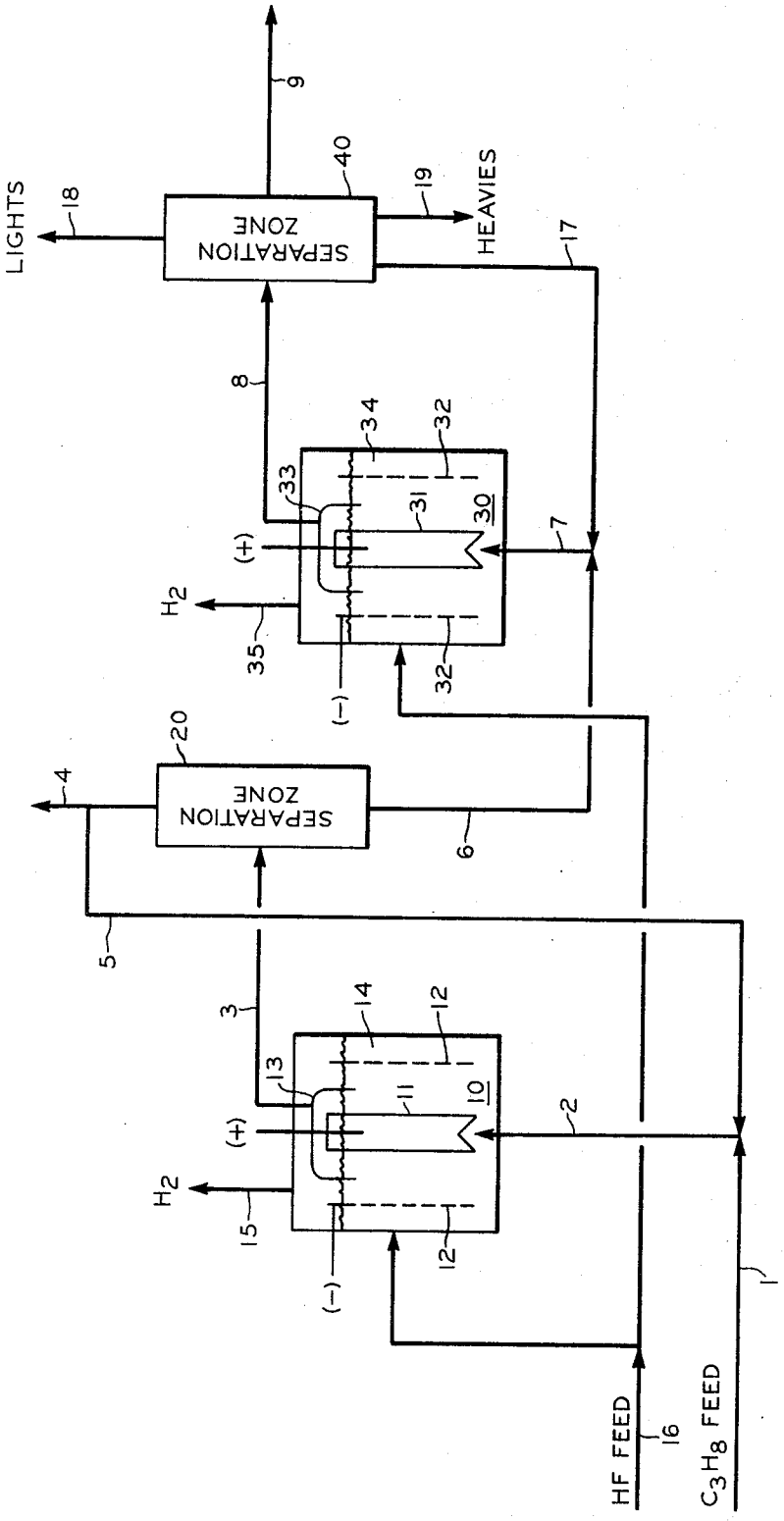
TWO-STAGE ELECTROCHEMICAL OCTAFLUOROPROPANE PRODUTION

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TWO-STAGE ELECTROCHEMICAL OCTAFLUOROPROPANE PRODUCTION

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ABSTRACT OF THE DISCLOSURE

A two-stage electrochemical process comprising: a first-stage fluorination wherein propane is fluorinated under regulated conditions in order to produce a maximum amount of partially fluorinated propanes and a minimum amount of octafluoropropane; a separation step wherein a propane-free stream of partially fluorinated propanes is isolated; and a second-stage fluorination wherein said partially fluorinated propanes are fluorinated under regulated conditions in order to maximize the formation of octafluoropropane (perfluoropropane).

This invention relates to a process and an apparatus for the preparation of octafluoropropane (perfluoropropane).

In this application, the phrase "partially fluorinated propanes" refers to fluorinated propane molecules containing at least one but not more than seven fluoride atoms. The phrase is used interchangeably with "octafluoropropane intermediates," "perfluoro intermediates," or simply "intermediates."

Electrochemical fluorination processes for converting organic compounds into desirable fluorinated compounds are generally known in the art. Recent advances in the state of the art include electrochemical fluorination processes wherein fluorination of organic compounds is carried out within the confines of a porous anode. Such an improved process is capable of producing a broad variety of partially and completely fluorinated products with very little carbon to carbon bond scission which results in undesirable by-products.

In such prior art electrolytic fluorination processes, when charging propane feedstock, there is obtained a mixture of partially and completely fluorinated propanes. There are about 29 such fluoropropanes and most are generally present. In the practice of the prior art processes for the preparation of octafluoropropane, there is the problem that mixtures of octafluoropropane and unconverted propane cannot readily be separated. These two materials have similar boiling points and tend to codistill with one another when using conventional fractionation methods. As a result, the conversion of propane to perfluoropropane is complicated because it is difficult to recycle the unconverted propane. Also, it is difficult to obtain a perfluoropropane product that is not contaminated with significant amounts of propane.

It is an object of this invention to provide an improved electrochemical process for the fluorination of propane to octafluoropropane. Anther object is to provide an improved electrochemical process which reduces or eliminates separation of octafluoropropane from mixtures including propane. Another object is to provide a process to regulate or control the fluorination of propane to reduce or eliminate the occurrence of mixtures of propane and octafluoropropane in the product. Another object is to provide a process for the preparation of mixtures of propane and perfluoropropane intermediates that can be conveniently separated. Still another object is to provide a process for the fluorination of perfluoropropane intermediates to provide mixtures of octafluoropropane and perfluoropropane intermediates. Still another object is to provide an improved electrochemical process for the continuous fluorination of propane and the recovery of octafluoropropane which avoids or substantially reduces the separation of octafluoropropane from unconverted propane feedstock. Other objects and advantages of this invention will be apparent to those skilled in the art in view of this disclosure and the appended claims.

According to this invention, there is provided a process for electrochemical fluorination of propane feedstock to octafluoropropane, which process comprises: (a) passing a feedstock comprising propane into a first electrochemical fluorination zone and therein partially fluorinating the propane under conditions sufficient to produce an effluent stream comprising partially fluorinated propane, unconverted propane, and little or no perfluoropropane; (b) passing said effluent into a separation zone to produce a first lower boiling mixture comprising propane and perfluoropropane, and a second higher boiling mixture comprising partially fluorinated propane; (c) returning said first mixture to said electrochemical fluorination zone as a portion of said feedstock; and (d) passing said second mixture to a second electrochemical fluorination zone operating under conditions sufficient to produce an effluent stream comprising a substantially quantity of perfluoropropane.

The advantages realized by operating the first fluorinating zone under conditions to minimize the production of octafluoropropane combined with operation of the second fluorinating zone under conditions to maximize the production of octafluoropropane permits the separation, isolation, and recovery of octafluoropropane conveniently and relatively inexpensively without the necessity for more complex and more costly methods for the separation of mixtures of octafluoropropane and propane. Thus, in the process of the present invention, mixtures of these difficultly separable materials are avoided or minimized.

Any suitable electrochemical fluorination process, which is capable of replacing the hydrogen atoms of propane with fluorine atoms, can be used in the fluorination zones of the present invention. However, the presently preferred electrochemical fluorination process comprises passing the propane or the perfluoropropane intermediates feedstock into the pores of a porous anode at a point near the bottom of the porous anode, e.g., porous carbon, immersed in a current-conducting, essentially anhydrous hydrogen fluoride-containing liquid electrolyte such as $KF \cdot 2HF$. The feedstock contacts the fluorinating species within the pores of the anode and, depending on the conditions, at least some of the hydrogen on the propane or perfluoropropane intermediates are replaced with fluorine. The vaporous fluorinated products leave the pores of the anode at a point above the liquid electrolyte level and exit the cell. Hydrogen is generated at the cathode and, with the aid of a simple cell divider, exits the cell without mingling with the fluorination products. HF is consumed in the process and is continuously or intermittently replaced.

The hydrogen fluoride electrolyte can contain an inorganic additive such as an alkali metal fluoride or ammonium fluoride which desirably reduces the hydrogen fluoride vapor pressure and assists in maintaining adequate conductivity in the electrolyte under the fluorinating conditions employed in this invention. The additives can be employed in any suitable molar ratios of additive to hydrogen fluoride, generally within the range of from 1:4.5 to 1:1.

Generally speaking, the fluorination process can be carried out at temperatures within the range of from −112 to 932° F. in which the vapor pressure of the electrolyte is not excessive, e.g., less than 250 millimeters Hg. It is preferred to operate at temperatures such that the vapor pressure of the electrolyte is less than about 50 millimeters Hg. Preferred operating temperatures are in the range 140 to 250° F.

Pressures substantially above or below atmospheric can be employed; however, the vapor pressure of the electrolyte must be taken into consideration as discussed hereinbefore. Generally speaking, the process of this invention is carried out conveniently at substantially atmospheric pressure.

Current densities within the range of 30 to 1000 or higher, preferably 50 to 500, amperes per square foot of anode geometric surface, are generally used. Voltage employed will vary depending upon the particular cell configuration as well as the current density desired. Under normal operating conditions, however, the cell voltage or potential will be less than that required to evolve or generate free elemental fluorine. Voltages within the range of 4 to 12 volts are typical. Generally speaking, the maximum normal voltage will not exceed 20 volts per electrolytic cell.

Feed rates which can be employed will preferably be within the range of from 0.5 to 10 milliliters per minute per square centimeter of anode geometric surface area. Since the anode can have a wide variety of geometrical shapes, which will affect the geometrical surface area, sometimes a more useful way of expressing the feed rate is in terms of anode cross-sectional area (taken perpendicular to the direction of flow). Thus, the feed rate can be 3–600 ml./min/cm. of porous anode cross-sectional area. Even more preferably, the feed rate will be such that there is established a pressure balance between the feedstock entering pores of the anode from one direction and the electrolyte attempting to enter the pores from another and opposing direction. Essentially all of the feedstock travels within the porous anode via the pores therein until it exits from the anode at a point above the surface of the electrolyte.

Further details of suitable electrochemical processes can be found in Fox et al. 3,511,760, Childs 3,511,762, application Ser. No. 75,292, filed Sept. 24, 1970, and application Ser. No. 226,039, filed Feb. 14, 1972.

The first electrochemical fluorination zone will operate in a manner essentially identical with that of the second electrochemical zone with two important exceptions. The first is that propane is a feed component to the first zone only; a propane-free stream is fed to the second zone. Thus, the feed stream, including recycle materials, to the first electrochemical fluorination zone is essentially propane and will comprise, including recycle materials, perfluoropropane, perfluoropropane intermediates and some hydrogen fluoride. Propane will be absent in the cell and in the recycling and separating stages of the second fluorination zone. There will, of course, be minor amounts of some heavy and some light products which can be removed from the process at any convenient time and location.

The second important condition which is different between the two fluorination zones is the degree of conversion of replaceable hydrogen on the feedstock molecules. In the first electrocehmical fluorination zone the electrical current and organic flow rates are such that only 1–20%, preferably 5–15%, of the replaceable hydrogens are converted. Since two Faradays are required to convert one hydrogen equivalent, this means that only about 2–40 Faradays are passed through the cell with the simultaneous passage of 100 hydrogen equivalents. Such a condition has the effect of maximizing the conversion of propane to intermediates yet minimizes the conversion of propane to perfluoropropane.

In the second electrochemical fluorination zone, the current and flow rate of organic feedstock are proportioned to provide a replaceable hydrogen conversion of 21–90%, preferably 25–50%. Such conditions have the effect of maximizing the efficient conversion of lower fluorinated intermediates to higher fluorinated intermediates and to perfluoropropane, with minimum losses to cracked or heavy products.

Other conditions can also differ between the two fluorination zones but these are less important and not critical in obtaining the advantage of the invention. For example, it can be advantageous to maintain a somewhat lower temperature in the first zone, e.g., 160–220° F., than the temperature of the second zone, e.g., 190–250° F. Similarly, somewhat lower current densities, e.g., 50–200 amp./ft.^{2} can be advantageous in the first fluorination zone as compared with 100–500 amp/ft.^{2} in the second zone. Also, to minimize perfluorination of propane in the first fluorination zone, it can sometimes be advantageous to maintain a relatively high organic flow rate, with respect to the cross-sectional area of the porous anode, to provide, in turn, a relatively high linear velocity through the anode. Thus, elongated anodes with relatively thin sections of porous carbon through which the vaporous feed migrates are sometimes advantageous in the first fluorination zone. This is less important in the second fluorination zone.

Referring now to the drawing, the sole figure is a simplified diagrammatic representation of the apparatus and process of the present invention. In the figure, there are represented, in combination, cell zone **10**, separation zone **20**, cell zone **30**, and separation zone **40**. Cell zone **10** and **30** each represent one or more cells which can be connected in series or parallel and which are suitable for electrochemical fluorination. Each cell in cell zone **10** contains a porous carbon anode **11**, a cathode **12**, a cell divider **13** which separates the vapor space of the cell into a cathode space and anode space, an HF-containing and current-conducting electrolyte **14**, and a hydrogen exit **15**. Similarly, each cell in cell zone **30** contains a porous carbon anode **31**, a cathode **32**, a cell divider **33**, an HF-containing electrolyte **34**, and a hydrogen exit **35**. Separation zones **20** and **40** each comprise one or more suitable fractionation means such as one or more fractionators, including suitable heaters, condensers, packed columns or the like, to effect the desired separations hereinafter described.

In operation, propane feed in line **1** is mixed with recycle materials from line **5** and passed into cell zone **10** through line **2**. The feedstock in line **2** passes into the bottom of each porous carbon anode **11** of cell zone **10** and travels upward through anode **11**, being fluorinated during this passage. The fluorinated products exit anode **11** into the vapor space defined by cell divider **13**, and then exit the cell zone through line **3**. Hydrogen exits the cell zone through line **15**.

The fluorinated mixture in line **3**, comprising perfluoropropane, intermediates, uncoverted propane, and some hydrogen fluoride is conducted to separation zone **20**. Perfluoropropane, unconverted propane, and some hydrogen fluoride are removed from separation zone **20** as a lower boiling overhead stream and are recycled back to cell zone **10** through lines **5** and **2**. Depending on the operation of the separation zone, a small amount of intermediates can also be present in line **5**. A portion, about 1–20 wt. percent, of the flow in line **5** can be removed from the process by line **4**, if desired, to prevent build-up of perfluoropropane.

An essentially propane-free stream comprising intermediates and some hydrogen fluoride is passed from separation zone **20** as a higher boiling bottom stream into cell zone **30** via lines **6** and **7**. Further fluorinated materials are passed from cell zone **30** through line **8** into separation zone **40**. A small amount of light (cracked) materials exit separation zone **40** through line **18** and a small amount of heavy products exit through line **19**. Essentially propane-free perfluoropropane is obtained as the principal product through line **9**. Intermediates leave separation zone **40** and are recycled to cell zone **30** through lines **17** and **7**. Hydrogen fluoride feed is passed, as required, into cell zone **10** and cell zone **30** through line **16**.

If desired, separation zones **20** and **40** can comprise means, such as caustic or bauxite aborbers, to remove hydrogen fluoride from the various streams. However,

except for the stream of the perfluoropropane product, this is not ordinarily considered to be necessary.

ILLUSTRATIVE EXAMPLE

Propane is electrochemically converted to octafluoropropane using the apparatus and the sequence of steps as generally outlined in FIG. 1. Cell zone **10** comprises a battery of cells containing a total of 42.88 ft.^{2} of porous carbon anode surface. The anodes are in the form of cylinders of porous carbon which are vertically immersed, almost completely, in the electrolyte. The cylinders are composed of a porous carbon having a total porosity of 51% and whose average pore size is 55 microns. Each cylinder contains a cavity at its bottom into which the gaseous feed is introduced. The feed diffuses upward through the porous carbon anode and exits the anode at a point above the liquid electrolyte level. An iron screen cathode surrounds each anode and each cell has a domed divider (skirt) which separates the vapor space of each cell into a cathode chamber, from which the cathodically-generated hydrogen gas is removed, and an anode chamber, from which the anodically-generated product vapors are removed. The electrolyte is KF, and HF is continuously added at a rate sufficient to maintain a molten composition similar to KF·2HF. Other operating conditions include a current density of 100 amp/ft.^{2} of anode surface, a current level of 4288 amps, a temperature of 180° F., atmospheric pressure, and a feed rate sufficient to convert 10% of the replaceable hydrogen in the feedstock.

Cell zone **30** is essentially identical to cell zone **10** except that it contains 32.16 ft.^{2} of porous carbon anode surface. It is operated at 200 amp/ft.^{2} of anode surface, at a current level of 6432 amps, at atmospheric pressure, at a temperature of 205° F., with a molten KF·2HF electrolyte, and at a feed rate sufficient to convert 30% of the replaceable hydrogen.

Exemplary simplified flow rates and stream compositions associated with the process are shown in Table I below.

TABLE I

	Lb. moles/hr.									
Stream number	1	2	3	4	5	6	7	8	9	17
Propane	32	100	75	7	68	----	----	----	----	----
Octafluoropropane	----	10	11	1	10	----	----	24	24	----
Fluorinated intermediates	----	----	24	----	----	24	120	96	----	96

NOTE.—(1) Some HF is carried out of cell zone 10 through line 3 and most of this is carried into cell zone 30 through lines 6 and 7. (2) Some HF is similarly carried out of cell zone 30 through line 8 and is returned to cell zone 30 through lines 7 and 17.

This example shows a process which utilizes a combination of two electrochemical fluorination zones to conveniently convert propane to octafluoropropane without the necessity of making the difficult separation of octafluoropropane from propane.

We claim:

1. A process for the preparation of octafluoropropane, which comprises:

passing an electric current through a current-conducting liquid hydrogen fluoride electrolyte contained in a first electrolysis cell provided with a cathode and an anode;

passing a first feedstock comprising propane into said first electrolysis cell and into contact with said anode and fluorinating said feedstock in said first electrolysis cell under first fluorinating conditions which favor the conversion of said feedstock to perfluoropropane intermediates as opposed to the conversion to octafluoropropane;

withdrawing from said first electrolysis cell a first effluent stream comprising unconverted propane, perfluoropropane intermediates, and octafluoropropane;

passing the first effluent stream into a first separation zone;

withdrawing from said first separation zone a first overhead stream comprising all of said unconverted propane and at least a major portion of octafluoropropane, and a first bottoms stream free of propane and comprising at least a major portion of said perfluoropropane intermediates;

passing an electric current through a current-conducting liquid hydrogen fluoride electrolyte contained in a second electrolysis cell provided with a cathode and an anode;

passing a propane-free second feedstock comprising at least a portion of said first bottoms stream from said first separation zone into said second electrolysis cell and into contact with the anode of said second electrolysis cell and fluorinating said second feedstock in said second electrolysis cell under second fluorinating conditions which favor the conversion of said second feedstock to octafluoropropane;

withdrawing from said second electrolysis cell a propane-free second effluent stream comprising perfluoropropane intermediates and octafluoropropane;

passing the second effluent stream to a second separation zone;

withdrawing from said second separation zone a second overhead stream comprising at least a major portion of the octafluoropropane contained in said second effluent stream, and a propane-free second bottoms stream comprising at least a major portion of the perfluoropropane intermediates contained in said second effluent stream;

returning at least a portion of said first overhead stream to said first electrolysis cell to form a portion of said first feedstock; and

returning at least a portion of said second bottoms stream to said second electrolysis cell to form a portion of said second feedstock;

wherein said first fluorinating conditions comprise replacement of from 1 to 20 percent of the replaceable hydrogen of said first feedstock with fluorine, and wherein said second fluorinating conditions comprise replacement of at least greater than 20 percent of the replaceable hydrogen of said second feedstock with fluorine.

2. A process in accord with claim **1** wherein said first fluorinating conditions comprise simultaneously passing proportionately from about 2 to 40 Faradays for each 100 hydrogen equivalents passing through said first electrolysis cell, and wherein said second fluorinating conditions comprise simultaneously passing proportionately at least greater than 40 Faradays for each 100 hydrogen equivalents passing through said second electrolysis cell.

3. A process in accord with claim **2** wherein said first fluorinating conditions comprise a first cell temperature within a range of from about 160° F. to about 220° F., and a first cell current density of from about 50 to about 200 amperes per square foot of anode surface, and wherein said second fluorinating conditions comprise a second cell temperature within a range of from about 190° F. to about 250° F., and a second cell current density of from about 100 to about 500 amperes per square foot of anode surface.

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