

TITLE OF THE INVENTION

PURIFICATION OF 2,3,3,3-TETRAFLUOROPROPENE

FIELD

[0001] This invention relates to processes for purifying fluoropropenes by reducing concentration of undesirable components in mixtures comprising fluorinated propenes, in particular, where the fluoropropene is 2,3,3,3-tetrafluoropropene.

BACKGROUND

[0002] Certain fluoroolefins, such as fluoropropenes, such as 2,3,3,3-tetrafluoropropene (HFO-1234yf) is known to be effective in applications as refrigeration, heat transfer, propellants, foaming agents, blowing agents, gaseous dielectrics, sterilant carriers, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents, displacement drying agents and power cycle working fluids.

[0003] Unlike most chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), most fluoroolefins pose no threat to the ozone layer. HFO-1234yf has also been found to be low global warming compounds with low toxicity. Accordingly, compositions containing fluoroolefins can meet increasingly stringent requirements are among leading materials being developed for use in many of the aforementioned applications.

[0004] Manufacturing processes for preparing fluoroolefins are known. These processes often involve starting from a hydrochloro(fluoro)carbon, that is a chlorinated alkane or chlorinated fluoroalkane.

[0005] Unfortunately, processes for making fluoroolefins may lead to the generation of undesirable components as by-products, which are difficult to remove.

[0006] A common method for removing impurities is via distillation. However, this method is difficult if the boiling points of the desired product and an impurity are close or if substance interactions between product and components bring otherwise dissimilar boiling compounds close together (such as azeotropes). Even after distillation, it is still possible that small quantities of impurities remain.

[0007] As a result, there is a need to identify impurities generated in the process of making fluoroolefins, e.g., HFO-1234yf and methods for removing these impurities (undesired components).

SUMMARY

[0008] It has been found that certain impurities can be effectively removed from fluoropropenes, in particular, HFO-1234yf, using an adsorption method in the liquid phase. In particular, the processes disclosed herein are effective to remove such impurities from fluorinated olefins. For example, the methods disclosed herein are effective to remove such undesired components from 2,3,3,3-tetrafluoropropene, wherein the impurities are one or more of 1,1,3,3,3-pentafluoropropene and hexafluoropropene.

[0009] Thus, the present invention provides a process to remove impurities from a fluoroolefin mixture comprising 2,3,3,3-tetrafluoropropene comprising contacting the fluoroolefin mixture with an alumina-based adsorbent to reduce the concentration of one or more impurities chosen from 1,1,3,3,3-pentafluoropropene and hexafluoropropene.

[0010] In certain embodiments of the process of this disclosure, the adsorbent is an alumina adsorbent. In certain embodiments of the process of this disclosure, the adsorbent is an alkali promoted alumina adsorbent, for example alumina loaded with alkali metal oxide, such as Na₂O.

DETAILED DESCRIPTION

[0011] Fluoropropenes have multiple uses in heat transfer fluid applications (e.g., for use in vehicle air conditioning and refrigeration, among others). Purification of the fluoropropene, HFO-1234yf, remains an important step in commercial production of this valued fluid.

Definitions

[0012] The present invention relates to purifying compositions comprising 1234yf and certain impurities. The compounds disclosed herein are defined in Table 1. The

term recited under the column “Compound” may be used herein, when referring to such compounds.

Table 1. Compounds

Compound	Chemical formula	Chemical name
1234yf	$\text{CF}_3\text{CF}=\text{CH}_2$	2,3,3,3-tetrafluoropropene
1225zc	$\text{CF}_3\text{CH}=\text{CF}_2$	1,1,3,3,3-pentafluoropropene
1225ye	E- and/or Z- $\text{CF}_3\text{CF}=\text{CHF}$	E- and/or Z-1,2,3,3,3-pentafluoropropene
1234ze	E- and/or Z- $\text{CF}_3\text{CH}=\text{CHF}$	E- and/or Z-1,3,3,3-tetrafluoropropene
152a	CHF_2CH_3	1,1-difluoroethane
124	CHClFCF_3	1-chloro-1,2,2,2-tetrafluoroethane
HFP	$\text{CF}_3\text{CF}=\text{CF}_2$	hexafluoropropene

[0013] With respect to compounds having unsaturation (double bond), the compound may have “E-” and “Z-” isomers. If neither “E-” nor “Z-” are identified, the compound disclosed may contain one or both isomers. Specific isomers are identified as “E-” or “Z-”. For example, 1225ye may include one or both of E-HFO-1225ye and Z-HFO-1225ye, whereas specific isomers are identified as “E-HFO-1225ye” and “Z-HFO-1225ye”.

[0014] 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 are true (or present).

[0015] As used herein, the term “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 “consists essentially of” or “consisting essentially of” occupies a middle ground between “comprising” and “consisting of”.

[0016] 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.

[0017] 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.

[0018] 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.

[0019] The present invention relates to purifying compositions comprising 2,3,3,3-tetrafluoropropene and certain undesired components or impurities. The terms “undesired component” or “undesired components” are used interchangeably herein with the terms “impurity” or “impurities”. Both have the same meaning for purpose of this invention, that is, an undesired component or an impurity both refer to a compound present in a mixture comprising 2,3,3,3-tetrafluoropropene that has been identified and is at least partially removed, that is, reduced in concentration in the mixture following processes as disclosed herein.

Description

[0020] The present invention relates to purifying compositions comprising 1234yf and certain undesired components.

[0021] The present disclosure provides a process comprising: contacting a mixture comprising 2,3,3,3-tetrafluoropropene and at least one impurity with an alumina-based adsorbent. In certain embodiments, the alumina-based adsorbent is an alumina loaded with alkali metal oxide, such as sodium oxide (Na₂O). In certain embodiments of the process of this disclosure, the alumina-based adsorbent is an alumina not loaded with alkali metal oxide.

[0022] The mixture to be treated typically comprises at least 98% or at least 99% or at least 99.5% or at least 99.8% or at least 99.9% of 1234yf, based on the total weight of said mixture.

[0023] The process of contacting may be performed by simply combining the mixture comprising 1234yf and the at least one undesired component in any suitable vessel at any suitable temperature and pressure, provided however, the contacting is performed at conditions of temperature and pressure to maintain the mixture in the liquid phase. Conveniently the contacting step may be performed at room temperature in a suitable vessel such as a cylinder. Alternatively, the contacting step may be performed by flowing the mixture through an adsorption bed in a continuous process.

[0024] In one embodiment, the mixture to be treated comprises 1234yf and 1225zc. In one embodiment, the mixture to be treated comprises 1234yf and HFP. In one embodiment, the mixture to be treated comprises 1234yf and 1225zc and HFP.

[0025] In certain embodiments, the process comprises contacting a mixture comprising 1234yf and at least one impurity chosen from 1225zc and HFP with an adsorbent, wherein the adsorbent comprises an alumina-based adsorbent.

[0026] In one embodiment, the process comprises contacting a mixture comprising 1234yf and at least one impurity chosen from 1225zc and HFP with an alumina-based adsorbent, wherein the at least one impurity is 1225zc, wherein the

alumina-based adsorbent is promoted with an alkali metal oxide, or alternatively, the alumina-based adsorbent is not promoted with an alkali metal oxide.

[0027] In one embodiment, the process comprises contacting a mixture comprising 1234yf and at least one impurity chosen from 1225zc and HFP with an alumina-based adsorbent, wherein the at least one impurity is HFP, wherein the alumina-based adsorbent is promoted with an alkali metal oxide, or alternatively, the alumina-based adsorbent is not promoted with an alkali metal oxide.

[0028] In one embodiment, the process comprises contacting a mixture comprising 1234yf and at least one impurity chosen from 1225zc and HFP with an alumina-based adsorbent, wherein the at least one impurity is 1225zc and HFP, wherein the alumina-based adsorbent is promoted with an alkali metal oxide, or alternatively, the alumina-based adsorbent is not promoted with an alkali metal oxide.

[0029] The alkali metal oxide can be, for example, sodium oxide.

[0030] The amount of adsorbent can be any amount suitable to achieve the desired reduction in the impurities present in the mixture comprising 1234yf.

[0031] The ratio of the mixture comprising 1234yf and at least one impurity chosen from 1225zc and HFP, to the adsorbent is typically in the range of 50:1 to 1:1, preferably 30:1 to 2:1, more preferably 20:1 to 3:1.

[0032] The temperature may range from -30°C to 50°C, preferably -20°C to 40°C, with pressure at the vapor pressure of 1234yf or pressure above such vapor pressure at the selected temperature to maintain a liquid phase.

[0033] Removing impurities from a mixture where the mixture has a purity of at least 98% or at least 99% or at least 99.5% or at least 99.8% or at least 99.9% of 1234yf can be particularly difficult using distillation methods.

[0034] In particular, with respect to certain impurities such as 1225zc and HFP, it is desirable to have very low concentrations. In certain embodiments, the process provides a product comprising 1234yf and less than 0.02% of 1225zc. In certain embodiments, the process provides a product comprising 1234yf and less than

0.01% or less than 0.005% or non-detectable concentration (less than 0.1 ppm) of HFP.

[0035] In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.02% or less of 1225zc. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.015% or less of 1225zc. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.01% or less of 1225zc. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.00001% or less of 1225zc (0.1 ppm, not detectable, "ND").

[0036] In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.01% or less of HFP. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.005% or less of HFP. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.00001% or less of HFP (0.1 ppm, not detectable, "ND").

EXAMPLES

[0037] General Procedure for Purification. 50 g of 1234yf was mixed with a 5 g pre-dried adsorbent at room temperature in a pre-dried cylinder. The mixture was shaken for a few minutes and then held at room temperature for 2 hours, then the liquid phase of the 1234yf mixture was analyzed by GC-MS-FID. At 24 hours after mixing, the liquid phase of 1234yf was analyzed by GC-MS-FID again to check the composition change. The drying conditions for each adsorbent are listed in Table 2.

Table 2

Adsorbent	Drying conditions
Johnson Matthey Puraspec™ 6259 zeolite	dried at 90°C for 8 hrs. then ramped to 200°C and hold at 200°C for 2 hours in He before use
Johnson Matthey Puraspec™ 3110 alkali promoted alumina adsorbent	used as received

Adsorbent	Drying conditions
BASF CL750 Al ₂ O ₃ based adsorbent	dried at 90°C for 8 hrs. then ramped to 200°C and held at 200°C for 2 hours in He before use
BASF HF-200 Al ₂ O ₃	dried at 250°C for 4 hrs. in He , then cooled down to room temperature with He purge
BASF HF-200XP Al ₂ O ₃	dried at 250°C for 4 hrs. in He , then cooled down to room temperature with He purge
BASF 4126 Al ₂ O ₃	dried at 250°C for 4 hrs. then cooled down to room temperature under He before use
BASF 3954 Al ₂ O ₃	dried at 250°C for 4 hrs. then cooled down to room temperature under He before use
Molecular sieve 13X	dried at 320°C with He purge for 16 hrs., then cooled down to room temperature with He purge

Example 1. 1225zc and HFP removal by Al₂O₃ based adsorbents.

[0038] The starting material composition is provided below, with each of Tables 2a, 2b, 2c, 2d, 2e, and 2f. The results of analyses before and after the tests with Al₂O₃ based adsorbents are summarized in Tables 2a, 2b, 2c, 2d, 2e, and 2f. The 1225zc and HFP level in 1234yf was reduced significantly with these Al₂O₃ based adsorbents.

Table 2a

	Starting material	BASF AI3954 Al ₂ O ₃	
		2hr	24hr
HFP	0.0116%	0.0076%	0.0016%
1234yf	99.9357%	99.9444%	99.9575%
1225zc	0.0201%	0.0174%	0.0086%
Z-1225ye	0.0113%	0.0125%	0.0124%
E-1234ze	0.0144%	0.0155%	0.0156%
152a	0.0029%	0.0027%	0.0025%
124	0.0017%	0.0017%	0.0018%

Table 2b

	Starting material	BASF Al4126 Al ₂ O ₃	
		2hr	24hr
HFP	0.0116%	0.0115%	0.0074%
1234yf	99.9357%	99.9351%	99.9412%
1225zc	0.0201%	0.0207%	0.0179%
Z-1225ye	0.0113%	0.0115%	0.0118%
E-1234ze	0.0144%	0.0146%	0.0147%
152a	0.0029%	0.0027%	0.0027%
124	0.0017%	0.0019%	0.0020%

Table 2c

	Starting material	JM 3110 Na ₂ O/ Al ₂ O ₃	
		2hr	24hr
HFP	0.0116%	0.0034%	ND
1234yf	99.9357%	99.9542%	99.9672%
1225zc	0.0201%	0.0106%	ND
Z-1225ye	0.0113%	0.0109%	0.0113%
E-1234ze	0.0144%	0.0140%	0.0147%
152a	0.0029%	0.0029%	0.0030%
124	0.0017%	0.0016%	0.0018%

Table 2d

	Starting material	BASF CL750 Al ₂ O ₃	
		2hr	24 hr
HFP	0.0116%	0.0033%	ND
1234yf	99.9357%	99.9500%	99.9655%
1225zc	0.0201%	0.0105%	ND
Z-1225ye	0.0113%	0.0118%	0.0116%
E-1234ze	0.0144%	0.0149%	0.0149%
152a	0.0029%	0.0027%	0.0027%
124	0.0017%	0.0017%	0.0019%

Table 2e

	Starting material	BASF HF-200 Al ₂ O ₃	
		2hr	24 hr
HFP	0.0116%	0.0087%	0.0022%
1234yf	99.9357%	99.9344%	99.9533%
1225zc	0.0201%	0.0186%	0.0113%
Z-1225ye	0.0113%	0.0117%	0.0116%
E-1234ze	0.0144%	0.0149%	0.0145%
152a	0.0029%	0.0028%	0.0027%
124	0.0017%	0.0018%	0.0018%

Table 2f

	Starting material	BASF HF-200XP Al ₂ O ₃	
		2hr	24hr
HFP	0.0116%	0.0116%	0.0093%
1234yf	99.9357%	99.9337%	99.9421%
1225zc	0.0201%	0.0207%	0.0173%
Z-1225ye	0.0113%	0.0116%	0.0121%
E-1234ze	0.0144%	0.0152%	0.0148%
152a	0.0029%	0.0028%	0.0028%
124	0.0017%	0.0020%	0.0016%

Example 2. Comparison : Treatment of 1234yf containing 1225zc and HFP with zeolite-based adsorbents.

[0039] The starting material composition is provided below, with each of Tables 3a and 3b. The results of analyses before and after the tests with zeolite-based adsorbents are summarized in Tables 3a and 3b. The zeolite-based adsorbents did not reduce the concentrations of 1225zc and HFP as did the alumina-based adsorbents.

Table 3a

	Starting material	Zeolite 13X		
		2hr	24hr	7 days
HFP	0.0116%	0.0118%	0.0114%	0.0114%
1234yf	99.9357%	99.9365%	99.9364%	99.9364%
1225zc	0.0201%	0.0208%	0.0206%	0.0206%
Z-1225ye	0.0113%	0.0116%	0.0116%	0.0116%
E-1234ze	0.0144%	0.0143%	0.0143%	0.0143%
152a	0.0029%	0.0012%	0.0011%	0.0011%
124	0.0017%	0.0017%	0.0016%	0.0016%

Table 3b

	Starting material	JM6259 Puraspec™ zeolite	
		2hr	24hr
HFP	0.0116%	0.0118%	0.0121%
1234yf	99.9357%	99.9353%	99.9370%
1225zc	0.0201%	0.0206%	0.0196%
Z-1225ye	0.0113%	0.0117%	0.0115%
E-1234ze	0.0144%	0.0143%	0.0141%
152a	0.0029%	0.0011%	0.0011%
124	0.0017%	0.0015%	0.0017%

CLAIMS

What is claimed is:

1. A process for removing an impurity from a fluoroolefin mixture comprising 2,3,3,3-tetrafluoropropene and at least one impurity wherein the process comprises contacting the fluoroolefin mixture with an alumina-based adsorbent in the liquid phase to reduce the concentration of the at least one impurity chosen from 1,1,3,3,3-pentafluoropropene and hexafluoropropene.
2. The process of claim 1 wherein the alumina-based adsorbent is an Al_2O_3 adsorbent.
3. The process of claim 1 wherein the alumina-based adsorbent is an alkali promoted alumina adsorbent.
4. The process of claim 3 wherein the alumina-based adsorbent is an alumina loaded with alkali metal oxide.
5. The process of claim 4 wherein the alkali metal oxide is sodium oxide.
6. The process of claim 1 wherein the alumina-based adsorbent is an alumina not loaded with alkali metal oxide.
7. The process of any of claims 1-6 wherein the one or more of impurities comprises 1,1,3,3,3-pentafluoropropene.
8. The process of any of claims 1-6 wherein the one or more of impurities comprises hexafluoropropene.
9. The process of any of claims 1-6, wherein the one or more of impurities comprises 1,3,3,3-pentafluoropropene and hexafluoropropene.
10. The process of claim 3 wherein the one or more of impurities comprises 1,1,3,3,3-pentafluoropropene.
11. The process of claim 3 wherein the one or more of impurities comprises hexafluoropropene.
12. The process of claim 3 wherein the one or more of impurities comprises 1,1,3,3,3-pentafluoropropene and hexafluoropropene.

13. The process of claim 4 wherein the one or more of impurities comprises 1,1,3,3,3-pentafluoropropene.
14. The process of claim 4 wherein the one or more of impurities comprises hexafluoropropene.
15. The process of claim 4 wherein the one or more of impurities comprises 1,1,3,3,3-pentafluoropropene and hexafluoropropene.
16. The process of claim 5 wherein the one or more of impurities comprises 1,1,3,3,3-pentafluoropropene.
17. The process of claim 5 wherein the one or more of impurities comprises hexafluoropropene.
18. The process of claim 5 wherein the one or more of impurities comprises 1,1,3,3,3-pentafluoropropene and hexafluoropropene.
19. The process of claim 6 wherein the one or more of impurities comprises 1,1,3,3,3-pentafluoropropene.
20. The process of claim 6 wherein the one or more of impurities comprises hexafluoropropene.
21. The process of claim 6 wherein the one or more of impurities comprises 1,1,3,3,3-pentafluoropropene and hexafluoropropene.
22. The process of any of claims 1-21 wherein the amount of 2,3,3,3-tetrafluoropropene in said mixture is at least 98 wt % based on the total weight of said mixture.
23. A composition comprising at least 99.9% of 2,3,3,3-tetrafluoropropene and 0.02% or less of 1,1,3,3,3-pentafluoropropene.
24. The composition of claim 23, wherein the composition comprises 0.015% or less of 1,1,3,3,3-pentafluoropropene.
25. The composition of claim 23, wherein the composition comprises 0.00001% or less of 1,1,3,3,3-pentafluoropropene.
26. A composition comprising at least 99.9% of 2,3,3,3-tetrafluoropropene and 0.01% or less of hexafluoropropene.

27. The composition of claim 26, wherein the composition comprises 0.005% or less of hexafluoropropene.
28. The composition of claim 26, wherein the composition comprises 0.00001% or less of hexafluoropropene.