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PROCESS FOR THE MANUFACTURE OF PERFLUOROOLEFINS

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This invention relates to the manufacture of perfluoroolefins, and more particularly to a process suitable for the co-synthesis of tetrafluoroethylene and hexafluoropropylene.

The term "pyrolysis" is employed hereinafter to signify the conversion of one chemical species to another by the action of heat, regardless of whether the molecular complexities of the final products are greater or less than that of the starting material.

The expression "useful fluorocarbons" is employed herein to denote hexafluoropropylene, tetrafluoroethylene, and perfluorocyclobutane. Tetrafluoroethylene and hexafluoropropylene may be polymerized or copolymerized with each other and with other vinyl monomers to form an exceedingly valuable series of resinous products. Such products as polytetrafluoroethylene and copolymers of tetrafluoroethylene with hexafluoropropylene are particularly valuable, being inert to almost all known chemicals with the exception of molten alkali metals, having extremely low coefficients of friction and having an extremely wide range of use temperature. Perfluorocyclobutane is valuable as a refrigerant and propellant and may also be converted to tetrafluoroethylene and hexafluoropropylene.

The yields of the various species referred to herein are calculated as the weight percent obtained from chlorodifluoromethane calculated on the basis of carbon and fluorine atoms only.

It has been known heretofore that tetrafluoroethylene may be pyrolysed to give hexafluoropropylene. Under certain critical conditions high yields may be obtained. See, for example, U.S. Patent 2,758,138 issued to D. A. Nelson on August 7, 1954.

It has also been known that chlorodifluoromethane may be pyrolysed to give tetrafluoroethylene, for example, as described by Downing in U.S. Patent 2,551,573 issued May 8, 1951.

It has not been known heretofore, however, that hexafluoropropylene can be prepared directly from chlorodifluoromethane by pyrolysis in high yield.

It has been discovered that when chlorodifluoromethane is pyrolysed at low conversion so that a high yield of tetrafluoroethylene is formed, a small amount of hexafluoropropylene is also formed. The quantity thus formed is too small to be of economic significance. As the percentage conversion is increased by increasing the temperature, or the contact time, or both, the amount of hexafluoropropylene formed also increases. On the other hand, the unwanted side products, hereinafter called "unrecoverables," also increase, and at a rate twice as great as the rate of increase of the hexafluoropropylene. However, in the range between 86% conversion and 94% conversion a highly surprising effect has been found. In that range the concentration of hexafluoropropylene suddenly increases until the proportion of hexafluoropropylene is comparable with and may exceed the concentration of tetrafluoroethylene. Moreover, the increase in yield with conversion is accompanied by an increase of 0.8 part of unrecoverables per part of hexafluoropropylene as compared with over 2.0 parts of unrecoverables per part of hexafluoropropylene at lower conversion. Above about 90% conversion, the yield of unwanted products

itself shows a sharp increase, and beyond about 94% conversion, the yield becomes less favorable economically. Again it has been found that, at conversions above 94%, carbon deposits form and rapidly choke the tubular furnaces which are the preferred form of reactor for the process of this invention.

In addition to tetrafluoroethylene and hexafluoropropylene, perfluorocyclobutane is formed by the pyrolysis of chlorodifluoromethane.

At conversions below about 80%, about two parts of perfluorocyclobutane are formed for each part of hexafluoropropylene. As the conversion is increased to a level within the range from about 86% to 94%, the percentage of perfluorocyclobutane in the useful product decreases rapidly, substantially vanishing at about 94% conversion.

An object of the present invention is to produce tetrafluoroethylene and hexafluoropropylene suitable for the production of fluorocarbon resins. Since tetrafluoroethylene may be readily obtained by modification of the process of the present invention in high yield, it is more especially an object to obtain hexafluoropropylene in economic yield directly from chlorodifluoromethane.

Other objects will be apparent hereinafter.

The above objects are achieved by the pyrolysis of a feed comprising chlorodifluoromethane at a pyrolytic conversion between 86% and 94% based on the chlorodifluoromethane charged. The temperature should be maintained in the range between about 700° C. and 900° C., and the pressure is preferably maintained between 0.5 and 1.2 atmospheres absolute. The pyrolysate is then cooled and tetrafluoroethylene and hexafluoropropylene are separated from the product.

It has also been discovered that greater overall yields can be obtained in the process of this invention by employing a tubular reactor and maintaining an ascending temperature profile along the reaction path. Another modification of this invention comprises separating octofluorocyclobutane and chlorodifluoromethane from the reaction product and recycling these compounds in the feed. In yet another modification, the octofluorocyclobutane product may be pyrolysed separately and the pyrolysis products of the octofluorocyclobutane may be added to the pyrolysis product of of the chlorodifluoromethane. Yet another modification of this invention is to employ a feed consisting of crude chlorodifluoromethane containing hydrofluoric acid.

In the process of this invention it is highly critical to maintain the level of conversion of chlorodifluoromethane between 86% and 94%. Generally speaking, the conversion process may be controlled by controlling the temperature or by controlling the time of the reaction, or in a flow-type system by the rate of flow of the reactants, or all of these variables may be employed to control the conversion. From a practical standpoint it is generally preferable to employ a tubular furnace, control the temperature, and preferably also the temperature profile as explained hereinafter, and then control the degree of conversion by controlling the rate of flow of the reactant stream to the pyrolysis furnace. This controlling operation may be performed by hand, on the basis of periodic analyses of the product. It is preferable, however, to monitor the product stream, measuring the concentration (and hence conversion) of the chlorodifluoromethane by such methods as mass spectrometry, infrared spectrometry, gas chromatography and the like, and hence electrically control a valve regulating the flow of reactant to the furnace in order to maintain the level measured in the product stream at the predetermined value. It will be understood that many other methods which will be obvious to one skilled in the art may be employed to control the level of conversion of chlorodifluormethane.

The lower limit of conversion, 86% appears to be substantially independent of other reaction conditions. The upper limit of about 94% represents a limit determined by economic yield and operability of the process and is somewhat dependent on the exact reaction variables selected. Generally, it is preferable to operate well below this limit of conversion, although operation is feasible up to the limit. The most pronounced effects are produced by pressure. Increasing the pressure reduces the yield of useful fluorocarbons substantially, and consequently lowers the limit of conversion at which the process is usefully operable. On the other hand, at very low pressure, improved overall yields of useful fluorocarbon may be obtained, although the amount of hexafluoropropylene does not increase.

The increased efficiency of the reaction, however, which may amount to as much as 15% greater yield to useful fluorocarbons at 0.1 atmosphere in comparison to results at 1 atmosphere, is counterbalanced to an increasing extent, as partial pressure of the chlorodifluoromethane is lowered by the decrease in convenience associated with operation at the lowered partial pressures.

For the above reason, the process may be operated with advantage at partial pressures 0.1 to 2 atmospheres, but preferably in most instances at 0.5 to 1.2 atmospheres.

For the above reasons the process should be operated at a partial pressure of chlorodifluoromethane between 0.1 atmospheres and 2 atmospheres and preferably between 0.5 and 1.2 atmospheres. The partial pressure may be varied by operating the process under increased or reduced pressure by methods well known to those skilled in the art, or by the dilution of the chlorodifluoromethane with a chemically unreactive gas such as nitrogen, or certain unreactive gases to be described hereinafter.

Generally speaking, the temperature at which pyrolysis takes place is not highly critical but a temperature in the range between about 700° C. and 900° C. should be employed. In this temperature range the contact time required is between about 0.1 second and 10 seconds. It is therefore highly convenient to employ a flow system for the pyrolysis whereby the reactant vapors are passed through a long furnace, and the pyrolytic reaction may be controlled by controlling the rate of flow or the heat input as explained hereinabove.

The process of the present invention is a pyrolytic reaction which depends on the transfer of heat to the reactant gas, and is accomplished by the agency of heat. Any material which will withstand the necessary temperatures, pressures and the chemical action of the reactants, reaction products, or intermediates at the aforesaid temperatures and pressures may be employed for the construction of the furnace. The noble metals are particularly preferred as materials of construction, or as a lining of the surface exposed to the reaction, but it will be realized that other materials may be employed, e.g. silver, carbon or Iconel. In any case the furnace should be constructed to have a high surface to volume ratio and a long length in order to promote effective heat transfer to the gas at short residence time. Preferably the furnace should have a surface/volume ratio of at least 5 inches^{-1}.

The pyrolysis furnace may be heated by any convenient means. Electrical resistance heaters have been employed very successfully but other heating means, such as natural or coal gas, oil and the like, may be used to heat the furnaces.

A study of temperature profiles along the furnace led to the surprising discovery that a furnace temperature between 700° C. and 900° C. which ascended along the length of the furnace in the direction of gas flow gave improved overall yields. Particularly good yields of useful fluorocarbons are obtained when the furnace temperature is maintained at a temperature between 700° C. and 800° C. over a major and initial portion of its length and at a temperature between 800° C. and 900° C. over a minor and final portion of its length.

The chlorodifluoromethane employed in the process of this invention as the starting material is an article of commerce. It may be manufactured at low cost by the catalytic fluorination of chloroform with hydrofluoric acid. The reaction product is distilled, and a crude chlorodifluoromethane is obtained which contains some 2% by weight of hydrofluoric acid which distills with the chlorodifluoromethane as an azeotrope. The hydrofluoric acid may be removed from the crude material by washing with water, and with alkali metal hydroxide solution, or by other suitable procedures. It has been found, however, that crude chlorodifluoromethane containing about 2% of hydrofluoric acid may be employed in the practice of this invention without appreciable loss in the yield of useful fluorocarbons.

The perfluorocyclobutane which is formed by the process of the reaction can be pyrolysed to give tetrafluoroethylene and hexafluoropropylene in good yield. Generally speaking, it has been found that the greatest yields of hexafluoropropylene are obtained when the perfluorocyclobutane is pyrolysed at high conversion, although there appears to be no critical range of conversion, as has been found in the case of chlorodifluoromethane. If it is desired to increase the yield of hexafluoropropylene and tetrafluoroethylene at the expense of perfluorocyclobutane, the perfluorocyclobutane may be separated, pyrolysed at a temperature between about 700° C. and 900° C. and the reaction product added to the effluent from the pyrolysis furnace employed for the pyrolysis of chlorodifluoromethane.

It has also been discovered that the perfluorocyclobutane may be pyrolysed concurrently with the chlorodifluoromethane by adding the perfluorocyclobutane separated from the product stream to the reagent chlorodifluoromethane entering the pyrolysis furnace. Under the conditions required for the pyrolysis of chlorodifluoromethane it has been established that perfluorocyclobutane is pyrolysed at high conversion, and that very little yield loss takes place on account of side reactions. The small yield loss encountered in this modification is offset by the simplicity of the resultant equipment.

The separation of the products of pyrolysis may be attained by distillation in an efficient fractionation column, and by extractive distillation in the presence of hydrocarbons, aromatic hydrocarbons or chlorinated hydrocarbons.

The invention is further illustrated by the following examples, which are given by way of illustration only, and are not intended to define the scope of the invention.

EXAMPLES

In the following examples three furnaces were employed. The first of these furnaces was a small laboratory furnace which consisted of a pure silver tube 30 inches in length and 0.5 inch in diameter, and having a wall thickness of $\frac{3}{32}$ inch. Two electrical resistance furnaces of 750 watt rated capacity were employed to heat this tube (which was maintained in a horizontal position), the heating zone of each was 12 inches. The furnace heaters were controlled with an autotransformer. Furnace temperatures were measured with a Chromel-Alumel thermocouple located in the center of the furnace. The reactant gas was taken from a cylinder, metered and mixed as needed with other gases. The gases that emerged from the furnace were passed through a coil of $\frac{3}{8}$ inch Inconel tubing immersed in a water bath. Samples of the cooled gases were then taken in gas sampling bottle mounted in a by-pass line of the line leading to an aspirator. The samples were analyzed, using gas chromotography. The gas chromotography column was standardized by using pure components. A constant volume syringe was employed to inject a series of standard volumes of air and pure compound. The factors relative to air were computed for the various compounds to be analyzed and hence

the concentration of the components in the mixture were determined, assuming a linear relationship between the concentration of each component and the peak height on the chromatogram. The validity of this analysis was verified by analytical distillation techniques.

The results of these analyses were employed to report the distribution of the various compounds in the product. This product distribution is expressed on a weight percentage basis of the theoretical yield of fluorocarbon (free from HCl).

The second furnace was constructed from a flattened tube made of Inconel lined with nickel and plated with platinum. The surface/volume ratio was 20.25 inches^{-1}. The heated length of the furnace was 14.5 ft. and it was heated by the radiant heat from a 2 inch diameter stainless steel tubular furnace to which were strapped three resistance heaters having a rated capacity of 7.5 kilowatts each. The assembly was contained inside a 5 inch mild steel pipe which was covered with 1½ inches of asbestos insulation.

The third furnace was similar to the second furnace except that the heaters were replaced with six resistance heaters, each having a rated capacity of 4.75 kilowatts, and was then capable of more uniform heating.

The temperature in the second and third furnaces were measured with the aid of thermocouples welded to the walls of the pyrolysis tube.

Examples 1 to 10, which are collected together for comparison in Table I, demonstrate the importance of the level of conversion in the process of this invention. Inspection of this table reveals the surprising increase in the concentration of hexafluoropropylene in the pyrolysis product which takes place at conversion levels above 86%. Again, the sharp decrease in the yield of useful fluorocarbons with increasing conversion and the formation of increasing amounts of unrecoverables is clearly shown in the same table.

EFFECT OF FURNACE TEMPERATURE ON THE PYROLYSIS OF $CHClF_2$

The effect of furnace temperature on the yield of useful fluorocarbon and in the distribution of the useful products is shown in Table III; (Examples 15 and 16). These examples represent two runs made with furnace No. 2, under substantially identical conditions with the exception of the temperature profile. In both cases a contact time in the pyrolysis tube of 2.1 seconds was employed.

TABLE III

	Example 15	Example 16
Temperature, ° C.:		
(i) 2 ft. from inlet end	720	810
(ii) 5 ft. from inlet end	735	815
(iii) 8 ft. from inlet end	750	775
(iv) 11 ft. from inlet end	764	764
(v) 14 ft. from inlet end (2 ft. from exit)	860	758
Product:		
C_2F_4	38.0	12.1
C_3F_6	35.3	15.4
C_4F_8		24.4
Percent $CHClF_2$ Converted	90.0	87.7
Yield to useful fluorocarbons	73.2	52.0

It will be noted that not only is the overall yield to useful fluorocarbons decreased substantially when a descending furnace temperature profile is employed rather than an ascending temperature profile, but that the distribution of products is also unfavorable, a much larger proportion of C_4F_8 being formed at the expense of the tetrafluoroethylene and hexafluoropropylene. C_4F_8 may, of course, be converted to the unsaturated compounds

TABLE I

Example	Furnace	Contact Time, Secs.	Temp.	Percent Conv.	C_2F_4	C_3F_6	C_4F_8	Yield to Useful Fluorocarbons
1	1	1.8	687	38.4	93.1	1.1	3.2	97.4
2	2	~2	797	69.1	78.9	3.7	9.7	92.3
3	2	~2	841	81.9	63.8	7.5	13.8	85.1
4	2	~2	907	89.0	31.2	31.9	6.5	69.6
5	3	~2	806	86.2	49.7	14.6	14.4	78.7
6	3	~2	866	93.6	46.3	17.5	14.3	78.1
7	1	1.8	869	91.9	31.2	36.8	4.8	72.8
8	1	1.8	881	94.9	12.8	49.4	3.1	65.3
9	1	0.19	923	92.0	48.5	29.2	2.7	80.4
10	1	0.19	931	93.0	36 4	36.5	3.2	76.1

The effect of pressure on the products of pyrolysis chlorodifluoromethane are shown in Examples 11 to 14, collected together in Table II.

C_2F_4 and C_3F_6 by subsequent pyrolysis, but this involves further loss of valuable material in the second pyrolytic step, and furthermore decreases the overall throughout

TABLE II

Example	Contact Time, Secs.	Hot Spot Temp.	Total Pressure in Atmospheres	Partial Pressure in Atmospheres of $CHClF_2$	Product Composition			Yield to Useful Fluorocarbons	Percent Conv.
					C_2F_4	C_3F_6	C_4F_8		
11	3.24	778	1	1	28.9	34.7	6.5	70.1	91.0
12	3.24	780	1	0.66	35.8	38.2	1.5	75.5	91.5
13	3.24	778	0.5	0.5	39.5	36.6	2.35	78.5	92.9
14	3.24	780	1	0.5	41.1	33.5	3.3	77.9	91.6

From Table II it can be seen that the partial pressure of the $CHClF_2$ is the major factor, rather than the total pressure, and hence that the effect of reduced pressure may be achieved by dilution of the reactants with an inert gas such as nitrogen or helium or carbon dioxide, thereby obviating the necessity of constructing equipment capable of operating at reduced pressures and high temperatures.

of the pyrolytic synthesis equipment, when the unsaturated fluorocarbon C_2F_4 and C_3F_6 are alone required for the production of the polymer resins.

RECYCLE OF C_4F_8 IN THE PYROLYSIS OF $CHClF_2$

Examples 17 to 22 were collected in Table IV to show the effect of adding perfluorocyclobutane to the feed of chlorodifluoromethane to the pyrolysis furnace.

The following definitions were employed to compute the degree of conversion of chlorodifluoromethane and perfluorocyclobutane.

Percent conversion ($CHClF_2$) =

$$\frac{\text{Wt. percent (CF) of } CHClF_2 \text{ in feed} - \text{Wt. percent (CF) in product}}{\text{Wt. percent (CF) of } CHClF_2 \text{ in feed}} \times 100$$

Percent conversion (C_4F_8) =

$$\frac{\text{Wt. percent } C_4F_8 \text{ in feed} - \text{Wt. percent } C_4F_8 \text{ in product}}{\text{Wt. percent } C_4F_8 \text{ in feed}} \times 100$$

i.e., the conversion of C_4F_8 does not account for the amount formed by the pyrolysis of $CHClF_2$, but only for the percentage by which C_4F_8 is reduced from feed to product.

Example No.	Feed Wt. Percent C_4F_8	Percent $CHClF_2$ converted	Percent C_4F_8 converted	Product, Wt. Percent		
				C_2F_4	C_3F_6	Unrecoverables
17	0	91	----------	30.9	37.2	31.9
18	15	90.9	99.3	29.9	40.4	29.7
19	30	89.3	79.2	35.9	30.3	24.8
20	30	90.4	100	22	47.4	30.6
21	45	88.7	78.6	39	39.1	21.9
22	100	----------	80	51	41	8

EXAMPLE 23.—PYROLYSIS OF CRUDE $CHClF_2$

Crude $CHClF_2$ obtained by distillation of the reaction mixture from the catalytic fluorination of chloroform with hydrofluoric acid, was employed in the synthesis of hexafluoropropylene by the process of this invention. The crude product consisted of an azeotropic mixture containing about 98% by weight of $CHClF_2$ and 2% by weight of hydrofluoric acid. This was pyrolysed at a contact time of 3.2 seconds and a conversion somewhat greater than 90% in the pyrolysis furnace No. 1. A second run under identical conditions was made with pure $CHClF_2$. The resultant products (Table V) were:

PRODUCT DISTRIBUTION OF PYROLYTIC PRODUCT FROM $CHCLF_2$ AT GREATER THAN 90% CONVERSION

Yield (Wt. percent)	(1) Crude $CHClF_2$	(2) Pure $CHClF_2$
C_2F_4	38.8	38.1
C_3F_6	29.6	27.6
C_4F_8	3.0	6.1
Unrecoverables	28.6	28.2

From this table it can be seen that the overall yield of useful fluorocarbon is substantially the same from chlorodifluoromethane containing 2% of HF as from pure chlorodimethane.

The process of this invention is extremely valuable for the production of tetrafluoroethylene and hexafluoropropylene which may be copolymerized with each other or with other vinyl monomers, using free radical catalysts to effect the polymerization. The present process offers great advantages in simplicity of operation and of economy in the necessary plant required to effect the synthesis of hexafluoropropylene.

I claim:

1. A process for the co-synthesis of hexafluoropropylene and tetrafluoroethylene which comprises pyrolysing chlorodifluoromethane at a temperature in the range between 700° C. and 900° C. at a partial pressure between 0.1 and 2.0 atmospheres and at a conversion level between 86% and 94% based on the chlorodifluoromethane charged, cooling the reaction product and thereafter separating tetrafluoroethylene and hexafluoropropylene from the reaction product.

2. A process for the co-synthesis of hexafluoropropylene and tetrafluoroethylene which comprises passing chlorodifluoromethane through a tubular furnace, said furnace being maintained at a temperature between 700° C. and 900° C., said chlorodifluoromethane being maintained at a partial pressure between 0.5 and 1.2 atmospheres; and controlling the temperature of the said furnace and the rate of flow of the said chlorodifluoromethane to maintain a level of conversion within the range between 86% and 94%, cooling the pyrolysis product and separating tetrafluoroethylene and hexafluoropropylene from the said reaction product.

3. The process of claim 2 wherein the temperature of the said furnace ascends along the direction of flow of the said chlorodifluoromethane.

4. The process of claim 2 wherein the temperature of a major and initial portion of the said furnace is maintained at a temperature within the range between 700° C. and 800° C. and the temperature of a minor and final portion is maintained at a temperature within the range between 800° C. and 900° C.

5. The process of claim 2 wherein the chlorodifluoromethane contains about 2% by weight of hydrofluoric acid.

6. A process for the co-synthesis of hexafluoropropylene and tetrafluoroethylene which comprises passing a mixture containing chlorodifluoromethane and perfluorocyclobutane through a tubular furnace, said tubular furnace being maintained at a temperature within the range between 700° C. and 900° C. said chlorodifluoromethane being at a partial pressure within the range between 0.5 atmospheres and 1.2 atmospheres, controlling the rate of flow of the said mixture and the temperature of the said furnace to maintain a level of conversion between 86% and 94% based on the chlorodifluoromethane charged, cooling the reaction product emerging from the said pyrolysis furnace, separating perfluorocyclobutane, hexafluoropropylene and tetrafluoroethylene from the said reaction product, and recycling the perfluorocyclobutane to the mixture passed into the said furnace.

7. A process for the co-synthesis of hexafluoropropylene and tetrafluoroethylene which comprises passing chlorodifluoromethane through a first tubular furnace, said furnace being maintained at a temperature within the range between 700° C. and 900° C., said chlorodifluoromethane being at a partial pressure between 0.5 to 1.2 atmospheres controlling the rate of flow of said chlorodifluoromethane to maintain the level of conversion within the range between 86% and 94% cooling the products

of reaction from the said first furnace and separating therefrom perfluorocyclobutane, hexafluoropropylene and tetrafluoroethylene, pyrolysing the said perfluorocyclobutane in a second furnace at a temperature in the range between 700° C. and 900° C. and adding the reaction product from the second furnace to the reaction product of the first furnace.

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