



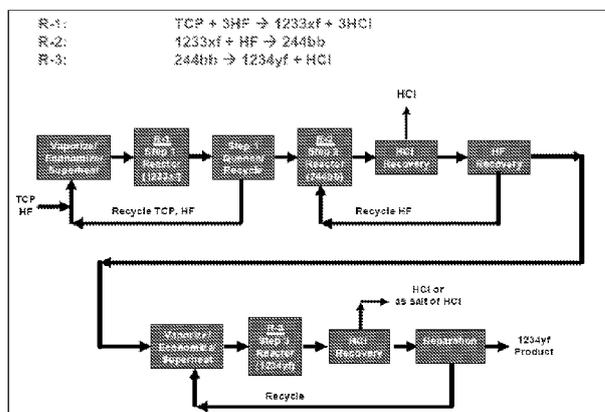
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[Continued on next page]

(54) Title: METHODS OF MAKING 2,3,3,3-TETRAFLUORO-2-PROPENE

FIGURE
Block Flow Diagram for Production of HFC-1234yf from TCP
Scheme 1



(57) Abstract: Disclosed is a process for the manufacture of 1234yf from 1,1,2,3-tetrachloro-propene, abbreviated herein as "TCP," in three integrated steps: (a) the R-1 hydrofluorination of TCP to form 1233xf in the vapor phase; (b) the R-2 hydrofluorination of 1233xf to form 244bb in either the liquid phase or in the liquid phase followed by the vapor phase; and (c) the R-3 dehydrochlorination of the 244bb in either the liquid or the vapor phase to produce 1234yf; wherein the vapor phase hydrofluorination of TCP in step (a) is carried out at a lower pressure than the liquid phase hydrofluorination of 123xf; and wherein the HCl generated during these steps is scrubbed with water to form an acid solution and the organic components are scrubbed with a caustic solution and then dried before further processing.





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METHODS OF MAKING 2,3,3,3-TETRAFLUORO-2-PROPENE

CROSS-REFERENCE TO RELATED APPLICATION

This application claims domestic priority from commonly owned, copending, U.S. Provisional Patent Application Serial No. 61/434,005, filed January 19, 2011, the disclosure of which is hereby incorporated herein by reference.

FIELD OF THE INVENTION

Fluorocarbons, particularly fluorinated olefins, as a class, have many and varied uses, including as chemical intermediates and monomers. In particular, the hydrogenated products are useful as refrigerants, monomers or intermediates for preparing refrigerants, particularly those identified as having low global warming potential.

BACKGROUND OF THE INVENTION

This invention especially relates to improvements in the production of 2,3,3,3-tetrafluoro-2-propene, also known as 1234yf, and having the chemical formula:

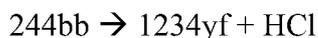
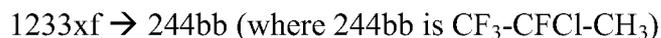
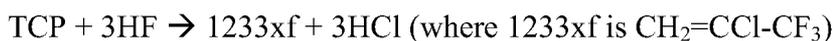


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This chemical compound has zero ozone depletion potential and low global-warming potential such that it may be useful and desirable as a replacement for existing materials used in refrigeration, foam blowing and other applications where fluorocarbons such as 1,1,1,2-tetrafluoroethane, also known as 134a, and known also by the chemical formula; $\text{CH}_2\text{F}-\text{CF}_3$, are currently utilized.

WO 2009/138764 discloses a process for the preparation of 1234yf comprising four steps; (1) contacting 1,1,2,3,3,3-hexafluoropropene (1216) with hydrogen in the presence of a hydrogenation catalyst to produce 1,1,2,3,3,3-hexafluoropropane (236ea); (2) dehydrofluorinating 236ea to produce 1,2,3,3,3-pentafluoropropene (1225ye); (3) contacting 1225ye with hydrogen in the presence of a hydrogenation catalyst to produce 1,2,3,3,3-pentafluoropropane (245eb); and (4) dehydrofluorinating (245eb) to produce (1234yf). Part of the process includes the use of H_2SO_4 in a drying tower for removal of water from the reactants.

It is known in the art to produce 1234yf from 1,1,2,3-tetrachloropropene (TCP or $\text{CCl}_2=\text{CCl}-\text{CH}_2\text{Cl}$) using a non-integrated three step route; see for example US Patent Pub. No. 2007/0197842, the disclosure of which is hereby incorporated herein by reference:



SUMMARY OF THE INVENTION

This invention provides an integrated process which will decrease the amount of processing equipment required for the process, thereby reducing the capital investment

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and operating cost, when comparing to a conventional design approach which required separate equipment to produce and isolate each individual process intermediate before subjecting it to further reaction. Hence, this invention provides a much more economical process both from capital and operating standpoints for the production of 2,3,3,3-tetrafluoro-2-propene (1234yf).

One embodiment of this invention is a process for the manufacture of 1234yf from TCP, i.e., 1,1,2,3-tetrachloropropene, in three integrated steps that includes:

- (a) the R-1 hydrofluorination of TCP to form 1233xf in the vapor phase;
- (b) the R-2 hydrofluorination of 1233xf to form 244bb in either the liquid phase or in the liquid phase followed by the vapor phase; and
- (c) the R-3 dehydrochlorination of the 244bb in either the liquid or the vapor phase to produce 1234yf;

wherein the vapor phase hydrofluorination of TCP in step (a) is carried out at a lower pressure than the liquid phase hydrofluorination of 123xf; and

wherein the HCl generated during these steps is scrubbed with water to form an acid solution and the organic components are scrubbed with a caustic solution and then dried before further processing.

As described above, the HCl generated during the process is scrubbed with water to form a solution and the remaining organic components are scrubbed with a caustic solution and dried before being collected. There are several options for drying the organic components:

- (1) passing the stream through a circulating packed tower with sulfuric acid;
- (2) passing the stream through a packed bed of alumina;
- (3) passing the stream through a packed bed of an appropriate molecular sieve, such as 3A;
- (4) passing the stream through a packed bed of silica gel;

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- (5) passing the stream through a packed bed of calcium sulfate and/or calcium chloride; and
- (6) combinations of these drying techniques.

As described above, this process advantageously includes steps to remove unwanted HCl formed during the reaction steps by washing with aqueous solutions, followed by drying steps to remove the water from the reaction streams. This washing and drying provides benefits to the overall reaction, including preventing corrosion by eliminating both moisture and acidity that could inhibit the reactions in subsequent processing steps.

Preferably, the hydrofluorination of TCP to 1233xf occurs in the vapor phase in the presence of a fluorination catalyst in a reactor selected from the group consisting of; a single reactor, a multistage reactor, or a series of reactors; using a combination of recycle streams, fresh HF and fresh TCP. The fluorination catalyst is at least one of the following selected from the group consisting of Cr_2O_3 , Sb/C, FeCl_3 , $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3/\text{AlF}_3$, $\text{Cr}_2\text{O}_3/\text{C}$, $\text{CoCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{NiCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CoCl}_2/\text{AlF}_3$.

Preferably, the hydrofluorination of 1233xf to 244bb in the liquid phase (or in the liquid phase followed by the vapor phase) and further includes treatment of any reactor effluent containing 1233xf, HCl, excess HF and any unreacted TCP plus intermediates, by feeding this stream into a Quench/Recycle Column for separation of unreacted TCP and excess HF for recycle use in step R-1 of the process.

Preferably, the 1233xf, HCl and HF is fed to a liquid phase reactor containing catalyst selected from SbCl_3 , SbCl_5 , SbF_5 , TiCl_4 , SnCl_4 and combinations thereof for hydrofluorination of 1233xf to 244bb. Preferably, a mixture of 244bb, HCl, unreacted 1233xf and HF exit the liquid reactor system via a catalyst stripper which is used such that most of the unreacted HF and catalyst is refluxed back to the reactor.

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Preferably, the effluent from the catalyst stripper may be passed through a bed containing SbCl_5 /Carbon catalyst for further conversion of 1233xf to 244bb. Advantageously, the effluent from the catalyst stripper or the effluent from SbCl_5 /C bed is fed to an HCl column to separate essentially pure HCl in the overhead from the mixture of 244bb, 1233xf, HF and HCl.

Advantageously, the mixture of 244bb, 1233xf, HF is fed to an HF Recovery section for recovery and recycle of a stream rich in HF and another stream that is rich in 244bb and 1233xf. One such method is cooling the mixture of 244bb, 1233xf, HF and subjecting to phase separation to separate an organic layer and an HF layer. Another method is the treatment of the mixture of 244bb, 1233xf, HF with a solution of H_2SO_4 , as disclosed in U.S. Patent No. 7,371,363, which is hereby incorporated herein by reference.

Preferably, the organic layer which contains minimal amount of HF is fed either directly to a dehydrochlorination reactor or further treated to remove the residual HF. Preferably, the crude 244bb stream is dehydrochlorinated using a vapor phase reactor containing dehydrochlorination catalyst. The catalyst is selected from Cr_2O_3 , Sb/C, FeCl_3 , $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3/\text{AlF}_3$, $\text{Cr}_2\text{O}_3/\text{C}$, $\text{CoCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{NiCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CoCl}_2/\text{AlF}_3$ and combinations thereof. Optionally, the crude 244bb stream is dehydrochlorinated in a liquid phase reactor in the presence of an aqueous base solution. The aqueous base solution is preferably either NaOH or KOH, but other aqueous base solutions may likewise be used herein. See Scheme 2 in the Figure.

Preferably, the effluent containing 1234yf, HCl and unreacted 244bb is deacidified in absorption equipment, dried, compressed and fed to a distillation train where 1234yf is recovered and unreacted 244bb recycled to the dehydrochlorination reactor. Advantageously, a portion of any unreacted 244bb is recycled to the liquid phase reactor in order to purge 1233xf. Advantageously, the effluent containing 1234yf, unreacted 244bb and water vapor is dried, compressed and fed to a distillation train where 1234yf is recovered and unreacted 244bb recycled to dehydrochlorination reactor.

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Preferably, a portion of the unreacted 244bb is recycled to the liquid phase reactor in order to purge 1233xf.

The drying operations that are required during the 3rd step of the process may be accomplished using several options:

- (1) passing the stream through a circulating packed tower with sulfuric acid;
- (2) passing the stream through a packed bed of alumina;
- (3) passing the stream through a packed bed of an appropriate molecular sieve, such as 3A;
- (4) passing the stream through a packed bed of silica gel;
- (5) passing the stream through a packed bed of CaSO₄ and/or CaCl₂; and
- (6) combinations of these drying techniques.

BRIEF DESCRIPTION OF THE DRAWING

The Figure shows two block flow diagrams (Scheme 1 and Scheme 2) with processing steps used for the production of 1234yf from TCP, 1,1,2,3-tetrachloropropene.

DETAILED DESCRIPTION OF THE INVENTION

The present invention can be generally described as an integrated process for the production of 1234yf from TCP, 1,1,2,3-tetrachloropropene, in three reaction steps wherein the first reaction is carried out at a higher pressure than the second reaction.

Key features of the integrated process of the present invention include operating the first step vapor phase fluorination reactor at a pressure sufficiently high such that no compression or isolation of intermediates is required for the subsequent liquid phase fluorination reactor. Also, the HCl gas generated in the first step is fed directly to the second step - both to promote mixing and to suppress over-fluorination in the second

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liquid phase fluorination reactor. The two fluorination reactors are operated with a large excess HF, typically on the order of 20 mol HF to 1 mol organic which, in the first step enhances the vaporization of TCP, and minimizes by-product formation and in the second step, minimizes byproduct formation. The term “integrated process” describes how the process steps are coordinated such that no isolation of intermediate reactants is required. This provides a better yield than non-integrated processes, and reduces the operational costs of the process.

Scheme 1 in the Figure describes a process for the manufacture of 1234yf from TCP, 1,1,2,3-tetrachloro-propene, in three integrated steps that include:

- (a) the R-1 hydrofluorination of TCP to form 1233xf in the vapor phase;
- (b) the R-2 hydrofluorination of 1233xf to form 244bb in the liquid phase (or in the liquid phase followed by the vapor phase); and
- (c) the R-3 dehydrochlorination of 244bb in either the liquid or the vapor phase to produce 1234yf.

Preferably, in the Scheme 1 process, the vapor phase hydrofluorination is carried out at a higher pressure than the liquid phase hydrofluorination. Advantageously, in the Scheme 1 process, the TCP, HF and recycle is fed to a vapor phase reactor containing catalyst selected from the group consisting of Cr_2O_3 , Sb/C, FeCl_3 , $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3/\text{AlF}_3$, $\text{Cr}_2\text{O}_3/\text{C}$, $\text{CoCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{NiCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CoCl}_2/\text{AlF}_3$, or a mixture of such catalysts. The reactor used for the hydrofluorination of TCP to 1233xf in the vapor phase is a reactor selected from the group consisting of; a single reactor, a multistage reactor, or a series of reactors; using a combination of recycle streams, fresh HF and fresh TCP.

As illustrated, the hydrofluorination of 1233xf to 244bb in the liquid phase further includes treatment of any reactor effluent containing 1233xf, HCl, excess HF and any

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unreacted TCP plus intermediates, by feeding this stream into a Quench/Recycle Column for separation of unreacted TCP and excess HF for recycle use in step (R-1) of the process. The 1233xf, HCl and HF is fed to a liquid phase reactor containing catalyst selected from SbCl_3 , SbCl_5 , SbF_5 , TiCl_4 , and SnCl_4 for hydrofluorination of 1233xf to 1,1,1,2-tetrafluoro-2-chloropropane (244bb). The hydrofluorination of 1233xf to 244bb in the liquid phase further includes treatment of any reactor effluent containing 1233xf and 244bb, by feeding this stream into a Quench/Recycle Column for separation of 1233xf for recycle use in step (R-2) of the process.

As illustrated, a mixture of 244bb, HCl, unreacted 1233xf and HF exit the liquid reactor system via a catalyst stripper which is used such that most of the unreacted HF and catalyst is refluxed back to the reactor. The effluent from the catalyst stripper may be passed through a bed containing catalyst for further conversion of 1233xf to 244bb. One preferred catalyst for this conversion is SbCl_5 supported on carbon. Preferably, the effluent from the catalyst stripper or the effluent from bed containing SbCl_5 supported on carbon is fed to an HCl column to separate essentially pure HCl in the overhead from the mixture of 244bb, 1233xf, HF and HCl.

The essentially pure HCl product is either recovered as is or passed through silica gel for residual HF removal and absorbed into water. HF is recovered from a mixture of 244bb, 1233xf, and HF. One method for HF recovery is by cooling and phase separation to separate a layer rich in organics and a layer rich in HF. This method further includes HF recovery by phase separation and azeotropic distillation. Yet another method for the HF recovery is via absorption into sulfuric acid. Each of these options for HF recovery may be used, alone or in conjunction with the other.

In the process of the present invention, the organic layer which contains minimal amount of HF is fed either directly to a dehydrochlorination reactor or is deacidified. When the crude 244bb stream is dehydrochlorinated, a vapor phase reactor containing a dehydrochlorination catalyst selected from Cr_2O_3 , Sb/C, and FeCl_3 , $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$,

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$\text{Cr}_2\text{O}_3/\text{AlF}_3$, $\text{Cr}_2\text{O}_3/\text{C}$, $\text{CoCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{NiCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CoCl}_2/\text{AlF}_3$ and combinations thereof is employed.

As illustrated in Scheme 2 of the Figure, when the crude 244bb stream is dehydrochlorinated in a liquid phase reactor, an aqueous base solution is employed. The aqueous base solution is preferably either NaOH or KOH. When the effluent containing 1234yf, HCl and unreacted 244bb is deacidified in absorption equipment, dried, compressed and fed to a distillation train, 1234yf is recovered and unreacted 244bb is recycled to the dehydrochlorination reactor. Preferably, a portion of any unreacted 244bb is recycled to the liquid phase reactor in order to purge 1233xf. When the effluent containing 1234yf, unreacted 244bb and water vapor is dried, compressed and fed to a distillation train, 1234yf is recovered and unreacted 244bb is recycled to dehydrochlorination reactor. Preferably, a portion of the unreacted 244bb is recycled to the liquid phase reactor in order to purge 1233xf.

A detailed description of one preferred embodiment of the integrated process of the present invention is as follows:

- (1) Hydrofluorination of TCP, 1,1,2,3-tetrachloro-propene, to form 1233xf using a single reactor or a multistage reactor or a series of reactors in the vapor phase containing catalyst using a combination of recycle stream(s), fresh HF and fresh TCP as illustrated in the Figure (at Scheme 1) as "R-1, Step 1 Reactor". In the preferred embodiment, the reaction is carried out under conditions effective to provide at least 50% conversion, preferably 80% to 85% conversion of TCP to 1233xf where the mole ratio of HF to TCP is about 20:1, reaction temperature is about 300°C and pressure is about 120 psig.
- (2) Cool the above (1) reactor effluent containing 1233xf, HCl, excess HF and any unreacted TCP plus intermediates and feed this stream into a Quench/Recycle Column for separation of unreacted TCP plus intermediates and excess HF for

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recycle to (1) and; 1233xf, HCl and HF to liquid phase reactor (3), as illustrated in the Figure (at Scheme 1) as "R-2 Step 2 Reactor".

- (3) Feed the 1233xf, HCl and HF to a liquid phase reactor containing catalyst (see the catalyst choices listed above) for hydrofluorination of 1233xf to 244bb. In the preferred embodiment, the reaction is carried out under conditions effective to provide at least 96% conversion, preferably 98% conversion of 1233xf to 244bb where the mole ratio of HF to TCP is about 20:1, reaction temperature is about 85°C and pressure is about 100 psig.
- (4) A mixture of 244bb, HCl, unreacted 1233xf and HF exit the liquid reactor system via a catalyst stripper which is used such that most of the unreacted HF and catalyst is refluxed back to the reactor.
- (5) The effluent from the catalyst stripper may be passed through a bed containing SbCl_5 /Carbon catalyst for further conversion of 1233xf to 244bb in order to achieve a total of 98% conversion as stated in (3) above.
- (6) The effluent from the catalyst stripper (4) or the effluent from SbCl_5 /C bed (5) is fed to an HCl column to separate essentially pure HCl in the overhead from the mixture of 244bb, 1233xf, HF and HCl.
- (7) The essentially pure HCl product from (6) above may be recovered as is or passed through silica gel for residual HF removal and absorbed into water.
- (8) The mixture of 244bb, 1233xf, HF from (6) above is fed to an HF recovery system to separate a stream rich in organic and a stream rich in HF. Such methods include phase separation and preferential absorption of HF into sulfuric acid.

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- (9) The organic stream which contains minimal amount of HF is fed either directly to a dehydrochlorination reactor or further deacidified before being fed to the dehydrochlorination reactor (10) below.
- (10) The 244bb stream is dehydrochlorinated using a vapor phase reactor containing dehydrochlorination catalyst. In the preferred embodiment, the reaction is carried out under conditions effective to provide at least 20% conversion, preferably at least 50% conversion of 244bb to 1234yf where the reaction temperature is about 400°C and pressure is about 15 psig. Optionally, this stream may be dehydrochlorinated in a liquid phase reactor in the presence of an aqueous base solution such as NaOH or KOH at temperatures of about 50°C. See Scheme 2 in the Figure.
- (11) If a vapor phase dehydrochlorination reactor is used, the effluent from (10) above containing 1234yf, HCl and unreacted 244bb is deacidified in absorption equipment (KOH or NaOH scrubbing), dried with 3A mole sieves or another suitable drying agent as disclosed herein, compressed and fed to a distillation train where 1234yf is recovered and unreacted 244bb recycled to dehydrochlorination reactor (10) above. A portion of the unreacted 244bb may be recycled to the liquid phase reactor (3) in order to purge this section of 1233xf.
- (12) If a liquid phase dehydrochlorination reactor is used, the effluent from (10) above containing 1234yf, unreacted 244bb and water vapor is dried with a suitable drying agent, compressed and fed to a distillation train where 1234yf is recovered and unreacted 244bb recycled to dehydrochlorination reactor (10) above. A portion of the unreacted 244bb may be recycled to the liquid phase reactor (3) in order to purge this section of 1233xf.
- (13) Drying can be done by any suitable drying method, such as for example, with

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sulfuric acid or a particulate desiccant. The term desiccant means any material which will absorb water without dissolving in or otherwise contaminating the fluorocarbon being dried. Such desiccants include alumina, silica gel, molecular sieves (e.g., 3A), calcium sulfate (CaSO_4) and CaCl_2 , and the like

- (14) In one embodiment, a packed tower is utilized and strong sulfuric acid is circulated over the column as a gaseous stream of the fluorocarbon feed material is fed to the column and the moisture in the stream is removed by reaction with the sulfuric acid.
- (15) In another embodiment, the particulate desiccant is packed into a drying vessel and the liquid or gaseous fluorocarbon is passed over the material such that the moisture in the stream is removed by the desiccant.

EXAMPLE

The following non-limiting example is prospective and represents results obtained from standard process simulation and physical property prediction procedures in order to illustrate the invention. In the table below:

“R-1 Inlet” is the stream fed to the first hydrofluorination reactor.

“R-1 Exit” is the resulting effluent with reactor operating under preferred conditions.

“Quench Overhead” and “R-1 Recycle” respectively are the overhead and bottoms streams exiting a distillation tower whose primary purpose is to separate TCP and HF from the reaction products for recycle back to the first hydrofluorination reactor.

Table 1: R-1

Composition percentages, wt% for various streams				
	R-1 Inlet	R-1 Exit	Quench Overhead	R-1 Recycle
Temperature °C	300	300	48.8	93.9
Pressure psig	119.73	119.5	110	110
TCP + 1231 + 1232	33.9%	5.7%	0.0%	10.1%
HF	65.8%	56.2%	14.2%	89.3%
HCl	0.0%	17.3%	39.3%	0.0%
245cb	0.3%	0.8%	1.1%	0.6%
244bb	0.0%	0.0%	0.0%	0.0%
1234yf	0.0%	0.1%	0.2%	0.0%
1233xf	0.0%	19.8%	45.1%	0.0%

In the table below:

“R-2 Inlet” is the stream fed to the second hydrofluorination reactor.

“R-2 Exit” is the resulting effluent with reactor operating under preferred conditions.

“Recovered HCl” is the overhead stream from a distillation tower whose primary purpose is to separate HCl from a mixture of reactants and reaction products.

“R-2 Recycle” is the stream resulting from the HF Recovery section of the process. It is the resulting stream from subjecting the bottoms of the above distillation tower to HF recovery.

Table 2: R-2

Composition percentages, wt% for various streams				
	R-2 Inlet	R-2 Exit	Recovered HCl	R-2 Recycle
Temperature °C	85	61.9	-42.8	85
Pressure psig	100	100	80	
TCP + 1231 + 1232	0.0%	0.0%	0.0%	0.0%
HF	49.8%	46.0%	21 ppm	93.8%
HCl	21.6%	21.7%	99.80%	0.0%
245cb	0.6%	1.2%	0.0%	0.0%
244bb	3.0%	30.4%	0.19%	6.1%
1234yf	0.1%	0.1%	nil	0.0%
1233xf	24.8%	0.5%	0.0%	0.1%

In the table below:

“R-3 Inlet” is the stream fed to the dehydrochlorination reactor.

“R-3 Exit” is the resulting effluent with reactor operating under preferred conditions.

“1234yf Product” is the recovered product from a purification train.

“R-3 Recycle” is a stream resulting from the purification train. In this example, this stream is recycled to the dehydrochlorination reaction. Optionally, a portion of it (or all of it) may be recycled to the second hydrofluorination reactor to reduce the 1233xf content.

Table 3: R-3

Composition percentages, wt% for various streams				
	R-3 Inlet	R-3 Exit	1234yf Product	R-3 Recycle
Temperature °C	400	400	27.1	86.9
Pressure psig	15	15	90	
TCP + 1231 + 1232	0.0%	0.0%	0.0%	0.0%
HF	0.0%	0.1%	0.0%	0.0%
HCl	0.0%	3.6%	0.0%	0.0%
245cb	0.7%	0.4%	0.5%	0.0%
244bb	73.3%	58.2%	0.0%	68.9%
1234yf	0.1%	11.5%	99.5%	0.0%
1233xf	25.9%	26.3%	0.0%	31.1%

As used herein, the singular forms "a", "an" and "the" include plural unless the context clearly dictates otherwise. Moreover, 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 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. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

While the present invention has been particularly shown and described with

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reference to preferred embodiments, it will be readily appreciated by those of ordinary skill in the art that various changes and modifications may be made without departing from the spirit and scope of the invention. It is intended that the claims be interpreted to cover the disclosed embodiment, those alternatives which have been discussed above and all equivalents thereto.

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WHAT IS CLAIMED IS:

1. A process for the manufacture of 1234yf from 1,1,2,3-tetrachloropropene (TCP) in three integrated steps that include:

- (a) the R-1 hydrofluorination of TCP to form 1233xf in the vapor phase;
- (b) the R-2 hydrofluorination of 1233xf to form 244bb in either the liquid phase or in the liquid phase followed by the vapor phase; and
- (c) the R-3 dehydrochlorination of the 244bb in either the liquid or the vapor phase to produce 1234yf;

wherein the vapor phase hydrofluorination of TCP in step (a) is carried out at a lower pressure than the step (b) liquid phase hydrofluorination of 1233xf; and

wherein HCl generated during steps (a), (b), and/or (c) is scrubbed with water to form an acid solution and organic components generated during steps (a), (b), and/or (c) are scrubbed with a caustic solution and then dried before further processing.

2. The process of Claim 1, wherein the drying steps employed for the organic components are selected from the group consisting of:

- (a) passing the stream through a circulating packed tower with sulfuric acid;
- (b) passing the stream through a packed bed of alumina;
- (c) passing the stream through a packed bed of a molecular sieve;
- (d) passing the stream through a packed bed of silica gel;
- (e) passing the stream through a packed bed of calcium sulfate and/or calcium chloride;
- (f) and combinations thereof.

3. The process of Claim 1, wherein the TCP, HF and recycle is fed to a vapor phase reactor containing catalyst selected from the group consisting of Cr₂O₃, Sb/C, FeCl₃, Cr₂O₃/Al₂O₃, Cr₂O₃/AlF₃, Cr₂O₃/C, CoCl₂/Cr₂O₃/Al₂O₃, NiCl₂/Cr₂O₃/Al₂O₃, and

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$\text{CoCl}_2/\text{AlF}_3$.

4. The process of Claim 1, wherein the hydrofluorination of TCP to 1233xf in the vapor phase occurs in a reactor selected from the group consisting of; a single reactor, a multistage reactor, or a series of reactors; using a combination of recycle streams, fresh HF and fresh TCP.

5. The process of Claim 1, wherein the hydrofluorination of 1233xf to 244bb in the liquid phase further includes treatment of any reactor effluent containing 1233xf, HCl, excess HF and any unreacted TCP plus intermediates, by feeding this stream into a Quench/Recycle Column for separation of unreacted TCP and excess HF for recycle use in step (a) of the process.

6. The process of Claim 1, wherein the 1233xf, HCl and HF is fed to a liquid phase reactor containing catalyst selected from SbCl_3 , SbCl_5 , SbF_5 , TiCl_4 , SnCl_4 for hydrofluorination of 1233xf to 1,1,1,2-tetrafluoro-2-chloropropane (244bb).

7. The process of Claim 6, wherein the hydrofluorination of 1233xf to 244bb in the liquid phase further includes treatment of any reactor effluent containing 1233xf and 244bb, by feeding this stream into a Quench/Recycle Column for separation of 1233xf for recycle use in step (b) of the process.

8. The process of Claim 7, wherein a mixture of 244bb, HCl, unreacted 1233xf and HF exit the liquid reactor system via a catalyst stripper which is used such that most of the unreacted HF and catalyst is refluxed back to the reactor.

9. The process of Claim 8, wherein the effluent from the catalyst stripper may be passed through a bed containing catalyst for further conversion of 1233xf to 244bb.

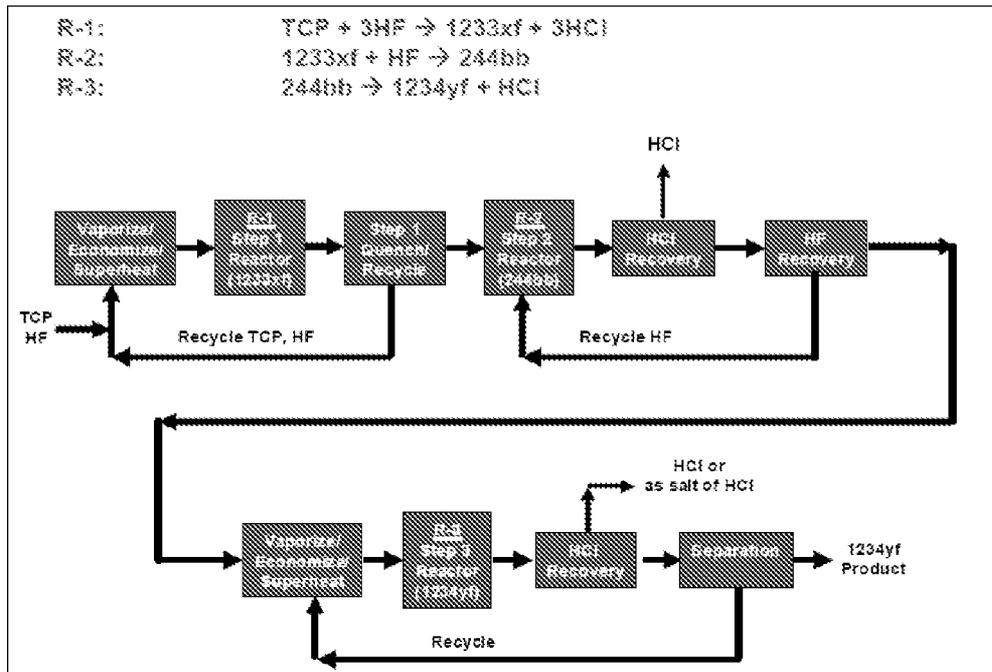
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10. The process of Claim 9, wherein the catalyst is SbCl_5 supported on carbon.

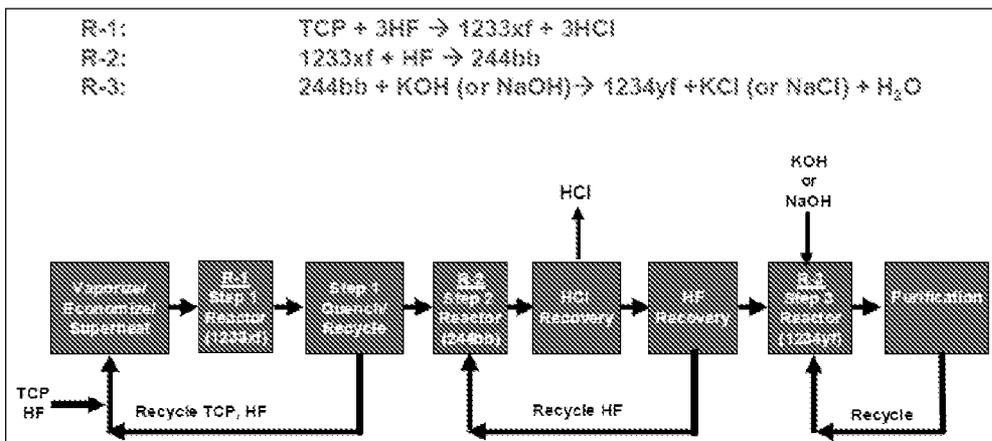
FIGURE

Block Flow Diagram for Production of HFO-1234yf from TCP

Scheme 1



Scheme 2



A. CLASSIFICATION OF SUBJECT MATTER*C07C 17/25(2006.01)i, C07C 21/18(2006.01)i, C07C 17/38(2006.01)i, B01J 23/18(2006.01)i*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C 17/25; C07C 21/18; C07C 17/20; C07C 17/23

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: 1234yf; 1,1,2,3-tetrachloropropene; TCP; 1233xf; 244bb; hydrofluorination; integrated process; scrub; caustic solution.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	WO 2011-056441 A2 (HONEYWELL INTERNATIONAL INC.) 12 May 2011 See abstract; paragraph [0034]; claims 1-11; Figure.	1-10
X	US 2009-0240090 A1 (MERKEL, DANIEL C. et al.) 24 September 2009 See abstract; Figures 1-7; paragraphs [0020]-[0046]; claims 1, 6, 10-11, 14 & 18.	1-10
A	US 2010-0036179 A1 (MERKEL, DANIEL C. et al.) 11 February 2010 See abstract; claim 20.	1-10
A	WO 2009-125201 A2 (INEOS FLUOR HOLDINGS LIMITED) 15 October 2009 See claims 1-3.	1-10

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/021158

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