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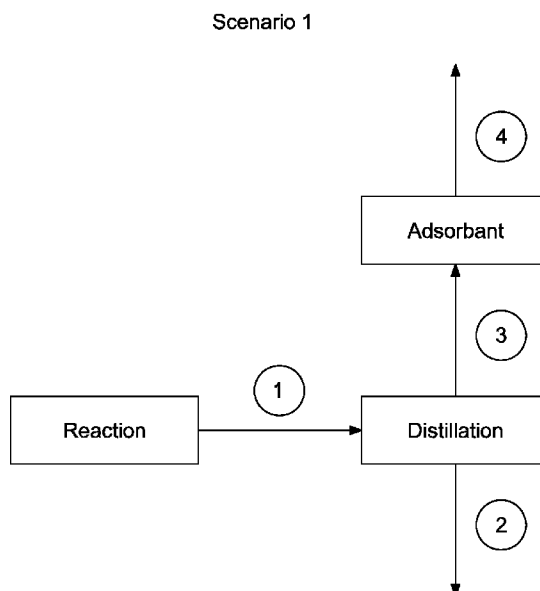


FIG. 1

(57) Abstract: The invention relates to HCl recovery and purification from fluorochemical raw product streams.

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TITLE

HCL RECOVERY IN FLUOROCHEMICAL PROCESSES TO PRODUCE HIGH QUALITY ANHYDROUS HCL OR AQUEOUS HCL OF SPECIFIC CONCENTRATION

FIELD

[0001] The invention relates to HCl recovery and purification of process streams from fluorochemical processes which are subjected to purification to produce anhydrous HCl or aqueous HCl suitable for use in the chemical, food, electrical and pharmaceutical industries, as well as HCl/HF-fluorochemical compositions.

BACKGROUND

[0002] Fluorochemicals, including, but not limited to, hydrofluoroolefins (HFOs) have been produced by fluorination, dehydrochlorination, hydrodechlorination and hydrogenation, and result in compounds with low ozone depletion potential (ODP) and low global warming potential (GWP). Hydrofluoroolefins (HFOs) have been replacing saturated CFCs (chlorofluorocarbons) and HCFCs (hydrochlorofluorocarbons) in a variety of applications for several years, as well as hydrofluorocarbons which tend to have high GWP values. As a result, the low ODP and GWP fluorochemicals are being used as refrigerants, solvents, foam expansion agents, cleaning agents, aerosol propellants, dielectrics, fire extinguishants, and power cycle working fluids, as well as starting materials.

[0003] To meet these increasing demands, new manufacturing techniques continue to be developed and additional manufacturing plants and suppliers come on-line. Often fluorochemicals of interest are produced from starting materials such as hydrochlorofluorocarbons and hydrochlorofluoroolefins. As a result HCl is a common byproduct made in the fluorochemical processes, and it is desirable to recover HCl either as gas or aqueous solution at high purity for use in the chemical, food, electrical and pharmaceutical industries. However, HCl produced in these reactions often contain trace amounts of HF, acid fluorides or lower boiling organic compounds, and these impurities could negatively impact the quality of the recovered HCl, and therefore, impede its end use, leading to disposing it as waste. Thus a need exists to provide more

effective and efficient HCl recovery in fluorochemical processes for environmental pollution reduction, and help improving process economics.

SUMMARY

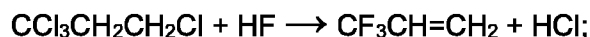
[0004] The invention relates to HCl recovery and purification from fluorochemical processes for producing anhydrous HCl or aqueous HCl for use in the chemical, food, electrical and pharmaceutical industries. See <https://balchem.com/performance-gases/products/anhydrous-hcl/#:~:text=It%20is%20used%20in%20chemical,electronic%20components%20and%20soap%20refining> and <https://labproinc.com/blogs/chemicals-and-solvents/top-5-uses-of-hydrochloric-acid>, the disclosure of each incorporated herein by reference in its entirety.

[0005] The present invention relates to recovering HCl from fluorochemical process product mixtures which comprises, consist essentially of, or consist of desired products, reaction intermediates, organic byproducts, HCl, trace HF and other impurities, by separatory techniques to produce anhydrous HCl and/or aqueous HCl stream of desired concentrations for use in the chemical, food, electrical and pharmaceutical industries.

[0006] In certain embodiments of the invention disclosed herein the desired products includes one of 3,3,3-trifluoropropene, 1,1,1,4,4,4-hexafluoro-2-butene (E), 2,4-dichloro-1,1,1,4,4,4-hexafluoro-2-butene(E) and 2,4-dichloro-1,1,1,4,4,4-hexafluoro-2-butene(Z), 2,3,3,3-tetrafluoropropene, 2-chloro-1,1,1,4-tetrafluoropropane and 1,1,1,4,4,4-hexafluoro-2-butene (E).

[0007] In certain embodiments of the invention disclosed herein the fluorochemical processes include, but not limited to,

(1) fluorination of 1,1,1,3-tetrachloropropane to 3,3,3-trifluoropropene:



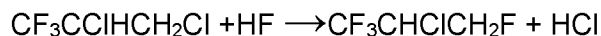
(2) catalytic coupling of 1,1,1-trifluorotrichloroethane in the presence of hydrogen:



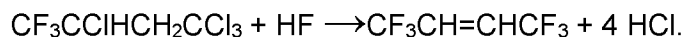
(3) Dehydrochlorination of 2-chloro-1,1,1,2-tetrafluoropropane $\rightarrow$ 2,3,3,3-tetrafluoropropene



(4) fluorination of 2,3-dichloro-1,1,1-trifluoropropane to 2-chloro-1,1,1,3-tetrafluoropropane:



(5) fluorination of 1,1, 1, 3-tetrachloro-4,4,4-trifluorobutane (343jfd) $\rightarrow$ trans-1,1,1,4,4,4-hexafluoro-2-butene + 4 HCl:



[0008] In one embodiment 1,1,1,3-tetrachloropropane contacts HF to form a product mixture including 3,3,3-trifluoropropene, as disclosed in U.S. Patent Pub. No. 20210317055, the disclosure of which is incorporated by reference in its entirety and the mixture is treated to obtain HCl.

[0009] In another embodiment 2-chloro-3,3,3-trifluoropropene contacts HF to form a reaction mixture comprising 2-chloro- 1,1, 1,2-tetrafluoropropene (244bb) or 1,1,2,3-tetrachloropropene (HCC-1230xa) contacts hydrogen fluoride to form a product mixture comprising 2-chloro-3,3,3-trifluoropropene (1233xf), HF and HCl as disclosed in International Publication WO2020247423 the disclosure of which is incorporated by reference in its entirety, and mixtures containing HF and HCl are treated to recover HCl and remove HF.

[0010] In one embodiment the 2-chloro-1,1,1,2-tetrafluoropropane contacts HF to form a product mixture including 2,3,3,3-tetrafluoropropene and HCl and the mixture is treated to obtain HCl.

[0011] In one embodiment 1,1,2,4-tetrachloropropene contacts hydrogen to form a product mixture comprising at least 2-chloro-3,3,3-trifluoropropene and HCl, as disclosed in U.S. Patent No. 9,943,717, the disclosure of which is incorporated by reference in its entirety and the mixture is treated to obtain HCl.

[0012] In one embodiment 2,3-dichloro-1,1,1-trifluoropropane contacts HF to form a product mixture comprising 2-chloro-1,1,1,3 tetrafluoropropane and HCl, and the mixture is treated to obtain HCl.

[0013] In one embodiment the 1,1,3-trichloro-4,4,4-trifluorobut-1-ene contacts HF, as disclosed in, for example, International Publication No. WO 2019/11305, the disclosure of which is incorporated herein by reference in its entirety, and the product mixture including E-1336mzz and 1333azd, 1336mt, 346mdf, 13351zz, Z-1336mzz, 356mff, 1326mxz and HCl is treated to obtain HCl.

[0014] In one embodiment the product mixture from the hydrogenation of 1,1,1-trifluorotrichloroethane (HCFC-113a), such as that disclosed in U.S. Patent Publication US 2016/0347694, the disclosure of which is incorporated herein by reference in its entirety, including HCl, E-1336, 356mff, 1345czf, Z-1336mzz, 346mdf, 1316mxx and 1326mxz is treated to obtain HCl.

[0015] In the fluorochemical processes disclosed herein involving hydrogenation or contact with HF, the HCl in the product mixture(stream) is treated to form anhydrous HCl, which can be used to make aqueous HCl at desired concentration and substantially free of HF and organics.

[0016] The present invention relates to processes where the product mixture from a fluorochemical process includes reactor effluent containing reaction products, reaction intermediates, organic byproducts, HCl and trace HF which can be sent to one or more distillation columns for separation. High boilers are separated at the bottom of the column and can be sent to another separation train, and the HCl and lower boilers that are separated at the top of the column can pass through one or more absorbent beds, including, but not limited to, silica gel (amorphous silica including pyrogenic silica, precipitated silica and silica gel) or alumina to remove HF and low boiling organics such as COF₂, and obtain anhydrous HCl at >99% purity, >99.5% purity. and substantially free of HF, and substantially free organics, e.g., <20 ppm, <10, ppm, <5 ppm.

[0017] In another embodiment disclosed herein the anhydrous HCl stream withdrawn from the one of more absorbers can be sent to an HCl absorber to make aqueous HCl at desired concentration which is substantially free of HF and organics.

[0018] In certain embodiments of the invention disclosed herein treatment operations for HCl bearing streams include, but are not limited to, distillation, decantation, absorption, adsorptions, etc.

[0019] In certain embodiments of the invention disclosed herein treatment operations for HCl bearing streams include membrane separation. In one such embodiment, there is a process comprising contacting a fluorochemical product stream containing at least one of a fluoroolefin, fluorochloroolefin, HCFO, HFC, HCO, HCFC, chloroolefin product, HCl, HF and optionally COF₂ and moisture with a membrane. The membrane may be an ion exchange membrane, particularly a fluorinated ion-exchange membrane. Membrane separation may comprise using a fluorinated ion-exchange membranes. Fluorinated ion exchange membranes include those commercially available, such as those sold under the Nafion™, FORBLUE™, FLEMION™ names.

[0020] In certain embodiments of the invention disclosed herein unit operations include, a reactor, plus one or more of the following units: at least one distillation column, a least one decanter, at least one absorber, and at least one sparging unit..

[0021] In another embodiment the anhydrous HCl stream can be sent to an HCl absorber to make aqueous HCl at desired concentration and substantially free of HF and organics.

[0022] In a still further embodiment the product mixture is removed from the reactor and sent to a HCl quench tank. Decanting, the high boilers from the bottom of the tank are removed for additional purification. Volatile organics are collected for additional purification. HCl solution is sent to a separate tank with gas sparging to remove the remaining organics. Optionally CaCl₂ in the tank is added to remove HF and obtain aqueous HCl at the desired concentration and substantially free of HF and organics.

[0023] Certain embodiments disclosed herein relate to compositions comprising HCl, HF and two or more, three or more additional compounds selected from one of 346mdf, 1336mzz(E), 1336mzz(Z), 356mff, 133a, 1327mz, 1336ft, 1243zf, 1242zf, 254eb, 254fb, 253fb, 113a, 123, 133a, 1316mxx(E), 1316mxx(Z), 1326mxz(E), 1326mxz(Z), 1234ze(Z), 1234ze(E), 1234yf, 244bb, 1233xf, 1233zd(E), 1233zd(Z), 245fa, optionally COF₂, and CO₂.

[0024] Certain embodiments disclosed herein relate to compositions comprising HCl, HF plus two more or three more of the following 346mdf, 1336mzz(E), 1336mzz(Z), 356mff, 133a, 1327mz, 1336ft, 1243zf, 1242zf, 254eb, 254fb, 253fb, 113a, 123, 133a, 1316mxx(E), 1316mxx(Z), 1326mxz(E), 1326mxz(Z), 1234ze(Z), 1234ze(E), 1234yf, 1233xf, 1233zd(E), 1233zd(Z), 245fa, optionally COF₂ and/or CO₂.

[0025] Certain embodiment disclosed herein relate to compositions comprising ., 346mdf, 1336mzz(E), 1336mzz(Z), HCl, HF, 356mff, 133a, 1327mz, and optionally COF₂, CO₂ wherein the amount of HCl present ≤ 500 ppm, ≤ 400 ppm, or ≤ 300 ppm.

[0026] Certain embodiment disclosed herein relate to compositions which comprise, consist essentially of, or consists of 346mdf, 1336mzz(E), 1336mzz(Z), greater than 100 ppm and ≤ 500 ppm HCl, HF, 356mff, 133a, 1327mz, optionally CO₂ and/or COF₂.

[0027] Certain embodiment disclosed herein relate to compositions which comprise, consist essentially of, or consists of one or more of 346mdf, 1336mzz(E), 356mff, 133a, 1327mz and 1336mzz(Z), greater than 100 ppm and ≤ 500 ppm HCl, HF, and optionally CO₂ and/or COF₂.

[0028] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, suitable methods and materials are described below. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] Figure 1 depicts a first treatment scenario of the invention.

[0030] Figure 2 depicts a second treatment scenario of the invention.

[0031] Figure 3 depicts a third treatment scenario of the invention.

DETAILED DESCRIPTION

[0032] The present invention relates fluorochemical processes which are conducted in the reaction zone of a reactor a product mixture/stream which includes the product of interest, reaction intermediates, organic byproducts, starting materials, HCl and trace HF. The Product mixture is sent to a distillation column. High boilers are separated at the bottom of the column and sent to another separation train. HCl and lower boilers separated at the top of the column optionally pass through an absorbent bed (silica gel (amorphous silica including pyrogenic silica, precipitated silica and silica gel), or alumina)) to obtain anhydrous HCl at >99% purity and substantially free of HF and organics.

[0033] In another embodiment the anhydrous HCl stream from the top of the column can be sent to an HCl absorber to make aqueous HCl at desired concentration and substantially free of HF, and organics .

[0034] In another embodiments first sent to a HCl quench tank. The high boilers at the bottom are decanted, removed and sent for additional purification. Volatile organics are collected for additional purification, HCl solution is sent to a separate tank with gas sparging to remove remain organics. HF is optionally removed by contact with CaCl_2 .

[0035] Before addressing details of embodiments described herein, some terms are defined or clarified as follows.

[0036] Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range. Moreover, all ranges set forth herein are intended to include not only the particular ranges specifically described, but also any combination of values therein, including the minimum and maximum values recited.

[0037] 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.

[0038] The term “hydrohaloalkane,” as used herein means a molecule containing hydrogen, carbon, fluorine and/or chlorine and/or bromine and/or iodine, with no carbon-carbon double bond (halo=fluoro, chloro, bromo, iodo). Examples are described throughout the instant specification.

[0039] The term “hydrohaloalkene” is intended to mean a chemical compound selected from the classes of hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) which include a double bond between adjacent carbon atoms and can contain 1 to 8 carbon atoms.

[0040] The term “dehydrohalogenation,” as used herein, means loss of HX from a hydrohaloalkane, where X=F, Cl, Br, I, where H and X are on adjacent carbons in the hydrohaloalkane. For example, the term “dehydrofluorination,” “dehydrofluorinating” or “dehydrofluorinated,” as used herein, means a process during which hydrogen and fluorine on adjacent carbons in a molecule are removed; the term “dehydrochlorination,” “dehydrochlorinating,” or “dehydrochlorinated,” as used herein, means a process during which hydrogen and chlorine on adjacent carbons in a molecule are removed.

[0041] Typically a heated reactor is used in the hydrogenation or fluorochemical processes described herein. A number of reactor configurations are possible including packed bed tube or column reactors, operated in batch, semi-batch or continuous modes. In addition to the reactors disclosed herein, preheaters and vaporizers, heat exchangers, feed and effluent lines, units associated with mass transfer, contacting vessels (pre-mixers), distillation columns, absorbers, and valving associated with reactors, heat exchangers, vessels, columns, and units that are used in the processes of various embodiments disclosed herein should be constructed of materials resistant to corrosion

[0042] As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following:

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

[0043] 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.

[0044] 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.’

[0045] 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.”

[0046] 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.

[0047] As used herein, the term “substantially free” means that less than about 0.0005 percent by weight is present (5 ppm), most preferably less than 1 ppm.

[0048] As used herein the term “about” in certain embodiments can mean $\pm 1\%$, $\pm 2\%$, $\pm 3\%$ and up to and including $\pm 10\%$ of an identified value, including all whole numbers and fractions thereof.

[0049] As used herein the term “substantially,” “main” or “major” and should be construed to mean at least 51 percent.

[0050] As used herein the terms Non-Condensable Gas (NCG) is meant to gases such as oxygen and nitrogen (air), carbon dioxide, argon and carbon monoxide. Non-absorbable gas (NAG), non-condensable gas (NCG), or simply non-condensables are all terms used to reference gases such as air, nitrogen, argon, carbon dioxide, and oxygen.

[0051] As used herein impurities comprise, but are not limited to moisture (water), non-absorbable gas (NAG), non-condensable gas (NCG), or simply non-condensables are all terms used to reference gases such as air, nitrogen, argon, carbon dioxide, and oxygen, and chlorine containing HCC, HCFC, HCFO and HCO compounds.

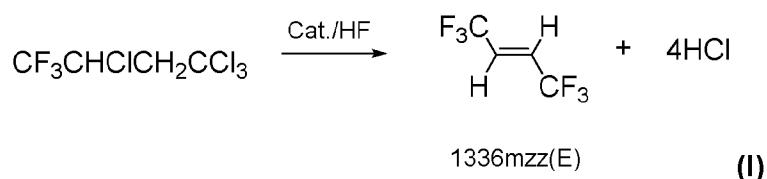
[0052] Compounds referred to in this disclosure may be referred to by code, based on fluorochemical naming convention, chemical structure and/or chemical name. For convenience and reference, selected compounds with codes, structures and chemical names are listed in Table 1.

TABLE 1

Code	Name-ASHRAE Designation	Formula
R-123	2,2-dichloro-1,1,1-trifluoroethane (HCFC-123)	
R-143a	1,1,1-trifluoroethane (HFC-143a)	
R-346mdf	2-chloro-1,1,1,1,4,4,4-hexafluorobutane (HCFC-346mdf)	
R-356mff	1,1,1,4,4,4-hexafluorobutane (HFC-356mff)	$\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$
R-1130a	1,1-dichloroethene (HCO-1130a)	$\text{CCl}_2=\text{CH}_2$
R-1326	E-2-chloro-1,1,1,4,4,4-hexafluoro -2-butene (HCFO-1326mxz(E),	$\text{E}-\text{CF}_3\text{CCl}=\text{CH}_2\text{CF}_3$
R-1326	Z-2-chloro-1,1,1,4,4,4-hexafluoro -2-butene (HCFO-1326mxz(Z),	$\text{Z}-\text{CF}_3\text{CCl}=\text{CH}_2\text{CF}_3$
R-1327me	1,1,1,2,4,4,4-hexafluoro-2-butene (HFO-1327me)	$\text{CF}_3\text{CF}=\text{CH}_2\text{CF}_3$
R-1336mzz(E)	E-1,1,1,4,4,4 hexafluoro-2-butene (HFO-1336mzz(E))	$\text{E}-\text{CF}_3\text{CH}=\text{CHCF}_3$
R-1336mzz(Z)	Z-1,1,1,4,4,4 hexafluoro-2-butene (HFO-1336mzz(Z))	$\text{Z}-\text{CF}_3\text{CH}=\text{CHCF}_3$

EXAMPLESExample 1

[0053] HCl recovery as anhydrous HCl



[0054] In the first scenario, illustrated in **Fig. 1**, raw product feed **1** containing products, reaction intermediates, organic byproducts, HCl and trace HF (e.g., raw feed comprising, e.g., 346mdf, 1336mzz(E), 1336mzz(Z), HCl, HF, COF₂, 356mff, 133a, 1327mz, CO₂ can be sent to a distillation column, and high boilers are separated at the bottom of the column and removed through (2) and sent to another separation train (not shown). HCl and lower boilers are separated at the top of the column in line (3) and optionally passes through an absorbent bed (silica gel (amorphous silica including pyrogenic silica, precipitated silica and silica gel), or alumina) to obtain anhydrous HCl at >99% purity and substantially free of HF and organics as stream (4). Before passing through the silica gel, stream (3) may contain HF < 500 ppm, organic < 500 ppm. After passing the silica gel, the amount of HF < 50 ppm, < 10 ppm, < 5 ppm, < 1 ppm, organic < 50 ppm, < 5 ppm < 1 ppm.

[0055] Alternatively, in scenario 2 shown in **Fig. 2**, the anhydrous HCl stream (4) can be sent to an HCl absorber to make aqueous HCl at desired concentrations and substantially free of HF and organics as stream (5).

[0056] Alternatively, in scenario 3 shown in **Fig. 3**, the raw production mixture (feed) from reaction (1) is first sent to a HCl quench tank to decant the high boilers which are removed from the bottom of the tank through line (6) for additional purification. Volatile organics (7) are collected for additional purification and HCl solution (8) is sent to a separate tank with gas sparging to remove remain organics (9), optionally adding CaCl₂ (10) (not shown) to remove HF to obtain aqueous HCl stream (11) at desired concentration and substantially free of HF and organics.

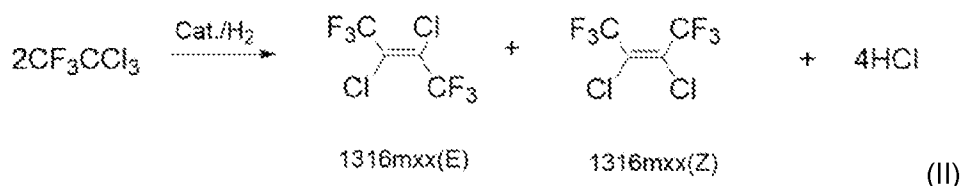
Example 1A

[0057] HCl recovery as aqueous HCl:

[0058] Anhydrous hydrogen chloride (AHCl) made from **Example 1** can be sent to a tank to make aqueous HCl solution in desired concentration.

Example 2

[0059] HCl recovery as aqueous solution via distillation



[0060] Trichlorotrifluoroethane (CFC-113a, CCl_3CF_3) is converted to a mixture of 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene (a mixture of the (E) and (Z) isomers (E-HCFO-1316mxx and Z-HCFO-1316mxx)) by contacting trichlorotrifluoroethane with hydrogen in the presence of a hydrogenation catalyst according to the reaction scheme (II). The crude reaction product comprises 113a, 123, 143a, 1316mxx(Z), 1316mzz(E), trace HF, HCl, H_2 is sent to a distillation column. 1316mxx(E) or 1316mxx(Z), 113a, H_2 , reaction byproducts such as 123 are separated at the bottom of the column and sent to another purification column. HCl containing trace amount of HF and low boiling organics, e.g., H_2 , 143a are distilled off from the top of the column, and optionally pass through silica gel (amorphous silica including pyrogenic silica, precipitated silica or silica gel) to remove HF and COF_2 , followed by going through an aqueous HCl absorber for HCl collection. The final aqueous HCl purity is greater than 99% with HF < 20 ppm.

Example 2A

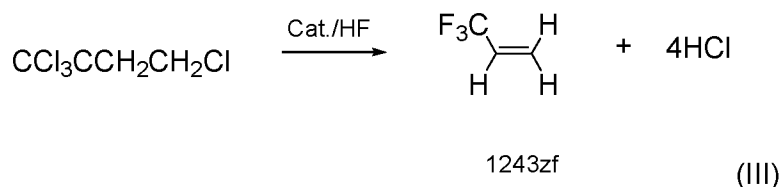
[0061] HCl recovery as aqueous solution from a Quench Tank

[0062] HCl recovery as aqueous solution: The reaction product mixture is sent to an aqueous quench tank. While 1316mxx(E) or 1316mxx(Z), 113a, reaction byproducts such as 123 are separated at the bottom of the reactor and sent to another purification column after drying. H_2 , 143a will be recycled after drying. Aqueous HCl is sparged for

organic removal, optionally adding CaCl₂ to remove HF. The final aqueous HCl purity is greater than 99% with HF < 20 ppm.

Example 3

[0063] HCl recovery as aqueous solution via distillation



[0064] 1,1,1,3-Tetrachloropropane (HCC-250fb, CCl₃CH₂CH₂Cl) is converted to a mixture of 3,3,3-trifluoropropene by contacting 250fb with Anhydrous HF in the presence of a fluorination catalyst according to the reaction scheme (III). The raw reaction product comprises 1243zf, 253fb, 1242zf, 1233zd, 1233zd(E), 1233zd(Z), 1233xf HF, HCl, optionally COF₂, and/or CO₂) is sent to a distillation column. 1243zf, 253fb, 1242zf, , 1233zd(E), 1233zd(Z), 1233xf, 254eb and 254fb HF are separated at the bottom of the column and sent to another purification column. HCl containing trace amount of HF and trace low boiling organics , e.g., 1243zf are distilled off from the top of the column, and optionally pass through silica gel (amorphous silica including pyrogenic silica, precipitated silica or silica gel) to remove HF and COF₂, followed by going through an aqueous HCl absorber for HCl collection. The final aqueous HCl purity is greater than 99% with HF < 20 ppm.

CLAIM EMBODIMENTS:

[0065] A process embodiment comprising passing a fluorochemical product stream containing at least two of a fluoroolefin, fluorochloroolefin, HCFO, HFC, HCO, HCFC, chloroolefin product, HCl, HF and optionally COF₂ and moisture to at least one distillation column, withdrawing an overhead stream from the column comprising at least HCl, HF and optionally COF₂ and moisture, contacting the overhead stream with an absorber adapted to remove HF, moisture and optionally COF₂, and withdrawing anhydrous HCl.

[0066] A process embodiment comprising passing a fluorochemical product stream containing at least HCl, HF, and at least three of a fluoroolefin, fluorochloroolefin, HCFO, HFC, HCO, HCFC, chloroolefin and optionally one of CO₂ COF₂ to at least one distillation column, withdrawing an overhead stream from the column comprising at least HCl, HF and optionally COF₂ and moisture, contacting the overhead stream with an absorber adapted to remove HF, moisture and optionally COF₂, and withdrawing anhydrous HCl.

[0067] A composition embodiment comprising greater than 100 ppm and ≤500 ppm of HCl and/or HF, at least one of 346mdf, 1336mzz(E), 1336mzz(Z), 356mff, 133a,1327mz, and optionally one of COF₂ and CO₂.

[0068] A composition embodiment comprising greater than 100 ppm and ≤500 ppm of HCl and/or HF, at least two of 346mdf, 1336mzz(E), 1336mzz(Z), 356mff, 133a,1327mz, and optionally one of COF₂ and CO₂.

[0069] A composition embodiment comprising greater than 100 ppm and ≤500 ppm of HCl and/or HF, at least three of 346mdf, 1336mzz(E), 1336mzz(Z), 356mff, 133a,1327mz, and optionally one of COF₂ and CO₂.

[0070] A composition embodiment comprising greater than 100 ppm and ≤500 ppm of HCl and/or HF, at least four of 346mdf, 1336mzz(E), 1336mzz(Z), 356mff, 133a,1327mz, and optionally one of COF₂ and CO₂.

[0071] A composition embodiment comprising greater than 100 ppm and ≤500 ppm of HCl and/or HF, at least five of 346mdf, 1336mzz(E), 1336mzz(Z), 356mff, 133a,1327mz, and optionally one of COF₂ and CO₂.

[0072] A composition embodiment comprising 113a, 123, 143a, 1316mxx(Z), 1316mzz(E), HF, HCl, H₂

[0073] A composition embodiment consists essentially of at least one, two or three of 346mdf, 1336mzz(E), 1336mzz(Z), 356mff, 133a,1327mz, at least one of HCl and HF, and optionally COF₂ or CO₂

[0074] A composition embodiment comprising HCl, trace amounts of HF, H₂, 143a and COF₂.

[0075] A composition embodiment comprising at least one of 1243zf, 253fb, 1242zf, 1233zd, 1233zd(E), 1233zd(Z), and 1233xf, HF, HCl, and optionally COF₂, and/or CO₂.

[0076] A composition embodiment comprising at least one of 1243zf, 253fb, 1242zf, 1233zd(E), 1233zd(Z), 1233xf, 254eb and 254fb, and HF.

[0077] A composition embodiment comprising 1243zf, 253fb, 1242zf, 1233zd, 1233zd(E), 1233zd(Z), and 1233xf, HF, HCl, and optionally COF₂, and/or CO₂).

[0078] A composition embodiment comprising 1243zf, 253fb, 1242zf, 1233zd(E), 1233zd(Z), 1233xf, 254eb and 254fb, and HF.

[0079] A process embodiment 1 comprising passing a fluorochemical product stream containing at least one of a fluoroolefin, fluorochloroolefin, HCFO, HFC, HCO, HCFC, chloroolefin product, HCl, HF and optionally COF₂ and moisture to at least one distillation column, withdrawing an overhead stream from the column comprising at least HCl, HF and optionally COF₂ and moisture, contacting the overhead stream with an absorber adapted to remove HF, moisture and optionally COF₂, and withdrawing anhydrous HCl.

[0080] The process embodiment 1 wherein the HCl stream is substantially free of moisture and HF.

[0081] The process embodiment 1 wherein the HCl stream includes less than 20 ppm of HF.

[0082] The process embodiment 1 wherein the HCl stream includes less than 10 ppm of HF.

[0083] The process embodiment 1 wherein the HCl stream includes less than 1 ppm of HF.

[0084] Any process embodiment 1 wherein the HCl stream is anhydrous HCl.

[0085] Any process embodiment 1 wherein the absorber is silica gel comprising one of: amorphous silica, pyrogenic silica, precipitated silica and silica gel.

[0086] Any process embodiment 1 where the absorber is an alumina compound.

- [0087]** Any process embodiment 1 where the absorber amorphous silica.
- [0088]** Any process embodiment 1 wherein there are two of more distillation columns.
- [0089]** The process embodiment 1 wherein distillation columns are in one of series or parallel.
- [0090]** The process embodiment 1 wherein and the overhead stream from a first distillation column is further purified to form a second overhead stream comprising HCl.
- [0091]** Any process embodiment wherein the absorber removes HF, moisture and COF₂.
- [0092]** A composition embodiment consisting essentially substantially pure of HCl containing between greater than 0 and <20 ppm, <10 ppm, <1 ppm, 0..1 ppm organics.
- [0093]** A composition embodiment of substantially pure HCl containing between greater than 0 and <20 ppm, <10 ppm, 1 ppm or 0.1 ppm organics.
- [0094]** An HCl composition embodiment containing > 99%, >99.5% or >99.9% HCl and between 0 and<20 ppm organics, between 0 and<10 ppm organics, between 0 and<5 ppm organics, between 0 and<1 ppm organics, or between 0 and<0.1 ppm organics

CLAIMS

What is claimed is:

1. A process comprising passing a fluorochemical product stream containing at least one of a fluoroolefin, fluorochloroolefin, HCFO, HFC, HCO, HCFC, chloroolefin product, HCl, HF and optionally COF₂ and moisture to at least one distillation column, withdrawing an overhead stream from the column comprising at least HCl, HF and optionally COF₂ and moisture, contacting the overhead stream with an absorber adapted to remove HF, moisture and optionally COF₂, and withdrawing anhydrous HCl.
2. The process of claim 1 wherein the HCl stream is substantially free of moisture and HF.
3. The process of claim 1 wherein the HCl stream includes less than 20 ppm of HF.
4. The process of claim 3 wherein the HCl stream includes less than 10 ppm of HF.
5. The process of claim 4 wherein the HCl stream includes less than 1 ppm of HF.
6. The process of any of claims 1-4 wherein the HCl stream is anhydrous HCl.
7. The process of claim 1 wherein the absorber is silica gel comprising one of: amorphous silica, pyrogenic silica, precipitated silica and silica gel.
8. The process of claim 1 with the absorber is an alumina compound.
9. The process of claim 1 where the absorber amorphous silica.
10. The process of claim 1 wherein there are two or more distillation columns.
11. The process of claim 11 wherein the distillation columns are in one of series or parallel.
12. The process of claim 1 wherein the overhead stream from the first distillation column is further purified to form a second overhead stream comprising HCl.
13. The process of any of claims 1 and 7-9 wherein the absorber removes HF, moisture and COF₂.

14. A system comprising,
- fluorochemical process reactor,
 - first and second reactant flow lines connected to said reactor, wherein the first flow line is connected to and in fluid communication with a contained source of HF or hydrogen and the second flowline is connected in flow communication with a source chloro(fluoro)organic material., and a discharge line for withdrawing the reactor product mixture,
 - at least one of a distillation column and/or a decanter, said discharge line being connected directly to one said distillation column or decanter, wherein the distillation column comprises an overhead line,
 - optionally at least one absorber unit connected to and in flow communication with said overhead line of said distillation column.,
 - optional purification units connected to and in flow communication with said overhead line of said distillation column,
- wherein said absorber includes one of silica gel, alumina or and optionally at least one of moisture and COF₂.
15. The system for performing the process of claim 1 including a distillation column and an absorber unit comprising an alumina compound.
16. The system for performing the process of claim 1 including a distillation column and an absorber unit comprising amorphous silica.
17. The system for performing the process of claim 1 including a distillation column and a unit absorber comprising a silica gel compound selected from one of amorphous silica, pyrogenic silica, precipitated silica and silica gel.
18. The system for performing the process of claim 8 wherein the are at least two different absorber units selected from silica gel, or alumina are present.
19. The system for performing the process of claim 7 wherein the fluorochemical process comprises fluorination of 1,1,1,3-tetrachloropropane to 3,3,3-trifluoropropene and HCl
20. The process of claim 1 wherein the fluorochemical process comprises catalytic hydrogenation of 1,1,1-trifluoro-2,2,2-trichloroethane to 2,4-dichloro-1,1,1,4,4,4--

- hexafluoro-2-butene (E) and 1,1,1,4,4,4-hexafluoro-2-butene and 2,4-dichloro-1,1,1,4,4,4-hexafluoro-2-butene (Z) and HCl.
21. The process of claim 1 wherein the fluorochemical process comprises catalytic fluorination of 2-chloro-1,1,1,2-tetrafluoropropane to 2,3,3,3-tetrafluoropropene and HCl
 22. The process of claim 1 wherein the fluorochemical process comprises catalytic fluorination of 2,3-dichloro-1,1,1-trifluoropropane to 2-chloro-1,1,1,3-tetrafluoropropane:.
 23. The process of claim 1 wherein the fluorochemical process comprises catalytic fluorination of 1,1,3-trichloro-4,4,4-trifluorobut-1-ene (343jfd) to trans-1,1,1,4,4,4-hexafluoro-2-butene and HCl.
 24. The process of any of claims 1-13 wherein the HCl is anhydrous HCl having a purity of at least 98% by weight.
 25. The process of any of claims 1-13 wherein the HCl is anhydrous HCl having a purity of at least 99% by weight.
 26. The process of any of claims 1-13 wherein the HCl is anhydrous HCl having a purity of >99.5% or greater than 99.9% by weight.
 27. The process of any of claims 1-13 wherein the HCl is anhydrous HCl and is converted to aqueous HCl at a concentration selected from one of 10%, 20%, 30%, 40%, or 50%.
 28. A composition comprising greater than 100 ppm and ≤ 500 ppm of HCl and/or HF, at least one of 346mdf, 1336mzz(E), 1336mzz(Z), 356mff, 133a, 1327mz, and optionally one of COF₂ and CO₂.
 29. A composition comprising 113a, 123, 143a, 1316mxx(Z), 1316mzz(E), HF, HCl, H₂
 30. A composition consists essentially of at least one, two or three of 346mdf, 1336mzz(E), 1336mzz(Z), 356mff, 133a, 1327mz, at least one of HCl and HF, and optionally COF₂.

31. A composition comprising HCl, trace amounts of HF, H₂, 143a and optionally COF₂.
32. A composition consisting essentially of HCl substantially free of organics to < 20 ppm.
33. The composition of claim 32, with less than 10ppm organics.
34. The composition of claim 32, with less than 5 ppm organics.
35. A process comprising contacting a fluorochemical product stream containing at least one of a fluoroolefin, fluorochloroolefin, HCFO, HFC, HCO, HCFC, chloroolefin product, HCl, HF and optionally COF₂ and moisture with a membrane.
36. The process of claim 35, wherein the membrane is an ion exchange membrane.
37. The process of claim 36, wherein the ion exchange membrane is a fluorinated ion exchange membrane.

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Scenario 1

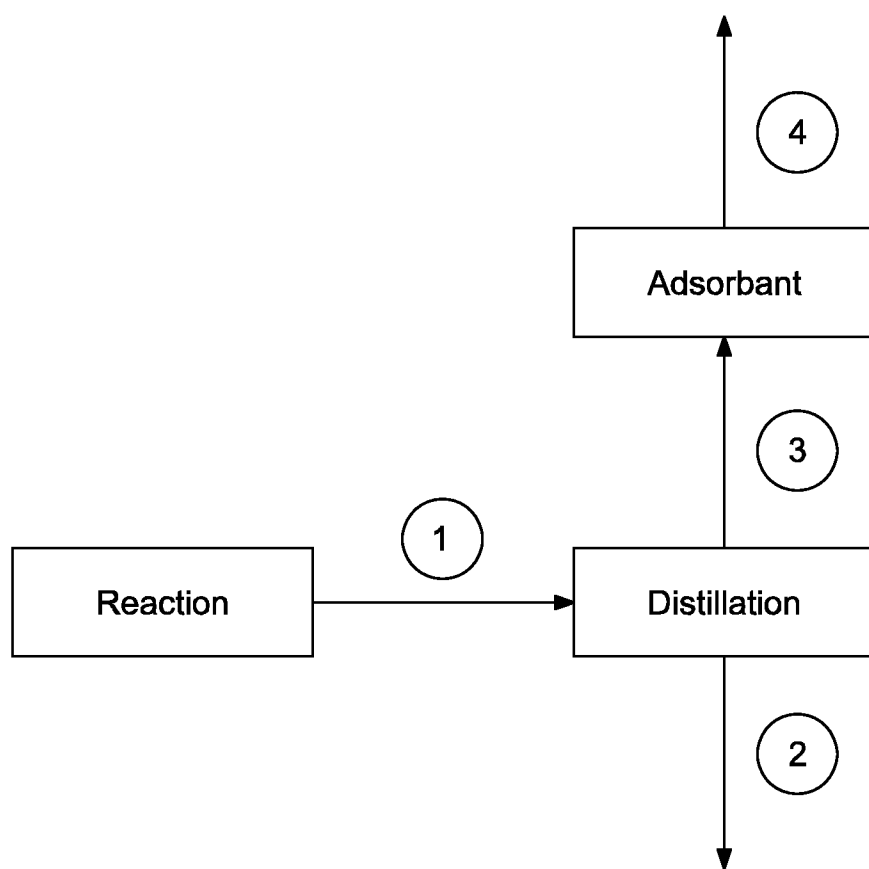


FIG. 1

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Scenario 2

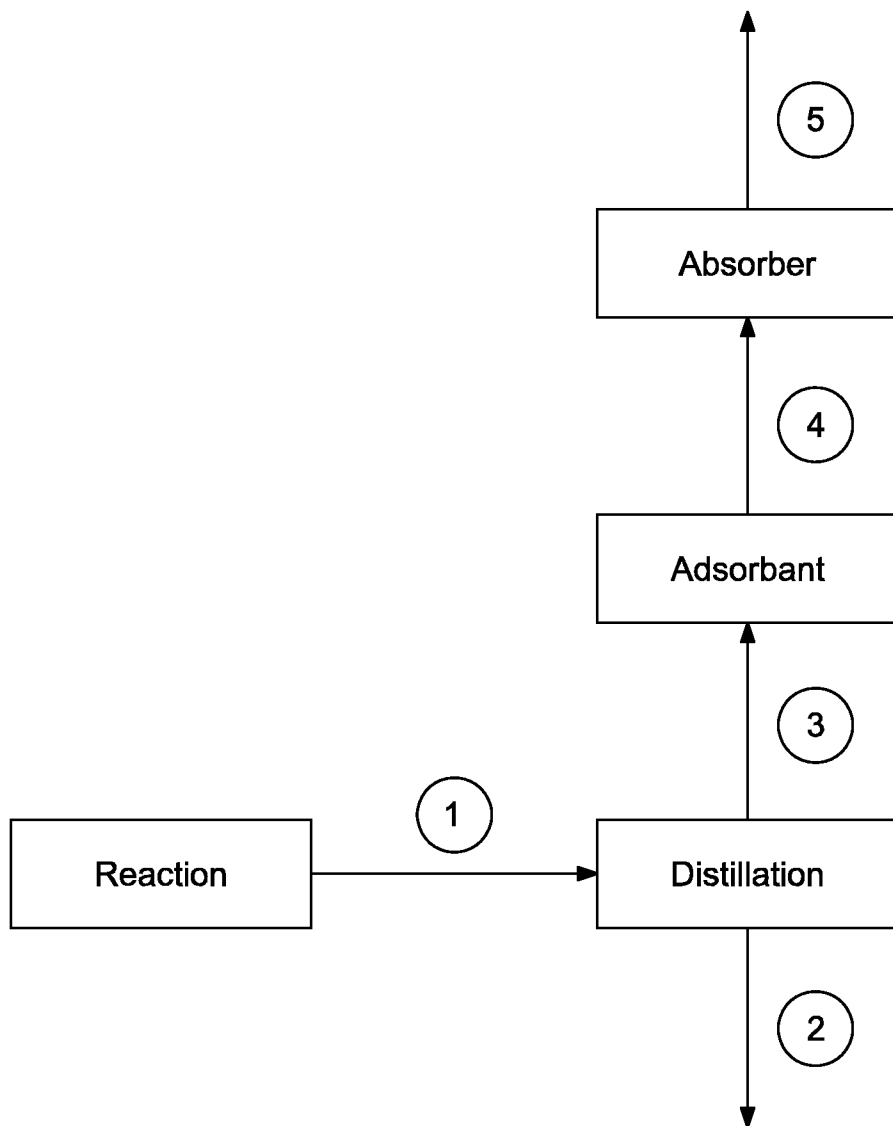


FIG. 2

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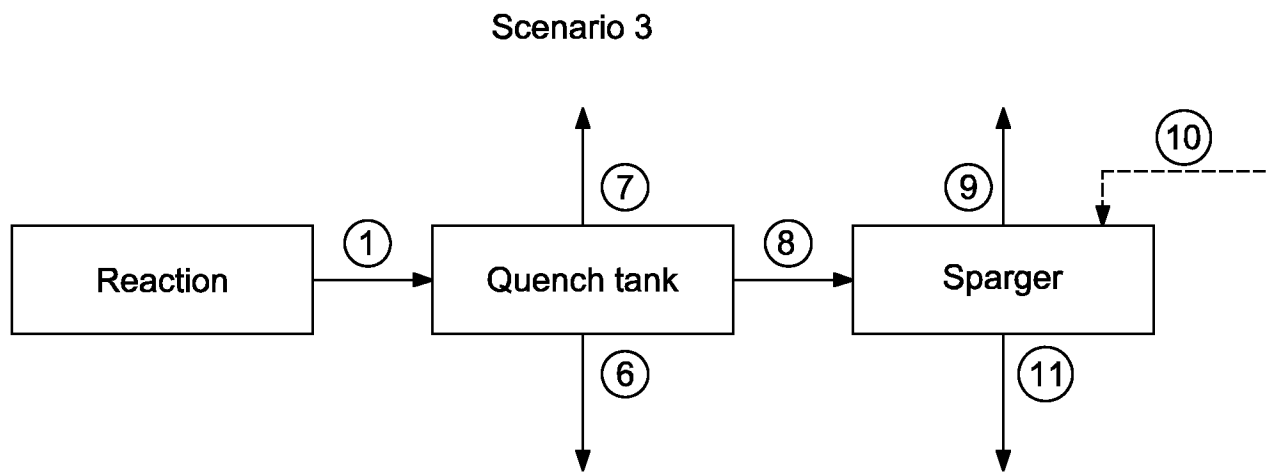


FIG. 3