



HU000031899T2

(19) **HU**(11) Lajstromszám: **E 031 899**(13) **T2****MAGYARORSZÁG**
Szellemi Tulajdon Nemzeti Hivatala**EURÓPAI SZABADALOM**
SZÖVEGÉNEK FORDÍTÁSA(21) Magyar ügyszám: **E 09 810828**(22) A bejelentés napja: **2009. 12. 23.**(51) Int. Cl.: **C07C 17/20** (2006.01)**C07C 21/18** (2006.01)**C07C 19/08** (2006.01)**C07C 17/087** (2006.01)(96) Az európai bejelentés bejelentési száma:
EP 20090810828(97) Az európai bejelentés közzétételi adatai:
EP 2516366 A1 **2011. 06. 30.**

(86) A nemzetközi (PCT) bejelentési szám:

PCT/IB 09/056055(97) Az európai szabadalom megadásának meghirdetési adatai:
EP 2516366 B1 **2016. 11. 16.**

(87) A nemzetközi közzétételi szám:

WO 11077192(72) Feltaláló(k):
DEUR-BERT, Dominique, 69390 Charly (FR)
WENDLINGER, Laurent, 69510 Soucieu en Jarrest (FR)
PIGAMO, Anne, 69340 Francheville (FR)(73) Jogosult(ak):
Arkema France, 92700 Colombes (FR)(74) Képviselő:
Danubia Szabadalmi és Jogi Iroda Kft.,
Budapest

(54)

1233XF-nek 1234YF-rá történő katalitikus gázfázisú fluorozása

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmas az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.



(11) **EP 2 516 366 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
16.11.2016 Bulletin 2016/46

(51) Int Cl.:
C07C 17/20 (2006.01) **C07C 21/18** (2006.01)
C07C 19/08 (2006.01) **C07C 17/087** (2006.01)

(21) Application number: **09810828.5**

(86) International application number:
PCT/IB2009/056055

(22) Date of filing: **23.12.2009**

(87) International publication number:
WO 2011/077192 (30.06.2011 Gazette 2011/26)

(54) **CATALYTIC GAS PHASE FLUORINATION OF 1233XF TO 1234YF**

KATALYTISCHE GASPHASENFLUORIERUNG VON 1233XF ZU 1234YF

FLUORATION CATALYTIQUE EN PHASE GAZEUSE DU 1233XF EN 1234YF

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL
PT RO SE SI SK SM TR**

(43) Date of publication of application:
31.10.2012 Bulletin 2012/44

(73) Proprietor: **Arkema France**
92700 Colombes (FR)

(72) Inventors:
• **DEUR-BERT, Dominique**
69390 Charly (FR)
• **WENDLINGER, Laurent**
69510 Soucieu En Jarrest (FR)

• **PIGAMO, Anne**
69340 Francheville (FR)

(74) Representative: **Hirsch & Associés**
137, rue de l'Université
75007 Paris (FR)

(56) References cited:
WO-A1-2009/003084 WO-A1-2010/059493
WO-A2-2009/137658 US-A1- 2009 124 837

Remarks:

The file contains technical information submitted after
the application was filed and not included in this
specification

EP 2 516 366 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

FIELD OF THE INVENTION

[0001] The present invention relates to the gas phase catalyzed fluorination of 2-chloro-3,3,3-trifluoro-1-propene (1233xf) to produce 2,2,2,3-tetrafluoropropene (1234yf). More particularly, the present invention relates to processes wherein 1233xf, optionally containing a low level of polymerization inhibitor, is contacted with hydrogen fluoride (HF) in a gas phase reaction, in the presence of a fluorination catalyst to produce 1234yf. The desired product, 1234yf is known to have utility as a foam blowing agent, refrigerant, aerosol propellant, heat transfer media, fire extinguisher, etc. Furthermore, 1234yf is known to have zero Ozone Depletion Potential (ODP) and very low Global Warming Potential (GWP) of much less than 150.

BACKGROUND OF THE INVENTION

[0002] The Montreal Protocol for the protection of the ozone layer mandated the phase out of the use of chlorofluorocarbons (CFCs). Materials more "friendly" to the ozone layer, such as hydrofluorocarbons (HFCs) e.g. HFC-134a replaced chlorofluorocarbons. The latter compounds have proven to be green house gases, causing global warming and were regulated by the Kyoto Protocol on Climate Change. With the continued concern over global climate change there is an increasing need to develop technologies to replace those with high ozone depletion potential (ODP) and high global warming potential (GWP). Though hydrofluorocarbons (HFCs), being non-ozone depleting compounds, have been identified as alternatives to chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) as solvents, cleaning agents and heat transfer fluids, they still tend to have significant GWP. Hydrofluoroolefins (HFO) have been identified as potential alternatives with zero ODP and low GWP.

[0003] Hence, numerous documents have provided such HFOs.

[0004] Methods of preparing hydrofluoroalkenes are known. For example, WO 2007/079431 discloses processes for the production of fluorinated olefins, including hydrofluoropropenes. The processes which are broadly described as a single reaction or two or more reactions involve fluorination of compound of the formula $C(X)_mC-Cl(Y)_nC(X)_m$ to at least one compound of formula $CF_3CF=CHZ$, where each X, Y and Z is independently H, F, Cl, I or Br and each m is independently 1, 2 or 3 and n is 0 or 1. 1234yf is prepared by fluorinating 1233xf into 1,1,1,2-tetrafluoro-2-chloropropane (HFC244bb), followed by dehydrochlorination. 1233xf is prepared by trifluorination of the corresponding chlorinated precursor ($CCl_2=CClCH_2Cl$).

[0005] EP-A-939071 discloses, among many possibilities, gas-phase fluorination of an halogenated propene (according to a very long list) into a fluorinated propene

(including in the list 1234yf).

[0006] WO 2008/054781 discloses a variety of processes for producing a variety of fluoropropenes and halofluoropropenes by reacting halopropenes or halopropenes with HF optionally in the presence of a catalyst. It discloses a process for making 1234yf by reacting 2,3-dichloro-1,1,1-trifluoropropane (243db) in the presence of HF, on a catalyst, especially Cr/Co 98/2. Reaction products comprise 1234yf and 2-chloro-3,3,3-trifluoro-1-propene (1233xf), the latter being the main product; other products being 1-chloro-3,3,3-trifluoro-1-propene (1233zd) as well as 245cb and 1234ze which are also formed.

[0007] WO 2008/002500 discloses a process for making a mixture of 2,3,3,3-tetrafluoro-1-propene (HFO 1234yf) and 1,3,3,3-tetrafluoro-1-propene (HFO 1234ze) by catalytic conversion of 1,1,1,2,3-pentafluoropropane (HFC 245eb) on a dehydrofluorination catalyst.

[0008] WO 2008/040969 discloses a process comprising dehydrochlorination of 243db into 1233 (xf as well as zd), followed by a reaction involving formation of 1,1,1,2-tetrafluoro-2-chloropropane (244bb) and later formation of the desired 2,3,3,3-tetrafluoro-1-propene through dehydrochlorination. Example 1 of said document discloses a gas phase reaction at atmospheric pressure of 243db with HF on a Zn/chromia catalyst, whereby 1234yf and 1233xf are formed, together with a small amount of 245cb. Example 2 of said document discloses a gas phase reaction at atmospheric pressure of 245cb in presence of HF on the same catalyst (contact time 5 sec) whereby 1234yf is formed.

[0009] WO 2009/015317 discloses the reaction of a chlorinated compound which can be 1,1,2,3-tetrachloro-1-propene (1230xa), 1,1,1,2,3-pentachloropropane (240db) or 2,3,3,3-tetrachloro-1-propene (1230xf) with HF, in gas phase, on a catalyst and in the presence of at least one stabilizer. This process allows obtaining 2-Chloro-3,3,3-trifluoro-1-propene (1233xf).

[0010] US 2009/0240090 discloses a process for making 2,3,3,3-tetrafluoro-1-propene (1234yf) starting from a compound of formula (I) $CX_2=CClCH_2X$, or formula (II) $CX_3CCl=CH_2$ or formula (III) $CX_3CHClCH_2X$ with X = F, Cl, Br, I. The process comprises three steps, which can be followed by purification. The process includes recycling steps allowing higher conversions and yields.

[0011] WO 2009/003084 is related to hydrofluoropropenes, and describes a 2 steps synthesis of 1234yf (2,3,3,3-tetrafluoropropene) from 1230xa (1,1,2,3-tetrachloropropane). In a first step: a non-catalytic fluorination in liquid phase of 1230xa leads to 1233xf. In the second step, is described the gas phase catalytic fluorination of the stream from 1st step comprising 1233xf, to form 1234yf. The reaction product of this second step also contains unreacted 1233xf, and co-products such as 245cb and/or 244bb, that can be separated from the desired hydrofluoropropene (1234yf), and the by products are recycled back to the gas phase catalytic fluorination reaction of the second step. No more information is given

but the possible separation and recycling to the gas phase. Nowhere in this prior document is given an information in favour of the importance of this possible recycling.

[0012] WO 2009/137658 is related to compositions comprising chloro fluoro propanes or chloro fluoro propenes HCFC-243db, HCFO-1233xf, HCFC-244db and/or HFO-1234yf. 1234yf is directly prepared from 1233xf via fluorination. 1233xf may be produced from 243db and then 1233xf may be converted directly to 1234yf. However no description of a full continuous process including recycling is described.

[0013] US 2009/124837 relates to a gas phase synthesis of 2,3,3,3-tetrafluoro-1-propene 1234yf from 2-chloro-3,3,3-trifluoro-1-propene 1233xf. It describes a multistep process: (a) contacting a starting material comprising 2-chloro-3,3,3-trifluoro-1-propene with hydrogen fluoride in the presence of activated first catalyst selected from the group consisting of antimony-halides, iron-halides, titanium halides, and tin-halides, to produce an intermediate composition; and (b) contacting said intermediate composition with a second catalyst of activated carbon to produce a final product comprising 2,3,3,3-tetrafluoro-1-propene. A full process conducted continuously is not described.

SUMMARY OF THE INVENTION

[0014] The present invention provides a process for preparing 2,3,3,3-tetrafluoropropene (1234yf), comprising:

- (i) contacting 2-chloro-3,3,3-trifluoro-1-propene (1233xf) with hydrogen fluoride HF in gas phase in the presence of a fluorination catalyst under conditions sufficient to produce a reaction mixture;
- (ii) separating the reaction mixture into a first stream comprising HCl, 2,3,3,3-tetrafluoropropene (1234yf) and a second stream comprising HF, unreacted 2-chloro-3,3,3-trifluoro-1-propene (1233xf) and 1,1,1,2,2-pentafluoropropane (245cb);
- (iii) recycling at least a part of the second stream at least in part back to step (i), wherein step (i) is carried out in the presence of O₂ and/or Cl₂, and wherein the process is continuous.

[0015] In one embodiment, the first stream is further separated into HCl and 2,3,3,3-tetrafluoropropene (1234yf), preferably in a distillation step.

[0016] The present invention also provides a process for preparing 2,3,3,3-tetrafluoropropene (1234yf), comprising :

- (i) contacting 2-chloro-3,3,3-trifluoro-1-propene (1233xf) with hydrogen fluoride HF in gas phase in the presence of a fluorination catalyst under conditions sufficient to produce a reaction mixture;
- (ii) separating the reaction mixture into HCl and a

stream containing the fluorinated products;

(iii) separating said stream containing the fluorinated products into a first stream comprising 2,3,3,3-tetrafluoropropene (1234yf) and a second stream comprising HF, unreacted 2-chloro-3,3,3-trifluoro-1-propene (1233xf) and 1,1,1,2,2-pentafluoropropane (245cb);

(iv) recycling at least a part of the second stream at least in part back to step (i), wherein step (i) is carried out in the presence of O₂ and/or Cl₂, and wherein the process is continuous.

[0017] Embodiments are the following:

- the reaction mixture obtained at step (i) comprises 2,3,3, 3-tetrafluoropropene (1234yf) and 1,1,1,2,2-pentafluoropropane (245cb) in a molar ratio of 1:5 to 3:1, preferably 1:4 to 2:1.
- the reaction mixture obtained at step (i) comprises 2,3,3, 3-tetrafluoropropene (1234yf), 1,1,1,2,2-pentafluoropropane (245cb) and 1,1,1,2-tetrafluoro-2-chloropropane (244bb) such that the molar ratio of 245cb to 244bb is from 1:1 to 70:1, preferably from 1.5:1 to 65:1.
- step (i) is carried out with a molar ratio HF:1233xf from 3:1 to 150:1, preferably 4:1 to 70:1, more preferably 5:1 to 50:1.
- step (i) is carried out at a pressure from 3 to 20 bars, preferably 5 to 15 bars, more preferably 7 to 10 bars.
- step (i) is carried out at a temperature of from 200 to 450°C, preferably from 300 to 430°C, more preferably from 320 to 420°C.
- step (i) is carried out with a contact time from 6 to 100 sec, preferably from 10 to 80 sec, more preferably from 15 to 50 sec.
- the ratio of O₂ and/or Cl₂ with respect to 2-chloro-3,3,3-trifluoro-1-propene (1233xf) is 0.05 to 15 mole%, preferably 0.5 to 10 mole%.
- the step of separating into a first stream and a second stream is a distillation step.
- step (i) is carried out in the presence of a polymerization inhibitor, preferably chosen from the group consisting of p-methoxyphenol, t-amylphenol, limonene, d,1-limonene, quinones, hydroquinones, epoxides, amines and mixtures thereof.
- step (i) is carried out in the presence of a catalyst comprising Ni-Cr, supported or unsupported.
- said catalyst is supported on a support selected from fluorinated alumina, fluorinated chromia, fluorinated activated carbon or graphite carbon.

BRIEF DISCLOSURE OF THE DRAWINGS

[0018]

Figure 1 is a scheme representing the possible reactions involved in the present invention.

Figure 2 is a scheme representing the process car-

ried out in the invention.

Figure 3 is a scheme representing the process carried out in the invention.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0019] Figure 1 provides a scheme of potential reactions involved in the instant process. 1233xf undergoes a series of possible reactions. Reaction with HF can lead directly to 1234yf or through an addition reaction to a saturated compound 244bb. This saturated compound can be dehydrochlorinated to give 1234yf. 244bb can also, upon fluorination with HF, give 245cb. 1234yf and 245cb form an equilibrium; the invention is based on this finding. Any 245cb formed can be recycled to the first reaction zone, whereby the equilibrium is displaced (1234yf being thus prevented from further conversion into 245cb). The 245cb flowrate in the recycling loop (either at the exit of the gas-phase reactor or in the second stream back exiting the distillation column and back to the gas-phase reactor) is thus substantially constant. No 245cb build up will thus take place in the recycling loop. In this instance, 1233xf fed into the reactor converts mainly into 1234yf since 245cb is already present in the recycling loop.

[0020] Figure 2 represents the process carried out in the invention. The gas-phase reactor is fed with 1233xf and HF. The reaction mixture exiting the reactor comprises HCl, unreacted 1233xf, unreacted HF, 1234yf, 245cb and a minor amount of 244bb. This reaction stream is separated by distillation into a first stream (light products) comprising HCl, 1234yf (possibly with a small amount of HF thereby forming an azeotropic mixture) and minor amounts of 245cb and 1233xf. A second, heavier, stream is obtained at the bottom of the distillation column, and comprises HF, 1233xf, 245cb and minor amounts of 244bb. The lighter fraction containing HCl, 1234yf (with HF) and minor amounts other products is again distilled. The top flow comprises HCl, while the bottom flow comprises 1234yf and HF, which can again be separated using appropriate known methods. Among known methods is the decantation, which produces an HF rich flow which can be recycled to the gas-phase reactor. This decreases the fluorine content downstream in the process, generating less side-products (e.g. CaF_2 which must be discarded). The streams exiting the decantation are treated according to known methods, including washing and scrubbing and distillations.

[0021] Figure 3 represents another embodiment, where HCl is removed in a first step before distillation of the organic fluorinated products takes place. The gas-phase reactor is fed with 1233xf and HF. The reaction mixture exiting the reactor comprises HCl, unreacted 1233xf, unreacted HF, 1234yf, 245cb and a minor amount of 244bb. This reaction stream is separated by a first distillation into a stream containing mainly HCl and another stream containing the other products. This other

stream is separated by distillation into a first stream (light products) comprising 1234yf (possibly with a small amount of HF thereby forming an azeotropic mixture) and minor amounts of 245cb and 1233xf. A second, heavier, stream is obtained at the bottom of the distillation column, and comprises HF, 1233xf, 245cb and minor amounts of 244bb. The lighter fraction containing 1234yf (with HF) and minor amounts other products is obtained at the top of the second distillation tower. This top flow can again be separated using appropriate known methods. Among known methods is the decantation, which produces a flow of HF which can be recycled to the gas-phase reactor. This decreases the fluorine content downstream in the process, generating less side-products (e.g. CaF_2 which must be discarded). The streams exiting the decantation are treated according to known methods, including washing and scrubbing and distillations.

[0022] The applicant has found that the stream exiting the gas-phase reactor has a specific composition, due to the recycling of 245cb. Hence, the invention provides also a composition containing 2,2,2,3-tetrafluoropropene (1234yf), 1,1,1,2,2-pentafluoropropane (245cb) and 1,1,1,2-tetrafluoro-2-chloropropane (244bb) such that the molar ratio of 245cb to 244bb is from 1:1 to 70:1, and the molar ratio of 1234yf:245cb is from 1:5 to 3:1; preferably the molar ratio of 245cb to 244bb is from 1.5:1 to 65:1, and the molar ratio of 1234yf:245cb is from 1:4 to 2:1. The composition may also comprise 1233xf, and optionally other compounds such as unreacted HF and HCl.

[0023] The gas phase reaction is carried out in the presence of a fluorination catalyst. The reaction is carried out in a single gas-phase reactor.

[0024] The level of the conversion and selectivity of the desired product can vary according to the processing conditions. The catalyst can be present in any suitable form, such as fixed or fluidized bed, preferably in a fixed bed. The direction of flow may be downward or upward.

[0025] This catalyst is for example a catalyst based on a metal including a transition metal oxide or a derivative or halide or oxyhalide such a metal. Catalysts are e.g. FeCl_3 , chromium oxyfluoride, chromium oxides (that can optionally be subject to fluorination treatments), chromium fluorides, and mixtures thereof. Other possible catalysts are the catalysts supported on carbon catalysts based on antimony, catalysts based on aluminum (as AlF_3 and Al_2O_3 and oxyfluoride of alumina and aluminum fluoride). Generally speaking, catalysts that can be used are chromium oxyfluoride, aluminium fluoride and oxyfluoride, and supported or unsupported catalyst containing a metal such as Cr, Ni, Zn, Ti, V, Zr, Mo, Ge, Sn, Pb, Mg. Reference can also be made to the disclosures of WO-A-2007/079431, at page 7, lines 1-5 and 28-32, EP-A-939071, at paragraph [0022], WO 2008/054781 at page 9 line 22 to page 10 line 34, WO 2008/040969 in claim 1.

[0026] Prior to its use, the catalyst is subjected to activation with HF at high pressure, typically above about 10 bars (typically at a pressure above the pressure used

in the gas-phase process), as described in US-A-7485598.

[0027] A preferred embodiment uses a particular catalyst, which is a mixed catalyst, containing both chromium and nickel. The molar ratio Cr: Ni, with respect to the metallic element is generally between 0.5 and 5, for example between 0.7 and 2, including close to 1. The catalyst may contain in weight from 0.5 to 20% chromium and 0.5 to 20% nickel, preferably between 2 and 10% of each metal.

[0028] The metal may be present in metallic form or as derivatives, including oxide, halide or oxyhalide. These derivatives, including halide and halide oxides, are obtained by activation of the catalytic metal. Although the activation of the metal is not necessary, it is preferred.

[0029] The support is preferably made from aluminum. There are several possible carriers such as alumina, activated alumina or aluminum derivatives. These derivatives include aluminum halides and halide oxides of aluminum, for example described in US-P-4902838, or obtained by the activation process described below.

[0030] The catalyst may include chromium and nickel in a non-activated or activated form, on a support that has been subjected to activation or not.

[0031] Reference can be made to WO 2009/118628, and especially to the disclosure of the catalyst from page 4, line 30 to page 7, line 16.

[0032] According to another embodiment, the process uses a high surface area Cr based catalyst which is preferably unsupported. The catalyst can optionally contain a low level of one or more co-catalyst such as Co, Zn, Mn, Mg and Ni salt. A preferred co-catalyst is nickel. Another preferred co-catalyst is Zn.

[0033] The preferred unsupported chromium catalyst can optionally contain low levels of one or more co-catalysts selected from cobalt, nickel, zinc or manganese, prepared by processes known in the art, such as impregnation, mixed powder and the like. The catalyst can be supported or unsupported. For supported catalyst, the catalyst support can be selected from materials known in the art to be compatible with HF at higher temperature and pressure. For example, fluorinated alumina, prefluorinated activated carbon, graphite or fluorinated graphite are suitable catalyst supports. A preferred chromium catalyst is a high surface area unsupported chromium oxide catalyst. The catalyst is activated before use. The catalyst activation typically comprises a high pressure, above 10 bars, procedure wherein the catalyst bed is heated to about 370-380° C, preferably with a continuous flow of nitrogen, after which a mixture of approximately equal volumes of HF and air or nitrogen (preferably nitrogen) are fed over the catalyst bed. The catalyst activation process can be as described in US7485598 Other fluorinated organic compounds such as CHF₂Cl, CHF₃, CF₃CH₂F, CF₃CH₂Cl and the like can be used for activation. Typically the high pressure catalyst activation procedure takes about 18 hours.

[0034] The resulted high-pressure activated catalyst

has a high surface area, such as from about 20 to about 250 square meters per gram. The fluorine content typically varies between about 20 to 25 wt%. The pore volume has an average value between 0.1 to 0.4 m³/g. Crushing strength is typically between about 8 to 15 kg/g. Percent attrition is typically on average between 1 to 5 wt%. Cr (VI) level is typically in the range of 100 to 300 ppm.

[0035] The level of the co-catalyst, when present, can be varied between 1 to 10 wt%, preferable between 1 to 5 wt%. Co-catalyst can be added to the catalyst by processes known in the art such as adsorption from an aqueous or organic solution, followed by solvent evaporation. The preferred catalyst in this embodiment is pure chromium oxide with nickel or zinc as a co-catalyst. Alternatively the co-catalyst can be physically mixed with the catalyst via grinding to produce an intimate mixture. An alternative catalyst is a mixed chromium/nickel catalyst supported on fluorinated alumina. US 5731481 discloses a method of preparation of this alternative catalyst which would be activated as described hereinabove.

[0036] For example, a catalyst which can be used in the invention can be prepared as follows. A Cr₂O₃ catalyst was activated at 16 bars and 350°C using HF and nitrogen gas. The chemical and physical properties of the resulting catalyst are shown in the table below.

%F Content wt%	22.2
Surface Area m ² /g ¹	43.9
Pore Volume m ³ /g ²	0.19
Crush Strength kg/g ³	10.6
Cr ^{+VI} content ppm	201
% Attrition ⁴	3.9
1. Surface area was determined by the BET surface area by Micrometrics ASAP 2400 2. Pore volume was evaluated using xylene porosity measurement. 3. Crush strength was evaluated by applying a specified rate of compression, until the integrity of the catalyst is compromised. 4. Percent Attrition was evaluated by using ASTM D-4058-92 Standard test method for attrition.	

[0037] The process of the present invention is run continuously.

[0038] The 1233xf fluorination process involves contacting 1233xf with HF in the reaction zone in a gas phase, under conditions sufficient to convert the 1233xf to fluorination products comprising unreacted 1233xf, 1234yf and 245cb. Such conditions are given below. In addition, other co-produced underfluorinated intermediates such as 244bb which may be present in minor amounts and unreacted 1233xf which are produced as part of the fluorination reaction are also recycled to the reactor. The re-

cycle stream contains the heavy fraction of the reaction stream which has been separated in the distillation step, and especially the equilibrated 245cb.

[0039] Typically, step (i) is carried out with a molar ratio HF:1233xf from 3:1 to 150:1, preferably 4:1 to 70:1, more preferably 5:1 to 50:1.

[0040] Typically, step (i) is carried out at a pressure from 3 to 20 bars, preferably 5 to 15 bars, more preferably 7 to 10 bars.

[0041] Typically, step (i) is carried out at a temperature of from 200 to 450°C, preferably from 300 to 430°C, more preferably from 320 to 420°C. The temperature of the bed can be substantially uniform in the reactor or can be adjusted along the path of the stream, decreasing or increasing along the direction of flow.

[0042] Contact times (catalyst volume divided by the total flow rate of reactants and co-feeds, adjusted to the operating pressure and temperature) are typically from 6 to 100 sec, preferably from 10 to 80 sec, more preferably from 15 to 50 sec.

[0043] An oxygen co-feed or chlorine co-feed is used to extend the catalyst lifetime, typically in an amount of from 0.05 to 15 mole%, preferably 0.5 to 10 mole% of oxygen or chlorine per 1230xa. The oxygen can be introduced as an oxygen-containing gas such as air, pure oxygen, or an oxygen/nitrogen mixture. Chlorine can be introduced as a chlorine-containing gas such as pure chlorine, or a chlorine/nitrogen mixture.

[0044] A polymerization inhibitor can be used to extend the catalyst life, typically in a concentration of from about 50-1000 ppm, more preferably between 100-500 ppm. The polymerization inhibitor can be p-methoxyphenol, t-amylphenol, limonene, d,1-limonene, quinones, hydroquinones, epoxides, amines and mixtures thereof. The preferred polymerization inhibitor is p-methoxyphenol or t-amylphenol. The co-feeding of a low level of a polymerization inhibitor can control such polymerization of chlorolefins and extend the life of the catalyst as described in US5714651.

[0045] The reactants can be fed to the reactor at the same location, at different locations, or using staged feeding at staged locations along the reactor. A preferred feeding system is to blow the gaseous reactants at the bottom of the reactor. Recycling can be done at the entry of the reactor or at an intermediate stage of the reactor; preferably at the entry of the reactor.

[0046] In another embodiment, the reaction stream exiting the gas-phase reactor can be recycled in part to the reactor, before it is subjected to the separation into a first, light, stream and a second, heavy stream. The recycling ratio can be as high as 0.7. This recycling allows dilution of 1233xf which is very reactive and avoids polymerisation.

[0047] Reactions are implemented in a dedicated reactor for reactions involving halogens. Such reactors are known to those skilled in the art and can include linings based eg Hastelloy®, Inconel®, Monel® or fluoropolymers. The reactor may also include means of heat ex-

change, if necessary.

[0048] As used herein, percentages are by molar percent unless specified otherwise.

[0049] The following examples illustrate the invention without limiting it. EXAMPLES.

[0050] In the following examples, use is made of a catalyst Ni-Cr/AlF₃ which is obtained as follows. The catalyst used is a mixed catalyst nickel/chromium of atomic ratio of Ni/Cr = 1, supported on alumina fluoride and is prepared by impregnating solutions of nickel and chromic anhydride (CrO₃). After impregnation and drying, the solid is treated at a temperature between 320°C and 390°C in the presence of a mixture of hydrofluoric acid and nitrogen (concentration by volume of 5 to 10% of this acid in nitrogen). The catalyst bed is placed on a grid welded to the lower end of reactor. The reactor is equipped with a temperature measurement at three locations along the catalyst bed.

20 Example 1. Fluorination of 1233xf.

[0051] 150 ml of catalyst Ni-Cr/AlF₃ are introduced into the reactor. The reactor was fed with 16.4 g/hr of HF and 4.1 g/h 1233xf. The reaction temperature is 352°C and atmospheric pressure. HF/1233xf molar ratio is 26.9 and the contact time of 4.9 seconds. The conversion rate is then 10.3%. The selectivities (amount of one product divided by the sum of all the products of reaction, this means without 1233xf) were 71.4% in 1234yf, 22.7% in 245cb. Other minor compounds detected are: 244bb, 1234ze and 245fa. (outlet gas flow contained 89.13 mol% 1233xf, 7.75 mol% 1234yf, 2.47 mol% 245cb and 0.65 mol% others).

35 Examples 2 to 6. Equilibrium 1234yf/245cb.

[0052] The fluorination reaction of 1233xf is performed according to example 1 described above. The flows of HF and 1233xf are adjusted to obtain a molar ratio HF/1233xf close to 5 but varying contact time: 9.5, 18.8, 26.7, 37.9 and 39 seconds. The products that are mainly obtained are 1234yf and 245cb (if one excludes the 1233xf, not completely converted). The molar compositions 1234yf and 245cb are summarized in table 1. It can be concluded that an equilibrium takes place between 1234yf and 245cb.

	Contact time	1234yf	245cb
	(s)	(%)	(%)
Ex. 2	9.5	72.53	27.47
Ex. 3	18.8	69.13	30.87
Ex. 4	26.7	66.49	33.51
Ex. 5	37.9	66.28	33.72
Ex. 6	39	66.18	33.82

Example 7.

[0053] The fluorination reaction of 1233xf is performed according to the embodiment described in Example 1 with an amount of 60 ml of catalyst introduced into the 60ml reactor. The 245cb is added to the feed. The flow of 245cb is 2.1 g/hr, the flow 1233xf is 4.5 g/hr and the flow of HF is 16.2 g/hr. Hence, 100 mol of 1233xf are used with 47 mol 245cb. HF/1233xf molar ratio is equal to 24.5 and the contact time is equal to 4.8s. Air is continuously added in order to preserve the life of the catalyst. The amount of oxygen introduced is expressed in molar ratio $O_2/(1233xf + 245cb)$ and is equal to 0.5%. The molar composition of gas leaving is analyzed by a gas chromatograph: 60.6% 1233xf, 26.6% 1234yf, 12.4% 245cb and some other impurities. (89.08 mol 1233xf; 39.07mol 1234yf; 18.17 mol 245cb and 0.72 mol others).

Claims

1. A process for preparing 2,3,3,3-tetrafluoropropene (1234yf), comprising:

- (i) contacting 2-chloro-3,3,3-trifluoro-1-propene (1233xf) with hydrogen fluoride HF in gas phase in the presence of a fluorination catalyst under conditions sufficient to produce a reaction mixture;
- (ii) separating the reaction mixture into a first stream comprising HCl, 2,3,3,3-tetrafluoropropene (1234yf) and a second stream comprising HF, unreacted 2-chloro-3,3,3-trifluoro-1-propene (1233xf) and 1,1,1,2,2-pentafluoropropane (245cb);
- (iii) recycling at least a part of the second stream at least in part back to step (i), wherein step (i) is carried out in the presence of O_2 and/or Cl_2 and wherein the process is continuous.

2. Process according to claim 1, wherein the first stream is further separated into HCl and 2,3,3,3-tetrafluoropropene (1234yf).

3. A process for preparing 2,3,3,3-tetrafluoropropene (1234yf), comprising:

- (i) contacting 2-chloro-3,3,3-trifluoro-1-propene (1233xf) with hydrogen fluoride HF in gas phase in the presence of a fluorination catalyst under conditions sufficient to produce a reaction mixture;
- (ii) separating the reaction mixture into HCl and a stream containing the fluorinated products;
- (iii) separating said stream containing the fluorinated products into a first stream comprising

2,3,3,3-tetrafluoropropene (1234yf) and a second stream comprising HF, unreacted 2-chloro-3,3,3-trifluoro-1-propene (1233xf) and 1,1,1,2,2-pentafluoropropane (245cb);

(iv) recycling at least a part of the second stream at least in part back to step (i),

wherein step (i) is carried out in the presence of O_2 and/or Cl_2

and wherein the process is continuous.

4. Process according to any one of claims 1 to 3, wherein the reaction mixture separated at step (ii) comprises 2,3,3,3-tetrafluoropropene (1234yf) and 1,1,1,2,2-pentafluoropropane (245cb) in a molar ratio of 1:5 to 3:1.

5. Process according to claim 4, wherein the reaction mixture separated at step (ii) comprises 2,3,3,3-tetrafluoropropene (1234yf), 1,1,1,2,2-pentafluoropropane (245cb) and 1,1,1,2-tetrafluoro-2-chloropropane (244bb) such that the molar ratio of 245cb to 244bb is from 1:1 to 70:1.

6. Process according to any one of claims 1 to 5, wherein step (i) is carried out with a molar ratio HF:1233xf from 3:1 to 150:1.

7. Process according to any one of claims 1 to 6, wherein step (i) is carried out at a pressure from 3 to 20 bars.

8. Process according to any one of claims 1 to 7, wherein step (i) is carried out at a temperature of from 200 to 450°C.

9. Process according to any one of claims 1 to 8, wherein step (i) is carried out with a contact time from 6 to 100 sec.

10. Process according to any one of claims 1 to 9, wherein the ratio of O_2 and/or Cl_2 with respect to 2-chloro-3,3,3-trifluoro-1-propene (1233xf) is 0.05 to 15 mole%

11. Process according to any one of claims 1 to 10, wherein the step of separating into a first stream and a second stream is a distillation step.

12. Process according to any one of claims 1 to 11, wherein step (i) is carried out in the presence of a polymerization inhibitor.

13. Process according to claim 12, wherein the polymerization inhibitor, is chosen from the group consisting of p-methoxyphenol, t-amylphenol, limonene, d,l-limonene, quinones, hydroquinones, epoxides, amines and mixtures thereof.

14. Process according to any one of claims 1 to 13,

wherein step (i) is carried out in the presence of a catalyst comprising Ni-Cr, supported or unsupported.

15. Process according to any one of claims 1 to 14, wherein said catalyst is supported on a support selected from fluorinated alumina, fluorinated chromia, fluorinated activated carbon or graphite carbon.

Patentansprüche

1. Verfahren zum Herstellen von 2,3,3,3-Tetrafluorpropen (1234yf), umfassend:

(i) Inkontaktbringen von 2-Chlor-3,3,3-trifluor-1-propen (1233xf) mit Fluorwasserstoff, HF, in der Gasphase in Gegenwart eines Fluorierungskatalysators unter Bedingungen, die ausreichend sind, um ein Reaktionsgemisch zu erzeugen;
(ii) Trennen des Reaktionsgemisches in einen ersten Strom, umfassend HCl, 2,3,3,3-Tetrafluorpropen (1234yf), und einen zweiten Strom, umfassend HF, nichtumgesetztes 2-Chlor-3,3,3-trifluor-1-propen (1233xf) und 1,1,1,2,2-Pentafluorpropan (245cb);
(iii) Zurückführen mindestens eines Teils des zweiten Stroms im Kreislauf mindestens teilweise zurück zu Schritt (i), wobei Schritt (i) in Gegenwart von O₂ und/oder Cl₂ durchgeführt wird und wobei das Verfahren kontinuierlich ist.

2. Verfahren nach Anspruch 1, wobei der erste Strom weiter in HCl und 2,3,3,3-Tetrafluorpropen (1234yf) getrennt wird.

3. Verfahren zum Herstellen von 2,3,3,3-Tetrafluorpropen (1234yf), umfassend:

(i) Inkontaktbringen von 2-Chlor-3,3,3-trifluor-1-propen (1233xf) mit Fluorwasserstoff, HF, in der Gasphase in Gegenwart eines Fluorierungskatalysators unter Bedingungen, die ausreichend sind, um ein Reaktionsgemisch zu erzeugen;
(ii) Trennen des Reaktionsgemisches in HCl und einen Strom, der die fluorierten Produkte enthält;
(iii) Trennen des Stroms, der die fluorierten Produkte enthält, in einen ersten Strom, umfassend 2,3,3,3-Tetrafluorpropen (1234yf), und einen zweiten Strom, umfassend HF, nichtumgesetztes 2-Chlor-3,3,3-trifluor-1-propen (1233xf) und 1,1,1,2,2-Pentafluorpropan (245cb);
(iv) Zurückführen mindestens eines Teils des zweiten Stroms im Kreislauf mindestens teilweise zurück zu Schritt (i), wobei Schritt (i) in Gegenwart von O₂ und/oder

Cl₂ durchgeführt wird und wobei das Verfahren kontinuierlich ist.

4. Verfahren nach einem von Anspruch 1 bis 3, wobei das Reaktionsgemisch, das in Schritt (ii) getrennt wird, 2,3,3,3-Tetrafluorpropen (1234yf) und 1,1,1,2,2-Pentafluorpropan (245cb) in einem Molverhältnis von 1 : 5 bis 3 : 1 umfasst.
5. Verfahren nach Anspruch 4, wobei das Reaktionsgemisch, das in Schritt (ii) getrennt wird, 2,3,3,3-Tetrafluorpropen (1234yf), 1,1,1,2,2-Pentafluorpropan (245cb) und 1,1,1,2-Tetrafluor-2-chlorpropan (244b) umfasst, derart, dass das Molverhältnis von 245cb zu 244bb von 1 : 1 bis 70 : 1 beträgt.
6. Verfahren nach einem von Anspruch 1 bis 5, wobei Schritt (i) bei einem Molverhältnis HF : 1233xf von 3 : 1 bis 150 : 1 durchgeführt wird.
7. Verfahren nach einem von Anspruch 1 bis 6, wobei Schritt (i) bei einem Druck von 3 bis 20 bar durchgeführt wird.
8. Verfahren nach einem von Anspruch 1 bis 7, wobei Schritt (i) bei einer Temperatur von 200 bis 450 °C durchgeführt wird.
9. Verfahren nach einem von Anspruch 1 bis 8, wobei Schritt (i) mit einer Kontaktdauer von 6 bis 100 s durchgeführt wird.
10. Verfahren nach einem von Anspruch 1 bis 9, wobei das Verhältnis von O₂ und/oder Cl₂ mit Bezug auf 2-Chlor-3,3,3-trifluor-1-propen (1233xf) von 0,05 bis 15 Mol-% beträgt.
11. Verfahren nach einem von Anspruch 1 bis 10, wobei der Schritt des Trennens in einen ersten Strom und einen zweiten Strom ein Destillationsschritt ist.
12. Verfahren nach einem von Anspruch 1 bis 11, wobei Schritt (i) in Gegenwart eines Polymerisationshemmers durchgeführt wird.
13. Verfahren nach Anspruch 12, wobei der Polymerisationshemmer aus der Gruppe ausgewählt wird, die aus p-Methoxyphenol, t-Amylphenol, Limonen, d,1-Limonen, Chinonen, Hydrochinonen, Epoxiden, Aminen und Gemischen davon besteht.
14. Verfahren nach einem von Anspruch 1 bis 13, wobei Schritt (i) in Gegenwart eines Katalysators, umfassend Ni-Cr, geträgert oder ungeträgert, durchgeführt wird.
15. Verfahren nach einem von Anspruch 1 bis 14, wobei der Katalysator auf einem Träger, ausgewählt aus

fluoriertem Aluminiumoxid, fluoriertem Chrom(III)-oxid, fluorierter Aktivkohle oder Graphitkohlenstoff, geträgert wird.

Revendications

1. Un procédé de préparation de 2,3,3,3-tétrafluoropropène (1234yf), comprenant :

(i) la mise en contact du 2-chloro-3,3,3-trifluoro-1-propène (1233xf) avec du fluorure d'hydrogène HF en phase gazeuse en présence d'un catalyseur de fluoration dans des conditions suffisantes pour produire un mélange réactionnel ;
 (ii) la séparation du mélange réactionnel en un premier courant comprenant HCl, du 2,3,3,3-tétrafluoropropène (1234yf) et un second courant comprenant HF, le 2-chloro-3,3,3-trifluoro-1-propène (1233xf) n'ayant pas réagi et le 1,1,1,2,2-pentafluoropropane (245cb);
 (iii) le recyclage d'au moins une partie du second courant au moins en partie vers l'étape (i), dans lequel l'étape (i) est mise en oeuvre en présence d'O₂ et/ou Cl₂ et dans lequel le procédé est continu.

2. Procédé selon la revendication 1, dans lequel le premier courant est ensuite séparé en HCl et le 2,3,3,3-tétrafluoropropène (1234yf).

3. Un procédé de préparation de 2,3,3,3-tétrafluoropropène (1234yf), comprenant :

(i) la mise en contact du 2-chloro-3,3,3-trifluoro-1-propène (1233xf) avec du fluorure d'hydrogène HF en phase gazeuse en présence d'un catalyseur de fluoration dans des conditions suffisantes pour produire un mélange réactionnel ;
 (ii) la séparation du mélange réactionnel en HCl et un courant contenant les produits fluorés ;
 (iii) la séparation dudit courant contenant les produits fluorés en un premier courant comprenant le 2,3,3,3-tétrafluoropropène (1234yf) et un second courant comprenant HF, le 2-chloro-3,3,3-trifluoro-1-propène (1233xf) n'ayant pas réagi et le 1,1,1,2,2-pentafluoropropane (245cb);
 (iv) le recyclage d'au moins une partie du second courant au moins en partie vers l'étape (i), dans lequel l'étape (i) est mise en oeuvre en présence d'O₂ et/ou Cl₂ et dans lequel le procédé est continu.

4. Procédé selon l'une des revendications 1 à 3, dans lequel le mélange réactionnel séparé à l'étape (ii) comprend le 2,3,3,3-tétrafluoropropène (1234yf) et le 1,1,1,2,2-pentafluoropropane (245cb) dans un

rapport molaire de 1:5 à 3:1.

5. Procédé selon la revendication 4, dans lequel le mélange réactionnel séparé à l'étape (ii) comprend le 2,3,3,3-tétrafluoropropène (1234yf), le 1,1,1,2,2-pentafluoropropane (245cb), et le 1,1,1,2-tetrafluoro-2-chloropropane (244bb) de telle sorte que le rapport molaire du 245cb au 244bb soit de 1:1 à 70:1.
6. Procédé selon l'une des revendications 1 à 5, dans lequel l'étape (i) est mise en oeuvre avec un rapport molaire HF:1233xf de 3:1 à 150:1.
7. Procédé selon l'une des revendications 1 à 6, dans lequel l'étape (i) est mise en oeuvre sous une pression de 3 à 20 bars.
8. Procédé selon l'une des revendications 1 à 7, dans lequel l'étape (i) est mise en oeuvre à une température de 200 à 450°C.
9. Procédé selon l'une des revendications 1 à 8, dans lequel l'étape (i) est mise en oeuvre avec un temps de contact de 6 à 100 sec.
10. Procédé selon l'une des revendications 1 à 9, dans lequel le rapport molaire de O₂ et/ou Cl₂ par rapport au 2-chloro-3,3,3-trifluoro-1-propène (1233xf) est 0,05 à 15% en moles.
11. Procédé selon l'une des revendications 1 à 10, dans lequel l'étape de séparation en un premier courant et un second courant est une étape de distillation.
12. Procédé selon l'une des revendications 1 à 11, dans lequel l'étape (i) est mise en oeuvre en présence d'un inhibiteur de polymérisation.
13. Procédé selon la revendication 12, dans lequel l'inhibiteur de polymérisation est choisi dans le groupe constitué par le p-méthoxyphénol, le t-amylphénol, le limonène, le d,1-limonène, les quinones, les hydroquinones, les époxydes, les amines et leurs mélanges.
14. Procédé selon l'une des revendications 1 à 13, dans lequel l'étape (i) est mise en oeuvre en présence d'un catalyseur comprenant du Ni-Cr supporté ou non supporté.
15. Procédé selon l'une des revendications 1 à 14, dans lequel ledit catalyseur est supporté sur un support choisi parmi l'alumine fluorée, l'oxyde de chrome fluoré, du charbon actif fluoré ou du carbone graphité.

Fig 1

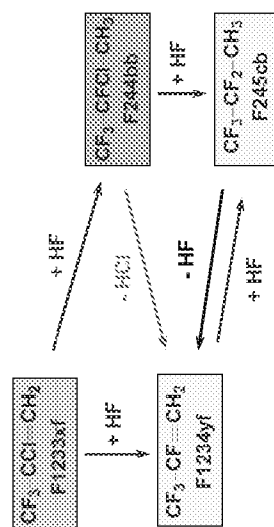


Fig 2

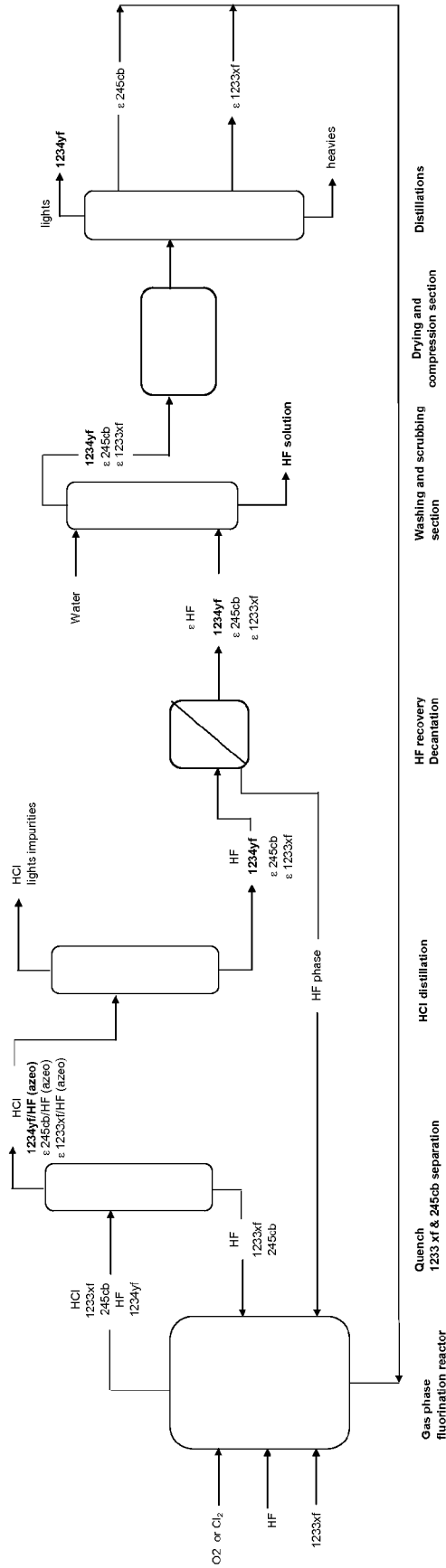
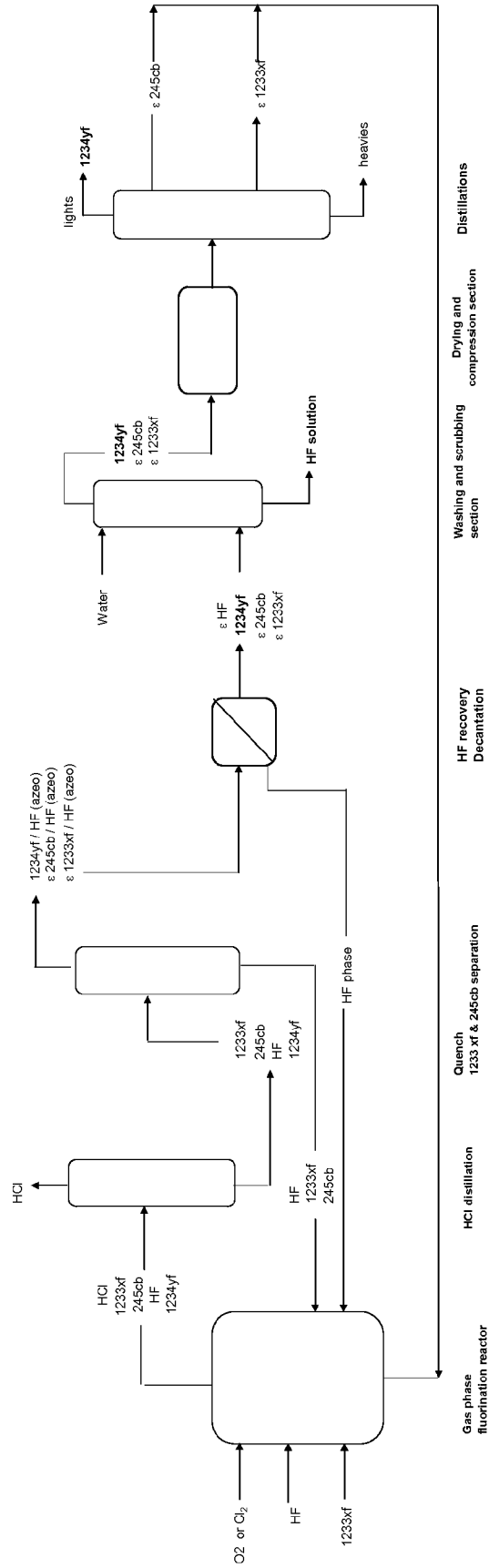


Fig 3



REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2007079431 A [0004] [0025]
- EP 939071 A [0005] [0025]
- WO 2008054781 A [0006] [0025]
- WO 2008002500 A [0007]
- WO 2008040969 A [0008] [0025]
- WO 2009015317 A [0009]
- US 20090240090 A [0010]
- WO 2009003084 A [0011]
- WO 2009137658 A [0012]
- US 2009124837 A [0013]
- US 7485598 A [0026]
- US 4902838 P [0029]
- WO 2009118628 A [0031]
- US 7485598 B [0033]
- US 5731481 A [0035]
- US 5714651 A [0044]



SZTNH-100002427

Szabadalmi igénypontok

1. Eljárás 2,3,3,3-tetrafluorpropén (1234yf) előállítására, amely tartalmazza:
 - (i) 2-klór-3,3,3-trifluor-1-propén (1233xf) kapcsolatba hozását HF hidrogén-fluoriddal gázfázisban fluorozó katalizátor jelenlétében, reakcióelegy előállításához megfelelő körülmények között;
 - (ii) a reakcióelegy szétválasztását egy első áramra, amely tartalmaz HCl-t, 2,3,3,3-tetrafluorpropént (1234yf), és egy második áramra, amely tartalmaz HF-t, elreagálatlan 2-klór-3,3,3-trifluor-1-propént (1233xf) és 1,1,1,2,2-pentafluorpropánt (245cb);
 - (iii) a második áram legalább egy részletének legalább részbeni visszaforgatását az (i) lépésbe, ahol az (i) lépést O_2 és/vagy Cl_2 jelenlétében végezzük és ahol az eljárás folytonos.
2. Az 1. igénypont szerinti eljárás, ahol az első áramot szétválasztjuk HCl-re és 2,3,3,3-tetrafluorpropénre (1234yf).
3. Eljárás 2,3,3,3-tetrafluorpropén (1234yf) előállítására, amely tartalmazza:
 - (i) 2-klór-3,3,3-trifluor-1-propén (1233xf) kapcsolatba hozását HF hidrogén-fluoriddal gázfázisban fluorozó katalizátor jelenlétében, reakcióelegy előállításához megfelelő körülmények között;
 - (ii) a reakcióelegy szétválasztását HCl-re és a fluorozott terméket tartalmazó áramra;
 - (iii) a fluorozott terméket tartalmazó áram szétválasztása egy 2,3,3,3-tetrafluorpropént (1234yf) tartalmazó első áramra, és egy második áramra, amely tartalmaz HF-t, elreagálatlan 2-klór-3,3,3-trifluor-1-propént (1233xf) és 1,1,1,2,2-pentafluorpropánt (245cb);
 - (iv) a második áram legalább egy részletének legalább részbeni visszaforgatását az (i) lépésbe, ahol az (i) lépést O_2 és/vagy Cl_2 jelenlétében végezzük, és ahol az eljárás folytonos.
4. Az 1-3. igénypontok bármelyike szerinti eljárás, ahol a (ii) lépésnél szétválasztott reakcióelegy 2,3,3,3-tetrafluorpropént (1234yf) és 1,1,1,2,2-pentafluorpropánt (245cb) 1:5 - 3:1 mólarányban tartalmaz.
5. A 4. igénypont szerinti eljárás, ahol a (ii) lépésnél szétválasztott reakcióelegy tartalmaz 2,3,3,3-tetrafluorpropént (1234yf), 1,1,1,2,2-pentafluorpropánt (245cb) és 1,1,1,2-tetrafluor-2-klórpropánt (244bb), és a 245cb-nek a 244bb-re vonatkoztatott mólaránya 1:1 - 70:1.
6. Az 1-5. igénypontok bármelyike szerinti eljárás, ahol az (i) lépést 3:1 - 150:1 HF:1233xf mólarány mellett végezzük.
7. Az 1-6. igénypontok bármelyike szerinti eljárás, ahol az (i) lépést 3-20 bar nyomáson végezzük.
8. Az 1-7. igénypontok bármelyike szerinti eljárás, ahol az (i) lépést 200-450°C hőmérsékleten végezzük.

9. Az 1-8. igénypontok bármelyike szerinti eljárás, ahol az (i) lépést 6-100 másodperc kontaktidő mellett végezzük.

10. Az 1-9. igénypontok bármelyike szerinti eljárás, ahol az O_2 -nek és/vagy Cl_2 -nak a 2-klór-3,3,3-trifluor-1-propénre (1233xf) vonatkoztatott aránya 0,05 - 15 mol%.

11. Az 1-10. igénypontok bármelyike szerinti eljárás, ahol az első áramra és második áramra történő szétválasztási lépés egy desztillációs lépés.

12. Az 1-11. igénypontok bármelyike szerinti eljárás, ahol az (i) lépést polimerizációs inhibitor jelenlétében végezzük.

13. A 12. igénypont szerinti eljárás, ahol a polimerizációs inhibitor a következők alkotta csoportból választott: p-metoxifenol, t-amilfenol, limonén, d,l-limonén, kinonok, hidrokinonok, epoxidok, aminos és ezek keverékei.

14. Az 1-13. igénypontok bármelyike szerinti eljárás, ahol az (i) lépést hordozós vagy hordozó nélküli, Ni-Cr-t tartalmazó katalizátor jelenlétében végezzük.

15. Az 1-14. igénypontok bármelyike szerinti eljárás, ahol a katalizátor hordozós, és a hordozó a következők közül választott: fluorozott alumínium-oxid, fluorozott króm(III)-oxid, fluorozott aktívszén vagy grafit szén.