

Method and facility for separating a mixture comprising at least one fluorinated fluid and one or more contaminants

TECHNICAL FIELD OF THE INVENTION

- 5 The invention relates to the field of hydrofluorocarbons (HFC), hydrofluoroolefins (HFO), and/or hydrochlorofluoroolefins (HCFO) and relates to a method for recycling substances contained in mixtures comprising at least one fluorinated fluid and one or more contaminants.

10 **TECHNICAL BACKGROUND**

The fluorinated chemical components used as refrigerants, aerosol propellants, extinguishing agents, or blowing agents are known as hydrofluorocarbons (HFC) (composed of hydrogen, fluorine, and carbon atoms), hydrofluoroolefins (HFO), and hydrochlorofluoroolefins (HCFO) molecules.

- 15 HFC, HFO, and HCFO allow a thermodynamic cycle to be implemented in a cold production device (such as a cold room or a freezer) or in a heat production device (such as a heat pump). They may also be used as aerosol propellants, extinguishing agents, or blowing agents.

- A fluorinated fluid commonly comprises a pure chemical component, a pure molecule, or a mixture of chemical components. The main HFC/HFO/HCFO components are R-1234yf/ze, R-134a, R-32, R-227ea, R-125, R-152a, and R-143a, used alone or in mixtures with other components.

- The document WO 2022/078755 A1 describes a method for separating a plurality of chemical components from a chemical mixture, said chemical mixture comprising a plurality of fluorinated fluids, each fluorinated fluid comprising at least one fluorinated component. This method comprises a step of identifying at least two sub-mixtures, a primary distillation step, and a secondary distillation step.

- The document WO 2011/053449 A1 describes a method for separating 1,1,1,2-tetrafluoropropane from a mixture also comprising 1,1,1,2,3-pentafluoropropane and hydrogen fluoride by distillation.

- 30 The document EP 1 038 857 A1 describes a method for separating a mixture comprising 1,1,1,3,3-pentafluorobutane and hydrogen fluoride by distillation.

- Today, HFCs have replaced both chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFC) as refrigerants, spray propellants, and in the manufacture of insulating foams, because they do not attack the ozone layer and have a

lower global warming potential (GWP) than CFCs. Nevertheless, their contribution to global warming is significant because, even though their service life is relatively short, their GWP over a hundred years may be several thousand times greater than that of CO₂.

As a result, F-Gas legislation limits their use and encourages the recycling and reuse of these products. Reducing their consumption, or at least their release into the atmosphere, is one of the challenges of the next few years. HFC emissions have been rising since the 1990s, while current regulations aim to reduce their use. Known alternatives to HFC comprise the use of HFO or hydrocarbons such as propane (R290), which have a much lower GWP. For example, the GWP of R32 is 675, and that of R125 is 3500, while that of R290 is 3 according to the 4th IPCC report.

Unfortunately, the replacement of some of the fluorinated chemical components by hydrocarbons in refrigerants or refrigerant mixtures complicates the refrigerant recycling process, and, in particular, the possibility of separating the various substances using conventional distillation methods. A solution, therefore, remains to be found to improve the recycling of mixed fluorinated fluid mixtures in that they comprise either different types of fluorinated chemical components, or both fluorinated chemical components and hydrocarbons.

The aim of the invention is to provide a solution to one or more problems and disadvantages encountered in the prior art. In particular, the aim of the invention is to provide a method for recycling a plurality of chemical components of a chemical mixture comprising at least one fluorinated chemical component and one or more contaminants selected from one or more hydrocarbons and/or one or more fluorinated contaminants.

SUMMARY

To this end, according to a first aspect, the invention relates to a method for recycling a mixture comprising at least one fluorinated fluid, which is remarkable in that it comprises:

- a) supplying, in the form of an initial flow, a mixture comprising at least one fluorinated fluid; the mixture comprising one or more fluorinated chemical components and one or more contaminants selected from one or more hydrocarbons and/or one or more fluorinated contaminants;
- b) membrane filtrating the initial flow to obtain a purified flow comprising a contaminant content lower than the contaminant content of the initial flow and a contaminant-enriched flow, said membrane filtration comprising at least two membrane filtration sub-steps carried out successively; and
- c) recovering the purified flow and/or contaminant-enriched flow for reuse and/or recycling.

As will be clear from the definition just given, the invention proposes to perform double membrane filtration of a mixture comprising at least one fluorinated fluid to obtain a purified flow depleted in contaminants and a contaminant-enriched flow. According to the invention, the purified flow is the permeate and the contaminant-enriched flow (for example hydrocarbons when present) is the retentate.

The invention has a particular application in the decontamination of refrigerant mixture flows comprising hydrocarbon contaminants and in the separation of fluorinated chemical compound mixtures. The purified and/or enriched flows generated in this way may be reused directly or sent to an additional recycling facility comprising one or more fluorinated chemical component separation units for recycling by conventional means.

The invention is remarkable in that it allows, through this specific contaminant separation step, to increase the overall efficiency of a method for recycling a mixture comprising at least one fluorinated fluid. The contamination of the mixtures comprising at least one fluorinated fluid by contaminants such as hydrocarbons may, when the content of the latter is too high, affect the yield of the distillation methods, or even allow to recycle certain mixtures. Implementing a preliminary contaminant separation step was found to improve the distillation capacity and, therefore, the overall efficiency of the recycling method. In the case of fluorinated contaminants, the separation and purification of fluorinated chemical components is improved.

In one embodiment, the initial flow comprises one or more fluorinated fluids selected from difluoromethane (R32), pentafluoroethane (R125), 1,1,1,2-tetrafluoroethane (R134a), 2,3,3,3-tetrafluoropropene (R1234yf), and trans-1,3,3,3-tetrafluoroprop-1-ene (R1234ze).

In one embodiment, the initial flow comprises one or more fluorinated contaminants, and the or at least one fluorinated contaminant is 1,1,1,2,3,3,3-heptafluoropropane (R227ea) ; and/or the initial flow comprises one or more fluorinated contaminants, and step c) comprises recovering the contaminant-enriched flow and recycling it.

In one embodiment, the initial flow comprises one or more hydrocarbons selected from the group comprising propane and isobutane; and/or the initial flow comprises one or more hydrocarbons, and step c) comprises recovering the purified flow and recycling it.

Preferably, the initial flow comprises one or more fluorinated chemical components chosen from Hydrofluorocarbons (HFC), HydroChloroFluoro-carbons (HCFC), Hydrofluoroolefins (HFO) and Hydrochlorofluoroolefins (HCFO); more preferably, the initial flow comprises one or more fluorinated chemical components chosen from Hydrofluorocarbons (HFC) and/or Hydrofluoroolefins (HFO).

According to the invention, step b) of membrane filtration comprises at least two successive membrane filtration sub-steps. As shown in the examples, the implementation of a two-stage filtration, i.e., where at least two membrane filtration modules are arranged in series, significantly improves the separation of contaminants such as hydrocarbons. As may be seen, each filtration sub-step generates a permeate and a retentate, and the second filtration sub-step is carried out on the permeate from the first filtration sub-step.

Preferably, as each membrane filtration sub-step generates a permeate and a retentate, the retentate from the second membrane filtration sub-step is recycled to be mixed into the initial flow.

- 10 According to a preferred mode of implementation, step b) of membrane filtration comprises at least one filtration sub-step using a membrane comprising at least one layer of a material chosen from a polyethersulfone (PES), a polysulfone (PSU), a polyvinylidene fluoride (PVDF), a polyether block amide (PEBA), a polypropylene (PP), a cellulose acetate (AC), a polytetrafluoroethylene (PTFE), a sulphonated polyphenylene sulphone (sPPSU), a cellulose acetate butyrate (CAB), a polyhedral oligomeric silsesquioxane (POSS), or a polydimethylsiloxane (PDMS). Preferably, step b) of membrane filtration comprises at least one sub-step of filtration using a membrane comprising at least one layer of a material chosen to be a polyether block amide (PEBA) and/or a polyether sulphone (PES).

- For example, step b) of membrane filtration comprises at least one filtration sub-step using a membrane comprising at least one layer of a material chosen to be a polyether block amide (PEBA); preferably, the polyamide block comprises at least one polyamide chosen from polyamide 6, polyamide 11 and polyamide 12; preferably, polyamide 6.

- For example, membrane filtration step b) comprises at least one filtration sub-step using a multi-layer membrane comprising a layer of a material chosen to be polyether block amide (PEBA), and a layer of polyether sulphone (PES); preferably, the polyamide block comprises at least one polyamide chosen from polyamide 6, polyamide 11 and polyamide 12; preferably, polyamide 6.

- For example, the initial flow supplied in step a) comprises a contaminant content greater than or equal to 0.5% by weight relative to the total weight of the initial flow; for example, greater than or equal to 1.0%. For example, the initial flow supplied in step a) comprises a contaminant content of 5.0% to 40% by weight relative to the total weight of the initial flow. When the contaminant or contaminants consist of or comprise at least one fluorinated contaminant, the initial flow supplied in step a) comprises a fluorinated contaminant content greater than or equal to 0.5% by weight relative to the total weight of the initial flow; for example, greater than or equal to 1.0%. For example, the initial flow supplied in step a)

comprises a fluorinated contaminant content of 5.0% to 40% by weight based on the total weight of the initial flow.

When the contaminant or contaminants consist of or comprise at least one hydrocarbon, the initial flow supplied in step a) comprises a hydrocarbon content greater than or equal to 0.5% by weight relative to the total weight of the initial flow; for example, greater than or equal to 1.0%. For example, step a) comprises a step of identifying one or more contaminants in the initial flow and in that when the hydrocarbon content is greater than 40% by weight based on the total weight of the initial flow, it further comprises a sub-step of diluting the initial flow with another hydrocarbon-free flow to adjust the hydrocarbon content to be less than 40% by weight based on the total weight of the initial flow.

For example, the initial flow supplied in step a) comprises a hydrocarbon content of 5.0% to 40% by weight based on the total weight of the initial flow.

For example, step b) is carried out to obtain a hydrocarbon content of less than 5.0% by weight relative to the total weight of the purified flow; preferably less than or equal to 4.0% by weight; even more preferably less than or equal to 3.0% by weight; even more preferably less than or equal to 2.5% by weight. In fact, it has been found that an excessively high hydrocarbon content, such as a content in excess of 5.0% by weight, will degrade the distillation yield when recycling the purified mixture and/or the contaminant-enriched flow that may be performed in step c).

For example, step b) is carried out to obtain a purified flow with a hydrocarbon content reduced by at least a factor of 4 compared with the hydrocarbon content of the initial flow, preferably by at least a factor of 5, even more preferably by at least a factor of 6; more preferably by at least a factor of 8.

In a preferred embodiment, the initial flow comprises at least two fluorinated chemical components, and the recycling step c) comprises separating said fluorinated chemical components by distillation.

In one embodiment, the purified flow comprises a fluorinated component, and step c) comprises recycling said purified flow through at least one purification step or sub-step; preferably, the purification step is performed by simple distillation on at least one simple distillation column.

In one embodiment, the purified flow is an azeotropic mixture, and step c) comprises recycling said purified flow that includes one or more distillation sub-steps selected from

- at least one simple distillation sub-step on a simple distillation column; and/or
- at least one advanced pressure balance distillation sub-step; and/or
- at least one advanced extraction distillation sub-step.

Preferably, the purified flow is an azeotropic mixture, and step c) comprises recycling said purified flow that includes one or more distillation sub-steps comprising at least one single distillation sub-step on a single distillation column, followed by one or more advanced distillation sub-steps selected from

- 5 - at least one advanced pressure balance distillation sub-step; and/or
- at least one advanced extraction distillation sub-step.

For example, the step of separating fluorinated chemical components by distillation comprises:

- 10 - a sub-step of identifying within the mixture of fluorinated chemical components at least two sub-mixtures, each sub-mixture being a simple sub-mixture comprising a single fluorinated chemical component or a complex sub-mixture comprising a combination of chemical components, each complex sub-mixture being associated with either a first group of secondary distillation by a pressure balance distillation method or a second group of secondary distillation by an extraction distillation method,
- 15 - a primary distillation step, using a single distillation column, to separate each identified sub-mixture,
- a secondary distillation step, using at least two auxiliary columns, of each complex sub-mixture of the first group and of the second group, the complex sub-mixtures of the first group being separated by the pressure balance distillation method and the complex sub-
- 20 mixtures of the second group being separated, using a solvent, by the extraction distillation method.

According to a second aspect, the invention relates to a facility for implementing the method according to the first aspect, which is remarkable in that it comprises a membrane filtration unit comprising at least two membrane filtration modules arranged in series.

25 Preferably, the facility also comprises a distillation unit comprising:

- one or more simple distillation columns; and/or
- one or more columns configured to allow the implementation of an advanced distillation by extraction, and/or
- one or more columns configured to allow the implementation of an advanced pressure
- 30 balance distillation.

Preferably, the facility also comprises a distillation unit comprising:

- one or more simple distillation columns; and
- one or more columns configured to allow the implementation of an advanced distillation by extraction.

PRESENTATION OF THE FIGURES

The invention will be well understood, and other aspects and advantages will become clear from the following description given with reference to the attached figures listed below.

[Fig.1] Figure 1 illustrates an example of an embodiment of a facility according to the invention.

[Fig.2] Figure 2 shows a thin-layer composite membrane stage with a flow model in the supplying and permeate flows.

[Fig.3] Figure 3 is a graph showing the concentration of HFC+HFO in the permeate flow versus the recovery of HFC+HFO as a function of the supply pressure (1-8 bar) and the membrane surface area. Each data point represents a combination of supply pressure and membrane surface area. Supply flow rate = 10 kg h^{-1} . Membrane thickness = $2 \text{ }\mu\text{m}$. The composition of the supply is 90% by weight HFC + HFO and 10% by weight HC (R600a + R290).

[Fig.4] Figure 4 is a graph showing the concentration of R32+R125 in the permeate flow versus the recovery of R32+R125 as a function of the supply pressure (1-8 bar) and the membrane surface area. Each data point represents a combination of supply pressure and membrane surface area. Supply flow rate = 10 kg h^{-1} . Membrane thickness = $2 \text{ }\mu\text{m}$. The composition of the supply is 40% by weight R32, 40% by weight R125, 10% by weight R600a, and 10% by weight R290.

[Fig.5] Figure 5 shows a comparison of one-step and two-step HFC+HFO purification: the concentration of HFC+HFO in the permeate flow versus the recovery of HFC+HFO as a function of the supply pressure (1-8 bar) and the membrane surface area. Each data point represents a combination of supply pressure and membrane surface area. Supply flow rate = 10 kg h^{-1} . Membrane thickness = $2 \text{ }\mu\text{m}$. The composition of the supply is 90% by weight HFC + HFO and 10% by weight HC (R600a + R290).

[Fig.6] Figure 6 shows a comparison of one-step and two-step purification of R32+R125: the concentration of R32+R125 in the permeate flow versus the recovery of R32+R125 as a function of the supply pressure (1-8 bar) and the membrane surface area. Each data point represents a combination of supply pressure and membrane surface area. Supply flow rate = 10 kg h^{-1} . Membrane thickness = $2 \text{ }\mu\text{m}$. The composition of the supply is 40% by weight R32, 40% by weight R125, 10% by weight R600a, and 10% by weight R290.

[Fig. 7] Figure 7 shows a comparison of the one-step and the two-step R227ea purification: the concentration of R227ea in the retentate flow versus R227ea the recovery as a function of the supply pressure (1-4 bar) and the membrane surface area. Each data point represents a combination of supply pressure and membrane surface area. Supply flow rate

= 10 kg h⁻¹. Membrane thickness = 2 µm. The supply composition is 70% by weight R227ea, 20% by weight R1234ze, and 10% by weight R134a.

DETAILED DESCRIPTION

- 5 In the following description, the term "comprise" is synonymous with "include" and is not limitative in that it authorizes the presence of other elements in the facility described or other steps in the method to which it refers. It is understood that the term "comprise" includes "consist of". Throughout the description, the various figures use the same reference signs to designate identical or similar entities.
- 10 The invention relates to a method for recycling a mixture comprising at least one fluorinated fluid and to a facility for implementing such a method. The method and the facility will now be described together with reference to Figure 1.

According to the invention, the method for recycling a mixture 1 comprising at least one
15 fluorinated fluid is remarkable in that it comprises:

- a) providing, in the form of an initial flow 3, a mixture 1 comprising at least one fluorinated fluid; the mixture 1 comprising one or more fluorinated chemical components (41, 43, 49, 51, 55) and one or more contaminants selected from one or more hydrocarbons and/or one or more fluorinated contaminants; and
- 20 b) membrane filtrating the initial flow 3 to obtain a purified flow 5 comprising a contaminant content lower than the contaminant content of the initial flow 3 and a contaminant-enriched flow 33, said membrane filtration comprising at least two membrane filtration sub-steps carried out successively; and
- c) recovering the purified flow 5 and/or the contaminant-enriched flow 33 for reuse and/or
25 recycling.

In one embodiment, step c) comprises recovering the purified flow 5 and/or the contaminant-enriched flow 33 for reuse. Depending on the composition of the initial mixture, the purified flow 5 and/or the contaminant-enriched flow 33 may be recovered and reused as they are (without any further separation or purification step).

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In a preferred embodiment, step c) comprises recovering the purified flow 5 for its recycling. The purified flow 5 is recycled by separating and/or purifying the fluorinated chemical components (41, 43, 49, 51, 55) contained in the purified flow 5 by distillation.

In a preferred embodiment, step c) involves recovering the contaminant-enriched flow 33
35 for its recycling. The contaminant-enriched flow 33 is recycled by separating and/or purifying

the fluorinated contaminant or contaminants and/or the hydrocarbon or hydrocarbons contained in the contaminant-enriched flow by distillation.

5 According to one embodiment, the method for recycling a mixture 1 comprising at least one fluorinated fluid is remarkable in that it comprises:

- a) supplying, as an initial flow 3, a mixture 1 comprising at least one fluorinated fluid; the mixture 1 comprising one or more fluorinated chemical components (41, 43, 49, 51, 55) and one or more hydrocarbons; and
- 10 b) membrane filtrating the initial flow 3 to obtain a purified flow 5 comprising a hydrocarbon content lower than the hydrocarbon content of the initial flow 3, said membrane filtration comprising at least two membrane filtration sub-steps carried out successively; and
- c) recovering and recycling the purified flow

15 According to one embodiment, the method for recycling a mixture 1 comprising at least one fluorinated fluid is remarkable in that it comprises:

- a) providing, as an initial flow 3, a mixture 1 comprising at least one fluorinated fluid; the mixture comprising one or more fluorinated chemical components (41, 43, 49, 51, 55) and one or more fluorinated contaminants; and
- 20 b) membrane filtrating the initial flow 3 to obtain a purified flow 5 comprising a contaminant content lower than the contaminant content of the initial flow 3 and a contaminant-enriched flow 33, said membrane filtration comprising at least two membrane filtration sub-steps carried out successively; and
- c) recovering and recycling the contaminant-enriched flow 33.

25 The invention also relates to a facility for implementing the method, the facility comprising a membrane filtration unit 7 comprising at least two filtration modules (9, 11).

Preferably, the facility also comprises a distillation unit 13 comprising

- one or more single distillation columns 15; and/or
- one or more columns (21, 23) configured to allow the implementation of an advanced
- 30 distillation by extraction, and/or
- one or more columns (17, 19) configured to allow the implementation of an advanced pressure balance distillation.

More preferably, the facility also comprises a distillation unit 13 comprising

- one or more single distillation columns 15; and/or

- one or more columns (21, 23) configured to allow the implementation of an advanced distillation by extraction.

Step a) supplies a mixture comprising at least one fluorinated fluid.

5 According to the invention, the initial flow 3 is a mixture 1 comprising at least one fluorinated fluid; the mixture comprises one or more fluorinated chemical components (41, 43, 49, 51, 55) and one or more contaminants chosen from one or more hydrocarbons and/or one or more fluorinated contaminants. Preferably, the initial flow 3 is a mixture 1 comprising one or more fluorinated chemical components (41, 43, 49, 51, 55) and one or more
10 hydrocarbons. Preferably, the initial flow 3 is a mixture 1 comprising one or more fluorinated chemical components (41, 43, 49, 51, 55) and one or more fluorinated contaminants.

According to the invention, a fluorinated contaminant is a fluorinated fluid that may be separated from the mixture in that it is present mainly in the membrane filtration retentate.

15 According to the invention, a fluorinated chemical component is a fluorinated fluid that may be separated from the mixture in that it is predominantly present in the membrane filtration permeate.

The components of the mixture have previously been used to allow the implementation of a thermodynamic cycle in a plurality of independent thermodynamic devices. By thermodynamic device, we mean a device for producing cold (such as a cold room, a
20 freezer, or a refrigerator), a device for producing heat (such as a heat pump), or an aerosol propellant, for example. The fluorinated fluids were used pure or in mixtures, then collected in separate collection reservoirs during a collective or selective recovery operation.

According to a preferred embodiment of the invention, the method further comprises a step of identifying one or more fluorinated fluids in the initial flow, this step being carried out
25 before step b) of membrane filtration. In particular, the method comprises a step of identifying one or more contaminants selected from one or more hydrocarbons and/or one or more fluorinated contaminants in the initial flow.

For example, the identification step is a qualitative and quantitative analysis step, preferably performed by chromatographic analysis, and the facility also comprises an identification
30 device, preferably a chromatographic analysis system.

For example, the initial flow 3 comprises one or more hydrocarbons selected from the group comprising methane (R50), ethane (R170), propane (R290), butane (R600), isobutane (R600a), pentane (R601), isopentane (R601a), and propene (R1270). Preferably, the initial flow 3 comprises propane (R290) and/or isobutane (R600a). In the context of the invention,

the hydrocarbon or hydrocarbons are contaminants in that they are present predominantly in the retentate.

For example, the initial flow 3 comprises at least one fluorinated contaminant being 1,1,1,2,3,3,3-heptafluoropropane (R227ea).

- 5 The contaminant content of the initial flow 3 is, for example, at least 0.3% by weight based on the total weight of the initial flow; preferably at least 0.5% by weight; more preferably at least 0.8% by weight; more preferably at least 1.0% by weight; more preferably at least 5.0% by weight and even more preferably at least 10.0% by weight.

- 10 For example, the contaminant content of the initial flow 3 is between 0.3 and 70% by weight based on the total weight of the initial flow; preferably, between 0.5 and 60% by weight; more preferably, between 1.0 and 50% by weight and even more preferably between 5.0 and 40% by weight; or even between 6.0 and 30% by weight.

- 15 When the contaminants comprise or consist of fluorinated contaminants, the fluorinated contaminant content of the initial flow 3 is, for example, at least 0.3% by weight based on the total weight of the initial flow; preferably at least 0.5% by weight; more preferably at least 0.8% by weight; more preferably at least 1.0% by weight; more preferably at least 5.0% by weight and even more preferably at least 10.0% by weight.

- 20 For example, the fluorinated contaminant content of the initial flow 3 is between 0.3 and 70% by weight based on the total weight of the initial flow; preferably, between 0.5 and 60% by weight; more preferably, between 1.0 and 50% by weight and even more preferably between 5.0 and 40% by weight; or even between 6.0 and 30% by weight.

- 25 When the contaminants comprise or consist of hydrocarbons, the hydrocarbon content of the initial flow 3 is, for example, at least 0.3% by weight based on the total weight of the initial flow; preferably at least 0.5% by weight; more preferably at least 0.8% by weight; more preferably at least 1.0% by weight; more preferably at least 5.0% by weight and even more preferably at least 10.0% by weight.

- 30 For example, the hydrocarbon content of the initial flow 3 is at most 70% by weight based on the total weight of the initial flow; preferably at most 60% by weight; more preferably at most 50% by weight, more preferably at most 40% by weight; more preferably at most 30% by weight; and even more preferably at most 25% by weight. When the hydrocarbon content is too high, for example when the initial flow has a hydrocarbon content of more than 40% by weight based on the total weight of the initial flow, it is possible to carry out a sub-step of diluting the initial flow with another hydrocarbon-free flow to adjust the hydrocarbon content to be equal to or less than 40%, preferably less than 30% by weight. This dilution

step increases the overall efficiency of the method. Step a) may therefore comprise a sub-step for adjusting the hydrocarbon content.

For example, the hydrocarbon content of the initial flow 3 is between 0.3 and 70% by weight based on the total weight of the initial flow; preferably, between 0.5 and 60% by weight; more preferably, between 1.0 and 50% by weight and even more preferably between 5.0 and 40% by weight; or even between 6.0 and 30% by weight.

For example, the initial flow 3 comprises one or more fluorinated fluids chosen from hydrofluorocarbons (HFC), HydroChloroFluoro-carbons (HCFC), hydrofluoroolefins (HFO) and hydrochlorofluoroolefins (HCFO); more preferably, the initial flow 3 comprises one or more hydrofluorocarbons (HFC) and/or one or more hydrofluoroolefins (HFO).

According to one implementation of the invention, the initial flow 3 comprises at least one fluorinated chemical component (41, 43, 49, 51, 55) and preferably at least two separate fluorinated chemical components (41, 43, 49, 51, 55).

In one embodiment, the initial flow 3 comprises one or more fluorinated fluids of the hydrofluorocarbon (HFC) type selected from trifluoromethane (R23), difluoromethane (R32), pentafluoroethane (R125), 1,1,2,2-tetrafluoroethane (R134), 1,1,1,2-tetrafluoroethane (R134a), 1,1,1-trifluoroethane (R143a), 1,1-difluoroethane (R152a), 1,1,1,2,3,3,3-heptafluoropropane (R227ea), 1,1,1,2,3,3-hexafluoropropane (R236ea), 1,1,1,3,3,3-hexafluoropropane (R236fa), trifluoropropane (R263), difluoropropane (R272), fluoropropane (R281), and 1,1,1,3,3-pentafluorobutane (R365mfc).

Preferably, the initial flow 3 comprises one or more fluorinated fluids of the hydrofluorocarbon (HFC) type selected from difluoromethane (R32), pentafluoroethane (R125), 1,1,1,2-tetrafluoroethane (R134a), and 1,1,1-trifluoroethane (R143a). Preferably, the initial flow 3 comprises one or more fluorinated fluids of the hydrofluorocarbon (HFC) type selected from difluoromethane (R32), pentafluoroethane (R125), and 1,1,1,2-tetrafluoroethane (R134a). Preferably, the initial flow 3 comprises at least one HFC being difluoromethane (R32), and/or pentafluoroethane (R125).

In one embodiment, the initial flow 3 comprises one or more fluorinated fluids of the hydrofluoroolefin (HFO) type chosen from cis-1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz-Z), trans-1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz-E), 2,3,3,3-Tetrafluoropropene (R1234yf) and trans-1,3,3,3-Tetrafluoroprop-1-ene (R1234ze). Preferably, the initial flow 3 comprises at least one HFO being 2,3,3,3-Tetrafluoropropene (R1234yf) and/or trans-1,3,3,3-Tetrafluoroprop-1-ene (R1234ze).

In one embodiment, the initial flow 3 comprises one or more fluorinated fluids of the hydrochlorofluorocarbon (HCFC) type chosen from chlorodifluoromethane (R22),

chlorofluoromethane (R31), 2,2-dichloro-1,1,1-trifluoroethane (R123), 1-chloro-1,2,2,2-tetrafluoroethane (R124), 1-chloro-1,1,2,2-tetrafluoroethane (R124a), 1,1-dichloro-1-fluoroethane (R141b), 1-chloro-1,1-difluoroethane (R142b), and 1,3-dichloro-1,1,2,2,3-pentafluoropropane (R225cb).

- 5 In one embodiment, the initial flow 3 comprises one or more fluorinated fluids of the hydrochlorofluoro-olefin (HCFO) type selected from trans-1-chloro-3,3,3-trifluoropropene (R-1233zd(E)), cis-1-chloro-3,3,3-trifluoropropene (R-1233zd(Z)), and (Z)-1-Chloro-2,3,3,3-Tetrafluoropropene (R-1224yd(Z)).

For example, the initial flow 3 comprises one or more fluorinated fluids chosen from
 10 difluoromethane (R32), pentafluoroethane (R125), 1,1,1,2-tetrafluoroethane (R134a), 2,3,3,3-tetrafluoropropene (R1234yf) and trans-1,3,3,3-Tetrafluoroprop-1-ene (R1234ze).

The content of fluorinated chemical components (41, 43, 49, 51, 55) in the initial flow 3 is, for example, at least 20% by weight based on the total weight of the initial flow 3; preferably
 15 at least 30% or at least 40% by weight; more preferably at least 50% by weight and most preferably at least 60% by weight.

For example, the content of fluorinated chemical components (41, 43, 49, 51, 55) in the initial flow 3 is at most 97% by weight based on the total weight of the initial flow; preferably at most 95% by weight; more preferably at most 92% by weight, and most preferably at
 20 most 90% by weight.

For example, the content of fluorinated chemical components (41, 43, 49, 51, 55) in the initial flow 3 is between 30 and 97% by weight based on the total weight of the initial flow; preferably, between 40 and 95% by weight; more preferably, between 50 and 92% by weight and most preferably between 60 and 90% by weight.

- 25 According to embodiments of the invention, step a) comprises at least one sub-step of pre-treatment of the refrigerant mixture 1 to obtain the initial flow 3. It is understood that the pre-treatment sub-step or sub-steps are carried out before step b) of membrane filtration using a pre-treatment unit 25.

For example, the mixture of fluorinated fluids 1 may or may not be compressed for storage
 30 purposes. When the fluorinated fluid mixture 1 is not compressed, step a) comprises a compression sub-step in a compression unit 27. In one embodiment of the invention, the initial flow 3 is compressed to a pressure of between 1 and 10 bar.

Preferably, before entering the membrane filtration unit 7, the initial flow 3 undergoes one or more pre-treatment sub-steps to remove any traces of water, oil, and particles that may
 35 damage the membrane surface. This task may be performed by one or more coalescing

filters (29, 31) placed in series, for example two coalescing filters (29, 31) with cartridges of 0.1 μm and 0.01 μm , respectively.

Alternatively, and according to an embodiment not shown, step a) comprises a sub-step of drying the refrigerant mixture in a dehydration unit. Advantageously, the dehydration sub-
 5 step is carried out using a molecular sieve. For example, the refrigerant mixture or part of the refrigerant mixture 1 is compressed to cause condensation of at least part of the water it contains to produce a two-phase current having liquid and gaseous phases. The gas phase is introduced into the dehydration unit to remove at least some of the water it contains and produce a dried gas phase.

10 Whichever pre-treatment is chosen, it will be to the advantage of the person skilled in the art that the initial flow 3 entering the membrane filtration unit 7 has a water content of at most 10 ppm by weight relative to the total weight of the initial flow.

For example, step a) comprises a sub-step of adjusting the hydrocarbon content of the refrigerant mixture 1 by mixing different harvested refrigerant flows. In fact, when the
 15 content of contaminants such as hydrocarbons is greater than 40% by weight of the total weight of the initial flow, it will be to the advantage of the person skilled in the art to dilute the initial flow with another hydrocarbon-free flow.

Membrane filtration step b) and membrane filtration unit

It will be understood that step b) of membrane filtration of the initial flow 3 to obtain a purified
 20 flow 5 comprising a hydrocarbon content lower than the hydrocarbon content of the initial flow 3, also allows for obtaining a contaminant-enriched flow 33.

The membrane separation takes place in a membrane filtration unit 7 comprising at least one filtration module 9, and preferably at least two filtration modules (9, 11) arranged in series. When the membrane filtration unit 7 comprises a single filtration module 9, the
 25 filtration is said to be in one stage. When the membrane filtration unit 7 comprises several filtration modules (9, 11) arranged in series, the filtration is said to be multi-stage. Figure 1 illustrates the embodiment wherein the membrane filtration unit 7 comprises two filtration modules (9, 11) arranged in series.

Each filtration module (9, 11) comprises one or more membranes arranged in parallel. The
 30 membrane or membranes may be single-layer or multi-layer, preferably with at least one selective layer for separating hydrocarbons. Two product flows leave a filtration module (9, 11): a permeate flow (5, 35) (or permeate) with the part of the supply flow that passes through the membrane, and the retentate flow (33, 37) (or retentate), which contains the part of the supply flow that does not pass through the membrane. According to the invention,
 35 the purified flow is the permeate, and the contaminant-enriched flow (e.g., hydrocarbons) is

the retentate. The retentate may then be treated as waste (for example, in the case of a hydrocarbon contaminant) or purified by recycling for reuse (for example, in the case of a fluorinated contaminant such as 1,1,1,2,3,3,3-heptafluoropropane (R227ea)). According to the invention, the method may also comprise recovering the filtration retentate obtained in
 5 step b) and recycling said retentate. Preferably, the retentate may be recycled by distillation. Filtration step b) may be a one-stage filtration comprising a single membrane filtration step or a multi-stage filtration wherein a plurality of membrane filtration sub-steps are carried out in succession.

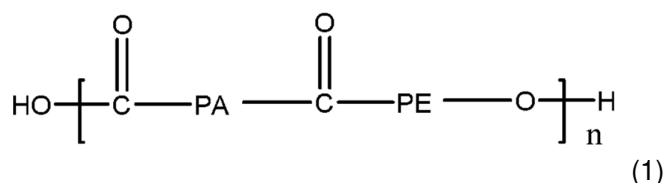
According to the invention, membrane filtration step b) comprises at least two membrane
 10 filtration sub-steps carried out successively. As shown in the examples, the implementation of a multi-stage filtration, i.e., wherein several filtration modules (9, 11) are arranged in series, improves hydrocarbon separation performance.

According to the invention, the membrane filtration is carried out in such a way that the contaminant or contaminants are predominantly in the filtration retentate (33, 37). As each
 15 filtration sub-step generates a permeate and a retentate, the filtration sub-steps, in addition to the first filtration, are carried out on the permeate from the previous filtration sub-step. In the case of a two-stage filtration, the second filtration sub-step is performed on the permeate 35 from the first filtration sub-step.

Preferably, the retentate from the filtration sub-steps, in addition to the first filtration, is
 20 recycled so that it is mixed into the initial flow 3. In the case of two-stage filtration, the retentate 37 from the second filtration sub-step is recycled so that it is mixed into the initial flow 3.

Preferably, the retentate 33 from the first filtration sub-step is discharged for further processing.

25 Preferably, the membrane or the membranes of the filtration module or modules (9, 11) comprise at least one layer of a material chosen to be a polyethersulfone (PES), a polysulfone (PSU), a polyvinylidene fluoride (PVDF), a polyether block amide (PEBA), polypropylene (PP), cellulose acetate (CA), polytetrafluoroethylene (PTFE), sulphonated polyphenylene sulphone (sPPSU), cellulose acetate butyrate (CAB), polyhedral oligomeric
 30 silsesquioxane (POSS), or polydimethylsiloxane (PDMS). More preferably, the membrane or membranes of the filtration module or modules (9, 11) comprise at least one layer of a polymer or a copolymer comprising repeating units of a tetramethylene oxide, propylene oxide or ethylene oxide monomer. For example, the polymer or copolymer comprises repeating units according to formula (1):



wherein PA is a polyamide chosen from polyamide 6, polyamide 11, and polyamide 12, and PE is poly(ethylene oxide) or poly(tetramethylene oxide); preferably, PA is polyamide 6.

According to a preferred implementation of the invention, the material of the or at least one layer of the filtration membrane is chosen to be a polyether block amide (PEBA). Preferably, the polyamide block comprises at least one polyamide chosen from polyamide 6, polyamide 11 and polyamide 12; preferably polyamide 6.

Copolymers containing polyamide (PA) blocks and polyether (PE) blocks are known to result from the copolycondensation of polyamide blocks with reactive ends with polyether blocks with reactive ends. For example, you may get a reaction from:

- polyether diol, and a polyamide dicarboxylic acid
- polyetherdiamine and a polyamide diacid, or
- polyetherdiol and a polyamide diamine.

The document FR 2 273 021 describes such block copolymers of polyether and polyamide, the polyamide blocks and polyether blocks being linked by an ester function. These products are sold under the trade name PEBAX® by ARKEMA. Examples of PEBA that may be used in the context of the invention are PEBAX® 1074, PEBAX® 2533 and PEBAX® 1657, which are commercially available from ARKEMA.

Thus, according to a preferred mode of implementation, step b) of membrane filtration comprises at least one filtration sub-step using a membrane comprising at least one layer of a material chosen from a polyethersulfone (PES), a polysulfone (PSU), a polyvinylidene fluoride (PVDF), a polyether block amide (PEBA), a polypropylene (PP), a cellulose acetate (AC), a polytetrafluoroethylene (PTFE), a sulphonated polyphenylene sulphone (sPPSU), a cellulose acetate butyrate (CAB), a polyhedral oligomeric silsesquioxane (POSS), or a polydimethylsiloxane (PDMS). Preferably, step b) of membrane filtration comprises at least one sub-step of filtration using a membrane comprising at least one layer of a material chosen to be a polyether block amide (PEBA) and/or a polyether sulphone (PES).

For example, membrane filtration step b) comprises at least one filtration sub-step using a multi-layer membrane, a layer of a material chosen to be a polyether block amide (PEBA), and a layer of polyethersulphone (PES).

Preferably, step b) is carried out to obtain a hydrocarbon content of less than 5.0% by weight relative to the total weight of the purified flow 5; preferably less than or equal to 4.0% by

weight, more preferably less than or equal to 3.0% by weight; and even more preferably less than or equal to 2.5% by weight.

For example, the purified flow comprises a hydrocarbon content of between 0.01% and less than 5.0% by weight relative to the total weight of the purified flow 5; preferably between
5 0.01 and 4.0% by weight, more preferably between 0.01 and 3.0% by weight; more preferably between 0.01 and 2.5% by weight.

Recycling step c)

Recycling step c) is carried out on the purified flow 5 and/or the contaminant-enriched flow 33. Preferably, when the initial flow 3 comprises one or more fluorinated contaminants, a
10 recycling step is performed on the contaminant-enriched flow 33. Preferably, when the initial flow 3 comprises one or more hydrocarbons, a recycling step is performed on the purified flow 5.

According to a preferred embodiment, the initial flow 3 comprises a single fluorinated chemical component (41, 43, 49, 51, 55) and one or more hydrocarbons, and the recycling
15 step c) is performed on the purified flow and is a step for purifying said fluorinated chemical component (41, 43, 49, 51, 55). This purification may be carried out by any means, preferably by distillation.

According to a preferred embodiment, the initial flow 3 comprises at least two fluorinated chemical components (41, 43, 49, 51, 55) and one or more hydrocarbons, and the recycling
20 step c) is at least performed on the purified flow and comprises at least one step of separating the fluorinated chemical components (41, 43, 49, 51, 55). This separation may be carried out by any means, preferably by distillation. Preferably, each separation step allowing the isolation of a fluorinated chemical component, or at least one of these separation steps, is followed by a purification step for the fluorinated chemical component
25 that has been isolated.

In a preferred embodiment, the initial flow 3 comprises at least one fluorinated chemical component (41, 43, 49, 51, 55) and one or more fluorinated contaminants, and step c)
30 comprises recycling the purified flow 5 and/or the contaminant-enriched flow 33. The recycling of each flow may be a step of recycling by purifying or separating the fluorinated contaminant or contaminants from the fluorinated chemical component or components.

According to the invention, a fluorinated contaminant is a fluorinated refrigerant that may be separated from the refrigerant mixture in that it is present mainly in the membrane filtration retentate.

According to the invention, a fluorinated chemical component is a fluorinated refrigerant that may be separated from the refrigerant mixture in that it is present in the majority in the membrane filtration permeate.

5 The methods for separating fluorinated refrigerants by distillation are known to the person skilled in the art. In the case of zeotropic mixtures, it is possible to separate the different components by a simple distillation method using simple distillation columns.

In the case of azeotropic or pseudo-azeotropic mixtures, two advanced distillation methods are known: pressure swing, and extraction using an entraining agent known as solvent 45. According to one implementation of the invention, the purified flow 5 is an azeotropic mixture and step c) is a step for separating a mixture of fluorinated chemical components (41, 43, 10 49, 51, 55) and/or fluorinated contaminants comprising one or more distillation sub-steps chosen from:

- a simple distillation sub-step on a simple distillation column 15,
- a pressure balance distillation sub-step using auxiliary distillation columns (17, 19), and
- 15 - an extraction distillation sub-step using auxiliary distillation columns (21, 23).

Preferably, the purified flow 5 is an azeotropic mixture and step c) is a step for separating a mixture of fluorinated chemical components (41, 43, 49, 51, 55) and/or fluorinated contaminants comprising at least one simple distillation sub-step and one or more advanced distillation sub-steps selected from:

- 20 - a pressure balance distillation sub-step, and
- an extraction distillation sub-step.

The pressure balance distillation methods are known to the person skilled in the art and implement two distillation columns (17, 19) operating at different pressures.

25 More specifically, a complex sub-mixture 39 moves successively in a continuous circuit through two columns (17, 19) set at different pressures. The role of each column (17, 19) is to separate one of the components (41, 43) of the complex sub-mixture 39 according to the pressure at which it is set.

In the first distillation column 17, which is mainly operated at low pressure (P1), one of the two components 41 may be removed at the bottom of the column 17, while the azeotrope 30 is removed at the top of the column and is introduced into the second column 19, which is operated at higher pressure (P2), causing the azeotrope mixture to disappear. In the second column 19, the second compound 43 may be removed from the bottom, while an azeotropic mixture 57 is formed at the top. The latter again has a composition significantly different from that of the sub-mixture 39. This azeotropic mixture 57 is reintroduced into the first 35 column 17.

The extractive distillation uses a solvent 45, called an entraining agent, which increases the volatility of one of the components or strongly modifies the activity coefficients of the substances to be separated in different directions, so that the separation factor becomes significantly different from 1 (1 = azeotropic). Two columns (21, 23) are used. Usually, the solvent 45 is supplied near the top of the first column 21 (called the extraction column) and the complex sub-mixture 47 to be separated is introduced into a lower area of this column 21 in order to obtain the best possible mixture. The solvent 45 may be removed from the bottom of this same column 21 along with one 51 of the substances to be separated. The second column 23 (called the regeneration column) is used to separate (regenerate) the solvent 45 and isolate the fluorinated chemical compound 51 to be extracted.

Such a method for separating a complex mixture of fluorinated chemical components (41, 43, 49, 51, 55) is known to the person skilled in the art and is described, for example, in the document FR3115036. Thus, preferably step c) of separation by distillation comprises the implementation of said method.

Preferably, the purified flow 5 is a complex mixture of fluorinated chemical components (41, 43, 49, 51, 55), and step c) comprises:

- a sub-step of identifying in the purified flow 5 at least two sub-mixtures (39, 47, 53), each sub-mixture being a simple sub-mixture 53 comprising a single fluorinated chemical component 55 or a complex sub-mixture (39, 47) comprising a combination of fluorinated chemical components (41, 43, 48, 51), each complex sub-mixture (39, 47) being associated with either a first group of secondary distillation by a pressure balance distillation method or a second group of secondary distillation by an extraction distillation method,
- a primary distillation step, using a single distillation column 15, to separate each identified sub-mixture (39, 47, 53), and
- a secondary distillation step, using at least two auxiliary extraction columns, of each complex sub-mixture (39, 47) of the first group and of the second group, wherein the complex sub-mixtures 39 of the first group are separated by the pressure balance distillation method and the complex sub-mixtures 47 of the second group are separated, using a solvent 45, by the extraction distillation method.

According to one implementation of the invention, the same auxiliary columns may carry out the pressure balance distillation and extraction distillation operations in succession. The advantage of this configuration is that it reduces the number of columns in the facility and therefore the associated costs.

Preferably, the solvent 45 is chosen from the following solvents: n-pentane, dichloromethane, methyl isobutyl ketone (MIBK), methyl ethyl ketone (MEK), heptanone, pentanone, cyclohexanone and dimethylether. Preferably, the compound used is Methyl isobutyl ketone (MIBK). Such a solvent advantageously provides a high separation factor and a high extraction capacity for the advanced distillation and the recovery of the chemical component.

Preferably, several secondary distillation steps are carried out successively for each complex sub-mixture (39, 47) from the first group and from the second group.

Optionally, the separation of a fluorinated chemical component 55 from a simple sub-mixture 53 comprises a purification step performed on said simple sub-mixture 53.

When step c) comprises both primary and secondary distillation sub-steps, the facility for the implementation of the method according to the invention comprises a distillation unit 13 comprising one or more single distillation columns 15; preferably, the distillation unit 13 also comprises at least two auxiliary columns (17, 19, 21, 23) configured to allow the implementation of an advanced distillation by extraction and/or advanced distillation by pressure balance to be implemented.

A similar procedure to that performed on the purified flow may be performed on the enriched flow when it comprises one or more fluorinated contaminants.

Preferably, the facility comprises:

- a simple distillation column 15 configured to receive the purified flow 5 and implement a primary distillation, to separate the purified flow 5 into at least two sub-mixtures,
- an electronic computer configured to:
 - identify the different sub-mixtures (39, 47, 53) in the chemical mixture, each sub-mixtures being a simple sub-mixture 53 comprising a single chemical component 55 or a complex sub-mixture (39, 47) comprising a combination of chemical components (41, 43, 49, 51),
 - associate each complex sub-mixture (39, 47) either with a first group of secondary distillation using a pressure balance method, or with a second group of secondary distillation using an extraction distillation method,
- at least two auxiliary columns (17, 19, 21, 23), configured to implement a secondary distillation and to allow a distillation by extraction using an entrainer, and/or a distillation by pressure balance, to separate all the chemical components (41, 43, 49, 51) from each sub-mixture (39, 47).

Preferably, two auxiliary columns are configured to implement a secondary distillation and to allow an extraction distillation to be carried out successively using an entrainer, followed

by a pressure balance distillation, to separate all the chemical components from each sub-mixture.

Examples

5 **Example 1 choice of the membrane and of the refrigerant mixtures**

The results presented in the examples below were obtained using a simulation software based on ideal (non-competitive) experimental permeability and selectivity data obtained on a laboratory scale.

10 The membrane material used in this project is a polyether block amide, i.e. a thermoplastic elastomer composed of flexible polyethylene oxide units (PEO, 60 wt.%) and glassy polyamide 6 hard segments (PA6, 40 wt.%). The polyamide segments give the polymer mechanical strength and prevent PEO crystallization, resulting in a polymer material with good film-forming properties and high gas permeability. The membrane is 2 μm thick.

15 The analysis of the experimental results concerning the pure permeation properties of HFC and HFO and 2 hydrocarbons through the polymer membrane led to the definition of two refrigerant mixtures M1 and M2, the composition of which is given in Table 1. A mixture of fluorinated refrigerants is also indicated in M3.

Table 1: Composition of the different refrigerant mixtures in percentage by mass in relation to the total weight of the mixture

20

Refrigerant (% by weight)	M1	M2	M3
R32	16	40	-
R125	26	40	-
R134a	21	-	10
R1234yf	20	-	-
R1234ze	7	-	20
R227ea	-	-	70
R600a	5	10	-
R290	5	10	-

The mixture M1 contains HFC, HFO and hydrocarbons. It is an R448A type mixture wherein 10% by weight of R32 has been replaced by hydrocarbons.

25 The mixture M2 contains HFC and hydrocarbons. This is a R410A type mixture wherein 20% by weight of the HFC have been replaced by hydrocarbons.

The mixture M3 contains an HFC-type fluorinated contaminant, 1,1,1,2,3,3,3-heptafluoropropane (R227ea).

HFC

- R32: difluoromethane
- R125: pentafluoroethane
- R134a: 1,1,1,2-tetrafluoroethane
- R227ea 1,1,1,2,3,3,3-heptafluoropropane

5 HFO

- R1234yf: 2,3,3,3-Tetrafluoropropene
- R1234ze: trans-1,3,3,3-Tetrafluoroprop-1-ene

Hydrocarbons

- R600a: isobutane
- 10 - R290: propane

Example 2 method implementing a one-stage membrane separation unit and hydrocarbons

15 The membrane separation step is carried out at a temperature of 25°C and a maximum pressure of 8.0 bar.

The mathematical model for a membrane separation unit has been constructed on the basis of the following assumptions:

- Gas permeability through the dense membrane layer is described by the solution-diffusion mechanism, which means that the permeability coefficient (P) is defined as the
- 20 product of the sorption coefficient (S) and of the diffusion coefficient (D).

$$P = D \cdot S \quad (1)$$

where S is an equilibrium term related to the concentration of a component in the polymer phase, and D is a kinetic term related to the molecular movement of the permeable component through the membrane.

- 25 - The transport of gas through a dense selective barrier is governed by the following expression.

$$J_i = \frac{P_i}{\delta} (p_{R,i} - p_{P,i}) \quad (2)$$

30 where J_i is the molar flow of the component i , P_i is the gas permeability coefficient, δ is the membrane thickness and $p_{R,i}$ and $p_{P,i}$ are the partial pressure of the component on either side of the membrane.

- Gas permeability is independent of the composition of the supply (ideal gas permeability), i.e. the simulation results do not take into account plausible competitive effects resulting from the supplying of the membrane with gas mixtures.
- Gas permeability depends on the pressure. Permeability data for each HFC, HFO and HC were described as a function of the pressure gradient applied through the membrane (Δp_i) following an exponential function.

$$P_i = P_{0,i} \cdot e^{m \cdot \Delta p_i} \quad (3)$$

where $P_{0,i}$ is a pre-exponential factor and m is a constant that provides information on the influence of the pressure on the gas permeability. A summary of the adjusted parameter values for each gas is given in Table 2.

- The piston flow concentration model is developed in both the supply gas and the permeate gas circulating through the channels on both sides of the membrane.
- Negligible pressure drop of the gaseous phase along the supply side.
- Isothermal operation.

Table 2: Parameters for exponential adjustment to Eq. (3) HFC, HFO and HC.

Parameter s	R32	R134a	R125	R143a	R227ea	R1234yf	R1234ze
$P_{0,i}$ (stri kethrough)	110.78	58.02	15.10	8.22	4.54	8.25	26.24
m (bar ⁻¹)	0.1375	0.2366	0.1686	0.0766	0.484	0.1254	0.2676
Parameters		R290			R600a		
$P_{0,i}$ (stri kethrough)			7.02			3.95	
m (bar ⁻¹)			0.066			0.193	

A schematic diagram of the gas separation process through a flat thin-layer composite membrane is shown in Figure 2.

- The differential mass balances around each component in a length slice dz are derived as follows,

$$dF_i^F(z) = -J_i(z) \cdot dA, \quad \forall i; \forall z \quad (4)$$

$$dF_i^P(z) = J_i(z) \cdot dA, \quad \forall i; \forall z \quad (5)$$

where F_i is the molar flow rate of the component i , A is the surface area of the membrane and z is the axial position along the length of the module. In addition, the transmembrane flow of each component (J_i) was defined in Eq. 2. The proposed mathematical model is therefore formed by the system of equations (2), (3), (4) and (5).

5 Performance of the separation process

The performance of the separation process is assessed in terms of product purity and product recovery from the flow of interest (either the retentate or the permeate, depending on the case study). In each case study, the recovery of the product is defined by Eq. (6) and the purity is given by the mass concentration of the target component or components
10 in the product flow.

$$\text{Product recovery} = \frac{\text{Flow rate of component } i \text{ in product stream}}{\text{Feed flowrate of component } i} \quad (6)$$

Filtration of the mixture M1

Figure 3 shows the concentration of HFC+HFO in the permeate flow versus the recovery of HFC+HFO as a function of the supply pressure (1-8 bar) and of the surface area of the
15 membrane for mixture 1. Each data point represents a combination of supply pressure and membrane surface area. Supply flow rate = 10 kg.h⁻¹. Membrane thickness = 2 µm. The composition of the supply is 90% by weight HFC + HFO and 10% by weight HC (R600a + R290).

Table 3 shows an example of the membrane separation performance for the mixture M1
20

Table 3

	M1	retentate	permeate
Flow rate (kg/h)	10	4.2	5.8
Pressure (bar)	3.7	3.7	1.01
Refrigerant (% by weight)			
R32	16	7.05	22.5
R125	26	29.86	23.2
R134a	21	11.16	28.2
R1234yf	20	30.98	12.0
R1234ze	7	5.97	7.8
R290	5	8.38	2.5
R600a	5	6.60	3.8

As may be seen, the recovery and the purity of HFC+HFO are 60.4% by weight (in the retentate) and 93.7% by weight (in the permeate), respectively. These product
25 specifications are obtained with a supply pressure of 3.7 bar and a membrane module with a permeation surface area of 17m².

Filtration of the mixture M2

Figure 4 shows the concentration of R32+R125 in the permeate flow versus the recovery of R32+R125 as a function of the supply pressure (1-8 bar) and of the membrane surface area. Each data point represents a combination of supply pressure and membrane surface area. Supply flow rate = 10 kg h⁻¹. Membrane thickness = 2 µm. The composition of the supply is 40% by weight R32, 40% by weight R125, 10% by weight R600a, and 10% by weight R290.

Table 4 shows an example of membrane separation performance for the mixture M2 (membrane surface area: 5.1 m²)

Table 4

	M2	retentate	permeate
Flow rate (kg/h)	10	4.8	5.2
Pressure (bar)	7.4	7.4	1.01
Refrigerant (% by weight)			
R32	40	12.7	65.0
R125	40	51.4	29.5
R290	10	17.4	3.3
R600a	10	18.5	2.2

As may be seen, the HC content in the product flow may be reduced from 20% by weight to 5.5% by weight with a single-stage membrane unit of 5m² permeation surface area applying a supply pressure of 7.4 bar. The recovery and the purity of R32+R125 are 61.4% and 94.5% by weight, respectively.

Table 5 shows another example of membrane separation performance for the mixture M2 (membrane surface area: 17 m²)

Table 5

	M2	retentate	permeate
Flow rate (kg/h)	10	4.8	5.2
Pressure (bar)	3.6	3.6	1.01
Refrigerant (% by weight)			
R32	40	18.9	59.4
R125	40	47.4	33.2
R290	10	16.0	4.5
R600a	10	17.7	2.9

In this case, a much lower pressure of 3.6 bar must be applied in order to achieve a R32+R125 recovery and a purity of 60.2% and 92.6% by weight, respectively.

Example 3 method using a 2-stage membrane separation unit and hydrocarbons

In the two-stage design, the permeate from the first membrane unit is generally recompressed and sent towards a second membrane unit, where further separation is performed. The final permeate is then enriched twice. In addition, as the volume of gas treated by the second-stage membrane unit is smaller than in the first stage, the membrane surface area of the second stage is smaller, and the compression power required does not increase significantly compared with the single-step method.

Filtration of the mixture M1

Figure 5 shows a comparison of the purification of HFC+HFO with one step and two steps. It shows HFC+HFO concentration in the permeate flow versus HFC+HFO recovery as a function of the supply pressure (1-8 bar) and of the membrane surface area. Each data point represents a combination of supply pressure and membrane surface area. Supply flow rate = 10 kg h⁻¹. Membrane thickness = 2 µm. The composition of the supply is 90% by weight HFC + HFO and 10% by weight HC (R600a + R290).

As may be seen, this configuration improves the product specification compared to the single-step method, as it would reduce the presence of HC in the permeate flow from the initial 10 wt% to a low hydrocarbon concentration (<2 wt%) with HFC+HFO recoveries around 60%.

A schematic representation of a two-stage membrane separation unit is shown in Figure 1. The unit comprises two filtration modules connected in series, the first module having a membrane surface area of 57m² and the second module having a membrane surface area of 5m². The initial flow alone initially supplies the first module and then, as soon as it is available, the retentate from the second module is recycled to the inlet of the first module, adding to the initial flow and therefore modifying the composition of the flow entering the first module. The results given in Table 6 illustrate a situation of equilibrium.

Table 6

	M1 Initial flow	Flows in the 1 st module (= initial flow + recycled flow)	Retentate of the 1 st module	Permeate from the 1 st module (after recompression)	Retentate from the 2 nd module (= recycled flow)	Permeate from the 2 nd module
Flow rate (kg/h)	10	23.6	3.7	19.9	13.6	6.3
Pressure (bar)	3.7	7.8	4.8	8	8	1.01
Refrigerant (weight %)						

R32	16	10.1	2.9	11.5	5.8	23.8
R125	26	32.7	25.1	34.1	37.6	26.6
R134a	21	16.0	5.0	18.1	12.4	30.5
R1234yf	20	23.9	39.3	21.0	26.8	8.4
R1234ze	7	8.1	3.7	8.9	8.9	9.0
R290	5	5.3	11.3	4.1	5.4	1.3
R600a	5	3.9	12.7	2.3	3.1	0.4

As may be seen, it is possible to achieve a target HFC+HFO purity of 98.3% by weight with a recovery of 68.8%. The specifications for this product are obtained with a supply pressure of 4.8 bar on the first stage and 8 bar on the second stage, and with modules of 57m² and 5m² membrane surface area.

The initial flow hydrocarbon content of 10% by weight is less than 2% by weight in the second permeate (a reduction of a factor of 5).

Filtration of the mixture M2

Figure 6 shows a comparison of R32+R125 purification in one step and two steps. It shows the concentration of R32+R125 in the permeate flow versus the recovery of R32+R125 as a function of the supply pressure (1-8 bar) and of the membrane surface area. Each data point represents a combination of supply pressure and membrane surface area. Supply flow rate = 10 kg h⁻¹. Membrane thickness = 2 µm. The composition of the supply is 40% by weight R32, 40% by weight R125, 10% by weight R600a, and 10% by weight R290.

The method illustrated in Figure 7 with recycling of the second retentate into the supply flow of the first module is also followed, with the difference that the membrane surface area is 80m² in the first module and 5m² in the second filtration module. The equilibrium results are shown in Table 7.

Table 7

	M2 Initial flow	Flows in the module (= initial flow + recycled flow)	Retentate of the 1 st module	Permeate from the 1 st module (after recompression)	Retentate from the 2 nd module (= recycled flow)	Permeate from the 2 nd module
Flow rate (kg/h)	10	22.3	4.7	17.6	12.3	5.3
Pressure (bar)	3.5	3.5	3.5	6.0	6.0	1.01
Refrigerant (weight %)						
R32	40	29.5	11.5	34.34	21.0	65.3

R125	40	53.3	48.3	54.73	64.2	32.6
R290	10	9.7	19.5	7.02	9.4	1.6
R600a	10	7.5	20.7	3.91	5.4	0.5

As may be seen, the two-stage filtration step reduces the presence of HC from the initial 20% by weight to around 2% by weight (a reduction by a factor of 10) and achieves a higher level of recovery (65%) than the single-step separation. This separation is achieved using
5 two membrane units of 80 and 5m² respectively. The recovery and the purity of R32+R125 are 64.8% and 97.9% by weight, respectively.

Example 4 method using a 2-stage membrane separation unit and a fluorinated contaminant.

10 In the two-stage design, the permeate from the first membrane unit is generally recompressed and sent towards a second membrane unit, where further separation is performed. The final permeate is then enriched twice. In addition, as the volume of gas treated by the second-stage membrane unit is smaller than in the first stage, the membrane surface area of the second stage is smaller, and the compression power required does not
15 increase significantly compared with the single-step method. When the contaminant is a fluorinated contaminant, it may be interesting to isolate this fluorinated chemical compound, qualified as a contaminant, so that it may also be recycled.

Filtration of the mixture M3

20 Figure 7 shows a comparison of the separation of the fluorinated chemical compound R227ea with one step and two steps. It shows the concentration of R227ea in the permeate flow versus the recovery of R227ea as a function of the supply pressure (1-4 bar) and of the membrane surface area. Each data point represents a combination of supply pressure and membrane surface area. Supply flow rate = 10 kg h⁻¹. Membrane thickness = 2 µm.
25 The supply composition is 70% by weight R227ea, 20% by weight R1234ze, and 10% by weight R134a.

The method illustrated in Figure 5 with recycling of the second retentate into the supply flow of the first module is also followed, with the difference that the membrane surface area is 15.3m² in the first module and 21.8m² in the second filtration module. The equilibrium results
30 are shown in Table 8.

Table 8

	M2 Initial flow	Flows in the 1 st module (= initial flow + recycled flow)	Retentate of the 1 st module	Permeate from the 1 st module	Retentate from the 2 nd module (= recycled flow)	Permeate from the 2 nd module
Flow rate (kg/h)	10	15.7	11.3	4.4	5.6	5.7
Pressure (bar)	3.0	3.0	3.0	1.01	3.0	1.01
Refrigerant (weight %)						
R227a	70	68.9	75.9	50.9	84.97	67.0
R134a	20	20.5	14.9	34.8	8.47	21.3
R1234ze	10	10.6	9.2	14.3	6.56	11.7

As may be seen, the two-stage filtration step allows recovery of the fluorinated chemical contaminant R227ea in the first and second retentates at 68% and 85%, respectively. This contaminant may then be purified and recycled.

CLAIMS

1. A method for recycling a mixture (1) comprising at least one fluorinated fluid, characterized in that it comprises:
 - 5 a) supplying, in the form of an initial flow (3), a mixture (1) comprising at least one fluorinated fluid; the mixture comprising one or more fluorinated chemical components (41, 43, 49, 51, 55) and one or more contaminants selected from one or more hydrocarbons and/or one or more fluorinated contaminants;
 - 10 b) membrane filtrating the initial flow (3) to obtain a purified flow (5) comprising a contaminant content lower than the contaminant content of the initial flow (3) and a contaminant-enriched flow (33); said membrane filtration comprising at least two membrane filtration sub-steps carried out successively; and
 - c) recovering the purified flow (5) and/or the contaminant-enriched flow (33) for reuse and/or recycling.
- 15 2. The recycling method according to claim 1, characterized in that the initial flow (3) comprises one or more fluorinated contaminants and the or at least one fluorinated contaminant is 1,1,1,2,3,3,3-heptafluoropropane (R227ea).
- 20 3. The recycling method according to claim 1 or 2, characterized in that the initial flow (3) comprises one or more fluorinated contaminants and step c) comprises recovering the contaminant-enriched flow (33) and recycling it.
4. The recycling method according to one of claims 1 to 3, characterized in that the
25 initial flow (3) comprises one or more hydrocarbons selected from the group comprising propane and isobutane.
5. The recycling method according to one of claims 1 to 4 in that the initial flow (3) comprises one or more hydrocarbons and step c) comprises recovering the purified flow (5)
30 and recycling it.
6. The recycling method according to one of claims 1 to 5, characterized in that step b) of membrane filtration comprises at least one filtration sub-step using a membrane comprising at least one layer of a polymeric material chosen from a polyethersulphone, a polysulphone a polyvinylidene fluoride, a polyether block amide, a polypropylene, a
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cellulose acetate, a polytetrafluoroethylene, a sulphonated polyphenylene sulphone, a cellulose acetate butyrate, a polyhedral oligomeric silsesquioxane, or a polydimethylsiloxane.

- 5 7. The recycling method according to one of claims 1 to 6, characterized in that step b) of membrane filtration comprises at least one filtration sub-step using a membrane comprising at least one layer of a material chosen to be a polyether block amide; preferably, the polyamide block comprises at least one polyamide chosen from polyamide 6, polyamide 11 and polyamide 12; preferably, polyamide 6.
- 10 8. The recycling method according to one of claims 1 to 7, characterized in that the initial flow (3) comprises one or more fluorinated chemical components (41, 43, 49, 51, 55) chosen from Hydrofluorocarbons (HFC), HydroChloroFluoro-carbons (HCFC), Hydrofluoroolefins (HFO) and Hydrochlorofluoroolefins (HCFO); more preferably, the initial
15 flow comprises one or more fluorinated chemical components chosen from Hydrofluorocarbons (HFC) and/or Hydrofluoroolefins (HFO).
- 20 9. The recycling method according to one of claims 1 to 8 in that the initial flow (3) comprises one or more fluorinated fluids (41, 43, 49, 51, 55) chosen from difluoromethane (R32), pentafluoroethane (R125), 1,1,1,2-tetrafluoroethane (R134a), 2,3,3,3-tetrafluoropropene (R1234yf) and trans-1,3,3,3-tetrafluoroprop-1-ene (R1234ze).
- 25 10. The recycling method according to one of claims 1 to 9, characterized in that the initial flow supplied in step a) comprises a contaminant content greater than or equal to 0.5% by weight relative to the total weight of the initial flow (3); preferably, a contaminant content of 5.0% to 40% by weight relative to the total weight of the initial flow.
- 30 11. The recycling method according to one of claims 1 to 10, characterized in that the initial flow supplied in step a) comprises a hydrocarbon content greater than or equal to 0.5% by weight relative to the total weight of the initial flow (3); preferably between 5.0 and 40% by weight.
- 35 12. The recycling method according to one of claims 1 to 11, characterized in that the initial flow supplied to step a) comprises one or more hydrocarbons and in that step b) is carried out to obtain a hydrocarbon content of less than 5.0% by weight relative to the total weight of the purified flow (5).

13. The recycling method according to one of claims 1 to 12, characterized in that the initial flow (3) comprises at least two fluorinated chemical components (41, 43, 49, 51, 55) and in that step c) of recycling the purified flow (5) comprises separating said fluorinated chemical components (41, 43, 49, 51, 55) by distillation.

14. The recycling method according to claim 13, characterized in that the step of separating the fluorinated chemical components (41, 43, 49, 51, 55) by distillation comprises:

- a sub-step of identifying within the mixture of fluorinated chemical components (41, 43, 49, 51, 55) at least two sub-mixtures (39, 47, 53), each sub-mixture being a simple sub-mixture (53) comprising a single fluorinated chemical component (55) or a complex sub-mixture (39, 47) comprising a combination of chemical components (41, 43, 49, 51), each complex sub-mixture (39, 47) being associated with either a first group of secondary distillation by a pressure balance distillation method or a second group of secondary distillation by an extraction distillation method,
- a primary distillation step, using a single distillation column 15, to separate each identified sub-mixture (39, 47, 53),
- a secondary distillation step, using at least two auxiliary columns (17, 19, 21, 23), of each complex sub-mixture (39, 47) of the first group and of the second group, the complex sub-mixtures (39) of the first group being separated by the pressure balance distillation method and the complex sub-mixtures (47) of the second group being separated, using a solvent (45), by the extraction distillation method.

15. The recycling method according to one of claims 1 to 14, characterized in that, as each membrane filtration sub-step generates a permeate and a retentate, the retentate from the second membrane filtration sub-step is recycled to be mixed into the initial flow.

16. The recycling method according to one of claims 1 to 15, characterized in that step a) comprises a step of identifying one or more contaminants in the initial flow and in that, when the hydrocarbon content is greater than 40% by weight based on the total weight of the initial flow, it further comprises a sub-step of diluting the initial flow with another hydrocarbon-free flow in order to adjust the hydrocarbon content to be less than 40% by weight based on the total weight of the initial flow.

17. A facility for implementing the method for recycling a mixture (1) comprising at least one fluorinated fluid according to one of claims 1 to 16, characterized in that it comprises a membrane filtration unit (7) comprising at least two membrane filtration modules (9, 11) arranged in series.