

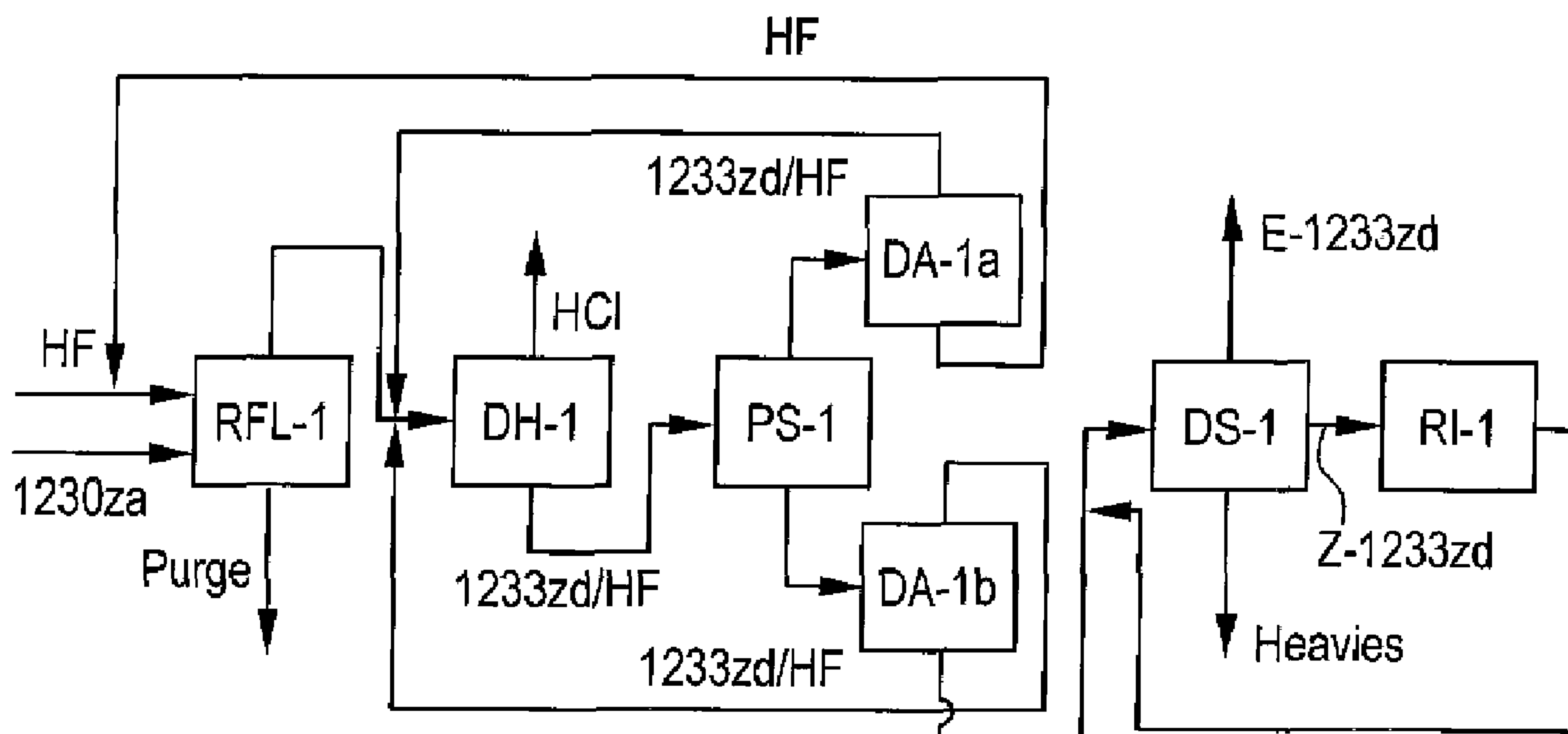


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(54) Titre : PROCEDE DE FABRICATION D'HYDROCHLOROFLUOROOLEFINES  
(54) Title: PROCESS FOR THE MANUFACTURE OF HYDROCHLOROFLUOROOLEFINS

**FIG. 1**



(57) **Abrégé/Abstract:**

The present invention provides a process for the manufacture of trans 1-chloro-3,3,3-trifluoropropene (E-1233zd). The first step of the process comprises the fluorination of 1,1,3,3-tetrachloropropene (1230za,  $\text{CCh}=\text{CH}-\text{CHCh}$ ) and/or 1,1,1,3,3-pentaachloropropane (240fa) to a mixture of cis 1233zd (Z-1233zd) and trans 1233zd (E-1233zd). The second step of the process comprises a separation of the mixture formed in the first step to isolate cis 1233zd (Z-1233zd) from the mixture. The third step of the process comprises isomerization of cis 1233zd (Z-1233zd) to trans 1233zd (E-1233zd).



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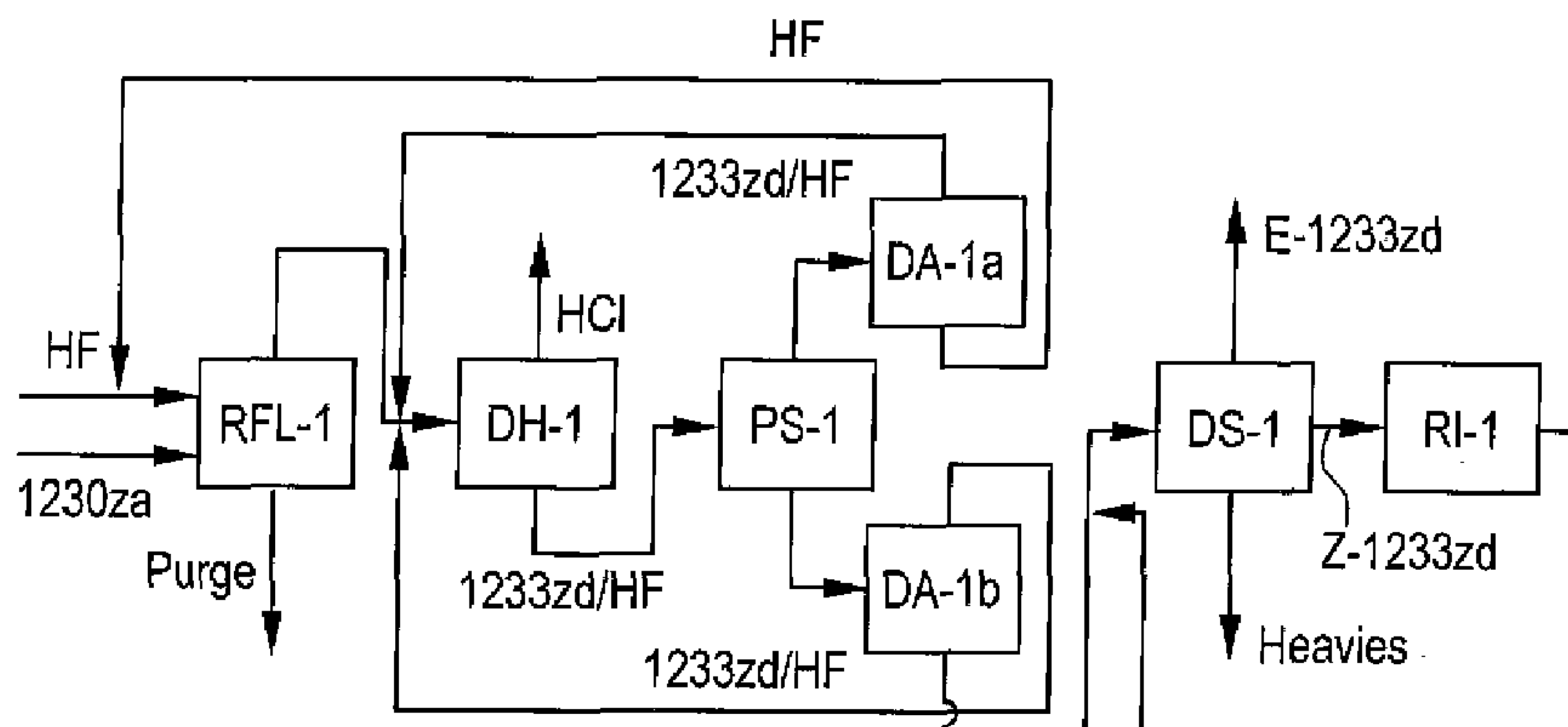
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(54) Title: PROCESS FOR THE MANUFACTURE OF HYDROCHLOROFLUOROOLEFINS

FIG. 1



(57) Abstract: The present invention provides a process for the manufacture of trans 1-chloro-3,3,3-trifluoropropene (E-1233zd). The first step of the process comprises the fluorination of 1,1,3,3- tetrachlororopropene (1230za, CCh=CH-CHCh) and/or 1,1,1,3,3- pentaachloropropane (240fa) to a mixture of cis 1233zd (Z-1233zd) and trans 1233zd (E-1233zd). The second step of the process comprises a separation of the mixture formed in the first step to isolate cis 1233zd (Z-1233zd) from the mixture. The third step of the process comprises isomerization of cis 1233zd (Z-1233zd) to trans 1233zd (E- 1233zd).

## PROCESS FOR THE MANUFACTURE OF HYDROCHLOROFLUOROOLEFINS

### Field of The Invention

The present invention relates to a process for the manufacture of  
5 hydrochlorofluoroolefins.

### Background of the Invention

The Montreal Protocol for the protection of the ozone layer mandates the phase out of the use of chlorofluorocarbons (CFCs). Materials more “friendly” to the ozone layer such as hydrofluorocarbons (HFCs) e.g. 134a replaced chlorofluorocarbons. The latter  
10 compounds have proven to be greenhouse gases, causing global warming and could be regulated by the Kyoto Protocol on Climate Change. Replacement materials are needed which are environmentally acceptable i.e. have negligible ozone depletion potential (ODP) and acceptable low global warming potential (GWP). The present invention describes a process for manufacturing of the hydrochlorofluoroolefin, trans 1233zd (E-  
15 1233zd, 1-chloro-3,3,3-trifluorpropene) which is useful as a low ODP and low GWP blowing agent for thermoset and thermoplastic foams, solvent, heat transfer fluid such as in heat pumps, and refrigerant such as a low pressure refrigerant for chillers.

US patent publications US2008/0051610 and US2008/0103342 disclose a process that includes a step of the catalytic isomerization of cis 1234ze to trans 1234ze. US 7,420,094  
20 discloses the isomerization of 1234ze to 1234yf with a Cr based catalyst.

US2008/0051611 discloses the recovery of trans 1234ze from a mixture that includes cis 1234ze and trans 1234ze via distillation.

### Summary of the Invention

The present invention relates a process for the manufacture of the  
25 hydrochlorofluoroolefin, trans 1-chloro-3,3,3-trifluorpropene (E-1233zd). The process comprises an isomerization step from cis 1233zd (Z-1233zd) to trans 1233zd (E-1233zd).



### Brief Summary of the Drawings

Figure 1 is a schematic of a liquid phase process in accordance with the present invention.

Figure 2 is schematic of a gas phase process in accordance with the present invention.

### 5 Detailed Description of the Invention

The present invention provides a process for the manufacture of trans 1-chloro-3,3,3-trifluoropropene (E-1233zd). The first step of the process comprises the fluorination of 1,1,3,3-tetrachlororopropene (1230za,  $\text{CCl}_2=\text{CH}-\text{CHCl}_2$ ) and/or 1,1,1,3,3-pentaachloropropane (240fa) to a mixture of cis 1233zd (Z-1233zd) and trans 1233zd (E-1233zd). The second step of the process comprises a separation of the mixture formed in the first step to isolate cis 1233zd (Z-1233zd) from the mixture. The third step of the process comprises isomerization of cis 1233zd (Z-1233zd) to trans 1233zd (E-1233zd).

The 1230za used in the first step can be obtained by the reaction of  $\text{CCl}_4$  and vinyl chloride monomer (VCM,  $\text{CH}_2=\text{CHCl}$ ) to form 1,1,1,3,3-pentachloropropane (240fa) which can be dehydrochlorinated to produce 1230za.

The present invention is directed toward a process for producing trans 1-chloro-3,3,3-trifluoro propene (E-1233zd) from 1,1,3,3-tetrachlororopropene (1230za,  $\text{CCl}_2=\text{CH}-\text{CHCl}_2$ ) and/or 1,1,1,3,3-tetrachloropropane (240fa) that comprises the steps of:

- a) fluorination of 1,1,3,3-tetrachlororopropene (1230za,  $\text{CCl}_2=\text{CH}-\text{CHCl}_2$ ) and/or 1,1,1,3,3-pentachloropropane (240fa) in gas phase, or liquid phase fluorination of 1230za to obtain a mixture of cis (Z) and trans (E) 1-chloro-3,3,3 trifluoro propene (1233zd,  $\text{CF}_3-\text{CH}=\text{CHCl}$ ); followed by
- b) separation of cis (Z) 1-chloro 3,3,3-trifluoropropene (1233zd,  $\text{CF}_3-\text{CH}=\text{CHCl}$ ) and trans (E) 1-chloro 3,3,3-trifluoropropene (1233zd,  $\text{CF}_3-\text{CH}=\text{CHCl}$ ); followed by
- c) isomerization of the cis 1233zd (Z-1233zd) from the second step to form trans 1233zd (E-1233zd).

The first step of the process, gas phase fluorination of 1230za and/or 240fa to 1233zd or liquid phase fluorination of 1230za to 1233zd; can be via any process known in the art. For example: the uncatalyzed liquid phase fluorination of 1230za is disclosed in US Patent No. 5,877,359; the catalyzed gas phase fluorination of 1230za is disclosed in US Patent No. 5,811,603; US Patent No. 6,166,274 discloses the fluorination of 1230za to 1233zd in the presence of catalyst such as trifluoroacetic acid or triflic acid. Fluorination catalysts such as  $\text{TiCl}_4$ ,  $\text{TiF}_4$ ,  $\text{SnCl}_4$ ,  $\text{SnF}_4$ ,  $\text{SbF}_5$ ,  $\text{SbCl}_5$ ,  $\text{SbF}_x\text{Cl}_y$  ( $x+y=5$ ), or an ionic liquid are described in US Patent No. 6,881,698. When an Sb type catalyst is used, it is preferred to feed low level of  $\text{Cl}_2$  to maintain the Sb species in an active form.

The second step of the process comprises the separation of the cis 1233zd and trans 1233zd formed in the first step via an appropriate separation means such as distillation, liquid phase separation, or extractive separation. The cis 1233zd and trans 1233zd formed in the first step may contain HF and HCl. Preferably, the HCl is first removed in a first distillation column. Thereafter, liquid phase separation coupled with azeotropic distillation can be used to remove HF. The boiling point difference of cis 1233zd and trans 1233zd enable them to be separated by conventional distillation, typically at atmospheric pressures.

The third step of the process involves the isomerization of the cis 1233zd from the second step into trans 1233zd. The isomerization step can be carried out in the gas phase or in the liquid phase using respectively a heterogeneous or a homogeneous catalyst.

The isomerization step is achievable with a gas phase process in the presence of a heterogeneous catalyst. A suitable heterogeneous catalyst is high surface area  $\text{Cr}^{(\text{III})}$  catalyst, supported or unsupported, that can optionally contains low levels of one or more co-catalysts selected from cobalt, nickel, zinc or manganese. For supported catalyst, the catalyst support can be selected from materials known in the art to be compatible with high temperature and pressure processes. For example, fluorinated alumina, HF treated activated carbon or carbon graphite are suitable catalyst supports. A preferred catalyst is a high surface area unsupported chromium oxide catalyst that is activated with HF before use, optionally at pressure above 50 psi. The level of the co-catalyst, when present, can be varied from 1 to 10 weight %, preferably from 1 to 5 weight % of the catalyst. Co-

catalyst can be added to the catalyst by processes known in the art such as adsorption from an aqueous or organic solvent, followed by solvent evaporation.

Suitable heterogeneous catalyst can also be selected from: Lewis acids supported catalysts selected from  $\text{Sb}^{\text{V}}$ ,  $\text{Ti}^{\text{IV}}$ ,  $\text{Sn}^{\text{IV}}$ ,  $\text{Mo}^{\text{VI}}$ ,  $\text{Nb}^{\text{V}}$  and  $\text{Ta}^{\text{V}}$ . The support itself is selected from the group such as fluorinated alumina; fluorinated chromia; HF activated carbon or graphite carbon. Supported antimony halides such as  $\text{SbF}_5$  are described in US Patent No. 6,528,691 and are preferred catalysts. Other solid catalysts such as NAFION<sup>®</sup> type polymer, acidic molecular sieves and, zeolites can be also used.

For the gas phase process, the temperature can be varied between 20-500°C, preferably between 100-400°C. Contact times can vary from 0.5 to 100 seconds. A low level of oxidizing agent such as oxygen or oxygen containing gas such as air or chlorine gas can be used at between .01- .1 volume percent to prolong the life of the catalyst.

The isomerization step is also achievable in a liquid phase process in the presence of a homogenous catalyst preferably selected from compounds of group 3, 4, 5, 13, 14 and 15 metal compounds of the Periodic Table of the elements (IUPAC 1988) and their mixtures (groups of the Periodic Table of the elements which were previously called IIIA, IVa, IVb, Va, Vb and VIb). The compounds of the metals are intended to include hydroxides, oxides and the organic or inorganic salts of these metals, as well as mixtures thereof. Preferred are the aluminum, titanium, tantalum, molybdenum, boron, tin and antimony derivatives such as  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{TaCl}_5$ ,  $\text{MoCl}_6$ ,  $\text{BF}_3$ ,  $\text{SnCl}_4$ , and  $\text{SbCl}_5$ . In the process according to the invention the preferred derivatives of the metals are the salts and these are preferably chosen from the halides and more particularly from chlorides, fluorides and chlorofluorides such as  $\text{AlF}_3$ ,  $\text{TiF}_4$ ,  $\text{TaF}_5$ ,  $\text{MoF}_6$ ,  $\text{SnF}_4$ ,  $\text{SbF}_5$ ,  $\text{SbF}_x\text{Cl}_y$  ( $x+y=5$ ). The catalyst must be subjected to activation (by HF or any molecule able to exchange fluorine) prior to the isomerization step. In the case of antimony type catalyst, a low level of chlorine gas as oxidizing agent can be used to maintain the antimony catalyst in the pentavalent oxidation state. In addition to the above mentioned Lewis acids catalyst, an ionic liquid derived from antimony, titanium, niobium and tantalum is suitable for liquid phase fluorination processes. A description of the preparation of such catalysts is disclosed in the US Patent No. 6,881,698.



The homogenous catalyst for a liquid phase process can also be selected from the Bronsted type family of acids such as (but not limited to) sulfuric acid  $\text{H}_2\text{SO}_4$ , sulfonic type acids such as  $\text{ClSO}_3\text{H}$  or  $\text{FSO}_3\text{H}$  or triflic acid  $\text{CF}_3\text{SO}_3\text{H}$  or methane sulfonic acid  $\text{CH}_3\text{SO}_3\text{H}$ . For the liquid phase process, the operating temperature can be varied between  
5 about 20-200°C, with a contact time between about 0.5-50 hours.

The process of the present invention may comprise additional separation steps between each step. The purpose of these separations could be:

1. to remove, totally or partially, any hydracid ( $\text{HF}$ ,  $\text{HCl}$ ) from the flow if required, or
- 10 2. to isolate a desired product in order to feed it in a subsequent step, or
3. to purify a product and removes organic impurities or by products, or
4. to dry a product ( $\text{H}_2\text{O}$  removal).

The means used to achieve these additional steps are known in the art and include but are not limited to: distillation, extractive distillation or adsorption.

15 The process of the present invention is exemplified in the figures, which set forth block flow diagrams of gas phase and liquid phase processes in accordance with the present invention. The processes in the figures are set out in the form of process modules designed to achieve a specific purpose and arranged in accordance with the process of the present invention. These modules comprise:

20 **RFL-** comprises a liquid phase fluorination reactor and rectification system comprising an unagitated, jacketed pressure vessel connected to a rectification column. The reactor also acts as the reboiler of the rectification column. The  $\text{HF}$  and organic (1230za) are fed directly to the reactor. The molar feed ratio of  $\text{HF}$  to organic is dictated by the reaction stoichiometry and the amount of  $\text{HF}$  leaving the reactor with the rectification column  
25 overhead and liquid phase purges. Mixing is provided by the boiling action of the reactor contents. For the most part, the reactor effluent leaves the reactor vessel as a gas and enters the bottom of the rectification column. A small purge from the liquid phase can

remove any non-volatiles that may form during the reaction. The rectification column contains either packing or trays designed to provide good mass transfer between up flowing gas and down flowing liquid. The condenser at the top of the column is cooled by either cooling water, chilled water, or some type of refrigeration. The condenser is a partial condenser where the liquid effluent is refluxed directly back to the column. The vapor effluent consists of HCl, HF and organic components.

**DH-** comprises an HCl distillation system whereby pure HCl is removed from the top of a distillation column. This column can operate between 100 psig and 300 psig. More typically, the HCl is distilled above 120 psig to allow the use of conventional (-40C) refrigeration at the top of the HCl column. The bottoms of this column contains HF and organic with a small residual amount of HCl. The ratio of HF to the organic component typically is close to the azeotropic composition.

**PS-** comprises a liquid phase separator to separate two liquid phases, one consisting primarily of a hydrochlorofluorocarbon (HCFC) and the other consisting primarily of HF. The HF phase is usually the less dense so that it exits from the top of the phase separator and the HCFC exits as the bottom phase. There is some HF in the HCFC phase and some HCFC in the HF phase. However, the compositions of both phases are far removed from any azeotropic composition. The operating temperature of the phase separator can be between -40°C and +20°C. However, the lower the temperature, the better the phase separation.

**DA-** comprises an azeotropic distillation column which distills overhead an azeotropic composition of HF and an organic consisting of one or more HCFC's (hydrochlorofluorocarbons) and HFC's (hydrofluorocarbons). These organic compounds can be either saturated or olefinic. The bottoms composition is either entirely HF or entirely organic, depending on whether the column feed composition is on the HF rich side or the organic rich side of the azeotrope. If the bottoms are HF, this stream is normally recycled back to the reactor. If the bottoms stream is organic, it is sent to a conventional distillation train.

**DS-** comprises a straight distillation normally done under pressure.



**RI** –comprises a gas phase isomerization reaction typically done at temperatures above 400°C in an adiabatic, packed bed reactor. The module consists of a feed vaporizer and superheater. It can include an “economizer”, whereby hot effluent is fed to one side and relatively cold reactor feed gases are fed to another side of a heat exchanger. The effluent gases are further cooled before entering a distillation column. Isomerization reactions can be run at varying conversions depending on the equilibrium distribution of isomers. The effluent isomers can have boiling points very close together. However, they typically exhibit close to ideal behavior so can be separated by conventional distillation. As an alternative to the gas phase, this reaction can be done as a homogeneously catalyzed liquid phase reaction. In this configuration, the reactor would be a continuous stirred tank with the effluent being removed as a vapor to effect separation from the catalyst.

**RFG-** comprises a gas phase fluorination reactor that is an adiabatic packed bed reactor that feeds a gas phase over a solid catalyst. No cooling is needed because of the reactor has a low conversion per pass and a high HF molar feed ratio. The adiabatic exotherm is typically less than 100°C. The feed HF and organic are vaporized in a common vaporizer and superheated to the reactor temperature. The common vaporizer allows the 1230za and/or 240fa to be vaporized at a lower temperature than would be possible if it were vaporized as a pure component, thereby minimizing thermal degradation. This module can also include an “economizer”, whereby hot effluent is fed to one side and relatively cold reactor feed gases are fed to another side of a heat exchanger. The effluent gases are further cooled before entering a distillation column. Reaction temperatures are between 200°C and 400°C. The pressure is high enough to allow the HCl by-product to be distilled with conventional refrigeration- preferably between 100 psig and 200 psig.

The lower case letter used to identify the modules distinguishes multiple appearances of the same type of module in the same process.

Figure 1 is a block flow diagram of a process in accordance with the present invention for converting 1230za to E-1233zd using a liquid phase fluorination step. The Figure incorporates the process modules described above. Figure 1 discloses a process wherein 1230za and HF are fed to reaction module RFL-1. Typically, the reaction takes place in a

predominantly HF rich medium without a catalyst. The HCl and the 1233zd/HF exit the top of the rectification column of RFL-1. The vapor effluent of RFL-1 enters DH-1 to remove HCl as a pure overhead product. The bottoms of DH-1 consists primarily of 1233zd (both E and Z isomers) and HF at a near azeotropic composition. This is fed to  
5 module PS-1 to effect a liquid phase separation. The top HF rich phase is sent to module DA-1a, where HF is separated as a bottoms stream for recycle to the reactor. The overhead azeotrope of 1233zd and HF is recycled back to DH-1 to allow any residual HCl and light organics to be stripped out in this column before the azeotrope gets recycled to phase separation. The bottoms stream from PS-1 goes to module DA-1b,  
10 which removes an organic stream devoid of HF as a bottoms stream. The overhead from DA-1b is recycled to DH-1 for the same reason that the DA-1a azeotrope was recycled to DH-1. The bottoms of DA-1b is sent to process module DS-1 that separates any heavies from the 1233zd. The overhead from DS-1 is E-1233zd, the desired trans isomer. The Z-1233zd is higher boiling and is recovered for feeding to process module RI-1. The  
15 effluent from the isomerization reactor is recycled to DS-1, which effects the separation of the E and Z isomers.

Figure 2 is a block flow diagram of a process in accordance with the present invention for converting 1230za or 240fa to E-1233zd using a gas phase fluorination step. The Figure incorporates the process modules described above. In Figure 2 the process is similar to  
20 Figure 1 except, for example, the liquid phase fluorination reactor (RFL-1) is replaced by a gas phase fluorination reactor (RFG-1) and azeotropic distillation column (DA-2a).

The process as outlined by Figure 2 comprises feeding 1230za and/or 240fa and HF to reaction module RFG-2. The reaction takes place in a gas phase with a catalyst. The reactor effluent consists of predominantly HCl, 1233zd, unreacted 1230za and excess HF.  
25 The reactor effluent of RFG-2 enters DA-2a to remove HF and unreacted F1230za as bottoms that is recycled to the reactor. The overhead, which consists predominantly of HCl and the azeotrope of HF and 1233zd (both E and Z isomers), is sent to DH-2, which removes HCl as a pure overhead product. The bottoms of DH-2 consists of primarily 1233zd (both E and Z isomers) and HF at a near azeotropic composition. This is fed to  
30 module PS-2 to effect a liquid phase separation. The top HF rich phase is sent to module

DA-2b, where HF is separated as a bottoms stream for recycle to the reactor. The overhead azeotrope of 1233zd and HF is recycled back to DH-2 to allow any residual HCl and light organics to be stripped out in this column before the azeotrope gets recycled to phase separation. The bottoms stream from PS-2 goes to module DA-2c, which removes an organic stream devoid of HF as a bottoms stream. The overhead from DA-2c is recycled to DH-2 for the same reason that the DA-2b azeotrope was recycled to DH-2. The bottoms of DA-2c is sent to process module DS-2 that separates any heavies from the 1233zd. The overhead from DS-2 is E-1233zd- the desired trans isomer. The Z-1233zd is higher boiling and is recovered for feeding to process module RI-2. The effluent from the isomerization reactor is recycled to DS-2, which effects the separation of the E and Z isomers.



What we claim

1. A process for preparing trans 1-chloro-3,3,3-trifluoropropene (E-1233zd) that comprises at least one step of isomerization of cis 1-chloro-3,3,3-trifluoropropene to trans 1-chloro-3,3,3-trifluoropropene.
2. The process of claim 1 wherein said isomerization is carried out in the liquid phase in the presence of a homogenous catalyst or in the gas phase in the presence of a heterogeneous catalyst.
3. The process of claim 2 wherein said heterogeneous catalyst is selected from the group consisting of a soluble Lewis acid of  $\text{Sb}^{\text{V}}$ ,  $\text{Ti}^{\text{IV}}$ ,  $\text{Sn}^{\text{IV}}$ ,  $\text{Mo}^{\text{VI}}$ ,  $\text{Nb}^{\text{V}}$  and  $\text{Ta}^{\text{V}}$ ; antimony halides; acidic molecular sieves; Cr and zeolites..
4. The process of claim 3 wherein said heterogeneous catalyst is supported or unsupported.
5. The process of claim 3 wherein said heterogeneous catalyst further comprises a co-catalyst selected from the group consisting of cobalt, nickel, zinc and manganese.
6. The process of claim 5 wherein said co-catalyst is present in amounts from about 1 to 5 weight percent of said catalyst.
7. The process of claim 2 wherein said homogenous catalyst is selected from the group consisting of: aluminum, titanium, tantalum, molybdenum, boron, tin, antimony and salts thereof and Bronsted acids.
8. The process of claim 7 wherein said salts are chlorides, fluorides or chlorofluorides.
9. The process of claim 4 wherein said support is selected from the group consisting of fluorinated alumina, fluorinated chromia, HF treated activated carbon and fluorinated graphite.
10. The process of claim 1 wherein said 1233zd is prepared via fluorination of 1230za and/or 240fa.
11. The process of claim 1 wherein said 1233zd is prepared via fluorination of 1230za in the gas or liquid phase.

12. The process of claim 11 wherein said 1230za is prepared via reaction of  $\text{CCl}_4$  and vinyl chloride monomer followed by dehydrochlorination.
13. The process of claim 11 wherein said fluorination is catalyzed or uncatalyzed.
14. The process of claim 1 wherein said 1233zd is prepared via fluorination of 240fa in the gas phase.
15. The process of claim 14 wherein said 240fa is prepared via reaction of  $\text{CCl}_4$  and vinyl chloride monomer followed by dehydrochlorination.
16. The process of claim 14 wherein said fluorination is catalyzed or uncatalyzed.
17. A process for manufacturing trans 1- chloro 3,3,3 trifluoro propene (E-1233zd) from 1,1,3,3- tetrachloropropene (1230za) and/ or 1,1,1,3,3- tetrachloropropane (240fa) comprising the steps of:
  - fluorination of 1,1,3,3- tetrachloropropene (1230za) and/ or 1,1,1,3,3- tetrachloropropane (240fa) to a mixture comprising cis 1233zd (Z-1233zd) and trans 1233zd (E- 1233zd); followed by
  - separation of said cis 1233zd (Z-1233zd) from said trans 1233zd (E- 1233zd); followed by
  - isomerization of said cis 1233zd (Z-1233zd) to from trans 1233zd (E- 1233zd).
18. The process of claim 17 wherein said isomerization process is carried out in the gas phase or the liquid phase.
19. The process of claim 18 wherein said isomerization is carried out in a liquid phase with a homogenous catalysts selected from the group consisting of soluble Lewis acid catalysts and Bronsted acid catalysts.
20. The process of claim 19 wherein said soluble Lewis acid catalyst is selected from  $\text{Sb}^{\text{V}}$ ;  $\text{Ti}^{\text{IV}}$ ;  $\text{Sn}^{\text{IV}}$ ;  $\text{Mo}^{\text{VI}}$ ;  $\text{Nb}^{\text{V}}$ ;  $\text{Ta}^{\text{V}}$ ; oxide supported catalysts; fluorinated alumina; fluorinated chromia; prefluorinated activated carbon; graphite carbon;  $\text{SiC}$ ;  $\text{Sb}^5$ .
21. The process of claim 20 wherein said oxide supported catalyst is selected from the group consisting of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ .

22. The process of claim 19 wherein said Bronsted acid catalyst is selected from the group consisting of triflic acid, methane sulfonic acid, sulfuric acid and sulfonic acid.
23. The process of claim 18 wherein said isomerization is carried out in the gas phase with a high surface area heterogeneous Cr catalyst, supported or unsupported.
24. The process of claim 23 wherein said catalyst further comprising a co-catalyst selected from the group consisting of Co, Ni, Zn and Mn.



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FIG. 1

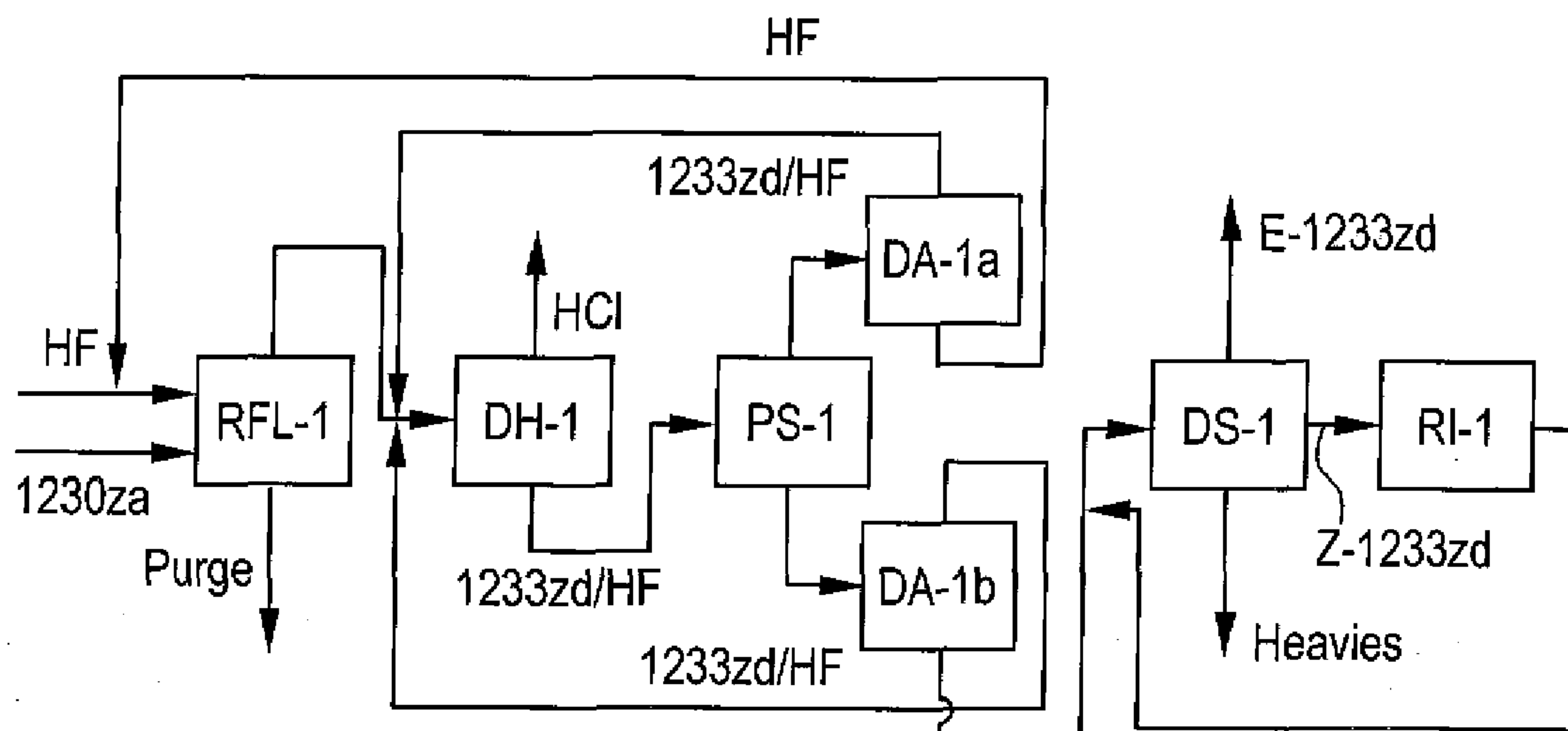


FIG. 2

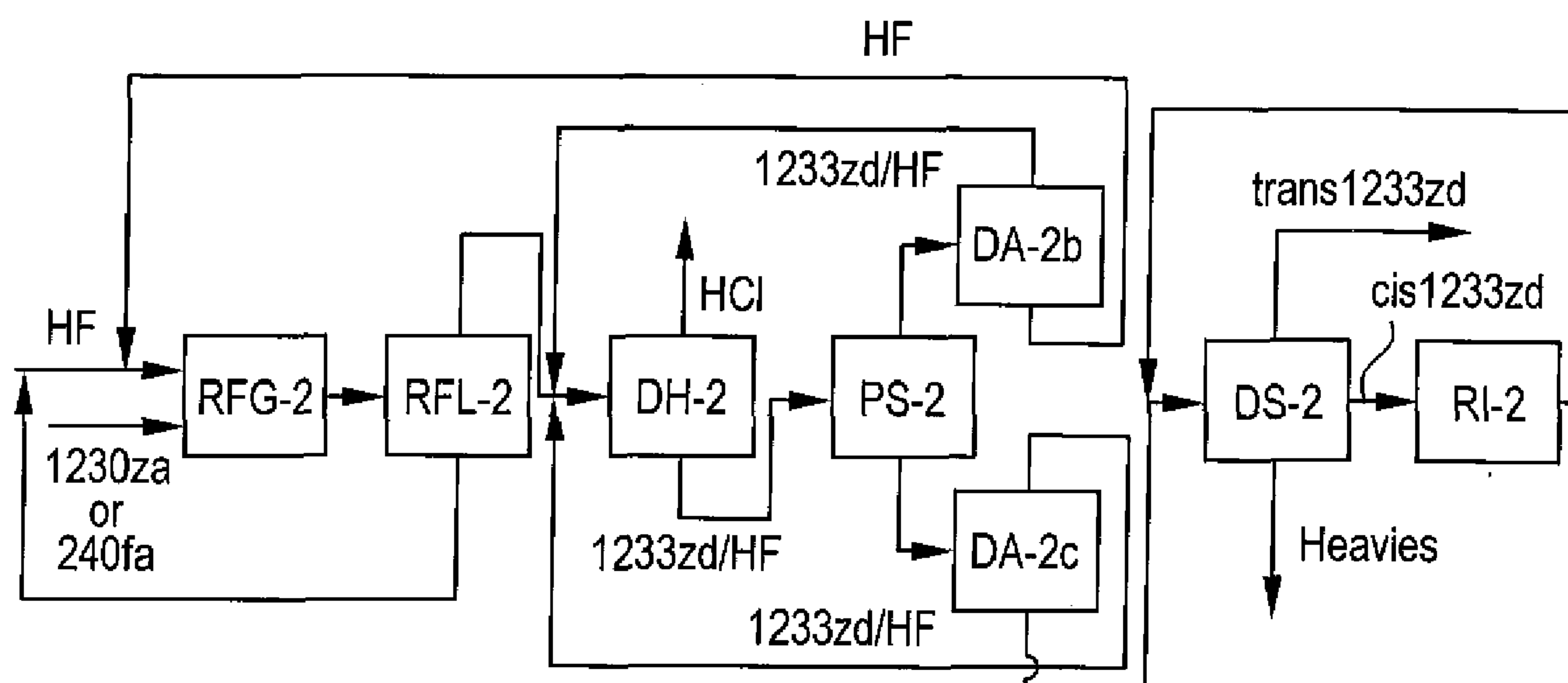


FIG. 1

