

TITLE**PURIFICATION OF FLUORINATED PROPENES BY LIQUID PHASE
ADSORPTION****FIELD**

[0001] This invention relates to processes for purifying fluoropropenes by reducing concentration of additional components in mixtures comprising fluorinated propenes.

BACKGROUND

[0002] Certain fluoroolefins, such as fluoropropenes, including 2,3,3,3-tetrafluoropropene (HFO-1234yf) and 1,3,3,3-tetrafluoropropene (HFO-1234ze) are known to be effective in applications as refrigerants, heat transfer media, 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. In addition, 3,3,3-trifluoropropene (HFO-1243zf) is a valuable intermediate in manufacture of other hydrofluoroolefins.

[0003] Unlike most chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), most fluoroolefins pose no threat to the ozone layer. HFO-1234yf, HFO-1234ze and HFO-1243zf have also been found to be low global warming compounds with low toxicity. Accordingly, compositions containing these fluoroolefins can meet increasingly stringent requirements and 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 additional components as by-products, which are difficult to remove.

[0006] A common method for removing additional components is via distillation. However, this method is difficult if the boiling points of the desired product and

additional component 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 additional components remain.

[0007] As a result, there is a need to identify additional components generated in the process of making fluoropropenes and methods for removing these additional components.

SUMMARY

[0008] It has been found that certain additional components can be effectively removed from fluoropropenes using an adsorption method and that adsorption performed in liquid phase process is more efficient when compared to previously disclosed methods performed in the vapor phase. In particular, the methods disclosed herein are effective to remove such additional components from fluorinated olefins. For example, the methods disclosed herein are effective to remove such components from 2,3,3,3-tetrafluoropropene, 1,3,3,3-tetrafluoropropene (Z- and E-isomers) and 3,3,3-trifluoropropene.

[0009] In one embodiment, the present disclosure provides a process to remove one or more additional components from a mixture comprising a fluoropropene, wherein the process comprises contacting the mixture in the liquid phase with molecular sieves chosen from one or more of 4A, 5A or 13X. The additional component comprises one or more of HF, HCl, vinyl chloride, 1131a, 245cb and 152a. The fluoropropene comprises 3,3,3-trifluoropropene, E-1,3,3,3-tetrafluoropropene, Z-1,3,3,3-tetrafluoropropene, 2,3,3,3-tetrafluoropropene, or a combination thereof.

[0010] In one embodiment, the present disclosure provides a process to remove vinyl chloride (1140) from a mixture comprising vinyl chloride and at least one fluoropropene, wherein the process comprises treating the mixture in the liquid phase with an adsorbent. The fluoropropene may be chosen from one or more of 3,3,3-trifluoropropene, E-1,3,3,3-tetrafluoropropene, Z-1,3,3,3-tetrafluoropropene, or 2,3,3,3-tetrafluoropropene.

[0011] In the process of this disclosure, the adsorbent is a molecular sieve chosen from 4A, 5A and 13X, or a combination of two or more thereof.

[0012] In the process of this disclosure, the purification process is done in a liquid phase with a molecular sieve chosen from 4A, 5A and 13X, or a combination of two or more thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] **Figure 1** and **Figure 2** show the uptake rate curves for Examples 1-5 and Examples 6-10, respectively, as a function of time.

[0014] **Figure 3** shows the liquid phase VCM loading isotherms after 24 hrs for 4A and 5A sieves, based on Tables 1 and 2.

[0015] **Figure 4** shows the uptake rate curves for Examples 1-5 and Examples 6-10 after 2 hours equilibration time as a function of dosage.

[0016] **Figure 5** shows the uptake rate curves for Examples 1-5 and Examples 6-10 after 24 hours equilibration time as a function of dosage.

[0017] **Figure 6** shows the VCM breakthrough curves for Example 11 using fresh and regenerated 4A molecular sieves.

[0018] **Figure 7** shows an enhanced version of the VCM breakthrough curves for Example 11, with extrapolation to show when the outlet concentration of VCM reaches 50% of the inlet.

[0019] **Figure 8** shows the VCM and 1131a breakthrough curves for Example 12 using fresh and regenerated 5A molecular sieves.

[0020] **Figure 9** shows a comparison of Examples 11 and 12.

DESCRIPTION

[0021] Fluoropropenes have multiple uses in heat transfer fluid applications (e.g., for use in vehicle air conditioning and refrigeration, among others). Purification of fluoropropenes remains an important step in commercial production of these valued fluids.

Definitions and Abbreviations

[0022] 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).

[0023] 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”.

[0024] 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.

[0025] 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.

[0026] 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.

[0027] The terms “additional component” or “additional components”, for purpose of this invention, refer to a compound present in a mixture comprising a fluoropropene that has been identified and is at least partially removed, that is, reduced in concentration in the mixture following processes as disclosed herein.

Description

[0028] This invention relates to a process for removing additional component(s) from fluoropropenes, which is performed in the liquid phase. Surprisingly, when performed in the liquid phase, improved removal of the additional component(s) is achieved relative to a vapor phase process. Such additional component(s) are produced in processes to prepare the fluoropropene.

[0029] This invention provides a process for removing one or more additional components from a mixture comprising a fluoropropene, wherein the process comprises treating the mixture in the liquid phase with molecular sieves chosen from one or more of 4A, 5A or 13X.

[0030] In this invention, the fluoropropene comprises 3,3,3-trifluoropropene, E-1,3,3,3-tetrafluoropropene, Z-1,3,3,3-tetrafluoropropene, 2,3,3,3-tetrafluoropropene, or a combination thereof.

[0031] In one embodiment, the present disclosure provides a process to remove one or more additional components from a mixture comprising a fluoropropene, wherein the process comprises contacting the mixture in the liquid phase with molecular sieves chosen from one or more of 4A, 5A or 13X. The additional component comprises one or more of HF, HCl, vinyl chloride, 1131a, 245cb and 152a. The fluoropropene comprises 3,3,3-trifluoropropene, E-1,3,3,3-tetrafluoropropene, Z-1,3,3,3-tetrafluoropropene, 2,3,3,3-tetrafluoropropene, or a combination thereof.

[0032] The mixture comprising a fluoropropene further comprises an additional component selected from the group consisting of vinyl chloride (1140 or vinyl chloride monomer, referred to herein as "VCM"), HF, HCl, 1-chloro-1-fluoroethylene (1131a), 1,1,1,2,2-pentafluoropropane (245cb) and 1,1-difluoroethane (152a). In some embodiments of this invention, the mixture comprises the fluoropropene and VCM. In some embodiments of this invention, the mixture comprises the fluoropropene and 245cb. In some embodiments of this invention, the mixture comprises the fluoropropene and 152a. In some embodiments of this invention, the mixture comprises VCM, 245cb and 152a.

[0033] In certain embodiments, the mixture comprises 1234yf and VCM. In some embodiments of this invention, the mixture comprises 1234yf and 245cb. In some embodiments of this invention, the mixture comprises 1234yf and 152a. In some embodiments of this invention, the mixture comprises 1234yf, VCM, 245cb and 152a.

[0034] In certain embodiments, the mixture comprises E-1234ze and VCM. In some embodiments of this invention, the mixture comprises E-1234ze and 245cb. In some embodiments of this invention, the mixture comprises E-1234ze and 152a. In some embodiments of this invention, the mixture comprises E-1234ze, VCM, 245cb and 152a.

[0035] In certain embodiments, the mixture comprises Z-1234ze and VCM. In some embodiments of this invention, the mixture comprises Z-1234ze and 245cb. In some embodiments of this invention, the mixture comprises Z-1234ze and 152a. In some embodiments of this invention, the mixture comprises Z-1234ze, VCM, 245cb and 152a.

[0036] In certain embodiments, the mixture comprises 1243zf and VCM. In some embodiments of this invention, the mixture comprises 1243zf and 245cb. In some embodiments of this invention, the mixture comprises 1243zf and 152a. In some embodiments of this invention, the mixture comprises 1243zf, VCM, 245cb and 152a.

[0037] In some embodiments of this invention, the amount of the fluoropropene in the mixture is at least 50 wt % based on the total weight of the mixture. In some embodiments of this invention, the amount of the fluoropropene in the mixture is at

least 70 wt % based on the total weight of the mixture. In some embodiments of this invention, the amount of the fluoropropene in the mixture is at least 90 wt % based on the total weight of the mixture.

[0038] In some embodiments of this invention, the fluoropropene is 1234yf, the one or more additional component comprises VCM, 245cb or 152a and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is 1234yf, the one or more additional component comprises VCM, 245cb or 152a and the adsorbent is 5A molecular sieve. In some embodiments of this invention, the fluoropropene is 1234yf, the one or more additional component comprises VCM, 245cb or 152a and the adsorbent is 13X molecular sieve.

[0039] In some embodiments of this invention, the fluoropropene is 1234yf, the one or more additional component comprises VCM and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is 1234yf, the one or more additional component comprises VCM and the adsorbent is 5A molecular sieve. In some embodiments of this invention, the fluoropropene is 1234yf, the one or more additional component comprises VCM and the adsorbent is 13X molecular sieve.

[0040] In some embodiments of this invention, the fluoropropene is E-1234ze, the one or more additional component comprises VCM, 245cb or 152a and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is E-1234ze, the one or more additional component comprises VCM, 245cb or 152a and the adsorbent is 5A molecular sieve. In some embodiments of this invention, the fluoropropene is E-1234ze, the one or more additional component comprises VCM, 245cb or 152a and the adsorbent is 13X molecular sieve.

[0041] In some embodiments of this invention, the fluoropropene is E-1234ze, the one or more additional component comprises VCM and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is E-1234ze, the one or more additional component comprises VCM and the adsorbent is 5A molecular sieve. In some embodiments of this invention, the fluoropropene is E-1234ze, the one or more additional component comprises VCM and the adsorbent is 13X molecular sieve.

[0042] In some embodiments of this invention, the fluoropropene is Z-1234ze, the one or more additional component comprises VCM, 245cb or 152a and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is Z-1234ze, the one or more additional component comprises VCM, 245cb or 152a and the adsorbent is 5A molecular sieve. In some embodiments of this invention, the fluoropropene is Z-1234ze, the one or more additional component comprises VCM, 245cb or 152a and the adsorbent is 13X molecular sieve.

[0043] In some embodiments of this invention, the fluoropropene is Z-1234ze, the one or more additional component comprises VCM and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is Z-1234ze, the one or more additional component comprises VCM and the adsorbent is 5A molecular sieve. In some embodiments of this invention, the fluoropropene is Z-1234ze, the one or more additional component comprises VCM and the adsorbent is 13X molecular sieve.

[0044] In some embodiments of this invention, the fluoropropene is 1243zf, the one or more additional component comprises VCM and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is 1243zf, the one or more additional component comprises VCM and the adsorbent is 5A molecular sieve. In some embodiments of this invention, the fluoropropene is 1243zf, the one or more additional component comprises VCM and the adsorbent is 13X molecular sieve.

[0045] In some embodiments of this invention, the fluoropropene is 1234yf, the one or more additional component comprises VCM and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is 1234yf, the one or more additional component comprises VCM and the adsorbent is 5A molecular sieve. In some embodiments of this invention, the fluoropropene is 1234yf, the one or more additional component comprises VCM and the adsorbent is 13X molecular sieve.

[0046] In some embodiments of this invention, the fluoropropene is E-1234ze, the one or more additional component comprises VCM and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is E-1234ze, the one or more additional component comprises VCM and the adsorbent is

5A molecular sieve. In some embodiments of this invention, the fluoropropene is E-1234ze, the one or more additional component comprises VCM and the adsorbent is 13X molecular sieve.

[0047] In some embodiments of this invention, the fluoropropene is Z-1234ze, the one or more additional component comprises VCM and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is Z-1234ze, the one or more additional component comprises VCM and the adsorbent is 5A molecular sieve. In some embodiments of this invention, the fluoropropene is Z-1234ze, the one or more additional component comprises VCM and the adsorbent is 13X molecular sieve.

[0048] In some embodiments of this invention, the fluoropropene is 1243zf, the one or more additional component comprises VCM and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is 1243zf, the one or more additional component comprises VCM and the adsorbent is 5A molecular sieve. In some embodiments of this invention, the fluoropropene is 1243zf, the one or more additional component comprises VCM and the adsorbent is 13X molecular sieve.

[0049] In some embodiments of this invention, the fluoropropene is 1243zf, the one or more additional component comprises VCM and the adsorbent is 4A molecular sieve. In some embodiments of this invention, the fluoropropene is 1243zf, the one or more additional component comprises VCM and the adsorbent is 5A molecular sieve. In some embodiments of this invention, the fluoropropene is 1243zf, the one or more additional component comprises VCM and the adsorbent is 13X molecular sieve.

[0050] During the process of the present invention, the adsorbent may become saturated with the one or more additional components, at which point the adsorbent will no longer effectively remove such components from the fluoropropene containing mixture. When saturation occurs, the adsorbent must be either replaced or regenerated. Saturation may be determined, for example, by periodically analyzing the product produced from the process disclosed herein. For example, the product may show increases in the concentration of the one or more additional components over time until the concentration reaches a set limit.

[0051] After reaching its saturation, the saturated adsorbent may be regenerated and then may be re-used. In an embodiment, the saturated adsorbent is regenerated by contacting the saturated adsorbent with an inert gas. An inert gas is any gas that isn't reactive with the adsorbent or compounds in the process and doesn't contain the additional component that the adsorbent is saturated with. The inert gas can be any suitable inert gas, including, but not limited to, N₂, Ar, He, and various combinations of these gases. The inert gas is preferably N₂. The contacting step may be performed at any suitable conditions, which include temperature of 150-325°C. The contacting step may be performed at subatmospheric pressure (under vacuum), at atmospheric pressure or at super atmospheric pressure, such as at a pressure up to about 50 psig.

[0052] In one embodiment, the process disclosed herein comprises a process to remove one or more additional component from a mixture comprising a fluoropropene, wherein the process comprises contacting the mixture in the liquid phase with an adsorbent chosen from one or more of 4A, 5A or 13X molecular sieves; saturating the adsorbent with at least one additional component, regenerating the saturated adsorbent by contacting with an inert gas. In one embodiment, the step of contacting with inert gas is performed at a temperature of about 150°C to about 325°C. In one embodiment, the step of contacting with inert gas is performed at a temperature of about 150°C to about 325°C and at subatmospheric pressure. In one embodiment, the step of contacting with inert gas is performed at a temperature of about 150°C to about 325°C and at atmospheric pressure. In one embodiment, the step of contacting with inert gas is performed at a temperature of about 150°C to about 325°C and at superatmospheric pressure, wherein superatmospheric pressure ranges from above atmospheric pressure to about 50 psig.

[0053] In one embodiment, the fluoroolefin is 1234yf and 1234yf is prepared by dehydrochlorination of 2-chloro-1,1,1,2-tetrafluoropropane (244bb), for example as disclosed in US Patent No. 9,493,384.

[0054] In one embodiment, the process of this invention comprises: (a) dehydrochlorinating 2-chloro-1,1,1,2-tetrafluoropropane to form a mixture comprising 1234yf and one or more additional components; (b) collect 1234yf product optionally

after one or more purification steps; (c) contacting the 1234yf product in step (b) with an adsorbent to reduce the concentration of said one or more additional components; and (d) recovering 1234yf having a reduced concentration of said one or more additional components.

[0055] The conditions for the contacting step are such that the fluoropropene is maintained in the liquid state. The vapor pressures are known for the fluoropropenes 1234yf, E-1234ze, Z-1234ze and 1243zf and those skilled in the art will appreciate conditions of temperature and pressure to maintain the fluoropropene in the liquid state.

[0056] In one embodiment, the molecular sieves are regenerated after the molecular sieves become saturated with the additional components.

[0057] This invention can be practiced with the molecular sieve contained in a packed bed and fluoropropene flow through the bed which additional components in the fluoropropene stream are absorbed and removed from fluoropropene stream. Variations to a packed bed are known in the art and are contemplated herein.

[0058] It is noted here, in case of vapor phase adsorption, the fluoropropene has to be vaporized into a gas and then gas flow through the adsorption bed and then re-condense back to liquid to collect. Both vaporization and condensation process require more equipment and utility.

[0059] In the case of liquid phase adsorption, when performed as a continuous process, the fluoropropene mixture flows through an adsorption bed as liquid and is collected as liquid. Thus, vaporization and re-condensation processes are not needed. The fluoropropene mixture may optionally be condensed before treatment by this invention, for example if it comprises the effluent from a vapor phase reactor and may be vaporized after treatment.

[0060] Liquid phase adsorption has an advantage over vapor phase adsorption as liquid phase adsorption can be readily performed as either a continuous or batch process, as well as using less equipment and utilities. Vapor phase adsorption is generally limited to a continuous process, as vapor phase adsorption would be difficult to perform as a batch process.

[0061] This invention can also be practiced in a batch process which fluoropropene is mixed with adsorbents with or without an agitation for a length of time to remove the additional components from fluoropropene.

[0062] The liquid phase adsorption in this invention has a surprising advantage over vapor phase adsorption that the same amount of adsorbent in liquid phase adsorption absorbs more far more of the additional components and is more efficient than a gas phase adsorption process.

[0063] Removing additional components from a mixture comprising a fluoropropene can be particularly difficult using distillation methods. In particular, with respect to certain components such as VCM, it is desirable to have very low concentrations. In certain embodiments, the process provides a product comprising a fluoropropene and less than 0.001% or less than 0.0005% or less than 0.0001% or less than 0.00005% or less than 0.00001% or non-detectable concentration (less than 0.1 ppm) of VCM. In one embodiment, the process provides a product comprising 1234yf and less than 0.001% or less than 0.0005% or less than 0.0001% or less than 0.00005% or less than 0.00001% or non-detectable concentration (less than 0.1 ppm) of VCM. In one embodiment, the process provides a product comprising E-1234ze and less than 0.001% or less than 0.0005% or less than 0.0001% or less than 0.00005% or less than 0.00001% or non-detectable concentration (less than 0.1 ppm) of VCM. In one embodiment, the process provides a product comprising Z-1234ze and less than 0.001% or less than 0.0005% or less than 0.0001% or less than 0.00005% or less than 0.00001% or non-detectable concentration (less than 0.1 ppm) of VCM. In one embodiment, the process provides a product comprising 1243zf and less than 0.001% or less than 0.0005% or less than 0.0001% or less than 0.00005% or less than 0.00001% or non-detectable concentration (less than 0.1 ppm) of VCM.

[0064] In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.001% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.0005% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.0001% or less of VCM. In another embodiment of this invention is provided a composition comprising

at least 99.9% of 1234yf and 0.00001% or less (non-detectable concentration of less than 0.1ppm) of VCM.

[0065] In another embodiment of this invention is provided a composition comprising at least 99.9% of E-1234ze and 0.001% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of E-1234ze and 0.0005% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of E-1234ze and 0.0001% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of E-1234ze and 0.00001% or less (non-detectable concentration of less than 0.1ppm) of VCM.

[0066] In another embodiment of this invention is provided a composition comprising at least 99.9% of Z-1234ze and 0.001% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of Z-1234ze and 0.0005% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of Z-1234ze and 0.0001% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of Z-1234ze and 0.00001% or less (non-detectable concentration of less than 0.1ppm) of VCM.

[0067] In another embodiment of this invention is provided a composition comprising at least 99.9% of 1243zf and 0.001% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1243zf and 0.0005% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1243zf and 0.0001% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1243zf and 0.00001% or less (non-detectable concentration of less than 0.1ppm) of VCM.

[0068] In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.001% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.0005% or less of VCM. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.0001% or less of VCM. In another embodiment of this invention is provided a composition comprising

at least 99.9% of 1234yf and 0.00001% or less (non-detectable concentration of less than 0.1ppm) of VCM.

[0069] The process of this invention is used to provide compositions as described wherein the compositions of purified 1234yf have improved stability. For example, removing VCM provides greater stability as VCM can be reactive forming oligomers under storage and/or use conditions of the compositions comprising 1234yf.

[0070] In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.003% or less of 1131a. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.0015% or less of 1131a. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.0005% or less of 1131a. In another embodiment of this invention is provided a composition comprising at least 99.9% of 1234yf and 0.00001% or less (non-detectable concentration of less than 0.1ppm) of 1131a.

[0071] The compositions as disclosed herein are stabilized by reducing and/or removing additional components.

[0072] The present invention also provides a process to prepare a purified and stabilized fluoropropene comprising (a) contacting a mixture comprising a fluoropropene and one or more additional components, in the liquid phase with molecular sieves chosen from one or more of 4A, 5A or 13X; and (b) adding an inhibitor comprising at least one member selected from the group consisting of limonene, α -terpinene, α -tocopherol, butylated hydroxytoluene, 4-methoxyphenol, benzene-1,4-diol to the composition obtained in step (a). In one embodiment, the limonene is d-limonene.

[0073] In certain embodiments, any of the compositions described hereinabove may be further stabilized by adding an inhibitor comprising at least one member selected from the group consisting of limonene, α -terpinene, α -tocopherol, butylated hydroxytoluene, 4-methoxyphenol, benzene-1,4-diol.

[0074] In certain embodiments, any of the compositions described hereinabove may be further stabilized by adding an inhibitor comprising at least one member

selected from the group consisting of limonene, α -terpinene, α -tocopherol, butylated hydroxytoluene, 4-methoxyphenol, benzene-1,4-diol. Optionally, the composition comprises at least one anti-oxidant. The anti-oxidant may be selected from the group consisting of butylated hydroxytoluene, butylated hydroxyanisole, tertiary-butylhydroquinone, gallate, 2-phenyl-2-propanol, 1-(2,4,5-trihydroxyphenyl)-1-butanone, bisphenol methane derivatives, 2,2'-methylene bis (4-methyl-6-*t*-butyl phenol), among other phenolics, and combinations thereof.

[0075] In certain embodiments, any of the compositions described hereinabove are further stabilized by adding at least one inhibitor comprising limonene or α -terpinene. In certain embodiments, any of the compositions described hereinabove are further stabilized by adding at least one inhibitor wherein the at least one inhibitor comprises d-limonene.

[0076] In any of the compositions described hereinabove, further stabilized by adding at least one inhibitor, the at least one inhibitor is present in an amount of about 30 to about 3,000 ppm.

[0077] 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.

[0078] The following Examples are provided to illustrate certain aspects of the invention and shall not limit the scope of the appended claims.

EXAMPLES

Examples 1-10: Liquid phase adsorption of VCM from 1234yf using 4A and 5A Molecular Sieves

[0079] A mixture of 1234yf with 94.67 ppmw VCM was prepared and used for Examples 1-10. Carefully weighed dosages of dry, activated 5A (Examples 1-5) and

4A (Examples 6-10) molecular sieves, “mol sieve”, (each, 1/16”, 0.16 cm) were charged into cylinders and then each cylinder was evacuated under vacuum, to which 50 g of the 1234yf/VCM mixture was added. The concentration of VCM in the starting material (at 0 hour) was 95.39 ppmw. The cylinders were then placed on an orbital shaker to effect mixing of the contents, and small samples of liquid were taken by gas-tight syringe and analyzed by GC-FID periodically to following the reduction of VCM over time. The results are provided in Table 1 (5A Molecular Sieves) and Table 2 (4A Molecular Sieves). Table 1 provides impact of 5A sieves over the course of time from 0 to 144 hours. Table 2 provides the impact of 4A sieves over the course of time from 0 to 24 hours and 5-11 days.

Table 1

Ex.	1234yf/VCM mixture, g	5A mol sieve, g	1234yf/mol sieve wt ratio	VCM (ppm) GC-FID area%			
				2 hr.	24 hr.	116 hr.	144 hr.
1	50	1.67	29.9	21.27	1.64	0	
2	50	0.67	74.6	50.31	4.09	1.27	
3	50	0.33	151.5	74.63	16.33	2.61	
4	50	0.17	294.1	84.75	24.96		13.81
5	50	0.083	602.4	89.75	53.6		19.56

Table 2

Ex.	1234yf/VCM mixture, g	4A mol sieve, g	1234yf/mol sieve wt ratio	VCM ppm GC-FID area%					
				2 hr.	3 hr.	24 hr.	5 day	7 days	11 days
6	50	1.67	29.9	6.74			1.3		
7	50	0.67	74.6	20.31			3.2		
8	50	0.33	151.5	48.34		7.32		16.63	
9	50	0.17	294.1	59.32		17.52			
10	50	0.083	602.4		76.46	38.32	52.26		88

[0080] The uptake rate curves for Examples 1-5 are shown in Figure 1. The uptake rate curves for Examples 6-10 are shown in Figure 2. As can be seen from Figures 1 and 2, initial VCM uptake was more rapid on the 4A sieves than on the 5A sieves, but the VCM concentrations began to rise on the 4A sieves after extended exposure times as can be seen when comparing the uptake rate curves in Figure 2 as compared to Figure 1.

[0081] Without wishing to be bound by theory, an explanation for the differences between results from the 4A sieves and the 5A sieves is that the smaller aperture in the 4A sieves (~4 Angstroms) significantly reduces the uptake rate of co-adsorbed 1234yf. The faster diffusing VCM molecule quickly enters the sorption cages, but over time, the more slowly diffusing 1234yf slowly catches up and ultimately is able to displace some of the VCM that adsorbed initially.

[0082] The liquid phase VCM loading isotherms after 24 hrs for 4A and 5A sieves are shown in Figure 3 (data in Tables 1 and 2). The loading at a VCM concentration of 8.8 ppmw (indicated by dashed line on Figure 3) was 15 mg/g on 4A sieves and 10 mg/g on 5A sieves.

[0083] The effects of both equilibrium limitations and kinetics combine to produce a VCM breakthrough curve specific for the operating conditions as can be seen in Figures 4 and 5. In the case of 4A sieves, for short time scales, such as after 2 hours (shown in uptake curve of Figure 4), uptake of VCM is superior to that of 5A sieves. In contrast, over long periods of time, such as after 24 hours, the kinetic advantage of 4A sieves diminishes as the hindered 1234yf co-adsorption catches up and displaces the VCM as shown in the uptake curve of Figure 5. Comparing the uptake curves for 4A and 5A at 2 hrs vs 24 hrs in Figures 4 and 5, respectively, clearly shows that 4A sieves are advantageous at shorter contact times.

Examples 11-12: Vapor phase adsorption of VCM from 1234yf using 4A and 5A Molecular Sieves

[0084] The removal of VCM from 1234yf vapor was explored using a column packed with 1/16" sieves. Separate runs for 4A and 5A sieves were performed under various conditions. The VCM breakthrough curves were used to extract equilibrium data by extrapolating the breakthrough data at 50% breakthrough ($C_{out} = 0.5 C_{in}$) and

assuming a symmetric breakthrough curve. C_{in} refers to concentration of VCM in the 1234yf feed (15.6 ppmv in both Examples 11 and 12) and C_{out} refers to the concentration of VCM in the 1234yf after passing through the mol sieve bed.

Examples 11: 4A Sieves

[0085] 1/16" 4A sieves were tested using 6 cc of sieves (4.52 g) in a 1/2" ID column. 1234yf vapor at 35 psig and 22°C containing 15.6 ppmv of VCM was passed through the column at ~50 sccm, and an online GC was used to quantify the breakthrough of VCM. The column was then regenerated at 175°C with N₂ and was run again. The breakthrough curves for both runs are in Figure 6.

[0086] As can be seen from both Figures 6 and 7, the reproducibility of the curves shows very effective regeneration. By extrapolating the breakthrough curve as shown in Figure 7, the amount 1234yf fed when the outlet VCM concentration reached 0.5 C_{in} (7.8 ppmv) was determined as indicated by the dashed lines. The mass of 1234yf fed at 0.5 C_{in} would have been 1250 g, which at 15.6 ppmv (= 8.55 ppmw) VCM gave 10.7 mg of VCM loaded on 4.43 g of sieves, or 2.31 mg VCM/g sieve. This represents a single isotherm point over 4A sieves at 25°C and a VCM partial pressure of 0.00078 psia and a 1234yf partial pressure of 49.696 psia.

Examples 12: 5A Sieves

[0087] Example 11 was repeated at the same conditions except with 5A sieves. The 1234yf feed for this example also contained 30 ppm of 1131a (CClF=CH₂). After the first breakthrough test, the column was regenerated and run again. The results are shown in Figure 8.

[0088] As can be seen from Figure 8, the reproducibility of the curves shows very effective regeneration. By extrapolating the breakthrough curve as shown in Figure 8, the amount 1234yf fed when the outlet VCM concentration reached 0.5 C_{in} (7.8 ppmv) was determined as indicated by the dashed lines. The mass of 1234yf fed at 0.5 C_{in} would have been 1650 g, which at 15.6 ppmv (= 8.55 ppmw) VCM gave 14.5 mg of VCM loaded on 4.65 g of sieves, or 3.1 mg VCM/g sieve. This represents a single isotherm point over 5A sieves at 22.5°C and a VCM partial pressure of 0.00078 psia and a 1234yf partial pressure of 49.696 psia.

[0089] As can be seen from Figure 8 breakthrough of 1131a occurred quickly, thus indicating that 1131a is not as strongly adsorbed as VCM. The reproducibility of the breakthrough responses after regeneration was excellent.

[0090] Figure 9 compares the 4A and 5A results from Examples 11 and 12 under the similar, with exceptions that the 5A tests had a mildly co-adsorbing 1131a present, while the 4A tests did not and the temperature was slightly different (22.5°C and 25°C, respectively).

[0091] Surprisingly, the 5A sieves demonstrated better capacity for VCM than 4A sieves under these conditions, despite a competing additional component, 1131a, being present at twice the initial concentration. This is surprising since 1234yf would be expected more easily enter the larger 5A sorption channels to reduce the effective loading of VCM. This would be particularly true if the 4A sieves excluded the 1234yf, allowing only VCM into the zeolite cages. Also, the breakthrough curves for VCM on 5A would be expected to be shifted even further to the right if 1131a wasn't present in the feed.

Examples 13-14. Comparison of Liquid and Vapor Phase Results

Example 13. 4A Molecular Sieves

[0092] The vapor phase tests were performed using flow-through column testing with a VCM feed concentration of 15.6 ppmv (= 8.8 ppmw). The performance between liquid and vapor phase is compared at this VCM concentration. As can be seen from Figure 3 and hereinabove, the observed loading of VCM in the liquid phase on 4A sieves at this concentration was 15 mg/g. The performance for vapor phase removal of the same concentration of VCM from 1234yf on 4A sieves at a total pressure of 35 psig and 20°C is shown in Figure 7 and the saturation VCM loading was determined to be 2.31 mg/g as described hereinabove in the paragraph describing Figures 6 and 7. VCM loading via liquid phase adsorption on 4A molecular sieves was about 6.5 times higher than that in the vapor phase!

Example 14. 5A Molecular Sieves

[0093] Again referring to Figure 3, the loading of VCM on 5A sieves at 8.8 ppmw was 10 mg/g in the liquid phase as described hereinabove. The loading of VCM in

the 5A vapor phase columns tests is also shown on Figure 8 and determined to be 1650 g 1234yf x 8.8 ppmw VCM = 14.5 mg VCM on 4.65 g of 5A sieves, or 3.1 mg/g as described hereinabove in the paragraph describing Figures 6 and 7. The liquid phase sorption of VCM is about 3x higher than in the vapor phase over 5A sieves! The true sorption would be even higher since the feed contained 30 ppmv of 1131a in addition to the VCM, which would increase the advantage of liquid phase over vapor phase on 5A sieves.

Example 15. VCM removal from 1243zf by adsorption of 4A molecular sieves

[0094] 50 g of 1243zf containing 83.3 ppmw VCM was mixed with 5 g 4A molecular sieves at room temperature in a cylinder. The mixture was shaken for a few minutes and then held at room temperature for 2 hours, then the liquid phase of the 1243zf/VCM mixture was analyzed by GC-MS-FID. The result of analysis is summarized in Table 9 below. The VCM level in 1243zf was reduced to 2.8 ppmw with contact of 4A molecular sieves.

Example 16. VCM removal from 1243zf by adsorption of 5A molecular sieves

[0095] 50 g of 1243zf containing 83.3 ppmw VCM was mixed with 5 g 5A molecular sieves at room temperature in a cylinder. The mixture was shaken for a few minutes and then held at room temperature for 2 hours, then the liquid phase of the 1243zf/VCM mixture was analyzed by GC-MS-FID. The result of analysis is summarized in Table 9 below. The VCM level in 1243zf was reduced to 0.9 ppmw with contact of 5A molecular sieves.

Table 9

	VCM, ppmw
Starting material	83.3
Example 15 – 4A sieves	2.8
Example 16 – 5A sieves	0.9

Example 17. VCM removal from 1243zf by adsorption of 4A molecular sieves

[0096] 50g of 1243zf containing 88.4 ppmw VCM was mixed with 4A molecular sieves at various ratio at room temperature in 5 cylinders. Each mixture was shaken

for a few minutes and then held at room temperature, then the liquid phase of the 1243zf/VCM mixture was analyzed by GC-MS-FID at 2 hours and at 24 hours. The results of the analyses are summarized in Table 10 below. The VCM level in each sample containing 1243zf and VCM was reduced by contact of the sample with 4A molecular sieves at various organic to molecular sieve ratios.

Table 10

Mix	1243zf , g	mol sieve, g	1243zf/mol sieve wt ratio, g / g	wt ppm	
				2 hr	24 hr
17A	50	1.67	29.9	7.7	3.0
17B	50	0.67	74.6	26.1	18.7
17C	50	0.33	151.5	48.7	33.3
17D	50	0.17	294.1	69.1	56.9
17E	50	0.083	602.4	78.8	75.3

Example 18. VCM removal from 1243zf by adsorption of 5A molecular sieves

[0097] 50g of 1243zf containing 88.4 ppmw VCM was mixed with 5A mol sieve at various ratios at room temperature in 5 cylinders. Each mixture was shaken for a few minutes and then held at room temperature, then the liquid phase of the 1243zf/VCM mixture was analyzed by GC-MS-FID at 2 hours and at 24 hours. The results of the analyses are summarized in Table 11 below. The VCM level in each sample containing 1243zf and VCM was reduced by contact of the sample with 5A mol sieve at various organic to molecular sieve ratios.

Table 11

Mix	1243zf , g	mol sieve, g	1243zf/mol sieve wt ratio, g / g	wt ppm	
				2hr	24hr
18A	50	1.67	29.9	24.0	13.7
18B	50	0.67	74.6	55.6	32.5
18C	50	0.33	151.5	74.5	62.5
18D	50	0.17	294.1	80.5	74.5
18E	50	0.083	602.4	86.5	83.0

Example 19: 245cb, 152a and VCM removal from 1243zf by adsorption of 4A mol sieve

[0098] 58.6 g of HFO-1243zf starting material was mixed with 12.1g g 4A molecular sieves at room temperature in a cylinder. The mixture was shaken for a few minutes and then remained at room temperature after which the liquid phase of the 1243zf mixture was analyzed by GC-MS-FID at 2hrs and 24 hrs. The result of analysis is summarized in Table 12 below. The 245cb, 152a and VCM level in 1243zf were reduced after contact of 4A mol sieve.

Table 12

Compound	GC-FID area		
	Starting Material	2hrs	24hrs
245cb	1.49 ppm	0 ppm	0 ppm
1243zf	99.9640%	99.9807%	99.9827%
152a	173.55 ppm	41.78	11.15
VCM	25.59 ppm	0 ppm	0 ppm

Example 20: 245cb, 152a and VCM removal from 1243zf by adsorption of 5A mol sieve

[0099] 61.2 g of HFO-1243zf starting material was mixed with 12.3g g 5A molecular sieves at room temperature in a cylinder. The mixture was shaken for a few minutes and then remained at room temperature after which the liquid phase of the 1243zf mixture was analyzed by GC-MS-FID at 2 hr and 24 hr. The result of analysis is summarized in Table 13 below. The 245cb, 152a and VCM level in 1243zf were reduced after contact of 5A mol sieve.

Table 13

Compound	GC-FID area		
	Starting Material	2 hrs	24 hrs
245cb	1.49 ppm	0 ppm	0 ppm
1243zf	99.9640%	99.9845%	99.9856%
152a	173.55 ppm	0 ppm	0 ppm
VCM	25.59 ppm	0 ppm	0 ppm

Example 21: 245cb, 152a and VCM removal from 1243zf by adsorption of 13X mol sieve

[0100] 58.52 of HFO-1243zf starting material was mixed with 12.03 g 13X molecular sieves at room temperature in a cylinder. The mixture was shaken for a few minutes and then remained at room temperature after which the liquid phase of the 1243zf mixture was analyzed by GC-MS-FID at 2 hr. The result of analysis is summarized in Table 14 below. The 245cb, 152a and VCM level in 1243zf were reduced after contact of 13X mol sieve.

Table 14

Compound	GC-FID area	
	Starting material	2hrs
245cb	1.49 ppm	0 ppm
1243zf	99.9641%	99.9834%
152a	173.55 ppm	10.14 ppm
VCM	25.59 ppm	3.28 ppm

CLAIMS

What is claimed is:

1. A process to remove one or more additional components from a mixture comprising a fluoropropene, wherein the process comprises contacting the mixture in the liquid phase with molecular sieves chosen from one or more of 4A, 5A or 13X.
2. The process of claim 1 wherein the fluoropropene comprises 3,3,3-trifluoropropene, E-1,3,3,3-tetrafluoropropene, Z-1,3,3,3-tetrafluoropropene, 2,3,3,3-tetrafluoropropene, or a combination thereof.
3. The process of claim 2 wherein the fluoropropene comprises 3,3,3-trifluoropropene.
4. The process of claim 2 wherein the fluoropropene comprises E-1,3,3,3-tetrafluoropropene.
5. The process of claim 3 wherein the fluoropropene comprises Z-1,3,3,3-tetrafluoropropene.
6. The process of claim 3 wherein the fluoropropene comprises 2,3,3,3-tetrafluoropropene.
7. The process of any of claims 1-6, wherein the one or more additional component comprises one or more of HF, HCl, vinyl chloride, 1131a, 245cb and 152a.
8. The process of claim 3 wherein the molecular sieve is 4A.
9. The process of claim 3 wherein the molecular sieve is 5A.
10. The process of claim 3 wherein the molecular sieve is 13X.
11. The process of any of claims 8-10, wherein the one or more additional component comprises one or more of HF, HCl, vinyl chloride, 1131a, 245cb and 152a.
12. The process of any of claims 8-10, wherein the one or more additional component comprises vinyl chloride.

13. The process of any of claims 8-10, wherein the one or more additional component comprises vinyl chloride, 245cb and 152a.
14. The process of any of claims 8-10, wherein the one or more additional component comprises 1131a.
15. The process of any of claims 8-10, wherein the one or more additional component comprises HF, HCl, or a combination thereof.
16. The process of claim 4 wherein the molecular sieve is 4A.
17. The process of claim 4 wherein the molecular sieve is 5A.
18. The process of claim 4 wherein the molecular sieve is 13X.
19. The process of any of claims 16-18, wherein the one or more additional component comprises one or more of HF, HCl, vinyl chloride, 1131a, 245cb and 152a.
20. The process of any of claims 16-18, wherein the one or more additional component comprises vinyl chloride.
21. The process of any of claims 16-18, wherein the one or more additional component comprises vinyl chloride, 245cb and 152a.
22. The process of any of claims 16-18, wherein the one or more additional component comprises 1131a.
23. The process of any of claims 16-18, wherein the one or more additional component comprises HF, HCl, or a combination thereof.
24. The process of claim 5 wherein the molecular sieve is 4A.
25. The process of claim 5 wherein the molecular sieve is 5A.
26. The process of claim 5 wherein the molecular sieve is 13X.
27. The process of any of claims 24-26, wherein the one or more additional component comprises one or more of HF, HCl, vinyl chloride, 1131a, 245cb and 152a.
28. The process of any of claims 24-26, wherein the one or more additional component comprises vinyl chloride.

29. The process of any of claims 24-26, wherein the one or more additional component comprises vinyl chloride, 245cb and 152a.
30. The process of any of claims 24-26, wherein the one or more additional component comprises 1131a.
31. The process of any of claims 24-26, wherein the one or more additional component comprises HF, HCl, or a combination thereof.
32. The process of claim 6 wherein the molecular sieve is 4A.
33. The process of claim 6 wherein the molecular sieve is 5A.
34. The process of claim 6 wherein the molecular sieve is 13X.
35. The process of any of claims 32-34, wherein the one or more additional component comprises one or more of HF, HCl, vinyl chloride, 1131a, 245cb and 152a.
36. The process of any of claims 32-34, wherein the one or more additional component comprises vinyl chloride.
37. The process of any of claims 32-34, wherein the one or more additional component comprises vinyl chloride, 245cb and 152a.
38. The process of any of claims 32-34, wherein the one or more additional component comprises 1131a.
39. The process of any of claims 32-34, wherein the one or more additional component comprises HF, HCl, or a combination thereof.
40. The process of claim 7 wherein the fluoropropene comprises 2,3,3,3-tetrafluoropropene and the 2,3,3,3-tetrafluoropropene is prepared by dehydrochlorination of 244bb.
41. A composition comprising at least 99.9% of 1234yf and 0.001% or less of vinyl chloride.
42. The composition of claim 41, wherein the composition comprises 0.0005% or less of vinyl chloride

43. The composition of claim 41, wherein the composition comprises 0.0001% or less of vinyl chloride.
44. The composition of claim 41, wherein the composition comprises 0.00001% or less of vinyl chloride
45. A composition comprising at least 99.9% of E-1,3,3,3-tetrafluoropropene and 0.001% or less of vinyl chloride.
46. The composition of claim 45, wherein the composition comprises 0.0005% or less of vinyl chloride.
47. The composition of claim 45, wherein the composition comprises 0.0001% or less of vinyl chloride.
48. The composition of claim 45, wherein the composition comprises 0.00001% or less of vinyl chloride
49. A composition comprising at least 99.9% of Z-1,3,3,3-tetrafluoropropene and 0.001% or less of vinyl chloride.
50. The composition of claim 49, wherein the composition comprises 0.0005% or less of vinyl chloride.
51. The composition of claim 49, wherein the composition comprises 0.0001% or less of vinyl chloride.
52. The composition of claim 49, wherein the composition comprises 0.00001% or less of vinyl chloride.
53. A composition comprising at least 99.9% of 3,3,3-trifluoropropene and 0.001% or less of vinyl chloride.
54. The composition of claim 53, wherein the composition comprises 0.0005% or less of vinyl chloride.
55. The composition of claim 53, wherein the composition comprises 0.0001% or less of vinyl chloride.
56. The composition of claim 53, wherein the composition comprises 0.00001% or less of vinyl chloride.

57. A composition comprising at least 99.9% of 2,3,3,3-tetrafluoropropene and 0.003% or less of 1131a.
58. The composition of claim 57, wherein the composition comprises 0.0015% or less of 1131a.
59. The composition of claim 57, wherein the composition comprises 0.0005% or less of 1131a.
60. The composition of claim 57, wherein the composition comprises 0.00001% or less of 1131a.
61. A process to prepare a purified and stabilized fluoropropene comprising (a) contacting a mixture comprising a fluoropropene and one or more additional components, in the liquid phase with molecular sieves chosen from one or more of 4A, 5A or 13X; and (b) adding an inhibitor comprising at least one member selected from the group consisting of limonene, α -terpinene, α -tocopherol, butylated hydroxytoluene, 4-methoxyphenol, benzene-1,4-diol to the composition obtained in step (a).
62. The composition of any of claims 41-60 further comprising at least one inhibitor comprising at least one member selected from the group consisting of limonene, α -terpinene, α -tocopherol, butylated hydroxytoluene, 4-methoxyphenol, benzene-1,4-diol.
63. The composition of claim 61, wherein the inhibitor is present in an amount of about 30 to about 3,000 ppm.
64. The composition of claims 61 or 62, further comprising an anti-oxidant.
65. The composition of claim 63, wherein the anti-oxidant is selected from the group consisting of butylated hydroxytoluene, butylated, tertiary-butylhydroquinone, gallate, 2-phenyl-2-propanol, 1-(2,4,5-trihydroxyphenyl)-1-butanone, bisphenol methane derivatives, 2,2'-methylene bis (4-methyl-6-*t*-butyl phenol), among other phenolics, and combinations thereof.
66. The composition of claims 61-64, wherein the inhibitor comprises limonene or α -terpinene.
67. The composition of claims 61-64, wherein the inhibitor comprises d-limonene.