

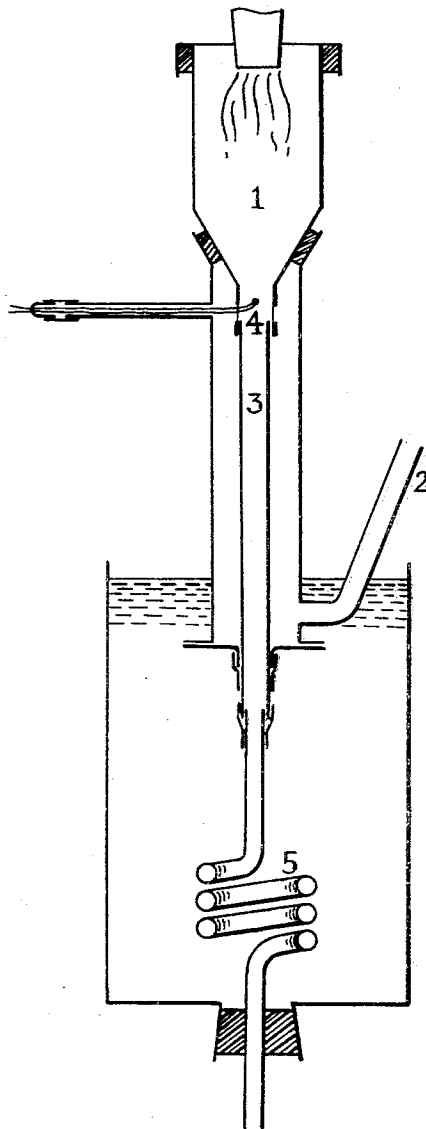
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MANUFACTURE OF TETRAFLUOROETHYLENE

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MANUFACTURE OF TETRAFLUOROETHYLENE
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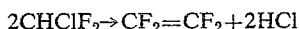
The present invention relates to a process for the manufacture of tetrafluoroethylene. The present application is a continuation-in-part of copending application Serial No. 790,937, filed February 3, 1959.

It is known from the literature that tetrafluoroethylene can be obtained by pyrolyzing monochlorodifluoromethane in a heated reaction tube. The optimum yields of 90–94%, calculated on the reacted monochlorodifluoromethane, are obtained if about 25–30% of the monochlorodifluoromethane undergoes conversion.

If the amount of monochlorodifluoromethane to undergo conversion is increased to about 50% by raising the temperature or permitting the starting material to remain in the reaction tube for a prolonged time, the yield of tetrafluoroethylene is reduced to 65–70% due to the formation of higher-boiling products which are increasingly formed at an increased rate of conversion of monochlorodifluoromethane (J. D. Park et al., Ind. Eng. Chem., 39, 354 (1947)). Experiments have shown that an optimum yield of tetrafluoroethylene is obtained if the monochlorodifluoromethane is treated at a fairly high temperature within a fairly short period of time.

An optimum yield can only be obtained at a given temperature if the time during which the starting material is permitted to remain in the reaction tube does not exceed a certain upper limit; in view of the fact that the conversion of the monochlorodifluoromethane depends on the time of stay in the reaction tube, it is impossible to increase the rate of conversion of monochlorodifluoromethane at will by increasing the time of stay without the yield of tetrafluoroethylene being impaired.

The reaction



takes place with an increase in volume so that according to the principle of least constraint (Braun-Le Chatelier) the formation of tetrafluoroethylene is favored when the reaction is carried out under reduced pressure or in the presence of an inert gas, for example nitrogen or helium. It is known from the literature that by reducing the pressure to 0.5 atmosphere absolute the conversion of monochlorodifluoromethane can be increased to 50% with a yield of tetrafluoroethylene of about 90%.

The present invention is based on the unexpected observation that the monochlorodifluoromethane conversion can be increased to about 65–70% with a 90–94% yield of tetrafluoroethylene, calculated on the reacted monochlorodifluoromethane, by subjecting a mixture prepared from monochlorodifluoromethane and, for example, 25 mol percent water vapor, to pyrolysis.

The addition, for example, of 25 mol percent water vapor, which results in a reduction of the partial pressure of the monochlorodifluoromethane used from 1 atmosphere absolute to 0.75 atmosphere absolute, thus enables the rate of conversion of monochlorodifluoromethane to be increased beyond the extent which would have been expected as a consequence of the reduction of the partial pressure.

The process of this invention offers the advantage that the water vapor on leaving the reactor together with the pyrolyzed gases can be condensed by cooling. All techni-

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cal difficulties pertaining to the apparatus used are thereby eliminated, difficulties which otherwise appear when working under reduced pressure or in the presence of an inert gas, for example nitrogen or helium, especially in condensing and distilling processes, where the removal of inert gas is always associated with a loss of substance.

Contrary to expectation, the monochlorodifluoromethane is not hydrolyzed by the water vapor at the relatively high temperatures employed, although it is known that halohydrocarbons containing fluorine are very sensitive to hydrolysis and that, more especially, monochlorodifluoromethane not only undergoes pyrolysis with strongly diluted alkalis at room temperature, but also with water under conditions such as prevail in refrigerating apparatus (cf. Handbuch der Kältetechnik, volume IV, Die Kältemittel, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1956, page 373, 345/48).

It was therefore surprising to see that in the process of this invention hot water vapor, even at 800° C., does not noticeably hydrolyze the monochlorodifluoromethane or the tetrafluoroethylene obtained.

The proportion of water vapor in the starting mixture cannot, however, be increased at will at a given temperature and time of stay without the yield of tetrafluoroethylene being reduced by splitting off of hydrogen fluoride; in other words the proportion of water vapor is not permitted to exceed a certain upper limit.

If the process of this invention is carried out with the use of a reaction tube and the starting mixture contains water vapor in a proportion of about 15–60 mol percent, preferably about 20–30 mol percent, it is most advantageous to permit the starting mixture to stay in said reaction tube for a period of time of between about 0.05 and 0.8 second, preferably between about 0.1 and 0.4 second at a temperature in the range of about 650° C. to 1,000° C., advantageously about 750° C. to 900° C. Under these conditions about 60–70% of the monochlorodifluoromethane used is converted and tetrafluoroethylene is obtained in a yield of about 90–94%, calculated on the monochlorodifluoromethane which underwent conversion.

The amount of heat necessary to produce the required reaction temperature can be supplied either by heating the mixture to undergo reaction by means of an appropriate heating device, or by heating the water vapor alone before it is mixed with the monochlorodifluoromethane to so high a temperature that, after the water vapor has been mixed with the monochlorodifluoromethane, the mixture obtained has the necessary reaction temperature.

If the whole mixture is heated by means of a heating device, it is advantageous to carry out the pyrolysis in a reaction device provided with an annular slit as described in patent application 790,937 filed February 3, 1959. The device comprises an inlet tube arranged concentrically within an enclosing tube which latter tube is surrounded by a jacket for heating the enclosing tube. The reaction zone proper in this device has a slit-shaped cross-sectional area. One wall of the reaction zone is heated while the opposing wall is cooled by the incoming gaseous starting material which is advantageously conducted in counter-current within and outside the reaction zone by means of a suitable device. In the other case, i.e. where the water vapor alone is heated, it is advantageous to use an oxyhydrogen flame and to mix the hot water vapor with monochlorodifluoromethane. Mixing may be performed, for example, with the use of a hydrogen-oxygen burner arranged in front of the reaction zone in which the monochlorodifluoromethane comes into contact with the hot water vapor.

If the aforesaid reaction device with annular slit is used, the water vapor is advantageously supplied by means of a dosing pump which transports the water to an evap-

orator. It is also advantageous to preheat the gas to a temperature of about 350° C. to 600° C. by means of a preheater connected in series with the reaction device in order favorably to influence uniform temperature distribution in the reaction device. This preheater may also be used to vaporize the water supplied by the dosing pump. The temperature is advantageously measured with a thermo-element.

The reaction device provided with an annular slit may be lined with all the materials listed as being suitable in the aforesaid patent application, for example carbon, copper, copper-nickel alloys, silver, platinum, platinum-iridium, platinum-rhodium or single or mixed sintered metal oxides, such as aluminum oxide, beryllium oxide or magnesium oxide or spinels, platinum being preferred.

The gases leaving the reactor are chilled in a cooler, washed with water, dried, condensed and subjected to fractional distillation.

If an oxyhydrogen flame is used as the source of heat to produce the necessary reaction temperature, the water vapor formed has the double function of a diluent and a heat carrier. An apparatus suitable for use in carrying out the process of the invention with the aid of an oxyhydrogen flame is shown diagrammatically in the accompanying drawing.

Referring to the drawing:

The oxyhydrogen flame burns in the cylindrical combustion chamber 1 which is conically tapered. The monochlorodifluoromethane is supplied through inlet pipe 2, flows around reaction tube 3 which is concentrically surrounded by a jacket steel tube, and is sucked into said reaction tube 3 by the suction effect of the flame gases. The temperature is measured by means of a thermo-element 4 at the inlet opening of the reaction tube, in other words at that place where the monochlorodifluoromethane comes into contact with the superheated water-vapor. The lower end of reaction tube 3 around which water flows has a rubber connection to the steel tube. The reaction products obtained are cooled to room temperature in the subsequent cooler 5. The combustion chamber 1 is made of ceramic material, preferably quartz, and the reaction tube 3 is preferably made of highly sintered aluminum oxide shaped into a tube, or platinum.

If the aforesaid oxyhydrogen burner is used, the most favorable results are obtained using a mixture which contains a proportion of water vapor of between about 20 mol percent and 70 mol percent, preferably about 25 mol percent and 50 mol percent, and permitting said mixture to stay in the reaction tube for a period of time of between about 0.005 and 0.2 second, preferably about 0.01 and 0.1 second, at a temperature within the range of about 700-1400° C., advantageously about 850-1100° C.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto:

Example 1

A mixture prepared from 3,580 grams (41.4 moles) monochlorodifluoromethane and 240 grams (13.3 moles) water vapor was passed within 28 minutes through a reaction device as described in the aforesaid patent application, so that 7,655 grams per hour monochlorodifluoromethane were passed through the reaction device. The inlet tube of the reaction device had a length of about 940 mm. and a diameter of 44 mm., and the jacket tube a diameter of 50 mm., so that the annular slit was 3 mm. wide. The temperature was measured at the outside wall of the tube. The medium time of stay of the gases in the reaction space was 0.2 second. The products leaving the reaction device were chilled to about room temperature in a cooler with condensation and elimination of the water vapor. The hydrogen chloride split off was washed with water and condensed in a cooling trap.

The condensate was distilled and yielded 1292 grams

(12.92 moles) tetrafluoroethylene, 1166 grams (13.5 moles) monochlorodifluoromethane and 121 grams higher boiling ingredients. 989 grams (27.1 moles) hydrogen chloride were determined titrimetrically. 67.4% of the monochlorodifluoromethane was converted and the yield of tetrafluoroethylene was 92.7%, calculated on the reacted monochlorodifluoromethane.

Example 2

In the reaction device shown in the accompanying drawing an oxyhydrogen flame was produced by introducing 230 liters/hour oxygen into 460 liters/hour hydrogen. The water vapor obtained had a temperature of 1400° C. at the inlet opening of the reaction tube. The temperature was measured with the thermo-element 4.

2,152 grams monochlorodifluoromethane were then supplied within 86 minutes and the temperature dropped to 800° C. When the hydrogen chloride split off had been washed, the reaction products leaving the cooler were dried and condensed in a cooling trap. 60-65% of the monochlorodifluoromethane underwent reaction; tetrafluoroethylene was obtained in a yield of 90-93%, calculated on the monochlorodifluoromethane which underwent reaction.

We claim:

1. In the process for the manufacture of tetrafluoroethylene by pyrolysis of difluoromonochloromethane, the improvement which comprises pyrolyzing a gaseous mixture comprising difluoromonochloromethane and water vapor, the water vapor being present as about 15 to about 70 mole percent of the gaseous starting mixture.

2. In the process for the manufacture of tetrafluoroethylene by pyrolysis of difluoromonochloromethane, the improvement which comprises pyrolyzing a gaseous mixture comprising difluoromonochloromethane and water vapor in a reaction zone having a cross-sectional area shaped as a slit, one side of said reaction zone being heated and its opposite side being cooled by the starting material which streams outside the reaction zone but along this opposite side, said water vapor being present in the gaseous starting mixture in an amount of about 15 to about 70 mole percent calculated upon the gaseous starting mixture.

3. A process as claimed in claim 2, wherein the reaction zone has a cross sectional area shaped as an end-less slit.

4. A process as claimed in claim 2, wherein the gaseous starting material is conducted in counter-current within and outside the reaction zone.

5. A process for the manufacture of tetrafluoroethylene, which comprises pyrolyzing a gaseous mixture consisting essentially of difluoromonochloromethane and water vapor in which the water vapor is contained in a proportion of between about 15 and about 70 mol percent calculated upon the gaseous mixture, at a temperature in the range of from about 650° C. to about 1400° C. within a period of about 0.005 to about 0.8 second.

6. A process for the manufacture of tetrafluoroethylene, which comprises pyrolyzing a gaseous mixture consisting essentially of difluoromonochloromethane and water vapor in which the water vapor is contained in a proportion of between about 20 and about 40 mol percent calculated upon the gaseous mixture, at a temperature in the range from about 750° C. to about 1000° C. within a period of about 0.02 to about 0.4 second.

7. In a process for the manufacture of tetrafluoroethylene by pyrolysis of difluoromonochloromethane, the improvement which comprises producing hot water vapor by burning hydrogen with oxygen, mixing said hot water vapor with difluoromonochloromethane so that the water vapor is present in an amount of about 15 to about 70 mole percent of the mixture, and then pyrolyzing difluoromonochloromethane contained in said mixture.

8. In a process for the manufacture of tetrafluoroethylene by pyrolysis of difluoromonochloromethane, the improvement which comprises pyrolyzing a mixture of difluoromonochloromethane and water vapor in a reaction zone with the use of an oxyhydrogen flame, and producing the temperature necessary to pyrolyze the mixture of difluoromonochloromethane and water vapor

by introducing superheated water vapor into the reaction zone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,551,573 Downing et al. ----- May 8, 1951