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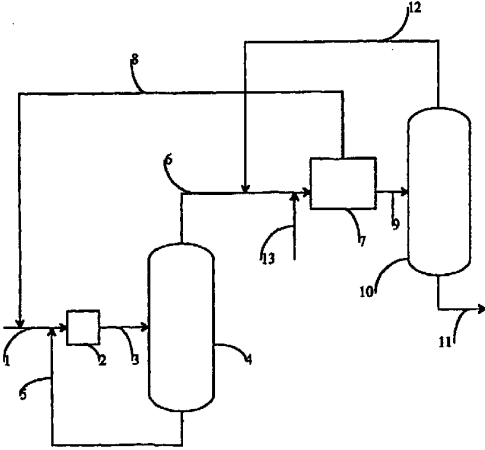
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<p>(21) International Application Number: PCT/GB00/01861 (22) International Filing Date: 15 May 2000 (15.05.00) (30) Priority Data: 9911475.3 18 May 1999 (18.05.99) GB 60/134,657 18 May 1999 (18.05.99) US <i>INEOS FLUOR HOLDINGS LIMITED</i> (71) Applicant (for all designated States except US): IMPERIAL CHEMICAL INDUSTRIES PLC (GB/GB); Imperial Chemical House, Millbank, London SW1E 3JE, (GB), First Floor <i>Queen's Gate 15-17 Queens Terrace Southampton Hampshire</i> (72) Inventors; and (75) Inventors/Applicants (for US only): GIBSON, Robin, Riyadh (GB/GB); Newton Cottage, Newton Lanc, Newton-by-Chester CH3 9AX (GB). SUMMERS, Greg, Lyndon (GB/GB); 3 Roosevelt Avenue, Lancaster LA1 5BJ (GB). (74) Agent: DEE, Ian, M.; Eric Potter Clarkson, Park View House, 58 The Ropewalk, Nottingham NG1 5DD (GB).</p>	<p>(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p> 	
<p>(54) Title: PRODUCTION OF 1,1,1,2,3,3,3-HEPTAFLUOROPROPANE</p>		
		
<p>(57) Abstract Preparation of HFC 227ea by reacting HFP with hydrogen fluoride comprising the steps of charging the reaction mixture therefrom to a liquid-phase separator, allowing a HFC 227ea-rich phase and a hydrogen fluoride-rich phase to separate under gravity, recycling the separated hydrogen fluoride-rich phase, charging the HFC 227ea-rich phase to a distillation column, recovering the HFC 227ea and an HF-rich mixture separately from the distillation column; and recycling the HF-rich mixture to the reactor.</p>		

Production of 1,1,1,2,3,3,3-heptafluoropropane

The present invention relates to a process for the production of 1,1,1,2,3,3,3-heptafluoropropane from hexafluoropropene and to a process for the separation of mixtures comprising 1,1,1,2,3,3,3-heptafluoropropane and hydrogen fluoride.

Hydrofluorocarbons are widely used as replacements for chlorofluorocarbon compounds in a variety of applications. Such applications include use in medical applications, for example as an aerosol propellant, use as a fire suppressant, use in refrigeration applications and in other applications. 1,1,1,2,3,3,3-heptafluoropropane, which is known in the art as Hydrofluorocarbon 227ea and will hereinafter be referred to as "HFC 227ea" for convenience, has zero ozone depletion potential and is particularly beneficial in medical applications in the light of its combination of properties including low toxicity, non-flammability, solvent properties and boiling point.

It is known to produce hydrofluorocarbons by the hydrofluorination of a fluoroalkene to the corresponding hydrofluoroalkane, optionally in the presence of a catalyst, in the liquid phase or vapour phase. Hydrogen fluoride is known for use as a hydrofluorination agent in such hydrofluorination processes.

A variety of materials may be employed as catalysts in such hydrofluorination processes.

For example, in the vapour phase reaction of hexafluoropropene, hereinafter referred to as "HFP" for convenience, with hydrogen fluoride for the preparation of HFC 227ea, DE 2712732 and GB 902590 disclose the use of a chromium oxyfluoride catalyst and an activated carbon catalyst respectively.

For example, in the liquid phase reaction of HFP with hydrogen fluoride for the preparation of HFC 227ea, WO 97/11042 and WO 96/0243 disclose the use of catalysts comprising an organic amine complexed with hydrogen fluoride and certain antimony catalysts respectively.

The disclosures in the aforementioned patent specifications are incorporated herein by way of reference.

A stoichiometric excess of hydrogen fluoride to HFP is normally employed in the aforementioned processes and the degree of conversion of HFP to HFC 227ea is dependent on *inter alia* the catalyst employed, if any, and the conditions in the reactor in which the conversion is carried out.

The product stream leaving the reactor typically comprises HFC 227ea, HFP, hydrogen fluoride and a ternary azeotrope thereof.

It is normal practice to recover as much as possible of the hydrogen fluoride from the product stream from such hydrofluorination reactions for re-use. This may be partially achieved by distillation. However, the presence in the product stream of an azeotrope or azeotrope-like mixture of HFC 227ea/hydrogen fluoride and an azeotrope or azeotrope-like mixture of HFP/hydrogen fluoride limits the extent to which hydrogen fluoride can be separated from the fluoro-organic compounds by simple distillation.

It is known that the stream comprising the HFC 227ea/hydrogen fluoride azeotrope and the HFP/hydrogen fluoride azeotrope, after recovery of a portion of the hydrogen fluoride by distillation, can be water-washed to allow recovery of both a mixture of organic compounds essentially free of hydrogen fluoride and aqueous hydrogen fluoride. However, such a treatment is wasteful of hydrogen fluoride since it is normal practice for aqueous hydrogen fluoride generated in this way to be neutralised with caustic solution and/or lime and ultimately disposed of.

Alternatively, the product stream from the reaction of a fluoroalkene with hydrogen fluoride, after recovery of a portion of the hydrogen fluoride by distillation, may be treated with a solution of alkali metal dissolved in anhydrous hydrogen fluoride as described in our patent specification WO 97/13719. However, although such a process recovers hydrogen fluoride for re-use within the process, it has the disadvantage of requiring additional equipment.

Furthermore, it is known that in the preparation of fluorine-containing organic compounds by the reaction of a haloalkene with hydrogen fluoride the haloalkene/hydrogen fluoride azeotrope can be separated from the fluorine-containing compound/hydrogen fluoride azeotrope by fractional distillation and hydrogen fluoride can be removed from the fluorine-containing organic compound/hydrogen fluoride azeotrope by treatment with water. However, treatment of the fluorine-containing organic compound/hydrogen fluoride azeotrope with water to remove hydrogen fluoride therefrom involves the use of expensive equipment and is wasteful of hydrogen fluoride.

It will be appreciated that whereas aqueous scrubbing is an effective way of removing hydrogen fluoride from the organic compound(s) after reacting hydrogen fluoride with a haloalkene aqueous scrubbing tends to be expensive in terms of hydrogen fluoride loss from the process. Preferably as much as possible, more preferably

essentially all, of the hydrogen fluoride is separated from the product stream before aqueous scrubbing and particularly more preferably aqueous scrubbing is avoided.

In our pending International Patent Application GB 98/03408 we disclose that where in the preparation of a fluorine-containing organic compound by the reaction of a haloalkene with hydrogen fluoride, for example the production of HFC 227ea from HFP, the haloalkene/hydrogen fluoride azeotrope is more volatile, ie has a lower boiling point, than the fluorine-containing organic compound/hydrogen fluoride azeotrope produced in the reaction both the fluorine-containing organic compound substantially free of hydrogen fluoride and the haloalkene/hydrogen fluoride azeotrope can be separated by charging the reaction product and the haloalkene to a distillation column and distilling the resulting mixture.

It should be noted that the discussion of the background to the invention herein is included to explain the context of the invention. This is not to be taken as an admission that any of the material referred to was published, known or part of the common general knowledge in Australia as at the priority date of any of the claims.

We have now found surprisingly that in the preparation of HFC 227ea by the reaction of HFP with hydrogen fluoride the reaction product phase-separates in the liquid phase to afford an organic-rich phase, which comprises HFC 227ea and HFP, and a hydrogen fluoride-rich phase. The mole fraction of HF to 227ea in the reaction product may be from about 0.1 to 0.9.

Furthermore, we have found that addition of HFP to the reaction product in the liquid phase enhances the aforementioned phase-separation.

According to the first aspect of the present invention there is provided a process for the production of HFC 227ea by the reaction of HFP with hydrogen fluoride including the Steps of:

- A. charging the reaction mixture from the reaction of HFP with hydrogen fluoride to a liquid-phase separator and allowing an organic phase and a hydrogen fluoride-rich phase to separate under gravity;
- B. recycling the hydrogen fluoride-rich phase separated in Step A to the reactor in which the reaction is carried out;

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- C. charging the organic-rich phase separated in Step A to a distillation column;
- D. recovering the HFC 227ea and an HF-rich mixture separately from the distillation column in Step (C); and
- E. recycling the HF-rich mixture recovered from Step D to the reactor or separator.

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Preferably the reaction mixture charged to the liquid-phase separator in Step (A) comprises an HFC 227ea/HF azeotrope, or azeotrope-like mixture, and optionally an HFP/HF azeotrope, or azeotrope-like mixture.

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The reaction mixture charged to the liquid-phase separator in Step A may be the mixture arising directly from the reactor in which HFP is reacted with hydrogen fluoride (direct mixture). It is often preferred, however, that the mixture charged to the liquid-phase separator is essentially an HFC 227ea/hydrogen fluoride azeotrope, for example
5 obtained from distillation of the direct mixture.

It will be appreciated that whereas the use of an HFC 227ea/HF azeotrope, or azeotrope-like mixture, in the process according to the present invention will not facilitate separation of the organic phase from the hydrogen fluoride-rich phase such use increases the amount of HFC 227ea to be removed per pass and, accordingly, reduces
10 the amount of material to be recycled.

We have found surprisingly that addition of HFP facilitates separation of the HFC 227ea/hydrogen fluoride azeotrope into its components. The HFP may be introduced into the process according to the present invention at one or more appropriate points. For example, it may be charged to the reactor and/or to the liquid-
15 phase separator in Step A and/or to the distillation column in Step C. Preferably the HFP is added to the liquid phase separator, either directly or mixed with the reaction mixture.

The reaction of HFP with hydrogen fluoride may be carried out in the liquid phase or in the vapour phase.
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To facilitate the separation in Step A of the process of the present invention, Step A is preferably carried out at below ambient temperature, typically at below 30°C.

To facilitate the separation in Step A of the process of the present invention, Step A is preferably carried out at supra-atmospheric pressure, typically 1-20 bars and preferably about 10 bars.
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The product of the reaction of HFP with hydrogen fluoride may be distilled to recover a portion of the hydrogen fluoride therefrom before the mixture comprising HFC 227ea/hydrogen fluoride azeotrope or azeotrope-like mixture thereof, HFP/hydrogen fluoride azeotrope or azeotrope-like mixture thereof, and hydrogen fluoride is charged to the liquid phase separator in Step A.
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The portion of hydrogen fluoride recovered by distillation in a recovery step prior to Step A, where such a recovery step is carried out, is preferably recycled to the reactor vessel.

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Alternatively, the product of the reaction of HFP with hydrogen fluoride may be charged directly to the liquid-phase separator in Step A.

Where HFC 227ea is prepared by reacting HFP with hydrogen fluoride in the liquid phase in the presence of a catalyst, eg TaF₅, NbF₅ or SbF₅, it is suitably carried out at a temperature in the range of 20 to 200°C, preferably 40 to 120°C and especially 50 to 100°C. Suitably the reaction is carried out at superatmospheric pressure such that the reactants are in the liquid phase for sufficient time to react to produce HFC 227ea. Preferably the pressure is at least 5 bar and more preferably the pressure is 10 to 50 bar.

A residence time in the reactor sufficient to permit conversion of HFP feedstock into HFC 227ea is required. The required residence time will be dependent on *inter alia* the degree of conversion required, the reactant ratio and the reaction conditions.

Where a low conversion rate of HFP into HFC 227ea is desired it is preferable that the feedstocks be recycled to increase the yield of HFC 227ea from the starting material. However, we do not exclude the possibility that recycling is employed where high single pass conversions are required.

The molar ratio of hydrogen fluoride (HF) to HFP fed to the reactor is suitably at least 1:1 and preferably between 1.2 and 10:1. It will be appreciated that where a molar ratio of HF to HFP of 0.1 up to 1:1 is employed the conversion ratio and/or the yield will be lower.

The molar ratio of HFP to the catalyst is suitably not more than 100:1 and is preferably between 1:1 and 50:1.

The levels of HF, HFP and catalyst in the process according to the present invention are suitably selected such that the catalyst and reactants are at least largely dissolved in the liquid phase under the reaction conditions employed.

The process according to the present invention may be operated in batch or continuous mode as desired. Semi-batch operation may also be employed in which one or more feedstocks are fed continuously to the process and one or more other feedstocks are fed to the process in batch-wise fashion.

Alternatively, reaction of HFP and HF may be carried out in the vapour phase. Suitable conditions and catalysts for use in carrying out the reaction of HFP and HF in the vapour phase are more fully described in DE 2712732 and GB 902590 mentioned hereinbefore.

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The present invention will be further illustrated by reference to the accompanying drawings which illustrate, by way of example only, schematic representations of plants for carrying out the process according to the present invention.

In the drawings:

5 Figure 1 is a schematic representation of a plant wherein HFP is fed to the liquid-phase separator;

Figure 2 is a schematic representation of a plant wherein HFP is fed to the reactor;

Figure 3 is a schematic representation of a plant wherein the product of the reaction is fed directly to the liquid-phase separator; and

10 Figure 4 is a ternary diagram illustrating HFC 227ea, HFP and HF separation.

In Figures 1 and 2, feed pipe (1) leads to a reactor (2), which optionally contains a fluorination catalyst. Product pipe (3) from the reactor (2) is in fluid-flow communication with a first distillation column (4), which is for example a single stage flash vessel. Distillation column (4) is typically operated at a pressure of 12 bars with a
15 bottoms temperature of 100°C and a tops temperature of around 50°C. Bottoms pipe (5) from distillation column (4) is in fluid-flow communication with feed-pipe (1). Tops line (6) from distillation column (4) is in fluid-flow communication with a liquid-phase separator (7). Tops line (8) from the liquid-phase separator (7) is in fluid-flow communication with fee-pipe (1). Bottoms line (9) from the liquid-phase separator (7)
20 is in fluid-flow communication with a second distillation column (10), which is for example a packed column. Distillation column (10) is typically operated at a pressure of around 12 bars with a tops temperature of 37°C and a bottoms temperature of around 60°C. Distillation column (10) is provided with an exit pipe for product (11) and a tops pipe (12).

25 In Figure 1, tops pipe (12) from distillation column (10) is in fluid flow communication with tops line (6) which is provided with a feed-pipe (13).



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In Figure 2, tops pipe (12) from distillation column (10) is in fluid flow communication with feed-pipe (1) which is provided with feed-pipe (13).

In operation, in Figures 1 and 2, the reactor (2) is charged through feed pipe (1) with a feed stream containing fresh hydrogen fluoride and recycled hydrogen fluoride (from lines (5) and (8) and, in Figure 2, line (12)). The product from reactor (2) comprising HFC 227ea, hydrogen fluoride and unconverted HFP, often in the form of a ternary azeotrope, travels through product pipe (3) to the first distillation column (4). In distillation column (4), hydrogen fluoride, which is recycled via bottoms line (5) to feed pipe (1), is separated from the mixture of HFC 227ea, hydrogen fluoride and unconverted HFP. The mixture of HFC 227ea, residual hydrogen fluoride and HFP is fed via tops line (6) from the distillation column (4) to the liquid-phase separator (7). The liquid-phase separator (7) is typically operated at 0-20°C to afford better separation. In Figure 1, HFP is fed via feed line (13) to liquid-phase separator (7). In Figure 2, HFP is fed via line (13) and feed-pipe (1) to reactor (2). In the liquid phase separator (7), an HF-rich phase separates from the organics-rich phase. The HF-rich phase is returned via tops-line (8) to feed-pipe (1). The organics-rich phase flows via bottoms line (9) to distillation column (10). A stream comprising HFP and essentially all the hydrogen fluoride content of the stream entering distillation column (10) via line (9) is removed from the top of distillation column (10) via line (12) and the product stream HFC 227ea is removed from the bottom of column (10) via exit pipe (11).

In Figure 3, feed pipe (1) leads to a reactor (2), which optionally contains a fluorination catalyst. Line (14) from reactor (2) is provided with a feed line (13) and is in fluid-flow communication with a liquid-phase separator (7). Tops line (8) from the liquid-phase separator (7) is in fluid-flow communication with feed-pipe (1). Bottoms line (9) from the liquid-phase separator (7) is in fluid-flow communication with a distillation column (10), which is for example a packed column. Distillation column (10) is typically operated at a pressure of around 12 bars with a tops temperature of 37°C and a bottoms temperature of around 60°C. Distillation column (10) is provided with an exit pipe for product (11) and a tops pipe (12) which is in fluid flow communication with line (14) to liquid-phase separator (7).

In operation, in Figure 3, the reactor (2) is charged through feed pipe (1) with a feed stream containing fresh hydrogen fluoride and recycled hydrogen fluoride from line (8). The product from reactor (2) comprising HFC 227ea, hydrogen fluoride and

unconverted HFP, often in the form of a ternary azeotrope, travels through product pipe (14) to the liquid-phase separator (7). HFP is fed via feed line (13) and product pipe (14) to liquid-phase separator (7). The liquid-phase separator (7) is typically operated at 0-20°C to afford better separation. In the liquid-phase separator (7), an HF-rich phase separates from the organics-rich phase. The HF-rich phase is returned via tops-line (8) to feed-pipe (1). The organics-rich phase flows via bottoms line (9) to distillation column (10). A stream comprising HFP and essentially all the hydrogen fluoride content of the stream entering distillation column (10) via line (9) is removed from the top of distillation column (10) via line (12) and returned to the liquid phase separator (7) via line (14). The product stream HFC 227ea is removed from the bottom of column (10) via exit pipe (11).

In the ternary diagram in Figure 4, compositions in the area of the figure designated A phase-separate, namely compositions comprising 0.4-0.6 mole fraction HF, greater than 0.4 mole fraction HFP and less than 0.6 mole fraction HFC 227ea.

The present invention is further illustrated by reference to the following Examples.

15 Examples 1-4

These examples 1-4 illustrate the liquid-phase separation of HFP 227ea from HF and the enhanced separation thereof in the presence of HFP.

In the Examples, HFC 227ea and HFP, where used, were added to HF in a 500 ml whitey bomb cooled in liquid nitrogen. The whitey bomb was provided with a double-dip arrangement such that the dip-pipes would sample from the middle of each phase. The mixture was allowed to warm to room temperature, agitated, allowed to stand for 2 hours and then analysed.

The HF phase was analysed for organics by transferring a portion of the HF phase (10g) to a smaller whitey bomb containing water. It was allowed to stand for 15 minutes then the headspace was analysed by G.C.

The organics phase was analysed for HF by bubbling a portion of the organics phase through water scrubbers containing fresh de-ionised water and ice. The water was then analysed for fluoride.

The results are shown in the Table from which it can be seen that (a) a mixture of HFC 227ea and HF phase-separates such that an organic layer and an HF-rich layer are formed (Example 1) and (b) addition of HFP to the HFC 227ea/HF mixture reduces the

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concentration of HF in the organic phase and significantly reduces the concentration of HFC 227ea in the HF phase (Examples 2-4).

Table

Example No.	Components	Mass (g)	%w/w	mole fraction	%w/w HF in organic phase	%w/w 227ea in HF phase	%w/w HFP in HF phase
1	HF	44.07	8.31	0.44	5.29		
	227ea	486	91.69	0.56		22.56	
2	HF	39.74	7.43	0.4	3.14		
	227ea	410.46	76.76	0.49		8.98	
	HFP	84.54	15.81	0.11			2.07
3	HF	33.32	6.16	0.35	3.54		
	227ea	367	67.88	0.45		10.81	
	HFP	140.3	25.96	0.2			5.47
4	HF	30.06	5.56	0.32	0.33		
	227ea	312.7	57.86	0.4		9.35	
	HFP	198	36.62	0.28			6.21

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the production of 1,1,1,2,3,3,3-heptafluoropropane (HFC 227ea) by the reaction of hexafluoropropene (HFP) with hydrogen fluoride including the steps of:
 - 5 A. charging the reaction mixture from the reaction of HFP with hydrogen fluoride to a liquid-phase separator and allowing an organic phase and a hydrogen fluoride-rich phase to separate under gravity;
 - B. recycling the hydrogen fluoride-rich phase separated in Step A to the reactor in which the reaction is carried out;
 - 10 C. charging the organic-rich phase separated in Step A to a distillation column;
 - D. recovering the HFC 227ea and an hydrogen fluoride-rich mixture separately from the distillation column in Step (C); and
 - E. recycling the hydrogen fluoride-rich mixture recovered from Step D to the reactor or separator.
- 15 2. A process as claimed in Claim 1 wherein the reaction mixture charged to the liquid-phase separator in Step (A) comprises an HFC 227ea/HF azeotrope, or azeotrope-like mixture.
3. A process as claimed in Claim 1 wherein in Step A the organic phase and the hydrogen fluoride-rich phase are allowed to separate under gravity at below
20 ambient temperature.
4. A process as claimed in Claim 1 wherein in Step A the organic phase and the hydrogen fluoride-rich phase are allowed to separate under gravity at supra-atmospheric pressure.
5. A process according to any one of the preceding claims in which HFP in addition
25 to that present in the reaction mixture from the reaction of HFP with hydrogen fluoride is introduced into the process.
6. A process as claimed in Claim 5, wherein the additional HFP is charged to the liquid-phase separator.
7. A process as claimed in Claim 5, wherein the additional HFP is charged to the
30 reactor.
8. A process as claimed in any one of the preceding claims wherein the mixture to be separated in the liquid-phase separator in Step (A) comprises a mole ratio of HF:HFC 227ea of between 3:7 and 6:4.

9. 1,1,1,2,3,3,3-heptafluoropropane made in accordance with the process of any one of claims 1 to 8.
10. A process for the production of 1,1,1,2,3,3,3-heptafluoropropane substantially as hereinbefore described with reference to the drawings.
- 5 11. 1,1,1,2,3,3,3-heptafluoropropane made in accordance with a process substantially as hereinbefore described with reference to the drawings.

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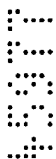

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Figure 1

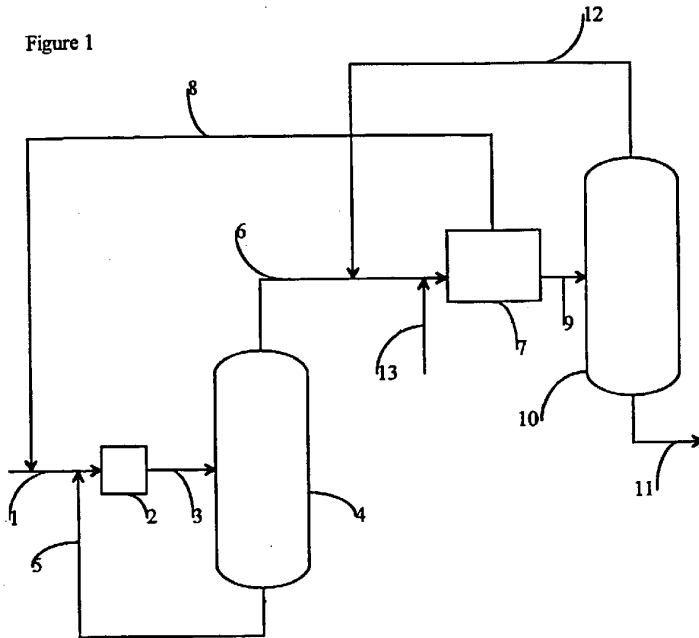


Figure 2

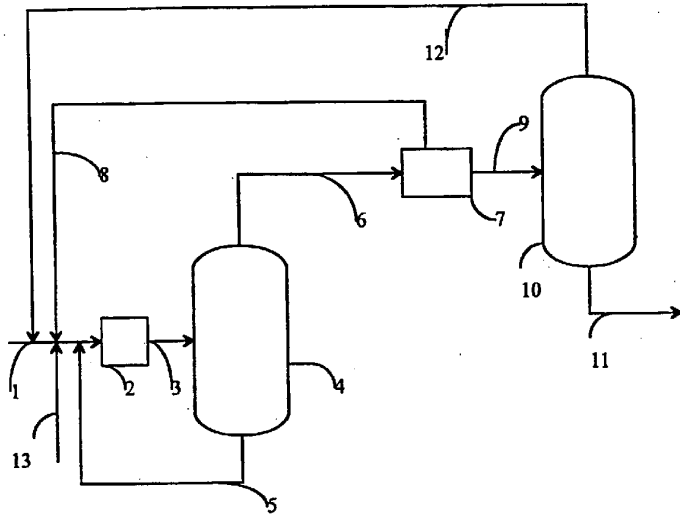


Figure 3

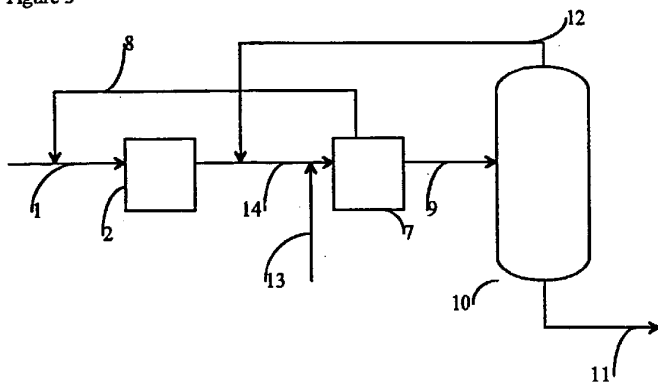


Figure 4

