxz) and Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz).

[0068] Embodiment 53: The system of any of Embodiments 50 to 52, alone or any combination thereof, wherein the base is selected from the group consisting of hydroxides, alkoxides, metal amides, metal hydrides and metal dialkylamides and arylamines

[0069] Embodiment 54: The system of Embodiment 53, wherein the base is selected from the group consisting of alkali metal hydroxides, calcium hydroxide, magnesium oxide, calcium oxide, sodium carbonate, potassium carbonate, sodium phosphate, potassium phosphate, and mixtures thereof.

[0070] Embodiment 55: The system of Embodiment 54, wherein the base comprises an alkali metal hydroxide, preferably sodium hydroxide or potassium hydroxide.

[0071] Embodiment 56: The system of Embodiment 55, wherein the base comprises potassium hydroxide and the salt is potassium chloride.

[0072] Embodiment 57: The system of Embodiment 55, wherein the base comprises sodium hydroxide and the salt is sodium chloride.

[0073] Embodiment 58: The system of any of Embodiments 50 to 57, alone or any combination thereof, wherein the recycled alkali metal halide salt has a purity of 90% or greater, preferably a purity of 95% or greater, most preferably a purity of 98% or greater.

[0074] Embodiment 59: The system of any of Embodiments 50 to 57, alone or any combination thereof, wherein the recycled alkali metal halide salt comprises less than about 5 mole percent, preferably less than about 3 mole percent, most preferably less than about 1 mole percent, of chlorine, fluorine and/or hydroxides.

[0075] Embodiment 60: The process of any of Embodiments 39 to 48, wherein the higher boiling fraction F_{4D30} comprising HCFO-1326mxz, water, alkali salts, excess PTC and other organic byproducts, and wherein the higher boiling fraction F_{4D30} is provided to one or more additional purification columns.

[0076] Embodiment 61: The system of Embodiment 60, the process further comprising:

optionally supplying a second portion of the higher boiling fraction F_{4D30} to the second distillation column and separating the second portion of the higher boiling fraction F_{4D30} into a lower boiling fraction F_{5D31} comprising HCFO-1326mxz, and a higher boiling fraction F_{6D31} comprising HCFO-1326mxz, water, alkali salts, excess PTC, other organic byproducts and distillation solvent; and

providing a distillation solvent as a separate feed to the second distillation column;

returning the lower boiling fraction F_{5D31} comprising HCFO-1326mxz from the second distillation column to the reactor, wherein the lower boiling fraction F_{5D31} further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z), R-336mdd, R-336maf and R-346mdf.

[0077] Embodiment 62: The system of Embodiments 60 and 61 wherein the distillation solvent is water.

[0078] Embodiment 63: The system of Embodiments 60 and 61 wherein the distillation solvent is carbon tetrachloride, chlorobenzene, dichlorobenzene, PCE or any high boiling point material that is miscible with PTC.

[0079] Embodiment 64: The system of Embodiments 62 and 63 where the distillation solvents are co-fed with the second portion of the higher boiling fraction F_{4D30} to the second distillation column.

[0080] Embodiment 65: The system of Embodiment 60, the process further comprising:

optionally supplying a third portion of the higher boiling fraction F_{4D30} to an additional extraction column and separating the third portion of the fourth higher boiling F_{4D30} into a lower density fraction F_{7A30} comprising HCFO-1326mxz,

extractant, water, alkali salts and PTC and an higher density fraction F8_{A30} comprising HCFO-1326mxz, water, other organic byproducts and extractant; and

providing the higher density fraction F8_{A30} to a third distillation column and separating the higher density fraction F8_{A30} into a lower boiling fraction F9_{D32} comprising HCFO-1326mxz, water, other organic byproducts and extractant and a higher boiling fraction F10_{D32} comprising HCFO-1326mxz, water, other organic byproducts;

returning the higher boiling fraction F10_{D32} comprising HCFO-1326mxz, water, other organic byproducts from the third distillation column to the reactor, wherein the higher boiling fraction F10_{D32} further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z), R-336mdd, R-336maf and R-346mdf.

[0081] Embodiment 66: The system of Embodiments 60 and 65 wherein the extractant is a water solution of methanol, ethanol or any solvent with low solubility in 1326mxz and solubility of PTC.

[0082] Embodiment 67: The system of Embodiments 66 where the extractant is co-fed with the third portion of the higher boiling fraction F4_{D30} to the extraction column.

DETAILED DESCRIPTION

[0083] The present invention generally relates to processes and systems for producing hexafluoro-2-butyne (HFB) by reacting a chlorinated reactant, and more particularly a chlorofluorocarbon, with a base in the presence of a phase transfer catalyst. In one embodiment, the chlorinated reactant includes a chlorofluorobutane or a chlorofluorobutene. In one embodiment, the chlorinated reactant comprises HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane), HCFO-1326mxz (E- or Z-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene), or a combination of two or more thereof. In one embodiment, the base comprises an alkali metal hydroxide.

[0084] In one embodiment, the process comprises first introducing the chlorinated reactant (e.g., HCFC-336mdd, HCFC-336maf, E- HCFO-1326mxz and/or Z-HCFO-1326mxz) to a reactor and subsequently introducing the base to the reactor in the presence of the phase transfer catalyst for dehydrochlorination of the chlorinated reactant to form HFB. In another embodiment, the chlorinated reactant (e.g., HCFC-336mdd, HCFC-336maf, E- HCFO-1326mxz and/or Z-HCFO-1326mxz) and the base are co-fed (optionally co-fed along with a metal halide solution along) to a reactor in the presence of the phase transfer catalyst for dehydrochlorination of the chlorinated reactant to form HFB.

[0085] 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).

[0086] 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.

[0087] 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”.

[0088] 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.”

[0089] 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.

[0090] 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.

[0091] 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.

[0092] 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.

[0093] 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.

[0094] As used herein, phase transfer catalyst is intended to mean a substance that facilitates the transfer of ionic compounds into an organic phase from an aqueous phase or from a solid phase. The phase transfer catalyst facilitates the reaction of these dissimilar and incompatible components. While various phase transfer catalysts may function in different ways, their mechanism of action is not determinative of their utility in the present invention provided that the phase transfer catalyst facilitates the dehydrochlorination reaction.

[0095] As used herein, the name HCFC-336 without a designation of positional isomers, refers to either or both of HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane) or HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane).

[0096] As used herein, the name HCFC-1326mxz without designation of stereochemistry refers to either or both of E- or Z-HCFC-1326mxz (E-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene or Z-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene).

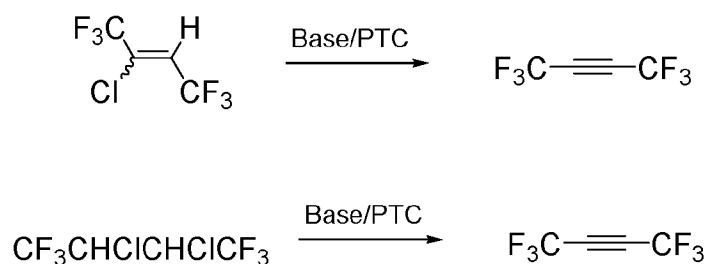
[0097] Referring to Fig. 1, in some embodiments of the invention, the process comprises steps of introducing first feed stream F30 comprising, consisting essentially of, or consisting of one or more chlorinated reactants selected from HCFC-336mdd, HCFC-336maf, Z-HCFO-1326mxz and E-HCFO-1326mxz, to a reactor R30. Subsequently, after the chlorinated reactant has been added to the reactor R30, a base is fed to the reactor R30 in second feed stream F31, for reaction with the chlorinated reactant in the presence of a phase transfer catalyst to form HFB. Thus, according to one embodiment of the claimed invention, the base is added to the organic chlorinated reactant in the presence of a phase transfer catalyst to form HFB.

[0098] In another embodiment, the process comprises a step of co-feeding first feed stream F30 comprising, consisting essentially of, or consisting of a chlorinated reactant selected from HCFC-336mdd, HCFC-336maf, Z-HCFO-1326mxz and E-HCFO-1326mxz, and second feed stream F31 comprising, consisting essentially of or consisting of a base to the reactor R30 for reaction in the presence of a phase transfer catalyst to form HFB. Thus, according to one embodiment of the claimed invention, the base and the organic chlorinated reactant are co-fed to the reactor R30 in the presence

of a phase transfer catalyst to form HFB. In one embodiment, one or more metal halides are preferably co-fed to the reactor R30 with the base and chlorinated reactant.

[0099] In one embodiment, two reactors may be utilized, where for example, the chlorinated reactant is formed in a first, upstream reactor (e.g., HCFC-336 may be converted to HCFO-1326mxz in first reactor) and then the chlorinated material may be sent to a second, downstream reactor (e.g., reactor R30) for dehydrochlorination to form HFB.

[0100] In the reactor R30, the chlorinated reactant is subjected to dehydrochlorination to form HFB. More particularly, the base is added to the chlorinated reactant in the presence of a phase transfer catalyst or the base and the chlorinated reactant are co-fed to a reactor in the presence of a phase transfer catalyst to form HFB. In one embodiment, the chlorinated reactant is selected from HCFC-336mdd, HCFC-336maf, Z-HCFO-1326mxz, E-HCFO-1326mxz, and combinations of two or more thereof. Representative reactions are shown below:



[0101] In one embodiment, the phase transfer catalyst (PTC) is fed to the reactor R30 in third feed stream F32 either before feeding first feed stream F30 (chlorinated reactant) and second feed stream F31 (base), or third feed stream F32 can be co-fed with first feed stream F30 and second feed stream F31 (base). The third feed stream F32 may comprise neat PTC or may comprise PTC dissolved in the chlorinated reactant. In one embodiment, the dehydrochlorination process is conducted by first flowing the chlorinated reactant into a bed comprising the phase transfer catalyst in the reactor R30 at a specified temperature and subsequently flowing the base into the phase transfer catalyst bed in the reactor R30 at a specified temperature. In another embodiment, the dehydrochlorination process is conducted by co-feeding the

chlorinated reactant and the base into the phase transfer catalyst bed in the reactor R30 at a specified temperature. In some embodiments, a carrier gas is utilized for introducing the chlorinated reactant and/or the base into the reactor. Examples of carrier gases include inert gases such as nitrogen, argon and helium.

[0102] 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. The anions of the salt can be halides such as chloride or bromide, hydrogen sulfate, or any other commonly used anion.

[0103] In one embodiment, the process according to the present invention comprises reacting a base with a chlorinated reactant in the presence of a quaternary alkylammonium salt having alkyl groups of from four to twelve carbon atoms, and mixtures thereof, wherein the base is added to the chlorinated reactant or wherein the chlorinated reactant and the base are co-fed to the reactor R30.

[0104] In one embodiment, the quaternary alkyl ammonium salt is a tetrabutylammonium salt. 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.

[0105] 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.

[0106] In another embodiment, the chlorinated reactant, such as HCFC-336mdd, can be twice dehydrochlorinated at temperatures well below 100°C using a base 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, mentioned above.

[0107] In yet another embodiment, dehydrochlorination of the chlorinated reactant, such as HCFO-1326mxz or HCFC-336mdd, 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.

[0108] 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.

[0109] 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.

[0110] 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.

[0111] In one embodiment, the process according to the present invention comprises reacting a base with a chlorinated reactant in the presence of a quaternary alkylammonium salt having alkyl groups of from four to twelve or four to ten carbon atoms, and mixtures thereof, and a non-ionic surfactant, wherein the base is added to the chlorinated reactant or wherein the chlorinated reactant and the base are co-fed to the reactor R30.

[0112] In some embodiments, dehydrochlorination of the chlorinated reactant, such as HCFO-1326mxz or HCFC-336mdd, 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.

[0113] 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.

[0114] In some embodiments, the base is selected from alkali metal hydroxides (e.g., lithium hydroxide, sodium hydroxide, potassium hydroxide), calcium hydroxide, magnesium oxide, calcium oxide, sodium carbonate, potassium carbonate, sodium phosphate, potassium phosphate, and mixtures thereof.

[0115] In some embodiments, the base comprises an alkali metal hydroxide. In some embodiments, the base comprises at least one of sodium hydroxide and potassium hydroxide.

[0116] In some embodiments, the base is an aqueous basic solution. As used herein, the “aqueous basic solution” or “base solution” is a liquid (whether a solution, dispersion, emulsion, or suspension and the like) that is primarily an aqueous liquid having a pH of over 7. In some embodiments, the aqueous basic solution has a pH of over 8. In some embodiments, the aqueous basic solution has a pH of over 10. In some embodiments, the aqueous basic solution has a pH of 12-14. In some embodiments, the aqueous basic solution contains small amounts of organic liquids which may be miscible or immiscible with water. In some embodiments, the liquid medium in the aqueous basic 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 is deionized water or distilled water.

[0117] In one embodiment, the aqueous basic solution comprises an alkali metal hydroxide. In one embodiment, the aqueous basic solution is an aqueous solution of an alkali metal hydroxide. In one embodiment, the base in the aqueous basic solution is potassium hydroxide or sodium hydroxide.

[0118] In one embodiment, the quaternary alkylammonium salt is added in an amount of from 0.5 mole percent to 1.0 mole percent of the chlorinated reactant. In another embodiment, the quaternary alkylammonium salts is added in an amount of from 1 mole percent to 5 mole percent of the chlorinated reactant. In yet another embodiment, the quaternary alkylammonium salts is added in an amount of from 1 mole percent to 3 mole percent of the chlorinated reactant. In one embodiment, the quaternary alkylammonium salt is added in an amount of from 1 mole percent to 1.5 mole percent of the chlorinated reactant and the weight of non-ionic surfactant added is from 1.0 to 2.0 times the weight of the quaternary alkylammonium salt.

[0119] In some embodiments, about 1 to about 5 molar equivalents of base is used based on one molar equivalent of the chlorinated reactant, for example, where the chlorinated reactant comprises HCFO-1326mxz and HCFC-336mdd. Preferably, 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 of base is used based on one molar equivalent of the chlorinated reactant. In some embodiments, about 1 to about 1.5 molar equivalents of base is used based on one molar equivalent of the chlorinated reactant. In some embodiments, a molar excess of base is used based on one molar equivalent of the chlorinated reactant.

[0120] In some embodiments, about 0.1 to about 1 molar equivalents of base is used based on one molar equivalent of the chlorinated reactant, for example where the chlorinated reactant comprises HCFO-1326mxz. Preferably, about 0.1 to about 0.9, about 0.1 to about 0.8, about 0.1 to about 0.7, about 0.2 to about 0.8, about 0.3 to about 0.8, about 0.2 to about 0.7, about 0.3 to about 0.7, about 0.4 to about 0.7, or about 0.4

to about 0.6 molar equivalents is used based on one molar equivalent of the chlorinated reactant. In some embodiments, about 0.5 to about 1 molar equivalents of base is used based on one molar equivalent of the chlorinated reactant. In some embodiments, a molar excess of base is used based on one molar equivalent of the chlorinated reactant.

[0121] In one embodiment, the conversion of the chlorinated reactant (e.g., HCFC-336 or HCFO-1326mxz or mixtures thereof) to HFB is at least 50% per hour.

[0122] 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.

[0123] The reaction zone temperature for the dehydrochlorination of the chlorinated reactant 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 (described in greater detail herein) can be reduced, and the deactivation of the catalyst can be suppressed by maintaining the reaction temperature within these ranges.

[0124] The contact time (CT) of the reactants and catalyst within the dehydrochlorination reactor R30 is determined by the following equation:

$$CT = VR/VF,$$

[0125] 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 chlorinated reactant 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.

[0126] 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 reaction is carried out at a pressure in a range from about -0.05 to 1.8 MPaG (gauge pressure) to achieve improved reaction selectivity.

[0127] 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.

[0128] The process of preparing the HFB may be conducted in a batchwise process or a continuous process. Preferably, the dehydrochlorination of the chlorinated reactant (e.g., HCFC-336mdd, HCFC-336maf, Z-HCFO-1326mxz, E-HCFO-1326mxz or combinations of two or more thereof) to form HFB is conducted as a batch process with the base being added to the organic reactant or the base and organic reactant being co-fed to the reactor, or as a continuous process with the base and organic reactant being co-fed to the reactor.

[0129] In one embodiment, upon completion of a batchwise or continuous dehydrochlorination process, the HFB is of sufficient purity to not require further purification steps.

[0130] 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.

[0131] The process according to the present invention may further comprise selective hydrogenation of the HFB to produce Z-HFO-1336mzz, as disclosed in International Application Publication No. WO2019/023572, the entire disclosure of which is incorporated herein by reference.

[0132] In one embodiment, the chlorinated reactant comprises, consists of or consists essentially of HCFC-336mdd. In some embodiments, the chlorinated reactant comprises, consists of or consists essentially of:

- (i) 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane (HCFC-336mdd); and
- (ii) one or more additional compounds selected from HCFO-1326mxz(Z), HCFO-1326mxz(E), HCFO-1316mxx(Z), HCFO-1316mxx(E), HCFC-356mff, HCFC-346mdf and HCFC-336maf.

wherein, in some embodiments, the chlorinated reactant composition comprises greater than about 95 mole percent HCFC-336mdd.

[0133] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of: (i) HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), and (ii) HCFO-1326mxz(E) or HCFO-1326mxz(Z), wherein the composition comprises greater than about 95 mole percent HCFC-336mdd, or greater than about 96 mole percent HCFC-336mdd, greater than about 97 mole percent HCFC-336mdd, greater than about 98 mole percent HCFC-336mdd, greater than about 99 mole percent HCFC-336mdd, greater than about 99.2 mole percent HCFC-336mdd, greater than about 99.5 mole percent HCFC-336mdd, greater than about 99.7 mole percent HCFC-336mdd, or greater than about 99.9 mole percent HCFC-336mdd.

[0134] In some embodiments, the chlorinated reactant comprises HCFC-336mdd and one of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336mdd 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 chlorinated reactant comprises HCFC-336mdd and each of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336mdd and from one to twenty-five of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336mdd and from one to twenty of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336mdd and from one to ten of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336mdd and from one to five of the additional compounds. In some

embodiments, the chlorinated reactant comprises HCFC-336mdd and from one to four of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336mdd and from one to three of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336mdd and from one to two of the additional compounds.

[0135] In some embodiments, the chlorinated reactant comprises greater than about 97 mole percent HCFC-336mdd, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 98 mole percent HCFC-336mdd, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99 mole percent HCFC-336mdd, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99.5 mole percent HCFC-336mdd, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99.9 mole percent HCFC-336mdd, with the remainder being one or more of the additional compounds.

[0136] In some embodiments, the chlorinated reactant consists essentially of or consists of the HCFC-336mdd and the one or more additional compounds.

[0137] The one or more additional compounds of the chlorinated reactant comprising HCFC-336mdd are selected from and listed in Table 1.

TABLE 1: COMPOUNDS OF HCFC-336MDD REACTANT COMPOSITION

Name	Code	Structure
Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene	Z-1326mxz	<chem>CF3-CCl=CH-CF3</chem>
E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene	E-1326mxz	<chem>CF3-CCl=CH-CF3</chem>
E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene	E-1316mxx	<chem>CF3-CCl=CCl-CF3</chem>
Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene	Z-1316mxx	<chem>CF3-CCl=CCl-CF3</chem>
2,2-dichloro-1,1,1,4,4,4-hexafluorobutane	336maf	<chem>CF3-CCl2-CH2-CF3</chem>
1,1,1,4,4,4-hexafluorobutane	356mff	<chem>CF3-CH2-CH2-CF3</chem>
2-chloro-1,1,1,4,4,4-hexafluorobutane	346mdf	<chem>CF3-CHCl-CH2-CF3</chem>

[0138] In one embodiment, the chlorinated reactant comprises, consists of or consists essentially of HCFC-336maf. In some embodiments, the chlorinated reactant comprises, consists of or consists essentially of:

- (iii) 2,2-dichloro-1,1,1,4,4,4-hexafluorobutane (HCFC-336maf); and
- (iv) one or more additional compounds selected from HCFO-1326mxz(Z), HCFO-1326mxz(E), HCFO-1316mxx(Z), HCFO-1316mxz(E), HCFC-356mff, HCFC-346mdf and HCFC-336mdd.

wherein, in some embodiments, the chlorinated reactant comprises greater than about 95 mole percent HCFC-336maf.

[0139] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of: (i) HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane), and (ii) HCFO-1326mxz(E) or HCFO-1326mxz(Z), wherein the composition comprises greater than about 95 mole percent HCFC-336maf, or greater than about 96 mole percent HCFC-336maf, greater than about 97 mole percent HCFC-336maf, greater than about 98 mole percent HCFC-336maf, greater than about 99 mole percent HCFC-336maf, greater than about 99.2 mole percent HCFC-336maf, greater than about 99.5 mole percent HCFC-336maf, greater than about 99.7 mole percent HCFC-336maf, or greater than about 99.9 mole percent HCFC-336maf.

[0140] In some embodiments, the chlorinated reactant comprises HCFC-336maf and one of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336maf 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 chlorinated reactant comprises HCFC-336maf and each of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336maf and from one to twenty-five of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336maf and from one to twenty of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336maf and from one to ten of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336maf and from one to five of the additional compounds. In some

embodiments, the chlorinated reactant comprises HCFC-336maf and from one to four of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336maf and from one to three of the additional compounds. In some embodiments, the chlorinated reactant comprises HCFC-336maf and from one to two of the additional compounds.

[0141] In some embodiments, the chlorinated reactant comprises greater than about 97 mole percent HCFC-336maf, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 98 mole percent HCFC-336maf, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99 mole percent HCFC-336maf, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99.5 mole percent HCFC-336maf, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99.9 mole percent HCFC-336maf, with the remainder being one or more of the additional compounds.

[0142] In some embodiments, the chlorinated reactant consists essentially of or consists of the HCFC-336maf and the one or more additional compounds.

[0143] The one or more additional compounds of the chlorinated reactant comprising HCFC-336maf are selected from and listed in Table 2.

TABLE 2: COMPOUNDS OF HCFC-336MAF REACTANT 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
2,3-dichloro-1,1,1,4,4,4-hexafluorobutane	336mdd	CF ₃ -CHCl-CHCl-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

[0144] In some embodiments, dehydrochlorination of HCFC-336 comprises adding the base to the HCFC-336 in the presence of a phase transfer catalyst or co-feeding the base and the HCFC-336 to a reactor in the presence of a phase transfer catalyst to convert the HCFC-336 to HFB, wherein the phase transfer catalyst is a quaternary alkylammonium salt which comprises at least one alkyl group 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. The anions of the salt can be halides such as chloride or bromide, hydrogen sulfate, or any other commonly used anion.

[0145] 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 HCFC-336. In another embodiment, the quaternary alkylammonium salts is added in an amount of from 1 mole percent to 2 mole percent of the HCFC-336. 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 HCFC-336. In one embodiment, the quaternary alkylammonium salt is added in an amount of from 1 mole percent to 1.5 mole percent of the HCFC-336 and the weight of non-ionic surfactant added is from 1.0 to 2.0 times the weight of the quaternary alkylammonium salt.

[0146] In one embodiment, the chlorinated reactant comprises, consists of or consists essentially of Z-HCFO-1326mxz. In some embodiments, the chlorinated reactant comprises, consists of or consists essentially of:

- (i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz);
- (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),

wherein, in some embodiments, the chlorinated reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz.

[0147] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of: Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene; 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 chlorinated reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz.

[0148] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of: Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene and HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), 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.

[0149] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of:

- (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-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 chlorinated reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz.

[0150] In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz and one of the additional compounds. In some embodiments, the chlorinated reactant 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 chlorinated reactant comprises Z-HCFO-1326mxz and each of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz and from one to twenty-five of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz and from one to twenty of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz and from one to ten of the additional compounds. In some

embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz and from one to five of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz and from one to four of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz and from one to three of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz and from one to two of the additional compounds.

[0151] In some embodiments, the chlorinated reactant comprises greater than about 97 mole percent Z-HCFO-1326mxz, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 98 mole percent Z-HCFO-1326mxz, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99 mole percent Z-HCFO-1326mxz, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99.5 mole percent Z-HCFO-1326mxz, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99.9 mole percent Z-HCFO-1326mxz, with the remainder being one or more of the additional compounds.

[0152] In some embodiments, the chlorinated reactant consists essentially of or consists of the Z-HCFO-1326mxz and the one or more additional compounds.

[0153] The one or more additional compounds of the chlorinated reactant comprising Z-HCFO-1326mxz are selected from and listed in Table 3.

TABLE 3: COMPOUNDS OF Z-HCFO-1326MXZ REACTANT COMPOSITION

Name	Code	Structure
Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene	Z-1326mxz	<chem>CF3-CCl=CH-CF3</chem>
E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene	E-1326mxz	<chem>CF3-CCl=CH-CF3</chem>
E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene	E-1316mxx	<chem>CF3-CCl=CCl-CF3</chem>
Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene	Z-1316mxx	<chem>CF3-CCl=CCl-CF3</chem>
1,1,1,2,4,4,4-heptafluoro-2-butene	E/Z-1327mz	<chem>CF3-CF=CH-CF3</chem>
1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene	E/Z-1325lxz	<chem>CClF2-CCl=CH-CF3</chem>
1,2-dichloro-3,3,4,4,4-pentafluoro-1butene	E/Z-1325dx	<chem>CHCl=CCl-CF2-CF3</chem>

Name	Code	Structure
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
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

[0154] In some embodiments, dehydrochlorination of Z-HCFO-1326mxz comprises adding the base to the Z-HCFO-1326mxz in the presence of a phase transfer catalyst or co-feeding the base and the Z-HCFO-1326mxz to a reactor in the presence of a phase transfer catalyst to convert the Z-HCFO-1326mxz to HFB, wherein the phase transfer catalyst is a quaternary alkylammonium salt which comprises at least one alkyl group 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. The anions of the salt can be halides such as chloride or bromide, hydrogen sulfate, or any other commonly used anion.

[0155] 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 Z-HCFO-1326mxz. In another embodiment, the quaternary alkylammonium salts is added in an amount of from 1 mole percent to 2 mole percent of the Z-HCFO-1326mxz. 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 Z-HCFO-1326mxz. In one embodiment, the quaternary alkylammonium salt is added in an amount of from 1 mole percent to 1.5 mole percent of the Z-HCFO-1326mxz and the weight of non-ionic surfactant added is from 1.0 to 2.0 times the weight of the quaternary alkylammonium salt.

[0156] In one embodiment, the chlorinated reactant comprises, consists of or consists essentially of Z-HCFO-1326mxz and E-HCFO-1326mxz. In some embodiments, the chlorinated reactant comprises, consists of or consists essentially of:

- (i) (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz);
- (ii) (E)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E-HCFO-1326mxz); and
- (iii) one or more additional compounds selected from:
 - 1,1,1-trifluoroethane;
 - (E)-1,1,1,4,4,4-hexafluoro-2-butene;
 - 1,1,1,4,4,4-hexafluorobutane;
 - 1-chloro-1,1-difluoroethane;
 - 2-chloro-1,1-difluoroethylene;
 - 1,1,4,4,4-Pentafluoro-1-butene;
 - 2-chloro-1,1,1,4,4,4-hexafluorobutane;
 - 1,1,1-trichloro-2,2,2-trifluoroethane;
 - 2,2-dichloro-1,1,1-trifluoroethane; and
 - 1,2-dichloro-2,2-difluoroethane,

wherein, in some embodiments, the chlorinated reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz and E-HCFO-1326mxz.

[0157] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of: 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 one or more additional compounds selected from:

- (E)-1,1,1,4,4,4-hexafluoro-2-butene;
- 1,1,1,4,4,4-hexafluorobutane;
- 1-chloro-1,1-difluoroethane;
- 2-chloro-1,1-difluoroethylene;
- 1,1,4,4,4-Pentafluoro-1-butene;
- 2-chloro-1,1,1,4,4,4-hexafluorobutane;
- 1,1,1-trichloro-2,2,2-trifluoroethane;
- 2,2-dichloro-1,1,1-trifluoroethane; and
- 1,2-dichloro-2,2-difluoroethane,

wherein, in some embodiments, the chlorinated reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz and E-HCFO-1326mxz.

[0158] In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz, E-HCFO-1326mxz and one of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz, E-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 chlorinated reactant comprises Z-HCFO-1326mxz, E-HCFO-1326mxz and each of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz E-HCFO-1326mxz and from one to twenty-five of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz, E-HCFO-1326mxz and from one to twenty of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz, E-HCFO-1326mxz and from one to ten of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz, E-HCFO-1326mxz and from one to five of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz, E-HCFO-1326mxz and from one to four of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz, E-HCFO-1326mxz and from one to

three of the additional compounds. In some embodiments, the chlorinated reactant comprises Z-HCFO-1326mxz, E-HCFO-1326mxz and from one to two of the additional compounds.

[0159] In some embodiments, the chlorinated reactant comprises greater than about 97 mole percent Z-HCFO-1326mxz and E-HCFO-1326mxz, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 98 mole percent Z-HCFO-1326mxz and E-HCFO-1326mxz, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99 mole percent Z-HCFO-1326mxz and E-HCFO-1326mxz, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99.5 mole percent Z-HCFO-1326mxz and E-HCFO-1326mxz, with the remainder being one or more of the additional compounds. In some embodiments, the chlorinated reactant comprises greater than about 99.9 mole percent Z-HCFO-1326mxz and E-HCFO-1326mxz, with the remainder being one or more of the additional compounds.

[0160] In some embodiments, the chlorinated reactant consists essentially of or consists of the Z-HCFO-1326mxz, E-HCFO-1326mxz and the one or more additional compounds.

[0161] The one or more additional compounds of the chlorinated reactant comprising Z-HCFO-1326mxz and E-HCFO-1326mxz are selected from and listed in Table 4.

TABLE 4: COMPOUNDS OF Z-HCFO-1326MXZ AND E-HCFO-1326MXZ REACTANT COMPOSITION

Name	Code	Structure
1,1,1-trifluoroethane	143a	CF ₃ CH ₃
(E)-1,1,1,4,4,4-hexafluoro-2-butene	E-1336mzz	CF ₃ CH=CHCF ₃
1,1,1,4,4,4-hexafluorobutane	356mff	CF ₃ -CH ₂ -CH ₂ -CF ₃
1-chloro-1,1-difluoroethane	142b	CClF ₂ CF ₃
2-chloro-1,1-difluoroethylene	1122	CHCl=CF ₂
1,1,4,4,4-pentafluoro-1-butene	1345czf	CF ₃ -CH ₂ -CH=CF ₂
2-chloro-1,1,1,4,4,4-hexafluorobutane	346mdf	CF ₃ -CHCl-CH ₂ -CF ₃

Name	Code	Structure
1,1,1-trichloro-2,2,2-trifluoroethane	113a	CF ₃ CCl ₃
2,2-dichloro-1,1,1-trifluoroethane	123	CF ₃ CHCl ₂
1,2-dichloro-2,2-difluoroethane	132b	CF ₂ ClCHCl ₂

[0162] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of: HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane), E-HCFO-1326mxz (E-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene), Z-HCFO-1326mxz (Z-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene), or a combination of two or more thereof.

[0163] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of: (i) HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane), E-HCFO-1326mxz (E-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene), Z-HCFO-1326mxz (Z-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene), or a combination of two or more thereof; (ii) one or more additional compounds selected from Table 1; (iii) one or more additional compounds selected from Table 2; (iv) one or more additional compounds selected from Table 3; and/or (v) one or more additional compounds selected from Table 4. In some embodiments, the chlorinated reactant comprises greater than about 95 mole percent of the compounds of (i), or greater than about 96 mole percent of the compounds of (i), greater than about 97 mole percent of the compounds of (i), greater than about 98 mole percent of the compounds of (i), greater than about 99 mole percent of the compounds of (i), greater than about 99.2 mole percent of the compounds of (i), greater than about 99.5 mole percent of the compounds of (i), greater than about 99.7 mole percent of the compounds of (i), or greater than about 99.9 mole percent of the compounds of (i), with the balance being the one or more additional compounds of Table 1, Table 2, Table 3 and/or Table 4.

[0164] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane) and Z-HCFO-1326mxz (Z-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene).

[0165] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of: (i) HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane) and Z-HCFO-1326mxz (Z-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene); (ii) one or more additional compounds selected from Table 1; and/or (iii) one or more additional compounds selected from Table 3, wherein in some embodiments, the chlorinated reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz and HCFC-336mdd, or greater than about 96 mole percent Z-HCFO-1326mxz and HCFC-336mdd, greater than about 97 mole percent Z-HCFO-1326mxz and HCFC-336mdd, greater than about 98 mole percent Z-HCFO-1326mxz and HCFC-336mdd, greater than about 99 mole percent Z-HCFO-1326mxz and HCFC-336mdd, greater than about 99.2 mole percent Z-HCFO-1326mxz and HCFC-336mdd, greater than about 99.5 mole percent Z-HCFO-1326mxz and HCFC-336mdd, greater than about 99.7 mole percent Z-HCFO-1326mxz and HCFC-336mdd, or greater than about 99.9 mole percent Z-HCFO-1326mxz and HCFC-336mdd, with the balance being the additional compounds.

[0166] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of: (i) HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), E-HCFO-1326mxz (E-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene) and Z-HCFO-1326mxz (Z-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene); (ii) one or more additional compounds selected from Table 1; and/or (iii) one or more additional compounds selected from Table 4, wherein in some embodiments, the chlorinated reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336mdd; or greater than about 96 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336mdd; or greater than about 97 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336mdd; or greater than about 98 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336mdd; or greater than about 99 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336mdd; or greater than about 99.2 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336mdd; or greater than about 99.5 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336mdd; or greater than about 99.7 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336mdd; or greater than about 99.9 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336mdd, with the balance being the additional compounds.

[0167] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of: (i) HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane) and Z-HCFO-1326mxz (Z-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene); (ii) one or more additional compounds selected from Table 2; and/or (iii) one or more additional compounds selected from Table 3, wherein in some embodiments, the chlorinated reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz and HCFC-336maf, or greater than about 96 mole percent Z-HCFO-1326mxz and HCFC-336maf, greater than about 97 mole percent Z-HCFO-1326mxz and HCFC-336maf, greater than about 98 mole percent Z-HCFO-1326mxz and HCFC-336maf, greater than about 99 mole percent Z-HCFO-1326mxz and HCFC-336maf, greater than about 99.2 mole percent Z-HCFO-1326mxz and HCFC-336maf, greater than about 99.5 mole percent Z-HCFO-1326mxz and HCFC-336maf, greater than about 99.7 mole percent Z-HCFO-1326mxz and HCFC-336maf, or greater than about 99.9 mole percent Z-HCFO-1326mxz and HCFC-336maf, with the balance being the additional compounds.

[0168] In some embodiments, the chlorinated reactant comprises, consists essentially of, or consists of: (i) HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane), E-HCFO-1326mxz (E-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene) and Z-HCFO-1326mxz (Z-1,1,1,4,4,4-hexafluoro-2-chloro-2-butene); (ii) one or more additional compounds selected from Table 2; and/or (iii) one or more additional compounds selected from Table 4, wherein in some embodiments, the chlorinated reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336maf; or greater than about 96 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336maf; or greater than about 97 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336maf; or greater than about 98 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336maf; or greater than about 99 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336maf; or greater than about 99.2 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336maf; or greater than about 99.5 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336maf; or greater than about 99.7 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336maf; or greater than about 99.9 mole percent Z-HCFO-1326mxz, E-HCFO-1326mxz and HCFC-336maf, with the balance being the additional compounds.

[0169] In some embodiments, the above-described system and process of dehydrochlorination of a chlorinated reactant comprising Z-HCFO-1326mxz and E-HCFO-1326mxz produces a composition comprising:

- i) hexafluoro-2-butyne; and
- ii) one or more additional compounds selected from:
 - 1,1,1,2,2,5,5,6,6,7,7,7-dodecafluorosept-3-ene;
 - 1,1,1,4,4,4-hexafluorobut-2-ene;
 - 1,1,1,2,4,4,4-septafluorobut-2-ene;
 - 1,1,1,4,4,4-hexafluorobutane;
 - 1,1,1-trifluoroethane;
 - Trifluoropropyne;
 - 1,1-difluoroethane;
 - 1,1,1-trifluoropropane;
 - 1-Chloro-1,1-difluoroethane;
 - Fluoromethane;
 - 1,2-dichloro-1,2-difluoroethylene;
 - Z-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene;
 - E-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene;
 - 1,2-dichloro-1,1-difluoroethane; and
 - Trifluoroacetone.

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

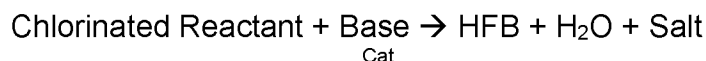
[0170] In some embodiments, the above-described system and process of dehydrochlorination of a chlorinated reactant comprising Z-HCFO-1326mxz produces a composition comprising:

- i) hexafluoro-2-butyne; 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-pentafluoro-1-butyne;
1-chloro-1,1,4,4,4-pentafluoro-2-butyne;
(Z)-1,2-dichloro-1,1,4,4,4-pentafluoro-2-butene;
1,2-dichloro-3,3,4,4,4-pentafluorobutene
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-trifluoropropyne;
1,2-dichloro-3,3,3-trifluoropropene;
(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-tetrafluoropropene;
1,1,3,3,3-pentafluoropropene; and
2-chloro-1,1,3,3,3-pentafluoropropene;

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

[0171] In addition to HFB and one or more additional compounds listed above, the product mixture produced from the dehydrochlorination of the chlorinated reactant (e.g., HCFC-336mdd, HCFC-336maf, Z-HCFO-1326mxz and/or E-HCFO-1326mxz) also comprises water and byproduct salts. In one embodiment, where the base comprises an alkali metal, and particularly an alkali metal hydroxide, the dehydrochlorination reaction produces an alkali metal halide salt. This reaction is shown below:



[0172] For example, where the base comprises potassium hydroxide, potassium chloride is produced as a byproduct of the dehydrochlorination reaction, or where the base comprises sodium hydroxide, sodium chloride is produced as a byproduct of the dehydrochlorination reaction.

[0173] In one embodiment, the dehydrochlorination of the chlorinated reactant (e.g., HCFC-336mdd, HCFC-336maf, Z-HCFO-1326mxz and/or E-HCFO-1326mxz) further comprises the addition of a salt to the reactor R30. Preferably, the added salt is an alkali metal halide salt. In one embodiment, the alkali metal is sodium or potassium. In one embodiment, the halide is chloride or bromide. In one embodiment, the alkali metal halide salt is sodium chloride or potassium chloride. Without wishing to be bound by any particular theory, it is believed that the alkali metal halide salt stabilizes the phase transfer catalyst and reduces the amount of fluoride ion measured in the water effluent from the reaction.

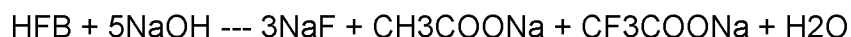
[0174] In one embodiment, the alkali metal halide salt is provided from an external source of the material, and is thus herein sometimes referred to as “fresh alkali metal halide salt”. In another embodiment, the alkali metal halide salt is recovered from the product mixture comprising HFB and is recycled to the reactor R30, and is thus herein sometimes referred to as “recycled alkali metal halide salt”. In some embodiments, either or both fresh alkali metal halide salt and/or recycled alkali metal halide salt may be added to the reactor R30 for the dehydrochlorination reaction.

[0175] In one embodiment, the base used for the dehydrochlorination reaction is sodium hydroxide (preferably an aqueous solution of sodium hydroxide) and the alkali metal halide salt produced as a byproduct is sodium chloride.

[0176] In one embodiment, the base used for the dehydrochlorination reaction is potassium hydroxide (preferably an aqueous solution of potassium hydroxide) and the alkali metal halide salt produced as a byproduct is potassium chloride.

[0177] In one embodiment, the dehydrochlorination reaction is carried out as a continuous process. In one embodiment, the reactor R30 is a continuously stirred tank. Preferably, the continuous process comprises co-feeding the chlorinated reactant, the base and the phase transfer catalyst to the reactor R30 to achieve at least partial conversion to HFB. In some embodiments, during the dehydrochlorination process, HFB is continuously removed, for example via a condenser (e.g., a partial condenser), optionally together with unreacted chlorinated reactant. The unreacted chlorinated reactant is preferably separated from the HFB, for example via distillation, and preferably sent back to the reactor R30 for use in the dehydrochlorination reaction, as is described below in more detail.

[0178] The boiling point of the HCFO-1326mxz starting material is about 35°C and the boiling point of HFB is about -25°C. The boiling point of di-HCFC-336mdd starting material is about 77°C-78°C and the boiling point of *meso*-HCFC-336mdd is about 85°C-86°C, while the boiling point of HFB is about -25°C. Thus, in one embodiment, the dehydrochlorination reactor R30 may be provided with a distillation column D33 or 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:



[0179] In one embodiment, the reaction mixture obtained in the dehydrochlorination reactor R30 from the dehydrochlorination of the chlorinated reactant comprises both vapor and liquid portions. A first stream S30 comprises the liquid portion of the reaction mixture and an fourteenth stream S3-13 comprises the vapor portion of the reaction mixture.

[0180] The first stream S30 (liquid portion) comprises, consists essentially of, or consists of water, unreacted chlorinated reactant (e.g., HCFC-336mdd, HCFC-336maf, Z-HCFO-1326mxz and/or E-HCFO-1326mxz), excess phase transfer catalyst and byproducts, such as salts (e.g., sodium chloride or potassium chloride) formed in the reaction forming the HFB. The first stream S30 is comprised of separate aqueous and organic liquid phases.

[0181] The first stream S30 is supplied from the reactor R30 to a decanter X30. In some embodiments, the decanter X30 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. In some embodiments, the decanter X30 operates a temperature of about 0°C to about 50°C.

[0182] The decanter X30 separates the aqueous liquid phase and the organic liquid phase contained in the first stream S30 into aqueous liquid phase and organic liquid phase fractions, respectively. More particularly, the decanter D30 separates the aqueous liquid and organic liquid phases contained in the first stream S30 into a lower density, aqueous fraction and a higher density, organic fraction.

[0183] The aqueous liquid phase fraction comprises, consists essentially of, or consists of water and salts formed by the dehydrochlorination reaction. The aqueous liquid phase fraction is removed from the decanter X30 in a second stream S31 and is preferably sent back to the reactor R30 to supply recycle alkali metal halide salt for use in the dehydrochlorination reaction. The recycled alkali metal halide salt second stream S31 may be co-fed to the reactor R30 with the second feed stream F31 (base) or may be pre-mixed with the second feed stream F31 (base) before being fed to the reactor R30.

[0184] In one embodiment, before returning to the reactor R30, the aqueous salt solution of the second stream S31 may optionally undergo sparging to remove residue organic compounds from the second stream S31, followed by optional concentration of the salt as a solid. Where the alkali metal halide salt has been concentrated to a solid, it may be mixed with water and co-fed to the reactor R30 with the second feed stream

base F31 (base), or may be pre-mixed with the second feed stream F31 (base) before being fed to the reactor R30.

[0185] In some embodiments, the recycled alkali metal halide salt (stream S31) preferably comprises greater than about 95 mole percent alkali metal halide salt, or greater than 96 mole percent alkali metal halide salt, or greater than 97 mole percent alkali metal halide salt, or greater than 98 mole percent alkali metal halide salt, or greater than 99 mole percent alkali metal halide salt. In some embodiments, the recycled alkali metal halide salt (stream 31) preferably comprises less than about 5 mole percent, or less than about 4 mole percent, or less than about 3 mole percent, or less than about 2 mole percent or less than about 1 mole percent, of metal acetate, carbonate, bicarbonate, fluoride and/or hydroxides.

[0186] The aqueous liquid phase fraction comprises, consists essentially of, or consists of water and salts formed by the dehydrochlorination reaction. A first portion of the second stream S31 returns to the reactor R30 via a third stream S32 (optionally passing through one or more filters) for further participation in the dehydrochlorination reaction. A second portion of the second stream S31 is removed from the process via a first outlet stream P30 to remove water and halide salts from the process.

[0187] The remaining (second) portion of the second stream S31 is removed from the process as stream P30. The proportion of the split of the first and second portions of the second stream S31 may vary between 0% removal from the process (i.e., the entirety of the second stream S31 is returned to the reactor) to 100% removal from the process (i.e., the entirety of the second stream S31 is removed from the process). The ratio of the split may be adjusted as needed to achieve the desired reaction results.

[0188] The organic liquid phase fraction comprises, consists essentially of, or consists of HCFO-1326mxz, excess PTC, and other organic byproducts. The organic liquid phase fraction is removed from the decanter X30 as a fourth stream S33. A first portion of the fourth stream S33 returns to the reactor R30 via a fifth stream S34 (optionally passing through one or more filters) for further participation in the dehydrochlorination reaction.

[0189] In some embodiments, where the chlorinated reactant comprises HCFO-1326mxz and/or HCFC-336, the fifth stream S34 (first portion of the fourth stream S33) comprises (i) HCFO-1326mxz; and (ii) one or more of the additional compounds selected from trifluoroacetone, R-346mdf, hexafluoro-2-butyne, R-1316mxx(E), R-1316mxz(Z), R-356mff, R-1327mz(E), R-1327mz(Z), R-1336mzz(E), R-1345czf, R-336mdd and R-336maf, or (iii) one or more of the additional compounds selected from trifluoroacetone, R-346mdf, hexafluoro-2-butyne, R-1316mxx(E), R-1316mxz(Z), R-1327mz(E), R-1327mz(Z), R-1345czf, R-1317mx(E) and R-1317mx(Z). In some embodiments, the composition of the fifth stream S34 comprises greater than about 95 mole percent HCFO-1326mxz, or greater than 96 mole percent HCFO-1326mxz, or greater than 97 mole percent HCFO-1326mxz, or greater than 98 mole percent HCFO-1326mxz, or greater than 99 mole percent HCFO-1326mxz.

[0190] In some embodiments, the water content of the composition of the fifth stream S34 is about 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 fifth stream S34 comprises about 1000 ppm or less of the base, and about 5000 ppm or more of the phase transfer catalyst.

[0191] The remaining (second) portion of the fourth stream S33 is supplied to a first distillation column D30 as a sixth stream S35. The proportion of the split of the first and second portions of the fourth stream S33 may vary between 0% direct return to the reactor R30 in the fifth stream S34 (i.e., the entirety of the fourth stream S33 is sent to the first distillation column D30 as the sixth stream S35) to 100% direct return to the reactor R30 via the fifth stream S34 (i.e., the entirety of the fourth stream S33 is sent directly to the reactor R30 without undergoing distillation). The ratio of the split may be adjusted as needed to achieve the desired reaction results.

[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.

[0193] In some embodiments, the operating pressure of the first distillation column D30 is slightly lower than the operating pressure of the decanter X30 to allow for flow from decanter X30 to the first distillation column D30.

[0194] In the first distillation column D30, the sixth stream S35 is separated, by distillation, into a lower boiling fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz and optionally other organic byproducts from the dehydrochlorination reaction, and a higher boiling fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz, excess PTC and other organic byproducts from the dehydrochlorination reaction. Most of the PTC supplied to the first distillation column D30 is removed from the column in the higher boiling fraction in an eighth stream S37, which is ultimately removed from the process.

[0195] In certain embodiments, HCFO-1326mxz is recovered by adding a solvent to remove HCFO-1326mxz from the lower boiling fraction. The solvent selected should be easily separated from HCFO-1326mxz. The solvent may be, for example, CCl₄, CC-1110, chlorobenzene, dichlorobenzene, and the like.

[0196] Most of the HCFO-1326mxz supplied to the first distillation column D30 is removed from the column in the lower boiling fraction in a seventh stream S36. The lower boiling fraction is removed from the first distillation column D30 via the seventh stream S36, which is returned to the dehydrochlorination reactor R30 for further participation in the dehydrochlorination reaction to produce HFB. .

[0197] In some embodiments, where the chlorinated reactant comprises HCFO-1326mxz, the seventh stream S36 (lower boiling fraction), which is recycled to the reactor R30 comprises HCFO-1326mxz and optionally one or more additional compounds selected from trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R1316(Z) and R-346mdf.

[0198] In some embodiments, where the chlorinated reactant comprises HCFO-1326mxz, the seventh stream S36 (lower boiling fraction), which is recycled to the reactor R30 comprises (i) HCFO-1326mxz; (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and optionally (iii) one or more of the additional compounds listed in Tables 3 or 4.

[0199] In some embodiments, where the chlorinated reactant comprises HCFO-1326mxz, the seventh stream S36 (lower boiling fraction) which is recycled to the reactor R30 comprises (i) HCFO-1326mxz; (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and optionally (iii) one or more additional compounds selected from R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, R-1336mzz(Z), R-1316mxx(E), R1316(Z) and R-346mdf.

[0200] In some embodiments, the composition of the seventh stream S36 which is recycled to the reactor R30 comprises greater than about 95 mole percent unreacted chlorinated reactant, or greater than 96 mole percent unreacted chlorinated reactant, or greater than 97 mole percent unreacted chlorinated reactant, or greater than 98 mole percent unreacted chlorinated reactant, or greater than 99 mole percent unreacted chlorinated reactant.

[0201] In some embodiments, where the chlorinated reactant comprises HCFC-336, the the seventh stream S36 (lower boiling fraction), which is recycled to the reactor R30 comprises (i) HCFO-1326mxz; (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and optionally (iii) one or more additional compounds selected from R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, R-1336mzz(Z), R-1316mxx(E), R1316(Z), R-336mdd, R-336maf and R-346mdf.

[0202] In some embodiments, the composition of the seventh stream S36 which is recycled to the reactor R30 comprises greater than about 95 mole percent HCFO-1326mxz, or greater than 96 mole percent HCFO-1326mxz, or greater than 97 mole percent HCFO-1326mxz, or greater than 98 mole percent HCFO-1326mxz, or greater than 99 mole percent HCFO-1326mxz.

[0203] In some embodiments, the water content of the composition of the seventh stream S36 is about 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 seventh stream S36 comprises about 100 ppm or less of the base. In some embodiments, the composition of the sixth stream S35 comprises about 500 ppm or less of the phase transfer catalyst.

[0204] In some embodiments, a portion of the eighth stream S37 is supplied to a second distillation column D31 as a ninth stream S38. The proportion of the split of the eighth stream S37 to the ninth stream S38 may vary between 0% to the ninth stream S38 (i.e., no feed to the second distillation column D31) to 100% to the ninth stream S38 (i.e., all of the feed to the second distillation column D31). The ratio of the split may be adjusted as needed to achieve the desired recycle purity and reaction results.

[0205] In some embodiments, water is optionally supplied as an additional feed to second distillation column D31 in fourth feed stream F33 to dissolve precipitated halide salts forming in the second distillation column. A distillation solvent is optionally supplied to second distillation column D31 in fifth feed stream F34 to dilute PTC in the second distillation column. The fourth feed stream F33 and fifth feed stream F34 can be fed to the column separately or combined into a single feed stream before entering second distillation column D31. The fourth feed stream F33 and fifth feed stream F34 can be combined with the ninth stream S38 before entering second distillation column D31.

[0206] 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 50 psig or less.

[0207] In some embodiments, the operating pressure of the second distillation column D31 is slightly lower than the operating pressure of first distillation column D30 to allow for flow from first distillation column D30 to the second distillation column D31 without pumping.

[0208] In some embodiments, water is added to the second distillation column D31 to dissolve any precipitated halide salts in the second distillation column. The amount of water added to second distillation column D31 could be ten times or more of the mass

of halide salts in the incoming ninth stream S38, or ten times or less of the mass of halide salts in the incoming ninth stream S38, or five times or less of the mass of halide salts in the incoming ninth stream S38, or one time or less of the mass of halide salts in the incoming ninth stream S38. No water may be added to the second distillation column D31.

[0209] In some embodiments, a distillation solvent is added to the second distillation column D31 to dilute PTC in the second distillation column. The amount of distillation solvent added to second distillation column D31 could be the four times or more of the mass of PTC in the incoming ninth stream S38, or four times or less of the mass of PTC in the incoming ninth stream S38, or two times or less of the mass of PTC in the incoming ninth stream S38, or one time or less of the mass of PTC in the incoming ninth stream S38.

[0210] In some embodiments, the distillation solvent is carbon tetrachloride.

[0211] In some embodiments, the distillation solvent is a chlorobenzene.

[0212] In some embodiments, the distillation solvent is a dichlorobenzene.

[0213] In some embodiments, the distillation solvent is a PCE.

[0214] In some embodiments, the distillation solvent is a mixture of solvents, or any higher boiling solvent miscible with PTC.

[0215] In the second distillation column D31, the ninth stream S38 is separated, by distillation, into a lower boiling fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz and optionally other organic byproducts from the dehydrochlorination reaction, and a higher boiling fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz, distillation solvent, excess PTC and other organic byproducts from the dehydrochlorination reaction. Most of the distillation solvent and PTC supplied to the second distillation column D31 is removed from the column in the higher boiling fraction in a second outlet stream P31, which is ultimately removed from the process.

[0216] Most of the HCFO-1326mxz supplied to the first distillation column D30 is removed from the column in the lower boiling fraction in a tenth stream S39. The lower boiling fraction is removed from the second distillation column D31 via the tenth stream S39 which is returned to the dehydrochlorination reactor R30 for further participation in the dehydrochlorination reaction to produce HFB.

[0217] In some embodiments, where the chlorinated reactant comprises HCFO-1326mxz, the tenth stream S39 (lower boiling fraction) which is recycled to the reactor R30 comprises HCFO-1326mxz and optionally one or more additional compounds selected from trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R1316(Z) and R-346mdf.

[0218] In some embodiments, where the chlorinated reactant comprises HCFO-1326mxz, the tenth stream S39 (lower boiling fraction) which is recycled to the reactor R30 comprises (i) HCFO-1326mxz; (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and optionally (iii) one or more of the additional compounds listed in Tables 3 or 4.

[0219] In some embodiments, where the chlorinated reactant comprises HCFO-1326mxz, the tenth stream S39 (lower boiling fraction) which is recycled to the reactor R30 comprises (i) HCFO-1326mxz; (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and optionally (iii) one or more additional compounds selected from R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, R-1336mzz(Z), R-1316mxx(E), R1316(Z) and R-346mdf.

[0220] In some embodiments, the composition of the tenth stream S39 which is recycled to the reactor R30 comprises greater than about 95 mole percent unreacted chlorinated reactant, or greater than 96 mole percent unreacted chlorinated reactant, or greater than 97 mole percent unreacted chlorinated reactant, or greater than 98 mole percent unreacted chlorinated reactant, or greater than 99 mole percent unreacted chlorinated reactant.

[0221] In some embodiments, where the chlorinated reactant comprises HCFC-336, the tenth stream S39 (lower boiling fraction) which is recycled to the reactor R30 comprises (i) HCFO-1326mxz; (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and optionally (iii) one or more additional compounds selected from R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, R-1336mzz(Z), R-1316mxx(E), R-1316(Z), R-336mdd, R-336maf and R-346mdf.

[0222] In some embodiments, the composition of the tenth stream S39 which is recycled to the reactor R30 comprises greater than about 95 mole percent HCFO-1326mxz, or greater than 96 mole percent HCFO-1326mxz, or greater than 97 mole percent HCFO-1326mxz, or greater than 98 mole percent HCFO-1326mxz, or greater than 99 mole percent HCFO-1326mxz.

[0223] In some embodiments, the water content of the composition of the tenth stream S39 is about 10000 ppm or less, or about 5000 ppm or less, or about 3000 ppm or less, or about 1000 ppm or less. In some embodiments, the composition of the tenth stream S39 comprises about 100 ppm or less of the base. In some embodiments, the composition of the tenth stream S39 comprises about 500 ppm or less of the phase transfer catalyst.

[0224] In some embodiments, a second portion of the eighth stream S37 is supplied to an extraction column A30 as an eleventh stream S3-10. The proportion of the split of the eighth stream S37 to the eleventh stream S3-10 may vary between 0% to the eleventh stream S3-10 (i.e., no feed to the extraction column A30) to 100% to the eleventh stream S3-10 (i.e., all of the feed to the extraction column A30). The ratio of the split may be adjusted as needed to achieve the desired recycle purity and reaction results.

[0225] In some embodiments, an extractant is supplied to extraction column A30 as a sixth feed stream F35. The sixth feed stream F35 can be fed to the column separately or combined into a single feed stream before entering extraction column A30.

[0226] In some embodiments, the extraction column A30 operates at a pressure of about 300 psig or less, or about 150 psig or less, or about 50 psig or less.

[0227] In some embodiments, the operating pressure of the extraction column A30 is slightly lower than the operating pressure of first distillation column D30 to allow for flow from first distillation column D30 to the extraction column A30 without pumping.

[0228] In some embodiments, extractant is added to the extraction column A30 to extract PTC from the incoming eleventh stream S3-10. The amount of extractant added to the extraction column A30 could be ten times or more of the mass of the PTC in the incoming eleventh stream S3-10, or ten times or less as the mass of PTC in the incoming eleventh stream S3-10, or five times or less as the mass of PTC in the incoming eleventh stream S3-10, or one time or less as the mass of PTC in the incoming eleventh stream S3-10.

[0229] In some embodiments, the extractant is a mixture of methanol and water. The amount of water in the extractant could be 0% (i.e., neat methanol), or the amount of water could be 25% or less in the extractant, or the amount of water could be 50% or less in the extractant, or the amount of water could be 75% or less in the extractant.

[0230] In some embodiments, the extractant is a mixture of ethanol and water. The amount of water in the extractant could be 0% (i.e., neat ethanol), or the amount of water could be 25% or less in the extractant, or the amount of water could be 50% or less in the extractant, or the amount of water could be 75% or less in the extractant.

[0231] In some embodiments, mixtures of methanol, ethanol and water in any proportions may be used as the extractant. Extractants that are not miscible in HCFO-1326mxz with solubility for PTC may be used.

[0232] In the extraction column A30 the eleventh stream S38 and extractant are contacted then separated, by gravity, into a lower density fraction comprising, consisting essentially of, or consisting of extractant, PTC, HCFO-1326mxz and optionally other organic byproducts from the dehydrochlorination reaction, and a higher density fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz, extractant, PTC and other organic byproducts from the dehydrochlorination reaction. Most of the extractant and PTC supplied to the extraction column A30 is removed from the column

in the lower density fraction in a fourth outlet stream P33, which is ultimately removed from the process.

[0233] Most of the HCFO-1326mxz supplied to the extraction column A30 is removed from the column in the higher density fraction in a twelfth stream S3-11. The higher density fraction is removed from the extraction column A30 via the twelfth stream S3-11 which is supplied to one or more additional distillation columns for purification of the HCFO-1326mxz.

[0234] In some embodiments, a third portion of the eighth stream S37 is removed from the process in the third outlet stream P32. The proportion of the split of the eighth stream S37 to the third outlet stream P32 may vary between 0% to the third outlet stream P32 (i.e., no material is removed from the process) to 100% to the third outlet stream P32 (i.e., all of the material is removed from the process). The ratio of the split between ninth stream S38, eleventh stream S3-10 and third outlet stream P32 may be adjusted as needed to achieve the desired recycle purity, yield and reaction results.

[0235] In some embodiments, the twelfth stream S3-11 is supplied to a third distillation column D32. In the third distillation column D32, the twelfth stream S3-11 is separated, by distillation, into a lower boiling fraction comprising, consisting essentially of, or consisting of extractant, water, HCFO-1326mxz and optionally other organic byproducts from the dehydrochlorination reaction, and a higher boiling fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz, PTC and other organic byproducts from the dehydrochlorination reaction. Most of the extractant supplied to the third distillation column D32 is removed from the column in the lower boiling fraction in a fifth outlet stream P34, which is ultimately removed from the process.

[0236] Most of the HCFO-1326mxz supplied to the third distillation column D32 is removed from the column in the higher boiling fraction in a thirteenth stream S3-12. The higher boiling fraction is removed from the third distillation column D32 via the thirteenth stream S3-12 which is returned to the dehydrochlorination reactor R30 for further participation in the dehydrochlorination reaction to produce HFB.

[0237] In some embodiments, where the chlorinated reactant comprises HCFO-1326mxz, the thirteenth stream S3-12 (higher boiling fraction) which is recycled to the reactor R30 comprises HCFO-1326mxz and optionally one or more additional compounds selected from trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R1316(Z) and R-346mdf.

[0238] In some embodiments, where the chlorinated reactant comprises HCFO-1326mxz, the thirteenth stream S3-12 (higher boiling fraction) which is recycled to the reactor R30 comprises (i) HCFO-1326mxz; (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and optionally (iii) one or more of the additional compounds listed in Tables 3 or 4.

[0239] In some embodiments, where the chlorinated reactant comprises HCFO-1326mxz, the thirteenth stream S3-12 (higher boiling fraction) which is recycled to the reactor R30 comprises (i) HCFO-1326mxz; (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and optionally (iii) one or more additional compounds selected from R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, R-1336mzz(Z), R-1316mxx(E), R1316(Z) and R-346mdf.

[0240] In some embodiments, the composition of the thirteenth stream S3-12 which is recycled to the reactor R30 comprises greater than about 95 mole percent unreacted chlorinated reactant, or greater than 96 mole percent unreacted chlorinated reactant, or greater than 97 mole percent unreacted chlorinated reactant, or greater than 98 mole percent unreacted chlorinated reactant, or greater than 99 mole percent unreacted chlorinated reactant.

[0241] In some embodiments, where the chlorinated reactant comprises HCFC-336, the thirteenth stream S3-12 which is recycled to the reactor R30 comprises (i) HCFO-1326mxz; (ii) one or more of trifluoroacetone and hexafluoro-2-butyne, and optionally (iii) one or more additional compounds selected from R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, R-1336mzz(Z), R-1316mxx(E), R1316(Z), R-336mdd, R-336maf and R-346mdf.

[0242] In some embodiments, the composition of the thirteenth stream S3-12 which is recycled to the reactor R30 comprises greater than about 95 mole percent HCFO-1326mxz, or greater than 96 mole percent HCFO-1326mxz, or greater than 97 mole percent HCFO-1326mxz, or greater than 98 mole percent HCFO-1326mxz, or greater than 99 mole percent HCFO-1326mxz.

[0243] In some embodiments, the water content of the composition of the thirteenth stream S3-12 is about 10000 ppm or less, or about 5000 ppm or less, or about 3000 ppm or less, or about 1000 ppm or less. In some embodiments, the composition of the tenth stream S3-9 comprises about 100 ppm or less of the base. In some embodiments, the composition of the thirteenth stream S3-12 comprises about 500 ppm or less of the phase transfer catalyst.

[0244] Referring back to the reactor R30, a fourteenth stream S3-13 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 fourteenth stream S3-13 is supplied from the dehydrochlorination reactor R30 to a fourth distillation column D33. In some embodiments, the fourth distillation column D33 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 fourth distillation column D33 is slightly lower than the operating pressure of the reactor R30 to allow for flow from reactor R30 to the fourth distillation column D33.

[0245] The fourth distillation column D33 separates, by distillation, the fourteenth stream S3-13 into a lower boiling fraction comprising, consisting essentially of, or consisting of HFB, HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction, and a higher boiling fraction comprising, consisting essentially of, or consisting of HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction. The higher boiling fraction is removed from the fourth distillation column in a sixteenth stream S3-15. In some embodiments, the water content of the composition of the sixteenth stream S3-15 is about 5000 ppm or less, or about 4000 ppm or less, or about 3000 ppm or less, or about 1000 ppm or less,

inclusive of all integers and ranges therebetween including zero ppm. The sixteenth stream S3-15 returns the higher boiling fraction comprising chlorinated reactant, water and other organic byproducts to the reactor R30 for further participation in the dehydrochlorination reaction.

[0246] In some embodiments, for example where the chlorinated reactant comprises HCFO-1326mxz, the sixteenth stream S3-15 (higher boiling fraction) comprises HCFO-1326mxz and optionally one or more additional compounds selected from trifluoroacetone, R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), trifluoropropyne, R-356mff and hexafluoro-2-butyne.

[0247] In some embodiments, for example where the chlorinated reactant comprises HCFC-336, the sixteenth stream S3-15 (higher boiling fraction) comprises HCFO-1326mxz and optionally one or more additional compounds selected from trifluoroacetone, R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), trifluoropropyne, R-356mff, R-336mdd, R-336maf and hexafluoro-2-butyne.

[0248] In some embodiments, the sixteenth stream S3-15 (higher boiling fraction) comprises (i) HCFO-1326mxz, and (ii) one or more of trifluoroacetone, trifluoropropyne, and hexafluoro-2-butyne, and optionally (iii) one or more of the additional compounds listed in Tables 1, 2, 3 and/or 4.

[0249] In some embodiments, the sixteenth stream S3-15 (higher boiling fraction) comprises (i) HCFO-1326mxz, (ii) one or more of trifluoroacetone, trifluoropropyne, and hexafluoro-2-butyne, and optionally (iii) one or more additional compounds selected from R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z) and R-356mff.

[0250] In some embodiments, the sixteenth stream S3-15 (higher boiling fraction) comprises (i) HCFO-1326mxz, (ii) one or more of trifluoroacetone, trifluoropropyne, and hexafluoro-2-butyne, and optionally (iii) one or more additional compounds selected from R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), R-336maf, R-336mdd and R-356mff.

[0251] In some embodiments, the composition of the sixteenth stream S3-15 comprises greater than about 95 mole percent HCFO-1326mxz, or greater than 96 mole percent HCFO-1326mxz, or greater than 97 mole percent HCFO-1326mxz, or greater than 98 mole percent HCFO-1326mxz, or greater than 99 mole percent HCFO-1326mxz, preferably Z-HCFO-1326mxz.

[0252] The majority of the HFB supplied to the fourth distillation column D33 is removed from the column in the lower boiling fraction fifteenth stream S3-14.

[0253] In one embodiment, the lower boiling fraction is removed from the fourth distillation column D33 via a fifteenth stream S3-14 which is comprised mostly of HFB. The desired product HFB may then be recovered from the fifteenth stream S3-14 and utilized, for example, to produce HCFO-1336mzz(Z).

[0254] In another embodiment, the lower boiling fraction is removed from the fourth distillation column D33 via a fifteenth stream S3-14 which is comprised mostly of HFB, as well as HCFO-1326mxz, water and other organic byproducts from the hydrochlorination reaction, and the lower boiling fraction (fifteenth stream S3-14) from the fourth distillation column D33 may be optionally supplied to a fifth distillation column D34. More particularly, the fifteenth stream S3-14 comprises, consists of or consists essentially of HFB and one or more additional compounds selected from HCFO-1326mxz(E), HCFO-1326mxz(Z), 356mff, trifluoroacetone, 1327mz, 1345czf, trifluoropropyne, and preferably has a moisture content of about 3% or less, or about 2% or less, or about 1% or less. The pressure of the fifth distillation column D34 is not specifically limited and may proceed at reduced, preferred and increased pressure. In one embodiment, the operating pressure of the fifth distillation column D34 is about 0.1 to about 0.5 MPaG.

[0255] The fifth distillation column D34 separates the components into lower boiling and higher boiling fractions. The lower boiling fraction F13_{D34} comprises the desired product from this process step, namely HFB, and is removed from the fifth distillation column D34 in sixth outlet stream P35. The majority of the HFB supplied to the fifth distillation column D34 is removed from the column in the sixth outlet stream P35

comprising the lower boiling fraction. The sixth outlet stream P35 is removed from the process. The higher boiling fraction F14_{D34} is removed from the fifth distillation column D34 in a seventeenth stream S3-16. The seventeenth stream S3-16 comprises, consists of or consists essentially of HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction. More particularly, the twelfth stream comprises, consists of or consists essentially of HCFO-1326mxz(E), HCFO1326mxz(Z), and one or more of the following: 356mff, trifluoroacetone, 1327mz, 1345czf, and has a moisture content of about 1% or less.

[0256] The higher boiling fraction from the fifth distillation column D34 may optionally be further supplied to a sixth distillation column D35 in the seventeenth stream S3-16. The sixth distillation column D35 separates the components into lower boiling and higher boiling fractions. The lower boiling fraction F15_{D35} 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 sixth distillation column D35 in a seventh outlet stream P36. The seventh outlet stream P36 is removed from the process. The higher boiling fraction F16_{D35} is removed from the sixth distillation column D35 in a eighteenth stream S3-17. The eighteenth stream S3-17 comprises, consists of or consists essentially of HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction. More particularly, the eighteenth stream S3-17 comprises, consists of or consists essentially of HCFO-1326mxz(E), HCFO-1326mxz(Z), and one or more of the following: 356mff, trifluoroacetone, 1327mz, 1345czf, and has a moisture content of about 1% or less.

[0257] The eighteenth stream S3-17 comprising HCFO-1326mxz, water and other organic byproducts is returned to the reactor R30 for further participation in the dehydrochlorination reaction to produce HFB.

[0258] In one embodiment, the operating pressure of the sixth distillation column D35 is slightly lower than the operating pressure of the fifth distillation column D34 to allow for flow from the fifth distillation column D34 to the sixth distillation column D35.

[0259] The HFB compositions provided by the invention may be used as intermediates for the production of Z-HFO-1336mzz, for example by selective hydrogenation of the HFB to produce Z-HFO-1336mzz, as disclosed in International Application Publication No. WO2019/023572, the entire disclosure of which is incorporated herein by reference.

[0260] Z-HFO-1336mzz compositions 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.

[0261] The Z-HFO-1336mzz compositions 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 polyolefins and polyurethane, gaseous dielectrics, fire extinguishing agents, and fire suppression agents, in liquid or gaseous form. In some embodiments, the Z-HFO-1336mzz compositions 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).

[0262] 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.

[0263] In some embodiments, the Z-HFO-1336mzz compositions may be useful in mobile heat transfer systems, including refrigeration, air conditioning, or heat pump systems or apparatus. In some embodiments, the Z-HFO-1336mzz compositions may be useful in stationary heat transfer systems, including refrigeration, air conditioning, or heat pump systems or apparatus.

[0264] 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).

[0265] 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.

[0266] Therefore, in accordance with the present invention, the Z-HFO-1336mzz compositions which may be produced from the reactive intermediates disclosed herein may be useful in methods for producing cooling, producing heating, and transferring heat.

[0267] In some embodiments, the present application provides a method for producing cooling comprising evaporating a Z-HFO-1336mzz composition produced from the reactive intermediates disclosed herein in the vicinity of a body to be cooled, and thereafter condensing said composition.

[0268] In some embodiments, the present application provides a method for producing heating comprising condensing a Z-HFO-1336mzz composition produced from the reactive intermediates disclosed herein in the vicinity of a body to be heated, and thereafter evaporating said compositions.

[0269] In some embodiments, the present application provides a method of using Z-HFO-1336mzz composition produced from the reactive intermediates disclosed herein as heat transfer fluid compositions. In some embodiments, the method comprises transporting said composition from a heat source to a heat sink.

[0270] The Z-HFO-1336mzz composition produced from the reactive intermediates disclosed 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.

[0271] In some embodiments, the Z-HFO-1336mzz composition produced from the reactive intermediates disclosed 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 Z-HFO-1336mzz composition produced from the reactive intermediates disclosed herein may provide heating performance (*i.e.*, heating capacity and energy efficiency) comparable to a refrigerant being replaced.

[0272] 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 a Z-HFO-1336mzz composition produced from the reactive intermediates disclosed herein 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 HCFC-123 with a POE lubricant).

[0273] In some embodiments, the Z-HFO-1336mzz compositions produced from the reactive intermediates disclosed herein may be used to top-off a refrigerant charge in a chiller. For example, if a chiller using HCFC-123 has diminished performance due to leakage of refrigerant, the Z-HFO-1336mzz compositions produced from the reactive intermediates disclosed herein may be added to bring performance back up to specification.

[0274] The present application further provides a heat exchange system containing any of the Z-HFO-1336mzz compositions produced from the reactive intermediates disclosed 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 Z-HFO-1336mzz compositions produced from the reactive intermediates disclosed herein 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.

[0275] 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.

[0276] The present application further provides foam expansion agent compositions comprising a Z-HFO-1336mzz composition produced from the reactive intermediates disclosed herein 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 Z-HFO-1336mzz compositions produced from the reactive intermediates disclosed herein 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.

[0277] The present application further provides a method of forming a foam comprising: (a) adding to a foamable composition a Z-HFO-1336mzz composition produced from the reactive intermediates disclosed herein; and (b) processing the foamable composition under conditions effective to form a foam.

[0278] The present application further provides the use of the Z-HFO-1336mzz compositions produced from the reactive intermediates disclosed herein 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 Z-HFO-1336mzz compositions produced from the reactive intermediates disclosed herein 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 intra-nasally.

[0279] The present invention further provides a process for producing aerosol products comprising the step of adding a Z-HFO-1336mzz composition produced from the reactive intermediates disclosed herein to a formulation to an aerosol container, wherein said composition functions as a propellant. Additionally, the present application further provides a process for producing aerosol products comprising the step of adding a Z-HFO-1336mzz composition produced from the reactive intermediates disclosed herein 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 functions as a propellant. Additionally, the present application further provides a process for producing aerosol products comprising the step of adding only a Z-HFO-1336mzz composition produced from the reactive intermediates disclosed herein to an aerosol package, wherein said composition functions as the active ingredient (e.g., a duster, or a cooling or freezing spray).

[0280] The present application further provides a process for converting heat from a heat source to mechanical energy, comprising heating a working fluid comprising a Z-HFO-1336mzz composition produced from the reactive intermediates disclosed herein 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.

[0281] 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).

[0282] 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.

[0283] 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.

[0284] 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.

[0285] 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.

[0286] 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.

[0287] 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

[0288] 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 (Adding Base to Chlorinated Reactant or Co-Feeding Base and Chlorinated Reactant)

[0289] KOH aqueous solution (12 mL, 0.12 mol) was added to a mixture of Z-1326mxz (20 g, 0.1 mol) and water (18 mL) in the presence of [CH₃CH(OH)CH₂]₂N(Bz)(C₁₂H₂₅))Cl (60 ac. 0.94 g, 0.001325 mol) at 35°C. The reaction temperature was raised to 70°C after the addition, and gas chromatography was used to monitor the reaction. The reaction was completed after 3 hours and 13.9 g product (yield: 86%) was collected in a dry ice trap.

Comparative Example 1 (Adding Chlorinated Reactant to Base)

[0290] Z-1326mxz (20 g, 0.1 mol) was added to a KOH aqueous solution (30 mL, 0.12 mol) in the presence of [CH₃CH(OH)CH₂]₂N(Bz)(C₁₂H₂₅))Cl (60 ac. 0.94 g, 0.001325 mol) at 35°C. The reaction temperature was raised to 70°C after the addition, and gas chromatography was used to monitor the reaction. After 3 hours, 5.2 g product (Conversion: 40%, yield: 78%) was collected in a dry ice trap.

[0291] Thus, it has been found that addition of the base to the chlorinated reactant (e.g., HCFC-336mdd, HCFC-336maf, Z-HCFO-1326mxz and/or E-HCFO-1326mxz) or co-feeding of the base and chlorinated reactant results in greater product yield than if the reaction were performed in the opposite order by addition of the chlorinated reactant to the base.

Example 2

[0292] KOH aqueous solution (12 mL, 0.12 mol) was added to a mixture of Z-1326/E-1326mxz (20 g, 0.1 mol) and water (18 mL) in the presence of 3.5 g fresh KCl and Aliquat® 336 (0.53 g, 0.001325 mol) at 35°C. The reaction temperature was raised to

70°C after the addition, and gas chromatography was used to monitor the reaction. The reaction was completed after 2.5 hours and 14.7 g product (conversion: 100%; yield: 91%) was collected in a dry ice trap.

[0293] Aqueous solution generated in the above reaction can go through sparging to remove residue organics, followed by concentrating to KCl salt as a solid. The salt can be recycled as in the following Example 3.

Example 3

[0294] KOH aqueous solution (12 mL, 0.12 mol) was added to a mixture of Z-1326/E-1326mxz (20 g, 0.1 mol) and water (18 mL) in the presence of 3.5 g recycled KCl and Aliquat® 336 (0.53 g, 0.001325 mol) at 35°C. The reaction temperature was raised to 70°C after the addition, and gas chromatography was used to monitor the reaction. The reaction was completed after 2.5 hours and 14.7 g product (conversion: 100%; yield: 91%) was collected in a dry ice trap.

Example 4

[0295] The dehydrochlorination reaction is performed as a continuous process by co-feeding caustic, organic (HCFO-1326mxz) and phase transfer catalyst to the reactor to achieve partial conversion. During the process, hexafluorobutyne is continuously removed via a partial condenser along with some 1326mxz. The vapor reaction mixture is sent to a distillation column for separation of 1326mxz. After separation via distillation, the 1326mxz is sent back to the reactor. The purity of the recycle is greater than 99% 1326mxz(Z) and 1326mxz(E) with one or more of the following components: trifluoroacetone, 1336mzz(E), 1336mzz(Z), 1345czf, 1327mz(E), 1327mz(Z), trifluoropropyne, 356mff, hexafluoro-2-butyne, and is substantially free of water (<1000 ppm). In parallel, the liquid reaction mixture of organic and aqueous phases is sent to a decanter for phase separation. The lower organic layer is sent to a distillation column and recycled back to the reactor. The purity of the recycle stream is greater than 99% 1326mxz(Z) and 1326mxz(E) with one or more of the following components: trifluoroacetone, 1336mzz(E), 1345czf, 1327mz(E), 1327mz(Z), 356mff, hexafluoro-2-

butyne, 1336mzz(Z), 1316mxx(E), 1316(Z), 346mdf and substantially free of water (<5000 ppm) and base (<100ppm) and phase transfer catalyst (<500 ppm).

[0296] 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 process of preparing hexafluoro-2-butyne (HFB), the process comprising adding a base to a chlorinated organic reactant for dehydrochlorination of the chlorinated organic reactant in a reactor in the presence of a phase transfer catalyst to form a composition comprising HFB.
2. A process of preparing hexafluoro-2-butyne (HFB), the process comprising co-feeding a base and a chlorinated organic reactant to a reactor for dehydrochlorination of the chlorinated organic reactant in the presence of a phase transfer catalyst to form a composition comprising HFB.
3. A process for producing hexafluoro-2-butyne (HFB), the process comprising:
 reacting a base with a chlorinated organic reactant in a reactor in the presence of a phase transfer catalyst and an alkali metal halide salt to form a product mixture comprising HFB,
 separating alkali metal halide salt from the product mixture, and
 returning the separated alkali metal halide salt to the reactor.
4. The process of any of claims 1, 2 or 3, wherein the chlorinated organic reactant comprises a chlororfluorobutane, a chlorofluorobutene, or a mixture thereof.
5. The process of any of claims 1 to 4, wherein the chlorinated organic reactant comprises one or more compounds selected from the group consisting of HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane), E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E-HCFO-1326mxz) and Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz).
6. The process of any of claims 1 to 5, wherein the chlorinated organic reactant comprises 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (HCFO-1326mxz).

7. The process of any of claims 1 to 6, wherein the chlorinated organic reactant comprises Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz) and 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).

8. The process of any of claims 1 to 6, wherein the chlorinated organic reactant comprises Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz) and one or more additional compounds selected from the group consisting of 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).
9. The process of any of claims 1 to 6, wherein the chlorinated reactant comprises Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene and HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane).
10. The process of any of claims 1 to 6, wherein the chlorinated reactant comprises (Z)-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene and one or more additional compounds selected from the group consisting of:
 - 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.

11. The process of any of claims 5 to 10, wherein the chlorinated organic reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz.

12. The process of any of claims 7 to 11, wherein the composition comprising HFB further comprises 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-heptafluorobut-2-ene;
(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-hexafluorobut-2-ene;
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-pentafluorobut-2-ene;
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-hexafluorobut-2-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-hexafluorobut-2-ene;
1,1,2-trichloro-1,2,2-trifluoroethane;

(Z)-2,3-dichloro-1,1,1,4,4,4-hexafluorobut-2-ene;

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-pentafluorobut-2-ene;

1-chloro-1,1,2,4,4,4-hexafluorobut-2-ene;

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.

13. The process of any of claims 1 to 6, wherein the chlorinated organic reactant comprises 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) and one or more additional compounds selected from the group consisting of:

(E)-1,1,1,4,4,4-hexafluoro-2-butene;

1,1,1,4,4,4-hexafluorobutane;

1-chloro-1,1-difluoroethane;

2-chloro-1,1-difluoroethylene;

1,1,4,4,4-Pentafluoro-1-butene;

2-chloro-1,1,1,4,4,4-hexafluorobutane;

1,1,1-trichloro-2,2,2-trifluoroethane;

2,2-dichloro-1,1,1-trifluoroethane; and

1,2-dichloro-2,2-difluoroethane).

14. The process of claim 13, wherein the chlorinated organic reactant comprises greater than about 95 mole percent Z-HCFO-1326mxz and E-HCFO-1326mxz.

15. The process of any of claims 13 to 14, wherein the composition comprising HFB further comprises one or more additional compounds selected from the group consisting of:
- 1,1,1,2,2,5,5,6,6,7,7,7-dodecafluorosept-3-ene,
 - 1,1,1,4,4,4-hexafluorobut-2-ene,
 - 1,1,1,2,4,4,4-septafluorobut-2-ene,
 - 1,1,1,4,4,4-hexafluorobutane,
 - 1,1,1-trifluoroethane,
 - Trifluoropropyne,
 - 1,1-difluoroethane,
 - 1,1,1-trifluoropropane,
 - 1-Chloro-1,1-difluoroethane,
 - Fluoromethane,
 - 1,2-dichloro-1,2-difluoroethylene,
 - Z-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene,
 - E-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene,
 - 1,2-dichloro-1,1-difluoroethane, and
 - Trifluoroacetone.
16. The process of any of claims 1 to 5, wherein the chlorinated organic reactant comprises 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane (HCFC-336mdd).
17. The process of any of claims 1 to 5 and 16, wherein the chlorinated organic compound comprises 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane (HCFC-336mdd) and one or more additional compounds selected from the group consisting of:
- Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
 - E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene,
 - E-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene,

Z-2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene,
2,2-dichloro-1,1,1,4,4,4-hexafluorobutane,
1,1,1,4,4,4-hexafluorobutane, and
2-chloro-1,1,1,4,4,4-hexafluorobutane.

18. The process of any of claims 1 to 5 and 16 to 17, wherein the chlorinated organic reactant comprises greater than about 95 mole percent HCFC-336mdd.
19. The process of any of claims 1 to 18, wherein the phase transfer catalyst is a quaternary alkylammonium salt wherein the alkyl groups are alkyl chains having from four to twelve carbon atoms
20. The process of any of claims 1 to 19, wherein the base is selected from the group consisting of hydroxides, alkoxides, metal amides, metal hydrides and metal dialkylamides and arylamines
21. The process of claim 20, wherein the base is selected from the group consisting of alkali metal hydroxides, calcium hydroxide, magnesium oxide, calcium oxide, sodium carbonate, potassium carbonate, sodium phosphate, potassium phosphate, and mixtures thereof.
22. The process of claim 21, wherein the base comprises an alkali metal hydroxide, preferably sodium hydroxide or potassium hydroxide.
23. The process of any of claims 1 to 22, further comprising feeding an alkali metal halide salt to the reactor, preferably by co-feeding the alkali metal halide salt with the base.
24. The process of any of claims 1 to 23, wherein the dehydrochlorination reaction produces an alkali metal halide salt.
25. The process of claim 24, wherein the alkali metal halide salt is recycled to the reactor.

26. The process of claim 25, wherein the recycled alkali metal halide salt has a purity of 90% or greater, preferably a purity of 95% or greater, most preferably a purity of 98% or greater.
27. The process of claim 25, wherein the recycled alkali metal halide salt comprises less than about 5 mole percent, preferably less than about 3 mole percent, most preferably less than about 1 mole percent, of chlorine, fluorine and/or hydroxides.
28. The process of any of claims 23 to 27, wherein the base comprises potassium hydroxide and the salt is potassium chloride.
29. The process of any of claims 23 to 27, wherein the base comprises sodium hydroxide and the salt is sodium chloride.
30. A process of preparing hexafluoro-2-butyne (HFB), the process comprising:
 - reacting a base comprising an alkali metal hydroxide with HCFO-1326mxz or HCFC-336 for dehydrochlorination of the HCFO-1326mxz or HCFC-336 in a reactor 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;
 - providing the vapor portion of the composition from the reactor to a fourth distillation column which separates the vapor portion into a lower boiling fraction F11_{D33} comprising HFB, and a higher boiling fraction F12_{D33} comprising HCFO-1326mxz; and
 - returning the higher boiling fraction F12_{D33} comprising HCFO-1326mxz from the fourth distillation column to the reactor, wherein the second fraction F12_{D33} further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), trifluoropropyne, R-356mff, R-336maf, R-336mdd and hexafluoro-2-butyne.

31. The process of claim 30, wherein the lower boiling fraction F_{11D33} comprises HFB, HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction, and wherein the lower boiling fraction F_{11D33} is sent to one or more additional distillation columns.
32. The process of any of claims 30 to 31, wherein the one or more additional compounds are selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), trifluoropropyne, R-356mff and hexafluoro-2-butyne.
33. The process of any of claims 30 to 32, wherein the base is added to the HCFO-1326mxz.
34. The process of any of claims 30 to 32, wherein the base and the HCFO-1326mxz are co-fed to the reactor.
35. The process of any of claims 30 to 34, wherein the higher boiling fraction F_{12D33} comprises greater than about 95 mole percent Z-HCFO-1326mxz, preferably greater than 97 mole percent Z-HCFO-1326mxz, most preferably greater than 99 mole percent Z-HCFO-1326mxz.
36. The process of any of claims 30 to 35, wherein a water content of the higher boiling fraction F_{12D33} is about 5000 ppm or less, preferably about 3000 ppm or less, most preferably about 1000 ppm or less.
37. The process according to any of claims 30 to 36, the process further comprising:
 - providing the liquid portion of the composition from the reactor to a decanter and separating the liquid portion into an aqueous liquid phase fraction F_{1X30} comprising water and the alkali metal halide salt and an organic liquid phase fraction F_{2X30} comprising HCFO-1326mxz and excess phase transfer catalyst;
 - optionally returning a first portion of the organic liquid phase fraction F_{2X30} from the decanter to the reactor;
 - providing a second portion of the organic liquid phase fraction F_{2X30} from the decanter to a first distillation column and separating the second portion of the

organic liquid phase second fraction $F2_{X30}$ into a lower boiling fraction $F3_{D30}$ comprising HCFO-1326mxz, and a higher boiling fraction $F4_{D30}$ comprising HCFO-1326mxz, water, alkali salts, excess PTC and other organic byproducts; and

returning the lower boiling fraction $F3_{D30}$ comprising HCFO-1326mxz from the first distillation column to the reactor, wherein the lower boiling fraction $F3_{D30}$ further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z), R-336mdd, R-336maf and R-346mdf; and

providing a first portion of the higher boiling fraction $F4_{D30}$ to a second distillation column and separating the first portion of $F4_{D30}$ into a lower boiling fraction $F5_{D31}$ comprising HCFO-1326mxz and optionally one or more additional compounds selected from trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z) and R-346mdf and a higher boiling fraction $F6_{D31}$ comprising HCFO-1326mxz, distillation solvent, excess PTC and other organic byproducts from the dehydrochlorination reaction; and

returning the lower boiling fraction $F5_{D31}$ from the second distillation column to the reactor, wherein the lower boiling fraction $F5_{D31}$ comprises HCFO-1326mxz and optionally one or more additional compounds selected from trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z) and R-346mdf; and

providing a second portion of the higher boiling fraction $F4_{D30}$ to an extraction column and separating the second portion of $F4_{D30}$ into a lower density fraction $F7_{A30}$ comprises extractant, water, HCFO-1326mxz, other organic byproducts from the dehydrochlorination reaction and a higher density fraction $F8_{A30}$ comprises HCFO-1326mxz, other organic byproducts from the dehydrochlorination reaction, extractant, and water; and

providing the higher density fraction F8_{A30} to a third distillation column and separating the higher density fraction F8_{A30} into a lower boiling fraction F9_{D32} comprises extractant, water, HCFO-1326mxz, other organic byproducts from the dehydrochlorination reaction and a higher boiling fraction F10_{D32} comprises HCFO-1326mxz, other organic byproducts from the dehydrochlorination reaction, extractant, and water; and

returning the higher boiling fraction F10_{D32} comprising HCFO-1326mxz from the third distillation column to the reactor, wherein the higher boiling fraction F10_{D32} comprises HCFO-1326mxz and optionally one or more additional compounds selected from trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R1316(Z) and R-346mdf.

38. The process of claim 37, wherein the one or more additional compounds are selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z) and R-346mdf.

39. A process of preparing hexafluoro-2-butyne (HFB), the process comprising:

reacting a base comprising an alkali metal hydroxide with HCFO-1326mxz and/or HCFC-336 in a reactor 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;

providing the liquid portion of the composition from the reactor to a decanter and separating the liquid portion into an aqueous liquid phase fraction F1_{X30} comprising water and the alkali metal halide salt and an organic liquid phase fraction F2_{X30} comprising the HCFO-1326mxz and excess phase transfer catalyst;

providing at least a portion of the organic liquid phase fraction $F2_{X30}$ from the decanter to the first distillation column and separating it into a lower boiling fraction $F3_{D30}$ comprising HCFO-1326mxz, and a higher boiling fraction $F4_{D30}$ comprising HCFO-1326mxz, water, alkali salts, excess PTC and other organic byproducts; and

returning the lower boiling fraction $F3_{D30}$ comprising HCFO-1326mxz from the first distillation column to the reactor, wherein the lower boiling fraction $F3_{D30}$ further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z), R-336mdd, R-336maf and R-346mdf; or from the group consisting of trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z) and R-346mdf; and

providing a first portion of the higher boiling fraction $F4_{D30}$ to a second distillation column and separating the first portion of $F4_{D30}$ into a lower boiling fraction $F5_{D31}$ comprising HCFO-1326mxz and optionally one or more additional compounds selected from trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z) and R-346mdf and a higher boiling fraction $F6_{D31}$ comprising HCFO-1326mxz, distillation solvent, excess PTC and other organic byproducts from the dehydrochlorination reaction; and

returning the lower boiling fraction $F5_{D31}$ from the second distillation column to the reactor, wherein the lower boiling fraction $F5_{D31}$ comprises HCFO-1326mxz and optionally one or more additional compounds selected from trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R-1316(Z) and R-346mdf; and

providing a second portion of the higher boiling fraction $F4_{D30}$ to an extraction column and separating the second portion of $F4_{D30}$ into a lower density fraction $F7_{A30}$ comprises extractant, water, HCFO-1326mxz, other organic byproducts

from the dehydrochlorination reaction and a higher density fraction F8_{A30} comprises HCFO-1326mxz, other organic byproducts from the dehydrochlorination reaction, extractant, and water; and

providing the higher density fraction F8_{A30} to a third distillation column and separating the higher density fraction F8_{A30} into a lower boiling fraction F9_{D32} comprises extractant, water, HCFO-1326mxz, other organic byproducts from the dehydrochlorination reaction and a higher boiling fraction F10_{D32} comprises HCFO-1326mxz, other organic byproducts from the dehydrochlorination reaction, extractant, and water; and

returning the higher boiling fraction F10_{D32} comprising HCFO-1326mxz from the third distillation column to the reactor, wherein the higher boiling fraction F10_{D32} comprises HCFO-1326mxz and optionally one or more additional compounds selected from trifluoroacetone, R-1336mzz(E), R-1345czf, R-1327mz(E), R-1327mz(Z), R-356mff, hexafluoro-2-butyne, R-1336mzz(Z), R-1316mxx(E), R1316(Z) and R-346mdf.

40. The process of claim 39, wherein the base is added to the HCFO-1326mxz and/or HCFC-336.
41. The process of claim 39, wherein the base is co-fed with the HCFO-1326mxz and/or HCFC-336 to the reactor.
42. The process of any of claims 39 to 41, wherein the lower boiling fraction F3D30 comprises greater than about 95 mole percent Z-HCFO-1326mxz, preferably greater than 97 mole percent Z-HCFO-1326mxz, most preferably greater than 99 mole percent Z-HCFO-1326mxz.
43. The process of any of claims 30 to 42, the process further comprising separating the alkali metal halide salt from the liquid portion and returning the alkali metal halide salt to the reactor.
44. The process of claim 43, wherein the recycled alkali metal halide salt has a purity of 90% or greater, preferably a purity of 95% or greater, most preferably a purity of 98% or greater.

45. The process of claim 43, wherein the recycled alkali metal halide salt comprises less than about 5 mole percent, preferably less than about 3 mole percent, most preferably less than about 1 mole percent, of chlorine, fluorine and/or hydroxides.
46. The process of any of claims 39 to 45, further comprising providing the vapor portion of the composition from the reactor to a fourth distillation column configured and separating the vapor portion into a lower boiling fraction F_{11D33} comprising HFB, and a higher boiling fraction F_{12D33} comprising unreacted HCFO-1326mxz; and returning the second fraction F_{12D33} comprising unreacted HCFO-1326mxz from the fourth distillation column to the reactor, wherein the higher boiling fraction F_{12D33} further comprises one or more additional compounds selected from the group consisting of trifluoroacetone, R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), trifluoropropyne, R-356mff and hexafluoro-2-butyne, or from the group consisting of trifluoroacetone, R-1336mzz(E), R-1336mzz(Z), R-1345czf, R-1327mz(E), R-1327mz(Z), trifluoropropyne, R-356mff and hexafluoro-2-butyne; and optionally, where the lower boiling fraction F_{11D33} comprises HFB, HCFO-1326mxz, water and other organic byproducts from the dehydrochlorination reaction, sending the lower boiling fraction F_{11D33} is sent to one or more additional distillation columns.
47. The process of any of claims 39 to 46, wherein a water content of the lower boiling fraction F_{3D30} is about 5000 ppm or less, preferably about 3000 ppm or less, most preferably about 1000 ppm or less.
48. The process of any of claims 39 to 46, wherein the lower boiling fraction F_{3D30} comprises about 100 ppm or less of the base.
49. The process of any of claims 39 to 48, wherein the lower boiling fraction F_{3D30} comprises about 500 ppm or less of the phase transfer catalyst.

50. A system for producing hexafluoro-2-butyne (HFB), the system comprising:
- a reactor for reacting a base with a chlorinated organic reactant in the presence of a phase transfer catalyst and an alkali metal halide salt to form a product mixture comprising HFB, and
 - a recycle stream for returning alkali metal halide salt separated from the product mixture to the reactor.
51. The system of claim 50, wherein the chlorinated organic reactant comprises a chlororfluorobutane, a chlorofluorobutene, or a mixture thereof.
52. The system of any of claims 50 to 51, wherein the chlorinated organic reactant comprises one or more compounds selected from the group consisting of HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane), HCFC-336maf (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane), E-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E-HCFO-1326mxz) and Z-2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (Z-HCFO-1326mxz).
53. The system of any of claims 50 to 52, wherein the base is selected from the group consisting of hydroxides, alkoxides, metal amides, metal hydrides and metal dialkylamides and arylamines.
54. The system of claim 53, wherein the base is selected from the group consisting of alkali metal hydroxides, calcium hydroxide, magnesium oxide, calcium oxide, sodium carbonate, potassium carbonate, sodium phosphate, potassium phosphate, and mixtures thereof.
55. The system of claim 54, wherein the base comprises an alkali metal hydroxide, preferably sodium hydroxide or potassium hydroxide.
56. The system of claim 55, wherein the base comprises potassium hydroxide and the salt is potassium chloride.

57. The system of claim 55, wherein the base comprises sodium hydroxide and the salt is sodium chloride.
58. The system of any of claims 50 to 57, wherein the recycled alkali metal halide salt has a purity of 90% or greater, preferably a purity of 95% or greater, most preferably a purity of 98% or greater.
59. The system of any of claims 50 to 57, wherein the recycled alkali metal halide salt comprises less than about 5 mole percent, preferably less than about 3 mole percent, most preferably less than about 1 mole percent, of chlorine, fluorine and/or hydroxides.

1/1

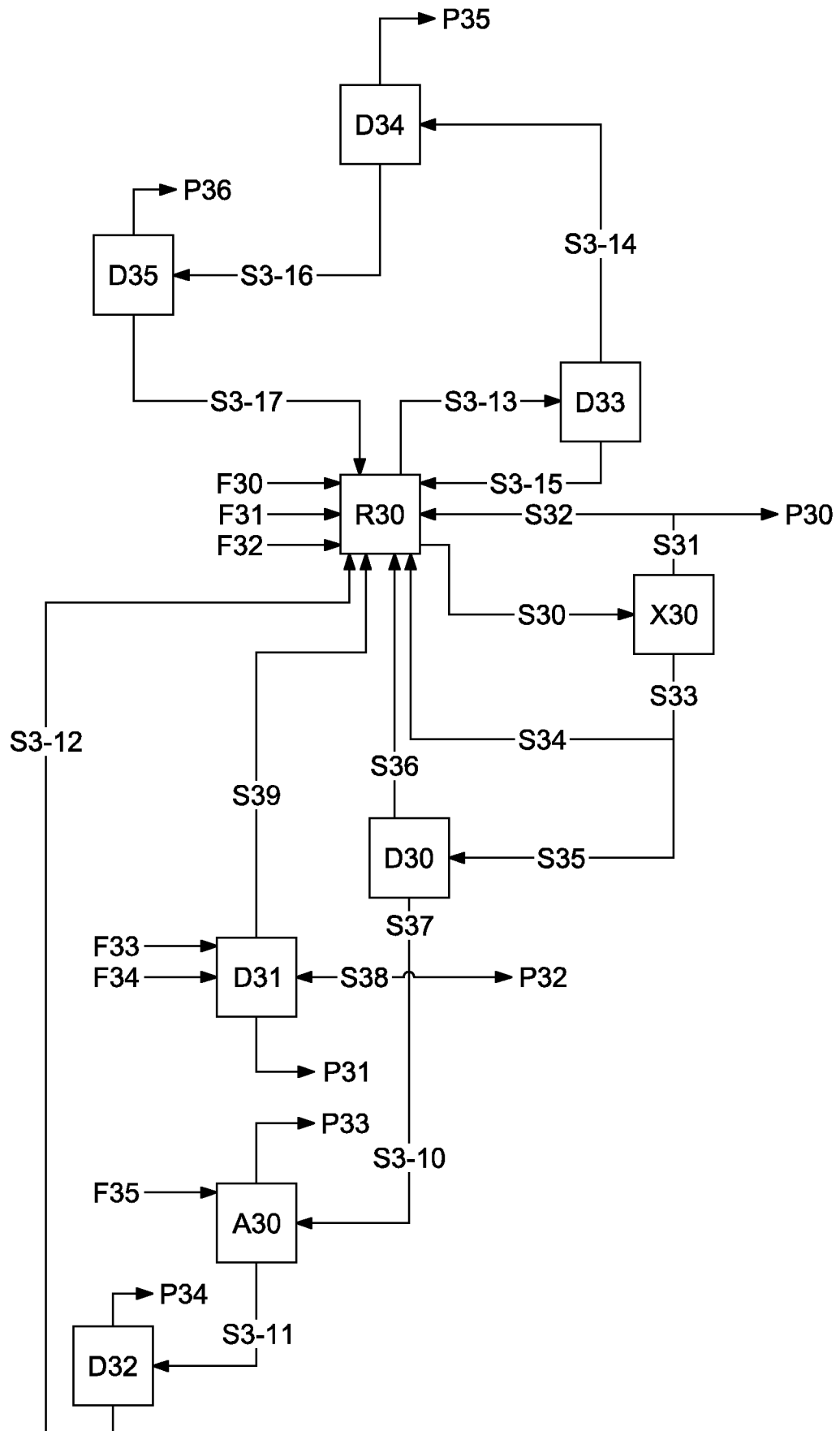


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/038700

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C17/25 C07C21/22 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 2020/206279 A1 (CHEMOURS CO FC LLC [US]) 8 October 2020 (2020-10-08) Paragraph "production of 1,1,1,4,4,4-hexafluoro-2-butyne", starting page 9, to bottom of page 13 Preferred embodiment page 10, lines 4-10: "The present disclosure further provides a process comprising contacting E- and/or Z-1326mxz with base to produce a product mixture comprising 1,1,1,4,4,4hexafluoro-2-butyne (CF ₃ C=CCF ₃) in a dehydrochlorination reaction. The base is preferably a basic aqueous medium. This reaction step is preferably performed in the presence of a catalyst. Preferably the basic aqueous medium comprises a solution of an alkali metal hydroxide or alkali metal halide salt or other base in water. Preferably the catalyst is a phase -/- -	1,4-29
☒ 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 15 October 2024		Date of mailing of the international search report 16/12/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Lange, Tim

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/038700

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	transfer catalyst". Example 6, page 22: Preparation of 1,1,1,4,4,4-Hexafluoro-2-butyne: NaOH aqueous solution (12 ml, 0.12 mol) was added to the mixture of Z-1326 (20 g, 0.1 mol) and water (18 ml) in the presence of tetra-n-butylammonium bromide (0.45 g, 0.001325 mol) at 35°C. The reaction temperature was raised to 70°C after the addition, and gas chromatography was used to monitor the reaction. The reaction was completed after 1 hour and 15.4 g product (conversion: 100%; yield: 95%) was collected in a dry ice trap. examples 7-20: Further processes of preparing HFB from ZE-1326mxz with NaOH as base, in the presence of a PTC. -----	
X	WO 2018/036076 A1 (WANG ZONGLING [CN]) 1 March 2018 (2018-03-01) examples 2-6: Adding potassium hydroxide aqueous solution and phase-transfer-catalysts (such as 18-K-6) together with hexafluoro-2-chlorobutene (chlorinated reactant) to the reaction vessel, and heating to 60-90°C. After collecting and condensing the gas-phase product produced during the reaction, a gas-phase product is obtained. -----	1,4-29
X	WO 2014/052695 A1 (DU PONT [US]) 3 April 2014 (2014-04-03) Process for preparing HFB whereby NaOH as base is added to HCFC-336mdd (2,3-dichloro-1,1,1,4,4,4-hexafluorobutane) in the presence of a quaternary alkylammonium salt as PTC and heating to 70°C, thereafter collecting the product hexafluorobutyne in a dry ice trap: see examples 1-3 Process for preparing HFB whereby NaOH as base is added to HCFC-336mfa (2,2-dichloro-1,1,1,4,4,4-hexafluorobutane) in the presence of a PTC and heating, thereafter collecting the product hexafluorobutyne in a dry ice trap: see comparative examples 2-3, page 13 Process for preparing HFB whereby NaOH as base is added to HCFO-Z/E-1326mxz (2-chloro-1,1,1,4,4,4-hexafluorobutene) in the presence of a quaternary alkylammonium salt as PTC and heating, thereafter collecting the product hexafluorobutyne in a dry ice trap: see examples 4-18 ----- -/-	1,4-29

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/038700

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/039728 A1 (PENG SHENG [US] ET AL) 11 February 2016 (2016-02-11) A process for preparing HFB by reacting a base (aq. basic solution) with chlorinated organic reactant (Z-1,1,1,4,4,4-hexafluoro-2-chloro-2-buten e) in a reactor in the presence of a PTC (quaternary alkylammonium salt) and an alkali metal halide salt to produce hexafluoro-2-butyne: see page 3, paragraph [42], step f -----	1,4-29
T	WO 2019/195251 A1 (BLUE CUBE IP LLC [US]) 10 October 2019 (2019-10-10) A system that comprises a reactor and a recycle stream: see claims 32-34 -----	50

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/038700

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 (completely) ; 4-29 (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.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2024/038700

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2020206279 A1	08-10-2020	AU 2020253606 A1	09-09-2021
		BR 112021018324 A2	23-11-2021
		CA 3131537 A1	08-10-2020
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		US 2022194881 A1	23-06-2022
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		MX 371333 B	27-01-2020
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US 2016039728 A1	11-02-2016	CN 105418361 A	23-03-2016
		US 2016039728 A1	11-02-2016
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		JP 2021520370 A	19-08-2021
		US 2021094897 A1	01-04-2021
		WO 2019195251 A1	10-10-2019

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 (completely); 4-29 (partially)

Processes for preparing HFB by reaction of a base and a chlorinated organic reactant in a reactor in the presence of a phase-transfer-catalyst (PTC), characterized in that a base is added to the chlorinated reagent.

2. claims: 2 (completely); 4-29 (partially)

Processes for preparing HFB by reaction of a base and a chlorinated organic reactant in a reactor in the presence of a phase-transfer-catalyst (PTC), characterized in that a base and a chlorinated reactant is co-fed to the reactor.

3. claims: 3 (completely); 4-29 (partially)

Processes for preparing HFB by reaction of a base and a chlorinated organic reactant in a reactor in the presence of a phase-transfer-catalyst (PTC), characterized in that an alkali metal halide is present in the reactor and the alkali metal halide salt is separated from the product mixture after reaction and returned to the reactor

4. claims: 30-38

Processes for preparing HFB by reaction of a base and a chlorinated organic reactant in a reactor in the presence of a phase-transfer-catalyst (PTC), characterized in that the process comprises a vapor portion and a liquid portion, and providing the vapor portion to a distillation column separating the vapor in a lower and a higher boiling fraction, and returning the higher boiling fraction to the reactor.

5. claims: 39-49

Processes for preparing HFB by reaction of a base and chlorinated organic reactant (either HCFO-1325mxz or HCFC-336) in a reactor in the presence of a phase-transfer-catalyst (PTC), characterized in that the process comprises a vapor portion and a liquid portion, and providing the liquid portion to a decanter, where the liquid portion is separated into an aqueous liquid and organic liquid phase

6. claims: 50-59

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

A system suitable for producing HFB, comprising a reactor
and a recycle stream.
