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## DESCRIPTION

## PROCESS FOR PRODUCING 1,1,1,2-TETRAFLUOROPROPENE

## 5      Technical Field

The present invention relates to a process for producing 1,1,1,2-tetrafluoropropene.

## Background Art

10        CFCs (chlorofluorocarbons) and HCFCs (hydrochlorofluorocarbons) were conventionally used as refrigerants. Since these substances can cause depletion of the ozone layer, HFCs (hydrofluorocarbons), particularly HFC-125 (pentafluoroethane) and HFC-32 (difluoromethane) 15 have widely been used as substitute refrigerants. However, HFC-125 and HFC-32 are potent global warming substances and cause concern of diffusion of these substances to adversely affect the global warming. Although these substances are recovered from disused apparatuses for the purpose of 20 preventing their diffusion and consequently the global warming, all of these substances cannot be recovered. Also, diffusion caused by leaking or the like cannot be neglected. Then, CO<sub>2</sub> and hydrocarbon compounds are studied to be used as other substitute refrigerants. However, the CO<sub>2</sub> 25 refrigerant has poor efficiency and requires a larger

device, so that there are a lot of problems in reducing overall greenhouse gas emission including consumption energy of the device. Also, the hydrocarbon compounds have problems about safety due to their high combustibility.

5 Recently, intense interest has been shown towards, as a substitute refrigerant being able to solve these problems, 1,1,1,2-tetrafluoropropene (or 2,3,3,3-tetrafluoropropene,  $\text{CF}_3\text{CF}=\text{CH}_2$ , hereinafter also referred to as "HFC-1234yf"), which is a HFC of an olefin having a low warming  
10 coefficient.

Some processes for producing HFC-1234yf have hitherto been disclosed. Patent Document 1 listed below describes a process of using  $\text{CF}_3\text{CH}=\text{CH}_2$  as a raw material, halogenating it and then subjecting to a dehydrofluorination reaction to  
15 obtain HFC-1234yf. Patent Document 2 listed below describes a process of hydrogenating a fluorinated olefin having 3 to 6 carbon atoms through at least two reaction stages to give an alkane, and dehydrofluorinating the alkane to produce a fluorinated olefin such as HFC-1234yf.  
20 Patent Document 3 listed below describes a process of directly obtaining HFC-1234yf from a mixture of  $\text{CF}_3\text{CF}_2\text{CHCl}_2$  (HCFC-225ca) and  $\text{CCl}_2\text{CF}_2\text{CHClF}$  (HCFC-225cb) using a Pd/C catalyst. Patent Document 4 listed below describes a process of coupling an alkane having 1 carbon atom with an  
25 alkane having 2 carbon atoms to produce an olefin having 3

carbon atoms such as HFC-1234yf. Patent Document 5 listed below describes a process of synthesizing an alkane having 3 carbon atoms by reacting an alkane having 1 carbon atom with an alkane having 2 carbon atoms, and

5 dehydrohalogenating the synthesized alkane to produce a fluorinated olefin such as HFC-1234yf. Patent Document 6 listed below describes a process of passing  $\text{CF}_3\text{CHFCH}_2\text{F}$  (HFC-236ea) and  $\text{CF}_3\text{CHFCH}_2\text{F}$  (HFC-245eb) simultaneously through a catalyst layer and subjecting them

10 dehydrofluorination to directly produce a mixture of HFC-1225ye (1,1,1,2,3-pentafluoropropene) and HFC-1234yf. Patent Document 7 listed below describes a process of fluorinating  $\text{CX}_3\text{CYCH}_3$  with HF concurrently with a dehydrofluorination reaction to produce HFC-1234yf.

15 Patent Document 1: WO 2007/056194

Patent Document 2: U.S. Patent Application Publication No. 2007/0179324

Patent Document 3: WO 2007/086972

Patent Document 4: WO 2007/056127

20 Patent Document 5: WO 2007/056128

Patent Document 6: WO 2007/117391

Patent Document 7: WO 2007/056148

Patent Document 8: WO 93/25510

25 Disclosure of Invention

However, these processes may often produce, in addition to HFC-1234yf as the aimed product and HFC-245eb as a precursor thereof, by-products which cannot be converted into HFC-1234yf. An object of the present 5 invention is to provide a process capable of producing HFC-1234yf with a higher selectivity than that of the conventional methods.

The present inventors have studied about use of hexafluoropropene (HFP) as a raw material for production of 10 HFC-1234yf, also intensively studied about appropriate procedure for carrying out hydrogenation, dehydrofluorination and distillation, and finally accomplished the present invention.

In a first aspect of the present invention, there is 15 provided a process for producing 1,1,1,2-tetrafluoropropene (HFC-1234yf), which comprises the steps of:

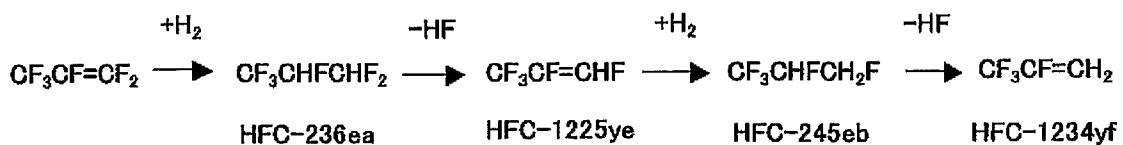
- a) hydrogenating a raw material of hexafluoropropene (HFP) together with 1,1,1,2,3-pentafluoropropene (HFC-1225ye) in the presence of a reducing catalyst to obtain a 20 reaction mixture containing 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and 1,1,1,2,3-pentafluoropropane (HFC-245eb);
- b) subjecting the reaction mixture obtained from the step a) to a dehydrofluorination reaction to obtain a reaction mixture containing 1,1,1,2,3-pentafluoropropene 25 (HFC-1225ye) and 1,1,1,2-tetrafluoropropene (HFC-1234yf);

c) subjecting the reaction mixture obtained from the step b) to distillation to separate into a 1A fraction containing 1,1,1,2-tetrafluoropropene (HFC-1234yf) and a 2A fraction containing 1,1,1,2,3-pentafluoropropene (HFC-1225ye); and

d) using 1,1,1,2,3-pentafluoropropene (HFC-1225ye) contained in the 2A fraction for the step a),

whereby 1,1,1,2-tetrafluoropropene is obtained in the 1A fraction.

10 It is considered that, in the process according to the first aspect of the present invention, for producing HFC-1234yf from HFP, the following reactions successively proceed via HFC-1225ye.



15 The present inventors have found that the hydrogenating reaction producing HFC-236ea from HFP and the hydrogenating reaction producing HFC-245eb from HFC-1225ye can proceed under the same conditions, and also the dehydrofluorination reaction producing HFC-1225ye from HFC-236ea and the dehydrofluorination reaction producing HFC-1234yf from HFC-245eb can proceed under the same conditions.

Thus, the hydrogenations and the dehydrofluorinations are respectively carried out in the same times (in other words, by "folding" the above successive reactions), and then distillation is carried out so that HFC-1234yf is obtained.

5 According to this process of the present invention, it becomes possible to produce HFC-1234yf with a higher selectivity.

In the process according to the above first aspect of the present invention,

10 the 2A fraction obtained from the step c) may contain, in addition to 1,1,1,2,3-pentafluoropropene (HFC-1225ye), at least one of 1,1,1,2,3-pentafluoropropane (HFC-245eb) and 1,1,1,2,3,3-hexafluoropropane (HFC-236ea); and

15 the step d) may comprise subjecting the 2A fraction to further distillation to separate into a 3A fraction containing at least one of 1,1,1,2,3-pentafluoropropane (HFC-245eb) and 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and a 4A fraction containing 1,1,1,2,3-pentafluoropropene (HFC-1225ye), subjecting the 3A fraction to the dehydrofluorination reaction of the step b) and subjecting the 4A fraction to the hydrogenating reaction of the step a).

20 Therefore, at least one of HFC-245eb and HFC-236ea as intermediates and HFC-1225ye can be used by returning to the each appropriate reaction stage.

However, the first aspect of the present invention is not limited thereto. For example, all of the 2A fraction as is may be subjected to the hydrogenating reaction of the step a).

5 In a second aspect of the present invention, there is provided a process for producing 1,1,1,2-tetrafluoropropene (HFC-1234yf), which comprises the steps of:

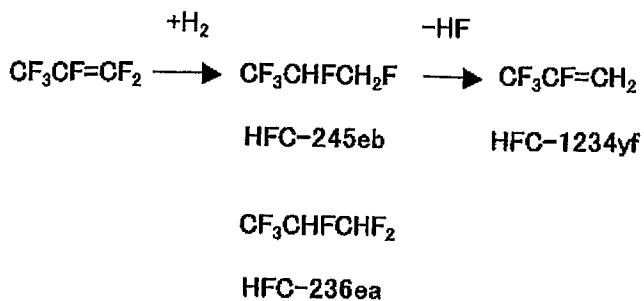
10 p) hydrogenating a raw material of hexafluoropropene in the presence of a reducing catalyst to obtain a reaction mixture containing 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and 1,1,1,2,3-pentafluoropropane (HFC-245eb);

15 q) subjecting the reaction mixture obtained from the step p) to distillation to separate into a 1B fraction containing 1,1,1,2,3-pentafluoropropane (HFC-245eb) and a 2B fraction containing 1,1,1,2,3,3-hexafluoropropane (HFC-236ea); and

r) subjecting the 1B fraction to a dehydrofluorination reaction to obtain a reaction mixture containing 1,1,1,2-tetrafluoropropene (HFC-1234yf),

20 whereby 1,1,1,2-tetrafluoropropene (HFC-1234yf) is obtained in the reaction mixture of the step r).

It is considered that, in the process according to the second aspect of the present invention, for producing HFC-1234yf from HFP, the following reactions proceed.



The present inventors have found that HFC-245eb is directly obtained, in addition to HFC-236ea, by 5 hydrogenating HFP under appropriate conditions, and the resulting HFC-245eb is separated by distillation and is bydehydrofluorinated to obtain HFC-1234yf. According to this process of the present invention, it becomes possible to produce HFC-1234yf with a higher selectivity.

10 The process according to the above second aspect of the present invention may further comprise supplying the 2B fraction obtained from the step q) to the hydrogenating reaction of the step p).

15 Therefore, HFC-236ea as an intermediate can be subjected to hydrogenation to obtain HFC-245eb.

However, the second aspect of the present invention is not limited thereto. It is not required to utilize the 2B fraction for hydrogenation.

According to the present invention, 1,1,1,2-tetrafluoropropene (HFC-1234yf) can be produced with a 20 higher selectivity by using hexafluoropropene (HFP) as a

raw material and appropriately combining hydrogenation, dehydrofluorination and distillation.

#### Brief Description of Drawings

5 Fig. 1 shows a schematic diagram for explaining a process for producing 1,1,1,2-tetrafluoropropene (HFC-1234yf) in one embodiment of the present invention.

Fig. 2 shows a schematic diagram for explaining a process for producing 1,1,1,2-tetrafluoropropene (HFC-1234yf) in another embodiment of the present invention.

Following numerals denote the following elements:

11-17, 21-25...line; R11, R21...reactor (hydrogenating reaction); R12, R22...reactor (dehydrofluorination reaction); T11, T12, T21...distillation column; F1, F2...feed (mixture); S11...first stream (reaction mixture); S12...second stream (reaction mixture); S13...third stream (1A fraction); S14...fourth stream (2A fraction); S15...fifth stream (3A fraction); S16...sixth stream (4A fraction); S21...first stream (reaction mixture); S22...second stream (1B fraction); S23...third stream (reaction mixture); and S24...fourth stream (2B fraction).

#### Best Mode for Carrying Out the Invention

25 Two embodiments of the present invention will be described in detail below with reference to the drawings.

## (Embodiment 1)

5 The present embodiment relates to a manner in which following a hydrogenating reaction, dehydrofluorination is carried out, and then distillation is carried out ("folding" type).

10 Referring to Fig. 1, a raw material of hexafluoropropene (HFP) is fed from the outside to a line 11, and a sixth stream (S16) taken out of a distillation column T12 through a line 17 as mentioned below is recycled to the line 11. The sixth stream (S16) is a 4A fraction containing 1,1,1,2,3-pentafluoropropene (HFC-1225ye). Thus, the mixture of HFP and HFC-1225ye, as a feed (F1), is fed to a reactor R11 through the line 11.

15 The mixture of HFP and HFC-1225ye fed as the feed (F1) is subjected to hydrogenation in the presence of a reducing catalyst in the reactor R11 (in Fig. 1, supply of H<sub>2</sub> is omitted) to produce 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and 1,1,1,2,3-pentafluoropropane (HFC-245eb). In 20 the reaction mixture, although the unreacted HFP and HFC-1225ye may slightly remain, it is preferred that there is substantially no material which would not be finally converted into HFC-1234yf.

25 As the reducing catalyst, for example, a general reducing catalyst can be used. A preferred reducing

catalyst is a supported metal such as Pd, Pt, Rh, Ru or Re on activated carbon, a metal oxide such as alumina, or a metal fluoride. The ratio of metal supported is from 0.1 to 20% by weight, preferably from 0.1 to 10% by weight, and 5 more preferably from 0.5 to 5% by weight.

Since ability of reduction varies depending on the kind of the catalyst and reduction may proceed excessively or may not proceed (a conversion ratio may not increase), the catalyst can be appropriately selected according to the 10 purposes of the present embodiment.

The reaction pressure is not particularly limited and the reaction may proceed under reduced pressure, normal pressure or increased pressure, but the reaction under normal pressure or increased pressure is preferred. The 15 pressure is preferably in a range from about 0 to 1.5 MPaG (gauge pressure), since such pressure has an advantage in that it does not require a comparatively large device for proceeding the reaction. However, it is also possible to apply a pressure out of the above range.

20 The reaction temperature is usually in a range from about 30 to 400°C, preferably from about 30 to 300°C, and more preferably from about 30 to 180°C. The amount of by-products can be suppressed to a comparatively small amount by the reaction temperature not being unnecessarily high.

25 Since this reaction is an exothermic reaction, a

temperature higher than the above range may occur locally (at a part of the catalyst).

The contact time is represented by  $W/F_0$  ( $g \cdot Nml^{-1} \cdot sec$ ) (in this case,  $F_0$  ( $Nml \cdot sec^{-1}$ ) denotes the amount of the feed ( $F_1$ ) supplied to the reactor R11, and  $W$  ( $g$ ) denotes the amount of the catalyst filling the reactor R11), it may be usually in a range from about 0.1 to 30, and is preferably in a range from about 0.5 to 15 (the symbol "N" in the unit means conversion into a normal condition of 0°C and 1 atm, the same shall apply hereinafter). The contact time exerts an influence on selectivity and conversion ratio, and therefore can be appropriately selected according to the purposes.

Hydrogen ( $H_2$ ) used for hydrogenation is usually mixed with HFP as the raw material and HFC-1225ye in a ratio not smaller than a theoretically equivalent amount and supplied to the reactor R11. Therefore, the molar ratio in supply of  $H_2$  / (HFP and HFC-1225ye) is usually in a range from 1 to 6, and more preferably from 1 to 3.

Then, the reaction mixture obtained in the reactor R11 is taken out as a first stream (S11) through a line 12 and supplied to a reactor R12. And, HFC-236ea and HFC-245eb in the reaction mixture are subjected to dehydrofluorination to produce 1,1,1,2,3-pentafluoropropene (HFC-1225ye) and 1,1,1,2-tetrafluoropropene (HFC-1234yf). In a reaction

mixture thus obtained, unreacted HFC-236ea, HFC-245eb and so on may remain.

For the dehydrofluorination reaction, a catalyst which can be used for a general dehydrohalogenation reaction can be used. The catalyst is specifically, for example, a metal oxyfluoride or a metal fluoride, and more specifically chromium oxyfluoride, aluminum oxyfluoride, niobium fluoride, magnesium fluoride, tantalum fluoride or antimony fluoride, but is not particularly limited thereto.

For another example, an activated carbon based catalyst as disclosed in Patent Document 8 listed above may also be used.

The reaction pressure is not particularly limited and the reaction may proceed under reduced pressure, normal pressure or increased pressure, but the reaction under normal pressure is preferred. The reaction under normal pressure is advantageous in comparison to the reaction under increased pressure in view of equilibrium, and has an advantage in comparison to the reaction under reduced pressure in that it does not require a comparatively large device.

The reaction temperature, in a case under normal pressure, can be in a range from about 200 to 600°C, and preferably in a range from 250 to 450°C.

The contact time is represented by  $W'/F0'$  (g·Nm<sup>-1</sup>

<sup>1</sup>·sec) (in this case,  $F_0'$  ( $Nml \cdot sec^{-1}$ ) denotes the amount of the first stream (S11) and, if any, a below-mentioned fifth stream (S15) supplied to the reactor R12, and  $W'$  (g) denotes the amount of the catalyst filling the reactor R12) 5 may be usually in a range from about 0.1 to 120, and is preferably in a range from about 0.5 to 60.

In the reactions of the present embodiment, the dehydrofluorination reaction is a rate-limiting step.

Then, the reaction mixture obtained in the reactor R12 10 after dehydrofluorination, is taken out as a second stream (S12) through a line 13 and supplied to a distillation column T11. The second stream (S12) contains HFC-1234yf (normal boiling point of about -29°C) and HFC-1225ye (normal boiling points of about -19.5°C (Z-isomer) and 15 about -15.3°C (E-isomer)) and is separated by distillation into a 1A fraction containing HFC-1234yf (low-boiling component) and a 2A fraction containing HFC-1225ye (high-boiling component).

The 1A fraction is taken out of the distillation 20 column T11 as a third stream (S13) through a line 14. The 1A fraction is preferably composed of HFC-1234yf substantially, and by the 1A fraction, HFC-1234yf can be obtained.

The 2A fraction is taken out of the distillation 25 column T11 as a fourth stream (S14) through a line 15. The

2A fraction may generally contain, in addition to HFC-1225ye, HFC-245eb (normal boiling point of about 23°C) and/or HFC-236ea (normal boiling point of about 6°C).

The 2A fraction thus obtained after taking out of the 5 distillation column T11 as the fourth stream (S14), is supplied to a further distillation column T12 and separated by distillation into a 3A fraction containing at least one of, generally both of, HFC-245eb and HFC-236ea (high-boiling components) and a 4A fraction containing HFC-1225ye 10 (low-boiling component). The 3A fraction is taken out of the distillation column T12 through a line 16 as a fifth stream (S15), and may be returned to the reactor R12, where it is subjected to the dehydrofluorination reaction. The 4A fraction is taken out of the distillation column T12 15 through a line 17 as the sixth stream (S16), and supplied to the reactor R11 together with HFP as the feed (F1) as mentioned above, where it is subjected to the hydrogenating reaction.

As described above, according to the present 20 embodiment, HFC-1234yf can be produced with a high selectivity by carrying out the successive reactions for obtaining HFC-1234yf from HFP through HFC-1225ye in the simplified process. The process of the present embodiment can be conducted continuously.

25 Although an amount of impurities produced in the

present embodiment is quite small, low-boiling and high-boiling impurities may be removed from the stream(s) (e.g. the product stream and the recycling stream) by distillation, if appropriate. Hydrogen fluoride (HF) produced during the step may be separated and removed by washing with water and/or distillation, if appropriate. Although the unreacted hydrogen ( $H_2$ ) may exist in the stream(s), it may be appropriately treated by, for example, separation and removal, or recycling to the reactor R11.

10

(Embodiment 2)

The present embodiment relates to a manner in which following a hydrogenating reaction, distillation is carried out, and then dehydrofluorination is carried out ("direct" type). Hereinafter, the present embodiment is similar to Embodiment 1 unless otherwise specified.

Referring to Fig. 2, a raw material of hexafluoropropene (HFP) is fed from the outside to a line 21 and a fourth stream (S24) taken out of a distillation column T21 through a line 24 as mentioned below is recycled to the line 21. The fourth stream (S24) is a 2B fraction containing HFC-236ea. Thus, the mixture of HFP and HFC-236ea, as a feed (F2), is fed to a reactor R21 through the line 21. However, it should be noted that feed of HFC-236ea is not essential to the present embodiment.

The mixture of HFP and HFC-236ea fed as the feed (F2) is subjected to hydrogenation in the presence of a reducing catalyst in the reactor R21 (in Fig. 2, supply of H<sub>2</sub> is omitted) to produce HFC-236ea and HFC-245eb. In the 5 present embodiment, even if only HFP is fed as the feed (F2), HFC-245eb can be produced directly from HFP. In the reaction mixture, HFC-1225ye may also be contained.

As the reducing catalyst, any appropriate reducing catalyst capable of directly producing HFC-245eb from HFP, 10 for example, those mentioned in Embodiment 1 may be used accordingly.

Since ability of reduction varies depending on the kind of the catalyst and reduction may proceed excessively or may not proceed (a conversion ratio may not increase), 15 the catalyst can be appropriately selected according to the purposes of the present embodiment.

The reaction pressure is not particularly limited and the reaction may proceed under reduced pressure, normal pressure or increased pressure, but the reaction under 20 normal pressure or increased pressure is preferred. The pressure is preferably in a range from about 0 to 1.5 MPaG (gauge pressure), since such pressure has an advantage in that it does not require a comparatively large device for proceeding the reaction. However, it is also possible to 25 apply a pressure out of the above range.

The reaction temperature is usually in a range from about 30 to 500°C, preferably from about 30 to 400°C, and more preferably from about 30 to 300°C. The amount of by-products can be suppressed to a comparatively small amount 5 by the reaction temperature not being unnecessarily high.

Since this reaction is an exothermic reaction, a temperature higher than the above range may occur locally (at a part of the catalyst).

The contact time is represented by  $W/F_0$  (g·Nml<sup>-1</sup>·sec) 10 (in this case,  $F_0$  (Nml·sec<sup>-1</sup>) denotes the amount of the feed ( $F_2$ ) supplied to the reactor R21, and  $W$  (g) denotes the amount of the catalyst filling the reactor R21), it may be usually in a range from about 0.1 to 30, and is preferably in a range from about 0.5 to 15. The contact 15 time exerts an influence on selectivity and conversion ratio, and therefore can be appropriately selected according to the purposes.

Hydrogen (H<sub>2</sub>) used for hydrogenation is usually mixed with HFP as the raw material (and HFC-236ea when it exists 20 in the feed as in the present embodiment) in a ratio not smaller than a theoretically equivalent amount and supplied to the reactor R21. Therefore, the molar ratio in supply (which corresponds to the volume ratio in a gaseous state) of H<sub>2</sub>/HFP (or H<sub>2</sub>/(HFP and HFC-236ea) when HFC-236ea exists 25 in the feed as in the present embodiment) is usually in a

range from 1 to 6, and more preferably from 1 to 4.

Then, the reaction mixture obtained in the reactor R21 is taken out as a first stream (S21) through a line 22 and supplied to a distillation column T21. The first stream 5 (S21) contains HFC-245eb and HFC-236ea and is separated by distillation into a 1B fraction containing HFC-245eb (high-boiling component) and a 2B fraction containing HFC-236ea (low-boiling component).

The 1B fraction is taken out of the distillation 10 column T21 through a line 23 as a second stream (S22) and supplied to a reactor R22. And, HFC-245eb in the 1B fraction is subjected to dehydrofluorination to produce HFC-1234yf.

The conditions of the dehydrofluorination reaction are 15 the same as those of Embodiment 1.

The reaction pressure is not particularly limited and the reaction may proceed under reduced pressure, normal pressure or increased pressure, but the reaction under normal pressure is preferred. The reaction under normal 20 pressure is advantageous in comparison to the reaction under increased pressure in view of equilibrium, and has an advantage in comparison to the reaction under reduced pressure in that it does not require a comparatively large device.

25 The reaction temperature, in a case under normal

pressure, can be in a range from about 200 to 600°C, and preferably in a range from 250 to 450°C.

The contact time is represented by  $W'/F_0'$  (g·Nml<sup>-1</sup>·sec) (in this case,  $F_0'$  (Nml·sec<sup>-1</sup>) denotes the amount of the second stream (S22) and, if any, the below-mentioned recycling stream supplied to a reactor R22, and  $W'$  (g) denotes the amount of the catalyst filling the reactor R22), it may be usually in a range from about 0.1 to 120, and is preferably in a range from about 0.5 to 60.

Although the unreacted HFC-245eb may also remain, the reaction mixture thus obtained preferably contains HFC-1234yf in high purity. Therefore, HFC-1234yf can be obtained. If desired, the reaction mixture may be separated into a fraction containing HFC-1234yf and a fraction containing HFC-245eb, and the latter fraction may be returned (recycling stream) to the reactor R22, where it is subjected to the dehydrofluorination reaction. Also in the reactions of the present embodiment, the dehydrofluorination reaction is a rate-limiting step.

On the other hand, the 2B fraction is taken out of the distillation column T21 through a line 24 as the fourth stream (S24), and supplied to the reactor R21 together with HFP as the feed (F2) as mentioned above, where it is subjected to the hydrogenating reaction. The 2B fraction may generally contain HFC-1225ye, in addition to HFC-236ea.

As described above, according to the present embodiment, HFC-1234yf can be produced with a high selectivity by the very simple process which utilizes the reaction capable of directly obtaining HFC-245eb from HFP.

5 The process of the present embodiment can also be conducted continuously.

Although an amount of impurities produced in the present embodiment is quite small, low boiling and high boiling impurities may be removed from the stream(s) (e.g. 10 the product stream and the recycling stream) by distillation, if appropriate. Hydrogen fluoride (HF) produced during the step may be separated and removed by washing with water and/or distillation, if appropriate. Although the unreacted hydrogen ( $H_2$ ) may exist in the 15 stream(s), it may be appropriately treated by, for example, separation and removal, or recycling to the reactor R21.

[Example 1]

The process of the present invention was carried out 20 in accordance with Embodiment 1 described in detail with reference to Fig. 1.

As a raw material, HFP was used in a gaseous state. This raw material and a sixth stream (S16) recycled from 25 the distillation column T12 were combined and then fed, as a feed (F1), to the reactor R11, where the feed was

subjected to the hydrogenation reaction in the presence of a reducing catalyst. As the reducing catalyst, an activated carbon-supported Pd catalyst (ratio of Pd supported: 3% by weight) was used. The reaction conditions 5 were as follows: The reaction temperature was 200°C, and the reaction pressure was normal pressure. The volume ratio in supply of H<sub>2</sub>/(HFP and HFC-1225ye) was adjusted to 3.  $W/F_0 = 8$  (g·Nml<sup>-1</sup>·sec), wherein F<sub>0</sub> (Nml·sec<sup>-1</sup>) denotes the amount of the feed (F<sub>1</sub>) supplied to the reactor R11, 10 and W (g) denotes the amount of the catalyst filling the reactor R11.

The reaction mixture obtained in the reactor R11 was taken out as a first stream (S11) and supplied to the reactor R12, where it was subjected to the 15 dehydrofluorination reaction. A fifth stream (S15) recycled from the distillation column T12 was also supplied to the reactor R12, and subjected to the dehydrofluorination reaction. As the catalyst, a chromium oxyfluoride catalyst (fluorine content: about 31.4% by 20 weight) was used. The reaction conditions were as follows: The reaction temperature was 400°C, and the reaction pressure was normal pressure.  $W'/F_0' = 20$  (g·Nml<sup>-1</sup>·sec), wherein F<sub>0'</sub> (Nml·sec<sup>-1</sup>) denotes the amount of the first stream (S11) and the fifth stream (S15) supplied to the 25 reactor R12, and W' (g) denotes the amount of the catalyst

filling the reactor R12.

The reaction mixture obtained in the reactor R12 after the dehydrofluorination was taken out as a second stream (S12) and transferred to the distillation column T11, where 5 it was separated into a third stream (S13) as a low-boiling part and a fourth stream (S14) as a high-boiling part. The resultant fourth stream (S14) was transferred to the distillation column T12, where it was separated into a fifth stream (S15) as a high-boiling part and a sixth 10 stream (S16) as a low-boiling part. The resultant fifth stream (S15) and sixth stream (S16) were recycled entirely to the reactor R12 and the reactor R11 respectively, as described above.

Twelve hours after starting the operation, 15 compositions of the feed (F1) and the first to sixth streams (S11 to S16) were analyzed by gas chromatography to determine the flow rate of each component excluding hydrogen ( $H_2$ ) and hydrogen fluoride (HF). The results are shown in Table 1. In the table, the symbol "--" means no 20 detection, and "trace" means existence only in a trace amount.

Table 1

	Flow rate (kmol/hr)						
	F1	S11	S12	S13	S14	S15	S16
HFP	0.51	-	-	-	-	-	-
HFC-236ea	-	0.51	0.08	-	0.08	0.08	-
HFC-245eb	-	0.49	0.05	-	0.05	0.05	-
HFC-1234yf	-	-	0.50	0.50	-	-	-
HFC-1225ye	0.49	-	0.49	-	0.49	-	0.49
Impurities	trace	trace	0.02	0.01	0.01	0.01	trace

It is confirmed from Table 1 that HFC-1234yf can be obtained as the third stream (S13), which corresponds to 5 the 1A fraction, with a high yield.

[Example 2]

The process of the present invention was carried out in accordance with Embodiment 2 described in detail with 10 reference to Fig. 2.

As a raw material, HFP was used in a gaseous state. This raw material and a fourth stream (S24) recycled from the distillation column T21 were combined and then fed, as a feed (F2), to the reactor R21, where the feed was subjected to the hydrogenation reaction in the presence of 15 a reducing catalyst. As the reducing catalyst, an activated carbon-supported Pd catalyst (ratio of Pd supported: 3% by weight) was used. The reaction conditions were as follows: The reaction temperature was 200°C, and 20 the reaction pressure was normal pressure. The volume

ratio in supply of  $H_2$  / (HFP and HFC-236ea) was adjusted to 4.

$W/F_0 = 8$  ( $g \cdot Nml^{-1} \cdot sec$ ), wherein  $F_0$  ( $Nml \cdot sec^{-1}$ ) denotes the amount of the feed (F2) supplied to the reactor R21, and  $W$  ( $g$ ) denotes the amount of the catalyst filling the reactor

5 R21.

The reaction mixture obtained in the reactor R21 was taken out as a first stream (S21) and supplied to the distillation column T21, where it was separated into a second stream (S22) as a high-boiling part and a fourth stream (S24) as a low-boiling part.

The resulting second stream (S22) was supplied to the reactor R22, where it was subjected to the dehydrofluorination reaction. As the catalyst, a chromium oxyfluoride catalyst (fluorine content: about 31.4% by weight) was used. The reaction conditions were as follows:

The reaction temperature was  $400^{\circ}C$ , and the reaction pressure was normal pressure.  $W'/F_0' = 20$  ( $g \cdot Nml^{-1} \cdot sec$ ), wherein  $F_0'$  ( $Nml \cdot sec^{-1}$ ) denotes the amount of the second stream (S22) supplied to the reactor R22, and  $W'$  ( $g$ ) denotes the amount of the catalyst filling the reactor R22.

On the other hand, the fourth stream (S24) was recycled entirely to the reactor 21, as described above.

25 Twelve hours after starting the operation, compositions of the feed (F2) and the first to fourth streams (S21 to S24) were analyzed by gas chromatography to

determine the flow rate of each component excluding hydrogen (H<sub>2</sub>) and hydrogen fluoride (HF). The results are shown in Table 2. In the table, the symbol "--" means no detection, and "trace" means existence only in a trace amount.

Table 2

	Flow rate (kmol/hr)				
	F2	S21	S22	S23	S24
HFP	0.2	-	-	-	-
HFC-1225ye	trace	trace	-	-	trace
HFC-236ea	0.9	0.9	-	-	0.9
HFC-245eb	-	0.2	0.2	0.016	-
HFC-1234yf	-	-	-	0.18	-
Impurities	trace	trace	trace	0.004	trace

It is confirmed from Table 2 that HFC-1234yf can be obtained in the third stream (S23), which corresponds to the reaction mixture after dehydrofluorination, in a yield of 90%. Since HFC-245eb in the third stream is an intermediate, a high yield of 97% or more can be expected when HFC-245eb is separated and recycled to the dehydrofluorinated reaction to obtain HFC-1234yf.

#### Industrial Applicability

1,1,1,2-tetrafluoropropene (HFC-1234yf) can be used as a refrigerant substance, and a process for producing HFC-1234yf using hexafluoropropene (HFP) as a raw material can

be expected to be useful as a process for producing a substitute refrigerant.

5 The present application claims a priority to United States Provisional Application No. 61/017,052 filed on December 27, 2007, entitled "PROCESS FOR PRODUCING 1,1,1,2-TETRAFLUOROPROPENE". The contents of that application are incorporated herein by the reference thereto in their entirety.

## CLAIMS

1. A process for producing 1,1,1,2-tetrafluoropropene, which comprises the steps of:

5 a) hydrogenating a raw material of hexafluoropropene together with 1,1,1,2,3-pentafluoropropene in the presence of a reducing catalyst to obtain a reaction mixture containing 1,1,1,2,3-hexafluoropropane and 1,1,1,2,3-pentafluoropropane;

10 b) subjecting the reaction mixture obtained from the step a) to a dehydrofluorination reaction to obtain a reaction mixture containing 1,1,1,2,3-pentafluoropropene and 1,1,1,2-tetrafluoropropene;

15 c) subjecting the reaction mixture obtained from the step b) to distillation to separate into a 1A fraction containing 1,1,1,2-tetrafluoropropene and a 2A fraction containing 1,1,1,2,3-pentafluoropropene; and

20 d) using 1,1,1,2,3-pentafluoropropene contained in the 2A fraction for the step a),

20 whereby 1,1,1,2-tetrafluoropropene is obtained in the 1A fraction.

2. The process according to claim 1, wherein the 2A fraction obtained from the step c) contains, in addition to 25 1,1,1,2,3-pentafluoropropene, at least one of 1,1,1,2,3-

pentafluoropropane and 1,1,1,2,3-hexafluoropropane; and  
the step d) comprises subjecting the 2A fraction to  
further distillation to separate into a 3A fraction  
containing at least one of 1,1,1,2,3-pentafluoropropane and  
5 1,1,1,2,3-hexafluoropropane and a 4A fraction containing  
1,1,1,2,3-pentafluoropropene, subjecting the 3A fraction to  
the dehydrofluorination reaction of the step b), and  
subjecting the 4A fraction to the hydrogenating reaction of  
the step a).

10

3. A process for producing 1,1,1,2-tetrafluoropropene,  
which comprises the steps of:

15 p) hydrogenating a raw material of hexafluoropropene  
in the presence of a reducing catalyst to obtain a reaction  
mixture containing 1,1,1,2,3-hexafluoropropane and  
1,1,1,2,3-pentafluoropropane;

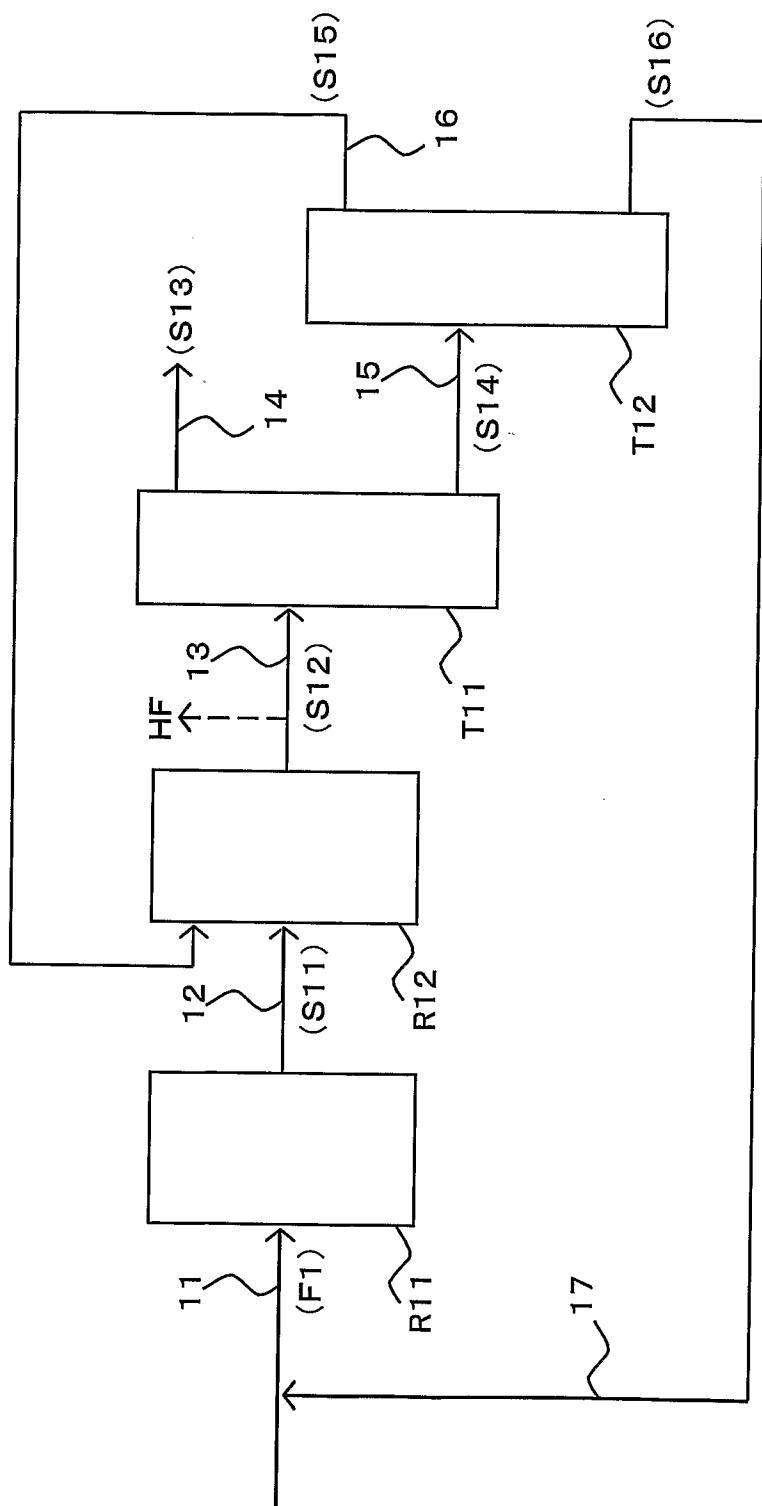
20 q) subjecting the reaction mixture obtained from the  
step p) to distilling to separate into a 1B fraction  
containing 1,1,1,2,3-pentafluoropropane and a 2B fraction  
containing 1,1,1,2,3-hexafluoropropane; and

r) subjecting the 1B fraction to a dehydrofluorination  
reaction to obtain a reaction mixture containing 1,1,1,2-  
tetrafluoropropene,

25 whereby 1,1,1,2-tetrafluoropropene is obtained in the  
reaction mixture of the step r).

4. The process according to claim 3, which further comprises supplying the 2B fraction obtained from the step q) to the hydrogenating reaction of the step p).

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**Fig. 1**

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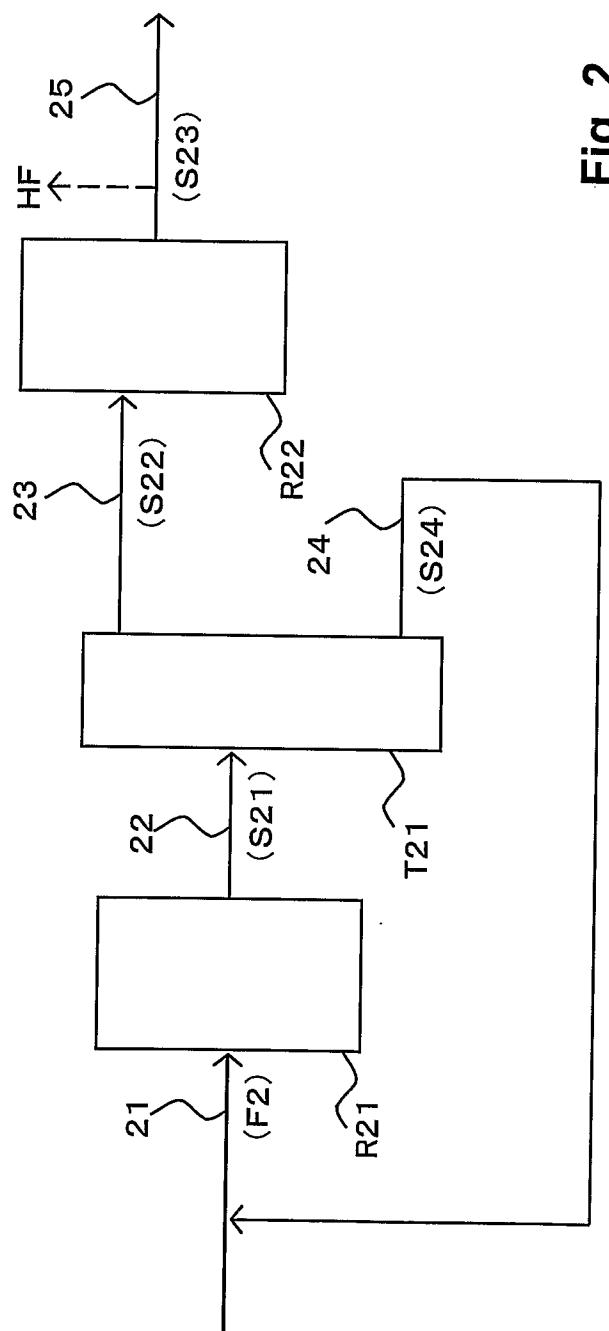


Fig. 2

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/JP2008/073902

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. C07C17/25 C07C17/354 C07C17/383 C07C19/08 C07C21/18

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C07C

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

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

EPO-Internal, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/179324 A1 (VAN DER PUY MICHAEL [US] ET AL) 2 August 2007 (2007-08-02) cited in the application abstract examples 1-8	1,3
A	US 4 086 407 A (FOZZARD GEORGE B) 25 April 1978 (1978-04-25) abstract examples 1,3	1,3



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

4 March 2009

Date of mailing of the international search report

11/03/2009

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**INTERNATIONAL SEARCH REPORT**

## Information on patent family members

International application No  
PCT/JP2008/073902

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 2007179324	A1 02-08-2007	WO	2008057794 A1	15-05-2008
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