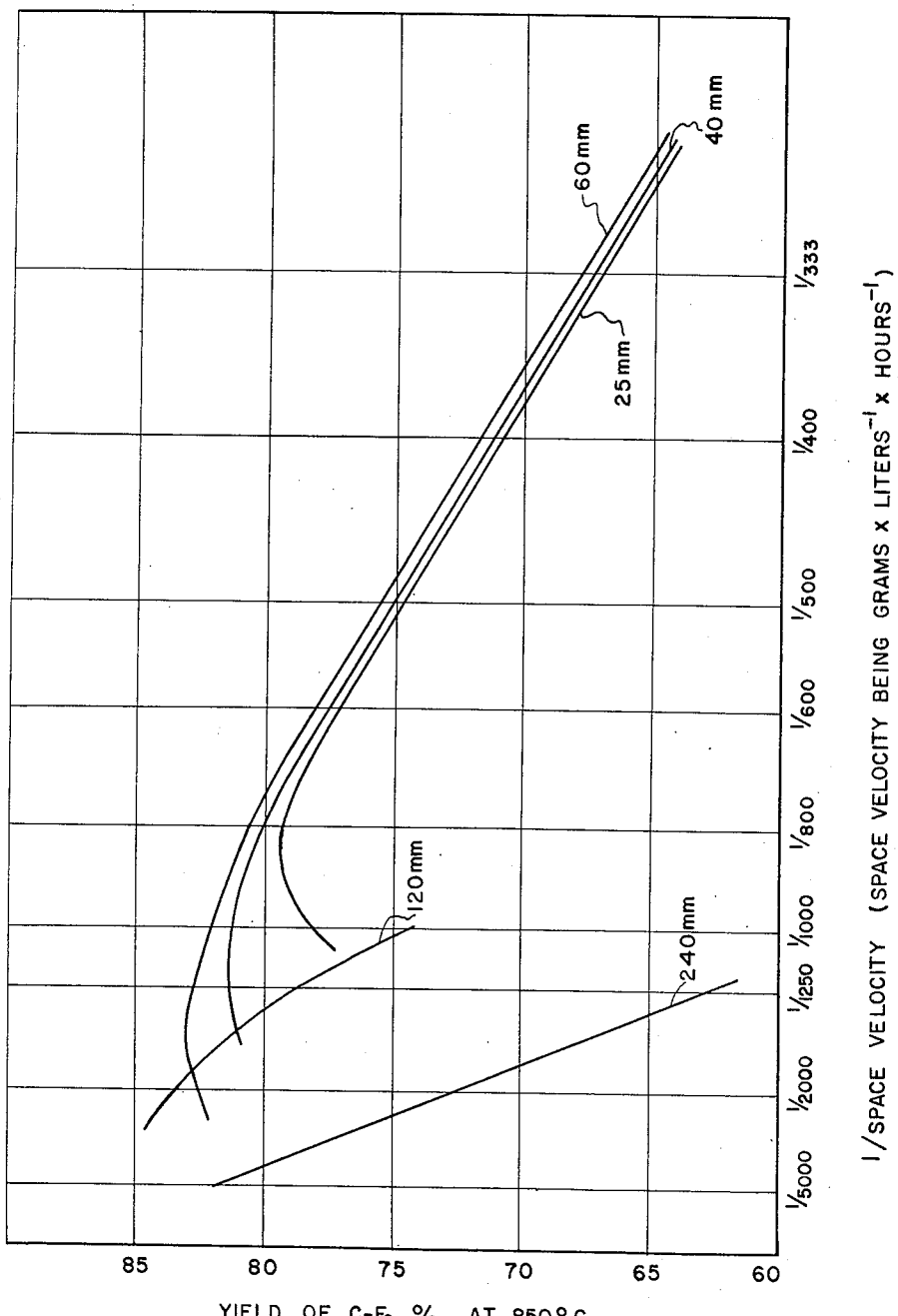
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PYROLYSIS PROCESS FOR MAKING PERFLUOROPROPENE FROM TETRAFLUOROETHYLENE

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PYROLYSIS PROCESS FOR MAKING PERFLUOROPROPENE FROM TETRAFLUOROETHYLENE

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This invention relates to a pyrolysis process and more particularly to a process for the manufacture of hexafluoropropene from tetrafluoroethylene in improved yields.

It has been reported (Slesser and Schram, "Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds," National Nuclear Energy Series VII–I, 1951, page 593) that the pyrolysis of monomeric tetrafluoroethylene at 665°±5° gives a 42% yield of hexafluoropropene at a contact time of 10 to 15 seconds, the yield of hexafluoropropene dropping to 4% when the temperature was raised to 750°±5°. Very recently it has been reported that at 800°, at atmospheric pressure, the yield of hexafluoropropene from tetrafluoroethylene is only 2.1% (J. C. S., 1953, page 2083). Thus, in these previously known procedures, the yields of hexafluoropropene were relatively small. In the pyrolysis of monomeric tetrafluoroethylene the maximum yield heretofore realized was 42%.

Hexafluoropropene has been, however, a highly valuable and useful intermediate in the manufacture of high quality tetrafluoroethylene-hexafluoropropene interpolymers (U. S. 2,598,283) and there has accordingly existed, for several years, a need for efficient methods for manufacturing this material.

An object of this invention is to provide an improved process for obtaining a relatively high yield of hexafluoropropene, especially yields in excess of 75% by weight, by pyrolysis of monomeric tetrafluoroethylene. Another object of this invention is to provide a process for obtaining improved yields of highly useful pyrolysis products, especially hexafluoropropene and mixtures of hexafluoropropene with the tetrafluoroethylene, while producing minimum quantities of less useful fluorinated compounds some of which may boil higher than hexafluoropropene. Other objects will appear in the description in the invention given below.

It has been discovered, according to this invention, that when the reaction temperature is maintained at 750° C. to 900° C., and the feed rate is maintained at 20 to 5000 grams of monomeric tetrafluoroethylene per liter of reaction space per hour, the initial tetrafluoroethylene pressure being from 25 to 200 mm. of mercury, the yield of hexafluoropropene, without recycling, is at a maximum. The pressure can be lower than 25 mm. if desired, although, as explained below, there is no advantage in using pressures below that level. At the optimum pressures, the yield is well above 75%.

The reaction involved can be formulated as follows:

$$C_2F_4 \rightarrow 2{>}CF_2$$

$$C_2F_4 + CF_2 \rightarrow C_3F_6$$

The pyrolysis of tetrafluoroethylene under the aforesaid conditions can be performed in a reaction tube made of or lined with alloy steel, or other material substantially inert to the reaction products and which will withstand the temperatures employed. The reaction tube may be heated by means of electric coils or other conventional heating means. The products of decomposition of the polytetrafluoroethylene can be cooled in a heat exchanger with water as the coolant, although other cooling means may be employed.

At low initial partial pressures of tetrafluoroethylene (below 25 mm.) maximum yields are not realized due to the formation of saturated fluorocarbons. The reaction mechanism for formation of these saturated products at such low pressures is not known. Relatively small amounts of these materials (e. g. C_2F_6, C_3F_8) are formed at pressures of 25 to 200 mm. The C_3 compounds can be removed readily from C_2 compounds by distillation hence give no serious problem so far as purging is concerned. On the other hand C_2F_6 is recovered with the recycled tetrafluoroethylene fraction, and gradually builds up to a rather sizable concentration amounting to 20–25% of the C_2F_6—C_2F_4 mixture. Fortunately when these concentrations of C_2F_6 are reached, the rate of conversion thereof to useful products is enhanced as a result of which the yield is maintained at levels above 75% even when this constant, and rather high, C_2F_6 concentration has been attained by prolonged recycling of the C_2F_6—C_2F_4 fraction.

When the process of this invention is performed in a continuous manner, the temperature inside the reaction tube near the entrance end through which the tetrafluoroethylene is fed continuously is generally lower than that at the center or exit end of the tube, as it takes more or less time for the tetrafluoroethylene to be raised from below its minimum decomposition temperature up to the maximum, or reaction zone, temperature reached within the reaction tube. Moreover, the temperature range in the reaction zone itself may spread over as much as one hundred or more degrees centigrade, without serious consequence. In order to note the temperature of the reaction mixture during a run, it is frequently helpful to place numerous thermocouples on the tube wall (preferably shielded from the heat source), at least one at the entrance end, others in the central portion, and others closer to the exit end of the tube. In general, the maximum temperature within the reaction tube is developed within the last half of the reaction tube, when a tubular continuous unit is used. The time at pyrolysis temperature, or within any particular temperature range, can be determined with sufficient accuracy from the profile of the temperature/distance curve, along the reactor. The reactor temperatures, as measured by means of the aforesaid thermocouples at the tube wall, correspond reasonably well with the actual temperatures in the gas stream flowing through the tube in close proximity to such thermocouples. Inert gases may be present, but are not generally preferred as a means of maintaining a low initial partial pressure of tetrafluoroethylene.

The following examples, in which proportions are given by weight unless otherwise indicated, illustrate specific embodiments of this invention.

Example 1.—A stainless steel reaction tube having an inside diameter of ⅜ inch was heated electrically, and several thermocouples were distributed along the length of the tube, protected from the heat source by glass tape. The reaction tube was evacuated to remove air and any other gases before feeding of the tetrafluoroethylene commenced. The rate of feed was 188 grams per liter of pyrolysis zone (750°–810° C.) per hour. A vacuum pump was connected with the reaction tube and the pressure inside the tube was maintained at 40 mm. of mercury throughout the period of the reaction, the product being caught in a vessel chilled with liquid nitrogen, said vessel being placed between the reaction vessel and the pump. The total conversion of tetrafluoroethylene to pyrolysis products was 72%, the yield of hexafluoro-

propene being 81.5%. The experiment was repeated using a pressure of 10 mm. Not only was conversion lowered to 16.5%, which was due very largely to the lower weight of reactant undergoing reaction per unit time by reason of the pressure being lowered to ¼ of its former value, but also the yield of hexafluoropropene decreased to 77.7%, the yield decrease being accompanied by an increase in the quantity of saturated fluorocarbons produced, relative to the amount of hexafluoropropene produced.

Example 2.—In an apparatus similar to that used in Example 1, the tetrafluorcethylene feed rate was increased to 3670 grams per liter per hour, and the temperature was increased to 760–860° C. The yield of hexafluoropropene was 84.8% and the total conversion of tetrafluoroethylene was 34.2%.

Example 3.—In a semi-works plant, tetrafluoroethylene was conducted through a tubular converter operating at 111 mm. pressure, and heated by means of an electric furnace to a minimum temperature of 850° C. The effluent gases were cooled, then chilled by means of refrigeration and the resulting condensate was distilled to produce tetrafluoroethylene. The tails from the still were conducted to another still for recovery of hexafluoropropene. The equipment was operated continuously for 180 hours, with recycle of the recovered tetrafluoroethylene, and addition of make-up tetrafluoroethylene in quantity sufficient to compensate for that which was consumed. During the last 100 hours of operation the average imput of make-up tetrafluoroethylene was 4.04 lbs. per hour, which was added to 4.21 lbs. per hour of recycle material containing 78.57 mol percent tetrafluoroethylene and 21.3 mol percent hexafluoroethane. The yield of hexafluoropropene was 81.5% and the conversion was 55.8%. Space velocity through the converter was 1470 grams tetrafluorcethylene per liter per hour.

The hexafluoroethane content of the recycled part of the charge is critical and represents the amount of this component which remains constant after prolonged operation when no effort is made to separate it from the recovered tetrafluoroethylene.

The foregoing examples are illustrative of the method of the invention. In order to determine the critical limits of operability, scores of experiments were performed under a wide variety of reaction conditions substantially in the manner described in the foregoing examples. These experiments established the relationships between yield, pressure, and space velocity. Surprisingly, the data obtained showed that there is a region of high yield, the existence of which was not heretofore suspected, corresponding to a combination of reaction conditions close to those employed in the foregoing examples. The data are shown in greater detail in the accompanying drawings which records the combined effect of pressure and residence time on yield. The data show that unless a moderately low pressure is used the residence times required for high yields are so short that they cannot practicably be attained even in small equipment. When the pressure is lowered to about 240 mm. the feed rates required for good yields are in a realizable range. At pressures below 200 mm., and especially at pressures as low as 120 mm., the maximum yield is obtained at a feed

of about 3000 grams per liter per hour, a feed rate which is attained without any difficulty. At a somewhat lower range of pressures, namely, about 40 to 120 mm. a rather wide range of feed rates can be used to achieve yields above 80%, as shown in the drawing, although at still lower pressures, e. g. 25 mm., the yield closely approaches 80% only at a narrower range of feed rates. Yields of 75–80% are attainable, however, over a far wider range of conditions than yields exceeding 80%, as shown in the drawing. The effect of temperature on yield is quite critical, the minimum temperature for yields exceeding 75% being about 750° C. At temperatures above 900° C., a yield loss is suffered with further increase in temperature, the chief product being CF_4 at temperatures of about 1000° C. Generally speaking, the best practical conditions for obtaining yields far above those of the prior art are as hereinabove specified, namely: 750°–900° C.; feed rates of 20 to 5000 grams per liter per hour; and pressures of 25 to 200 mm.

Hexafluoropropene, obtained as above described, may be copolymerized by known techniques with other monomers such as tetrafluoroethylene, ethylene, vinyl fluoride, vinyl chloride, methyl methacrylate, and the like to yield products which are particularly useful for molding and extruding into fibers, films and other shapes, including the manufacture of articles which are of value in the electrical insulation field.

I claim:

1. A process for preparing hexafluoropropene which comprises continuously feeding monomeric tetrafluoroethylene into a reaction zone heated to a pyrolysis temperature within the range of 750° C. to 900° C., at the rate of 20 to 5000 grams per hour per liter of said reaction zone, at an initial tetrafluoroethylene pressure of 25 to 200 mm., cooling the resulting products, and separating hexafluoropropene therefrom, the yield of hexafluoropropene being at least 75% of the tetrafluoroethylene consumed.

2. Process for preparing hexafluoropropene which comprises conducting a mixture consisting essentially of tetrafluoroethylene and hexafluoroethane into a reaction zone heated to a temperature of 750° to 900°, at the rate of 20 to 5000 grams of tetrafluoroethylene per hour per liter of said reaction zone at an initial tetrafluoroethylene pressure of 25 to 200 mm., recovering a mixture consisting essentially of tetrafluoroethylene and hexafluoroethane from the resulting products, continuing the recycling of the said recovered tetrafluoroethylene and hexafluoroethane with make-up tetrafluoroethylene until the ratio of hexafluoroethane:tetrafluoroethylene has risen to a constant level, whereby the tetrafluoroethylene is converted to hexafluoropropene in yields exceeding 75%, and thereafter continuing the operation in the same manner and recovering hexafluoropropene from the resulting reaction products.

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