PROCESS FOR REDUCING THE FORMATION OF POLYMER ATTENDANT THE PYROLYSIS OF TETRAFLUOROETHYLENE


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6 Claims

ABSTRACT OF THE DISCLOSURE

The pyrolysis of tetrafluoroethylene to higher molecular weight perfluorocarbon compounds, e.g., hexafluoro- propylene, is accompanied by polymer formation which, according to the present invention, is suppressed by intimately contacting the pyrolyzate before it cools sufficiently for polymerization to occur with such compounds as HCl, HF, KF or NaF.

This invention relates to the pyrolysis of tetrafluoroethylene and more particularly, to a process for suppressing the formation of polymer attending this pyrolysis.

The pyrolysis of tetrafluoroethylene to useful higher molecular weight fluorocarbon compounds, such as hexafluoropropylene and octafluorocyclobutane, is disclosed in U.S. Pat. No. 2,404,374 (Reissue 23,425) to Harmon and U.S. Pat. No. 2,436,142 to Harmon. An improved method for pyrolyzing tetrafluoroethylene to hexafluoropropylene is disclosed in U.S. Pat. No. 2,758,138 to Nelson, in which the pyrolysis is conducted at 750 to 900° C., 20 to 5,000 grams per liter, and 25 to 200 mm. Hg. A process which is conducted at higher pressures namely, 0.2 to 65 p.s.i., is disclosed in U.S. Pat. No. 2,970,176 to Ten Eyck et al., wherein the tetrafluoroethylene starting material contains at least 5 weight percent of dimer and other high boilers.

Still another method for obtaining hexafluoropropylene by pyrolysis is disclosed in U.S. Pat. No. 3,306,940 to Halliwell, wherein instead of tetrafluoroethylene being the starting material, the starting material is chlorodifluoromethane, and the pyrolysis is conducted to a conversion of from 80 to 94 percent of the chlorodifluoromethane to produce a pyrolyzate containing both tetrafluoroethylene and hexafluoropropylene. While this copolymer synthesis process has the advantage of producing a high yield of useful products relative to the amount of waste products formed, it also has the disadvantage of low productivity of hexafluoropropylene relative to the capacity of the equipment being used. In other words, if hexafluoropropylene is the desired product, then higher productivity of this product is obtained from a given furnace when the starting material is tetrafluoroethylene rather than chlorodifluoromethane.

Unfortunately, however, when tetrafluoroethylene has been used as the starting material, such as in the above described patent disclosed processes, the formation of the desired higher molecular weight perfluorocarbon compounds, e.g., hexafluoropropylene and/or octafluorocyclobutane, has been accompanied by the formation of solid polymer which builds up in the recovery system following the pyrolysis to eventually cause plugging.

It has now been discovered that the formation of polymer accompanying the pyrolysis of tetrafluoroethylene to higher molecular weight perfluorocarbon compounds can be suppressed by intimately contacting the pyrolyzate with an effective polymer suppressing amount of gaseous HCl or HF, or a solution of fluoride ion or HCl, before the pyrolyzate cools to a temperature at which polymerization occurs, which is believed to be at about 500° C.

In one embodiment, the gaseous HCl or HF is injected into the gases exiting the pyrolysis furnace (the pyrolyzate) to obtain intimate contact therewith. The amount of HCl or HF so injected will generally be in amounts from 3 to 10 percent of the weight of the tetrafluoroethylene feed to the pyrolysis furnace.

In another embodiment, the gaseous HCl or HF is supplied by copolymerization of compounds which convert thereto, with the tetrafluoroethylene feed to the pyrolysis furnace. Exemplary of compounds which convert to HCl and HF under tetrafluoroethylene pyrolysis conditions are chlorodifluoromethane and fluorofom, respectively. This endogenous formation of HCl or HF is preferably that amount under the pyrolysis conditions employed to supply the 3 to 10 percent range of HCl or HF contents previously described herein.

This copolymerization can be conducted by several methods. In one method, the compound convertible to either HCl or HF is fed to the pyrolysis furnace with the tetrafluoroethylene feed. Generally, no greater than 35 percent by weight of the convertible compound, particularly in the case of chlorodifluoromethane, based on the total weight of the feed to the furnace is used under this method, because at higher amounts the overall yield of useful products decreases significantly. Usually, at least 10 percent by weight of the convertible compound, based on the total weight of the feed, is required to get noticeable improvement in polymer suppression.

In another copolymerization method, the compound convertible to HCl or HF is injected into the pyrolysis furnace, slightly upstream of the end of the pyrolysis zone therein, so that some pyrolysis to HCl or HF occurs before leaving the furnace. Equipment suitable for making such injection is shown, e.g., in FIG. 1 of U.S. Pat. No. 2,979,539 to Errede et al. In this copolymerization method, less of the injected compound will be converted to the desired HCl or HF than in the previous method because of the shorter exposure to pyrolysis conditions. Consequently, the use of greater proportions of the convertible compound will be necessary. The lower conversion generally accompanying this method, however, has the advantage of producing lesser amounts of undesirable by-products.

These copolymerization methods can be used in combination with one another, or the copolymerization method of feeding the convertible compound with the tetrafluoroethylene feed into the furnace can be used in combination with intimate contacting by HCl or HF added to the pyrolyzate. In these combinations of embodiments, the feed of convertible compound or injection thereof or addition of HCl or HF to the pyrolyzate are proportioned to give the 3 to 10 percent range of HCl or HF in the pyrolyzate prior to its cooling to temperatures where polymerization occurs. Generally, at least 20 percent by weight of the total HCl or HF present in the pyrolyzate will be derived from each source thereof when these combinations of embodiments are employed.

In another embodiment of the present invention, the pyrolyzate from the pyrolysis of tetrafluoroethylene is bubbled through or otherwise scrubbed with an aqueous solution of HCl or fluoride ion supplied by such compounds as HF and the alkali metal salts, e.g., KF and NaF. The pyrolyzate is above temperatures at which the polymerization occurs when brought into contact with the aqueous solution which quenches the pyrolyzate. The concentration of the solution and its contact time with
the pyrolyzate can be widely varied to suppress the formation of polymer.

The improvement obtained by the present invention is generally applicable to the pyrolysis of tetrafluoroethylene to useful higher molecular weight perfluorocarbon compounds, which are mainly hexafluoropropylene and octafluorocyclobutane. Thus, the pyrolysis can be conducted at both sub-atmospheric and at super-atmospheric pressures, such as from 25 mm. Hg to 65 ps.i. Temperatures of from 600 to 1000° C. can be used. The feed rate of the tetrafluoroethylene through the pyrolysis furnace is adjusted to give the exposure time required at the particular furnace operating conditions employed to give the conversion desired, which will generally be between 30 and 90 percent. The separation of unreacted constituents from the pyrolyzate and purification of the reaction products therein are done by conventional procedures, such as disclosed in U.S. Pat. No. 2,406,794 to Benning et al.; U.S. Pat. No. 3,009,966 to Hauptscchein et al.; and U.S. Pat. No. 3,101,934 to Wist.

Examples of the present invention are as follows: parts and percents are by weight unless otherwise indicated.

EXAMPLE 1
Tetrafluoroethylene (TFE) was fed at one atmosphere pressure and 5 ml./sec. STP to a 0.7 cm. diameter, 28 cm. long Inconel pyrolysis tube heated by an electric furnace to 790° C. The exit gases were cooled to room temperature and analyzed by gas chromatography. Polymer was collected in the cold lines at the exit of the reaction tube. The results were as follows: TFE conversion = 75.59 percent; yield to hexafluoropropylene (HFP) and octafluorocyclobutane (dimer) = 88.3 percent; amount of polymer collected in three hours = 0.454 g.; total amount TFE fed = 241 g.; amount of TFE polymerized = 0.188 weight percent.

This experiment was repeated, except that the feed to the tube consisted of 4 ml./sec., the pyrolysis temperature was 780° C. and chlorodifluoromethane was at 25° C. injected at 1 ml./sec., into the exit gases at the exit end of the pyrolysis tube, with the following results: TFE conversion = 75.7 percent; chlorodifluoromethane conversion = 13.4 percent; yield to HFP and dimer = 92.2 percent. Total amount of TFE fed in 3 hours and 25 minutes = 219 g. No polymer collected in exit lines.

EXAMPLE 2
7.9 ml./sec. TFE and 2.25 ml./sec. chlorodifluoromethane were premixed at room temperatures and fed to the pyrolysis tube described in Example 1, at a temperature of 692° C. and at one atmosphere pressure, with the following results: TFE conversion = 35.8 percent; chlorodifluoromethane conversion = 61.8 percent; yield to HFP and dimer = 93.8 percent (3 percent HFP); polymer collected in the exit lines = 0.235 g. The total amount of TFE fed over one hour and 45 minutes = 272.2 g.; TFE polymerized = 0.086 weight percent.

EXAMPLE 3
6 ml./sec. TFE plus 2.35 ml./sec. chlorodifluoromethane were premixed and fed to the pyrolysis tube described in Example 1, at a temperature of 795° C. and a pressure of one atmosphere, with the following results: TFE conversion = 73.3 percent; chlorodifluoromethane conversion = 94.0 percent; yield to HFP and dimer = 66 percent. The total amount of TFE fed over 2 hours and 30 minutes = 241 g.

Less than one milligram polymer was detected in the exit lines, which corresponds to 0.004 percent of the TFE fed being polymerized.

EXAMPLE 4
3.8 ml./sec. TFE plus 1.7 ml./sec. chlorodifluoromethane were premixed and pyrolyzed at 763° C. in the pyrolysis tube described in Example 1, at one atmosphere pressure. 0.9 ml./sec. chlorodifluoromethane at 25° C. were injected at the exit. The injection tube extended 5 cm. into the 28 cm. long pyrolysis tube. The following results are obtained: TFE conversion = 70.7 percent; chlorodifluoromethane conversion = 61.8 percent; yield to HFP + dimer = 61.8 percent. The total amount of TFE fed over three hours = 183.2 g. No polymer was detected in exit lines.

EXAMPLE 5
1.7 ml./sec. chlorodifluoromethane and 8 ml./sec. TFE were premixed at room temperature and fed to the pyrolysis tube described in Example 1. The tube was heated to 690° C. 3.3 ml./sec. chlorodifluoromethane of room temperature were injected at the tube exit. The following results were obtained: TFE conversion = 39.8 percent; chlorodifluoromethane conversion = 29.6 percent; yield to HFP and dimer = 94.3 percent. Total amount of TFE fed in 2 hours and 35 minutes = 332 g.; polymer formed = 0.0426 gram; TFE polymerized = 0.0128 weight percent.

EXAMPLE 6
2.2 ml./sec. of TFE were fed to the pyrolysis tube described in Example 1. The tube was heated to 658° C. and was at one atmosphere pressure. The exit gases were immediately scrubbed by bubbling through a 0.05 percent solution of sodium fluoride in water at room temperature. The following results were obtained: TFE conversion = 85.1 percent; yield to HFP and dimer = 95.4 percent; total amount of TFE fed = 94.4 g. No polymer in lines downstream of scrubber. Similar results were obtained when HCl, HF and KF were individually substituted for NaF.

EXAMPLE 7
5 ml./sec. TFE plus 1.8 ml./sec. chlorodifluoromethane were mixed and fed to the pyrolysis tube described in Example 1. The pressure was reduced to 0.35 atmosphere and the tube heated to 863° C., with the following results being obtained: TFE conversion = 52.7 percent; chlorodifluoromethane = 91.8 percent; yield to HFP and dimer = 81.2 percent.

395 g. TFE were fed over 4 hours and 55 minutes. Less than 10 milligrams polymer deposited on walls in the exit lines. This is 0.0025 weight percent of total TFE fed.

The conversions and yields in the foregoing examples were calculated using the following equations wherein only the carbon and fluorine content of each component in the feed and pyrolyzate is calculated, to the exclusion of hydrogen and chlorine:

\[ \text{Percent chlorodifluoromethane converted} = \frac{\text{CF wt. percent (chlorodifluoromethane in feed) - chlorodifluoromethane in pyrolyzate)}}{\text{CF wt. percent chlorodifluoromethane in feed}} \times 100 \]

\[ \text{Percent TFE converted} = \frac{\text{CF wt. percent (TFE in feed)}}{\text{TFE in pyrolyzate}} \times 100 \]

\[ \text{Percent yield to HFP + dimer} = \frac{\text{CF wt. percent (HFP in pyrolyzate + dimer in pyrolyzate)}}{\text{TFE converted}} \times 100 \]

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof as described in the appended claims.

What is claimed is:

1. A process for pyrolyzing tetrafluoroethylene to higher molecular weight perfluorocarbon compounds which comprises feeding tetrafluoroethylene into the feed end of a pyrolyzing furnace and withdrawing pyrolyzate...
from the exit end of said furnace, and intimately contacting the pyrolyzate at a temperature above about 500°F. With between about 3% and about 10% by weight, based upon the weight of tetrafluoroethylene fed into said furnace, of gaseous HCl or HF or bubbling through or otherwise scrubbing said pyrolyzate with an aqueous solution of HCl, HF or alkali metal fluoride salts.

2. The process of claim 1 wherein said HCl is formed by copolymerizing chlorodifluoromethane with said tetrafluoroethylene.

3. The process of claim 2 wherein said chlorodifluoromethane is supplied with the tetrafluoroethylene feed to said furnace.

4. The process of claim 2 wherein said chlorodifluoromethane is injected into the exit end of the pyrolysis zone of said furnace.

5. The process of claim 2 wherein a portion of said chlorodifluoromethane is supplied with the tetrafluoroethylene feed to said furnace and the remainder thereof is supplied by injection into the exit end of the pyrolysis zone of said furnace.

6. The process of claim 1 wherein the compound used for polymer suppression is HCl in gaseous form and a portion thereof is supplied by copolymerization of chlorodifluoromethane supplied with the tetrafluoroethylene feed to said furnace.

References Cited

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