

Depolymerization of Clean Unfilled PTFE Waste in a Continuous Process

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ABSTRACT: A continuous process is described whereby waste PTFE was converted into tetrafluoroethylene (C₂F₄, TFE), hexafluoroethane (C₂F₆, HFE), hexafluoropropylene (C₃F₆, HFP), and octafluorocyclobutane (c-C₄F₈, OFCB). The waste PTFE was depolymerized inside a reactor that was heated by a radiofrequency induction generator. The reactor was capable of operating at various temperatures (600–900°C) as well as various reduced pressures (5–80 kPa). The depolymerization reaction conditions could be changed while the reactor was in operation in order to manipulate the reaction product composition. Under certain conditions, high yields of TFE

(> 94%) and low concentrations of by-products were formed. The PTFE was fed vertically downward from the hopper, with the screw feeder, into the reactor where the depolymerization process took place. The hot intermediate products were continuously evacuated through a self-cleaning quench probe, where it was quenched to form the final products. The depolymerized products were analyzed with a gas chromatograph. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2752–2759, 2006

Key words: continuous depolymerization; PTFE; PTFE waste conversion; fluoropolymer waste conversion

INTRODUCTION

Polytetrafluoroethylene (PTFE) has a high melting point, high chemical resistance, and high surface tension; is not biodegradable; and is very stable. Therefore, special uses for the polymer are possible, such as chemical- and thermal-resistant PTFE coatings on cookware, high-resistance chemical containers, gaskets, and thermally stable parts with excellent working properties in industrial machinery, and numerous other uses.

The inert properties of PTFE can, however, also be a disadvantage when looking at the waste generated during manufacturing and processing. Waste can be in the form of shavings, off-cuts, chunks, etc., and can amount to approximately 50% of the originally manufactured PTFE. It is not possible to reuse PTFE waste by melt processing, as is the case with other polymers, such as polyethylene. Some of the clean (clean PTFE is PTFE free of all contamination, e.g., cutting oils, dirt) unfilled PTFE is ground into a fine powder form and used as a filler material in paint and cement. PTFE processors are therefore forced to dispose of PTFE waste in landfills. This is an expensive option, due to the cost of landfilling as well as the loss of the highly valuable fluorine contained in the waste.

It is further expected that future environmental legislation will force manufacturers and processors of PTFE to be responsible for the waste they generate. This will cause companies to look for other suitable techniques to treat PTFE as an alternative to disposing of the waste in landfills.

The process of treating PTFE via pyrolysis vacuum depolymerization is described extensively in the literature.^{1–4} Various methods of heating are used, including resistance heating, in which the depolymerization reactor is heated by means of an electrical heater; steam heating, in which the depolymerization reactor is heated by means of the addition of steam into a reactor to reduce the partial pressure of the product with a resulting increase in the TFE yield, at ambient pressure;⁵ and superheated gas heating, in which earth gas or oil burners are used to heat the depolymerization reactor.

Steam heating has the advantage that the system operates at atmospheric pressure with a smaller chance of air leaking inward, causing a possible explosion. One of the disadvantages is the large amount of waste produced by condensation of the steam (10–20 parts steam for 1 part TFE). The steam is contaminated with a low percentage of hydrofluoric acid (HF) and must be treated accordingly. When vacuum depolymerization is used, instead of reducing the partial pressure of the product with steam, the amount of waste decreased to an almost negligible amount. It also decreased the capital cost of the reactor system,

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because normal stainless steel could be used instead of exotic materials that are HF resistant (e.g., Inconel).

Literature studies revealed that most of these depolymerization experiments were performed in a laboratory for research purposes only and were not scaled up for production purposes. These laboratory scale experiments were performed successfully for many years, but not yet continuously on bench, pilot, or commercial scale by means of a complete, comprehensive vacuum fluoropolymer waste conversion system.⁶⁻⁹

Another depolymerization method is cracking of the PTFE chain by means of radiolysis. This method was investigated to try to solve the problem of dealing with PTFE waste. This work was however stopped during the 1990s because of the stigma surrounding large-scale radiolysis work.¹⁰

Recently research was done on the optimization of TFE, HFP, and C_4F_8 isomers.¹¹ This research was done on a batch type reactor with a flow rate of 250–1000 g h⁻¹ PTFE and nitrogen as a carrier gas or as a partial pressure reducer. The product was frozen in sample holders and analyzed by means of a gas chromatograph.

In 2001, Van der Walt described¹² a process that was able to convert clean unfilled PTFE into high-purity TFE in a continuous and cost-effective process.

BASIC PROCESS DESCRIPTION

A schematic diagram of the basic process is presented in Figure 1. This system could be operated at temperatures of 600–950°C and under reduced pressures. No carrier gas was added.

A radiofrequency (RF) induction generator was used as a heating source. Induction heating can be up to 95% effective. The generator was operated at a frequency of 800 kHz and a maximum power of 10 kW could be applied. The main reason for using RF induction as a heating source was the quick startup and

shutdown times, and the quick response time for in situ temperature changes to take effect.

The depolymerization reactor consisted of a graphite crucible situated inside a quartz tube. This reactor was positioned inside the working coil of the RF induction heating system. The RF induction generator heated the reactor evenly in a relatively short period of time (5–10 min) to the desired working temperature.

The PTFE granules were fed from the hopper, downward into the reactor, where it was depolymerized, via a screw feeder. The product gas was continuously, countercurrently evacuated through an automated self-cleaning quench probe, situated next to the feeder inlet at the top of the reactor. A suitable filter was used to remove any fine particulates that might still be present in the product gas stream after quenching. The product gasses were analyzed online with a gas chromatograph (GC).

OPTIMIZATION OF THE CONTINUOUS DEPOLYMERIZATION PROCESS OF PTFE

Batch PTFE depolymerization was performed in the laboratory in a tubular reactor that was heated by resistance heaters. To convert the PTFE into > 90% TFE, the system was operated under reduced pressure and the product was quenched. To convert the batch process into a continuously depolymerizing process changes necessitated changes in the following equipment: the feeding system, the depolymerization reactor, and the quench probe. Similar vacuum and analytical systems could be used.

Feeding system

Constant transport of the PTFE into the reactor is an important operating criterion. The feed rate of the PTFE must be carefully controlled to correlate with the capacity of the system and the amount of energy being supplied by the RF generator. A feed rate that is too high can block the reactor.

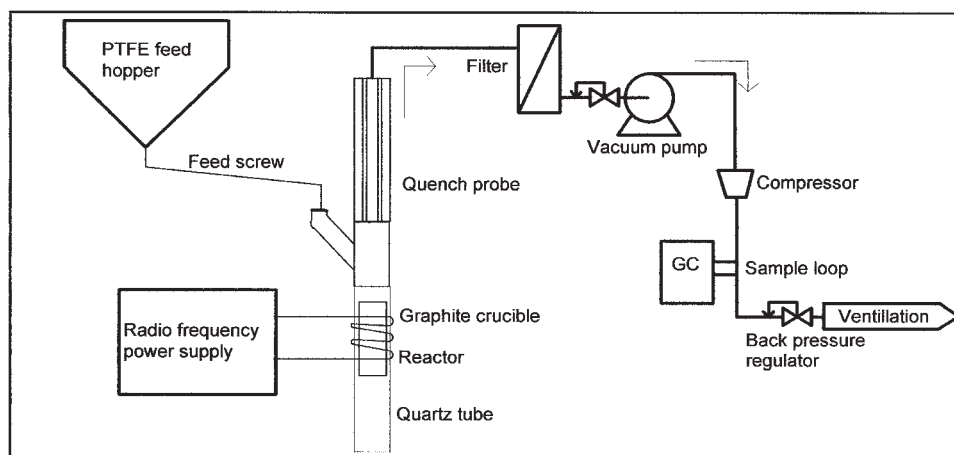


Figure 1 Schematic presentation of the continuous PTFE depolymerization system.



Figure 2 Granulated PTFE particles (in cm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PTFE waste (e.g., shavings, off-cuts, used parts) comes in a wide variety of different shapes and sizes. These physical differences make it difficult to feed PTFE waste at a constant continuous rate by means of a screw feeder. This problem was overcome by compressing the scrap PTFE at an elevated temperature into billets and then granulating it into roughly equal-sized particles of 1–2 mm in size (Fig. 2). These granulated particles are free flowing and could easily be fed by the screw feeder, without any blockages.

In this system, PTFE is supplied continuously to the screw feeder from a hopper that is connected to

the top of the screw feeder body with a vacuum seal. This is schematically presented in Figure 3.

A variable speed motor was used to regulate the rotating speed of the feeding screw. The interface between the feeder and the reactor was called the feeder interface. The reactor was situated at the bottom and the quench probe at the top, while the feeder inlet protruded from the side. This reactor was able to depolymerize 2 kg h^{-1} PTFE on a continuous basis.

Depolymerization reactor

The depolymerization reactor consisted of a cylindrical graphite crucible (200-mm length, 63-mm outer diameter, and with a 5-mm wall thickness), situated inside a quartz tube (300-mm length and 70-mm outer diameter). This reactor was situated inside the working coil of the RF generator. The quartz tube enabled observation of the depolymerization process inside the reactor, as well as temperature measurements. The temperature of the reactor was measured by means of a Minolta Land Cyclops infrared (IR) optical pyrometer, suitable to measure temperatures of 600–3000°C. The pyrometer was situated at right angles to the reactor for temperature measurement at the centre of the heated zone.

Quench probe

Quenching is a very important step to ensure high yield (> 93%) of TFE. This was achieved by means of a water-cooled, double-tube, annular, self-cleaning quench probe (Fig. 4). The quench probe consists of an inner and outer annulus with scrapers. During operation, the inner annulus was continuously rotated tangentially backward and forward with respect to the outer annulus. Any solid particles that deposited or repolymerized on the walls of the quench probe were scraped off and fell back into the

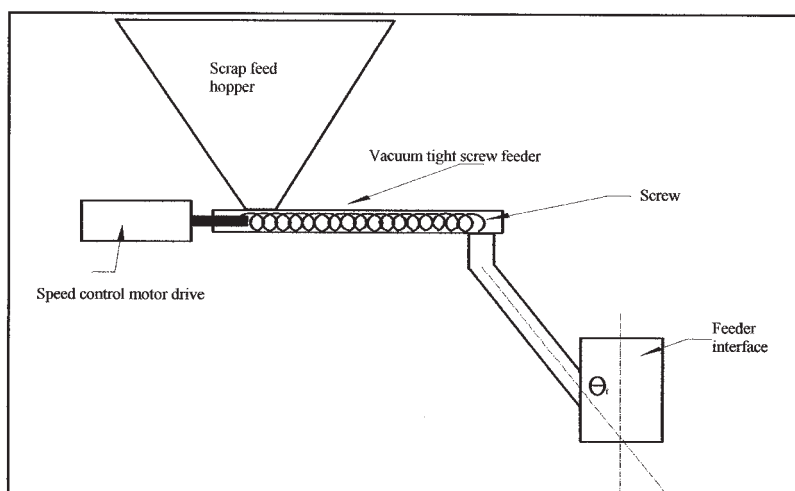


Figure 3 Schematic presentation of the PTFE feed system.

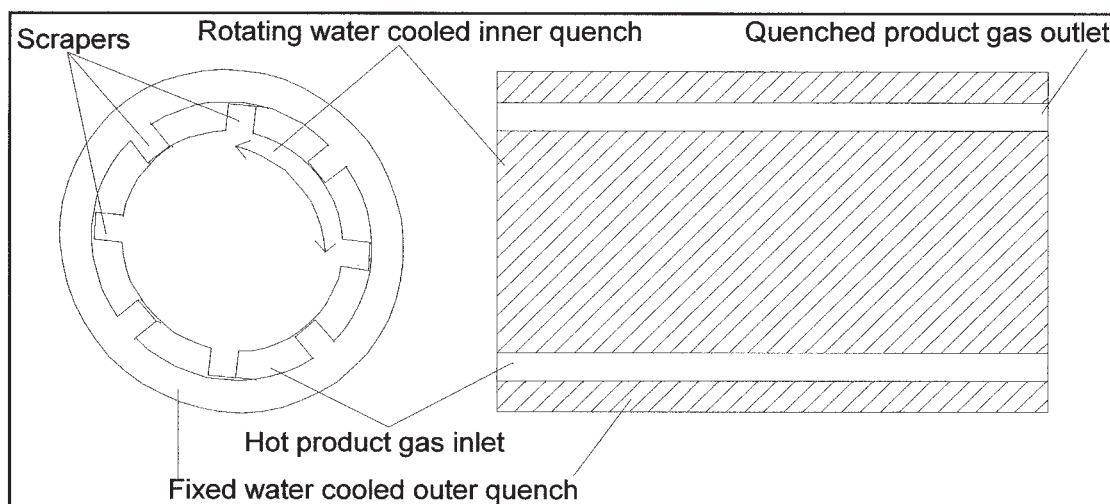


Figure 4 Schematic diagram of the quench probe.

reactor, or were removed from the gas stream by the filter. The vacuum system ensured transfer of the product gas through the annulus of the probe.

Vacuum system

A Varian Star, 25-m³/h, dry vacuum pump was used to achieve the reduced pressures inside the reactor as indicated in Figure 1. A dry pump was used to prevent the product from being contaminated with vacuum oil.

Analytical system

A Varian Star 3600 GC was used for online analysis of the product gas. The GC was equipped with a pneumatically actuated six-port valve with a 1-ml sample loop, a 2-m Poropak N packed column, and a thermal conductivity detector (TCD). It was calibrated with a specially prepared standard that simulated the expected composition of the product gas mixture. The GC was operated within a temperature range of 25–30°C, and the humidity inside the laboratory was not controlled.

The following temperature program on the GC was used for the product analysis. The starting temperature was 60°C for 1 min, after which the column temperature was increased from 60°C to 140°C over a period of 6 min, where it was kept constant for another 3 min. The total time for analysis was 10 min. The sampling point was installed between the filter and the vacuum pump. Before a sample was injected into the GC, it was compressed to 100 kPa.

EXPERIMENTAL CONDITIONS

The typical experimental conditions for the continuous depolymerization laboratory system is summar-

ized in Table I. The system was operated continuously for 24 h with analysis taken at 30-min intervals. The depolymerization product almost always comprises TFE, HFE, HFP, and OFCB as the main products. When the depolymerization parameters were kept constant for a typical 24-h experiment, the concentration of the products as determined by the on-line GC varied with less than 5%. During this 24-h cycle, no blockages occurred.

The higher the PTFE feed rate, the more power must be supplied to the working coil to keep the reactor at the desired temperature. For the purpose of these experiments, the mass flow of PTFE fed into the reactor was kept constant at 2 kg h⁻¹. For depolymerization at 600°C, for example, an enthalpy of 0.91 kW h kg⁻¹ PTFE was required.

RESULTS

The experimental results are summarized in Table II. Figures 5–8 graphically present the average molar percentage of the product gas for the experiments performed at 600–930°C and at different pressures (10, 20, 50, and ~80 kPa). The energy applied to the crucible varied between 1.82 and 5.02 kW for the temperature range that was investigated.

In order for the TFE molar percentage to be optimized, three sets of experimental conditions could be

TABLE I
Typical Experimental Parameters

Parameter	Value
Energy (kW)	1.82–5.04
Pressure (kPa abs)	5–80
Temperature (°C)	600–930
PTFE feed (kg h ⁻¹)	2
Enthalpy (kWh kg ⁻¹ PTFE)	0.91–2.52

TABLE II
GC Results of the Products Gas Composition and Concentration at Different Temperatures and Pressures

Temperature (°C)	Pressure (kPa)	C ₂ F ₆ (%)	C ₂ F ₄ (%)	C ₃ F ₆ (%)	C ₃ F ₈ (%)	c-C ₄ F ₈ (%)	C ₄ F ₈ isomers (%)	Total
607	5	ND	93.9	5.3	ND	0.7	ND	99.9
612	21	ND	81.4	12.4	ND	6.0	ND	99.8
631	84	ND	55.0	22.4	ND	22.4	0.05	99.8
704	9	ND	87.2	6.3	ND	6.4	0.1	100
715	53	0.7	39.6	38.5	1.3	19.0	0.5	99.6
720	82	2.4	23.5	45.3	1.7	25.1	1.7	99.7
809	9	0.7	81.1	12.0	0.2	6.1	0.5	99.9
817	52	15.8	14.8	60.6	5.0	2.7	0.8	99.7
805	82	9.0	12.8	61.0	4.5	10.7	1.7	99.7
923	10	0.4	78.5	17.9	0.1	2.4	0.5	99.8
923	55	77.1	3.3	10.1	0.8	0.5	0.1	92.1 ^a
902	83	3.9	67.9	18.7	1.0	8.3	ND	99.8

ND, not detected.

^a 7.9% CF₄ was formed as a by-product.

applied. For > 90% TFE, a temperature of 600–660°C and a pressure of < 10 kPa was needed; > 67% TFE was observed over a temperature range of 600–900°C; and a pressure of < 10 kPa as well at a temperature of 902°C and a pressure of > 83 kPa.

When it is needed for the HFP molar percentage to be maximized, two experimental conditions could be applied: a sharp maxima of 64% HFP was observed at a temperature of > 800°C and a pressure of ~ 20 kPa. A much broader maximum of > 57% HFP was observed at a temperature of 800°C and a pressure of 80 kPa.

When the OFCB molar percentage must be maximized within the present experimental window, a 25% value could be obtained at a temperature of 700°C and a pressure of 80 kPa. With all the products there is a definite trend for higher yields by increasing either the temperature or the pressure.

No HFE was detected at the lower temperatures and pressures. At 700–900°C, however, HFE was detected in significant amounts. The highest yield of HFE was recorded at 800°C and 50 kPa. Other simple perfluorinated products were also formed during depolymerization: 1-, 2-, and iso-octafluorobutylene. These products are very toxic, but they have significance in the production of other fluorinated products.

DISCUSSION

As indicated above, the depolymerization process was performed at different temperatures and different pressures. After analyzing these data, HFE was not found at lower temperatures. This is an indication of two different mechanisms at the two different temperature ranges. The first mechanism dominates the lower range (620–700°C), and the second mecha-

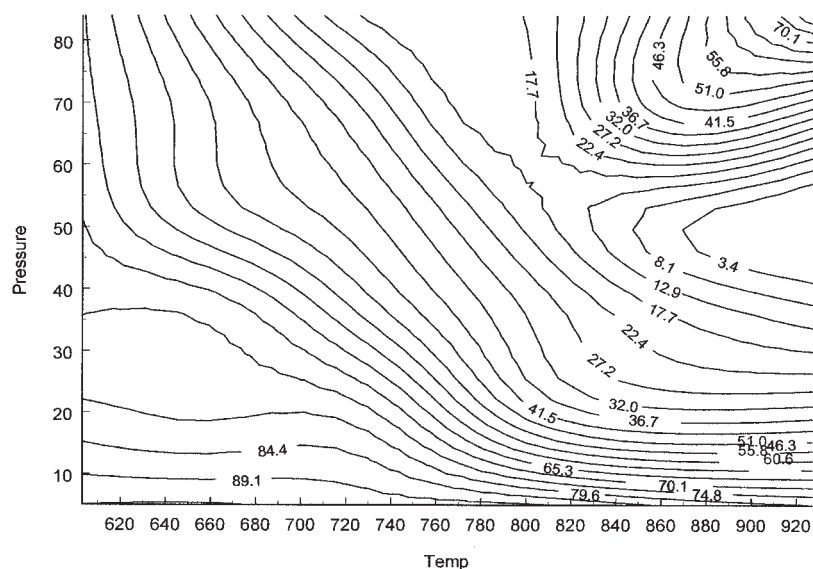


Figure 5 Concentration of TFE obtained as a function of temperature and pressure.

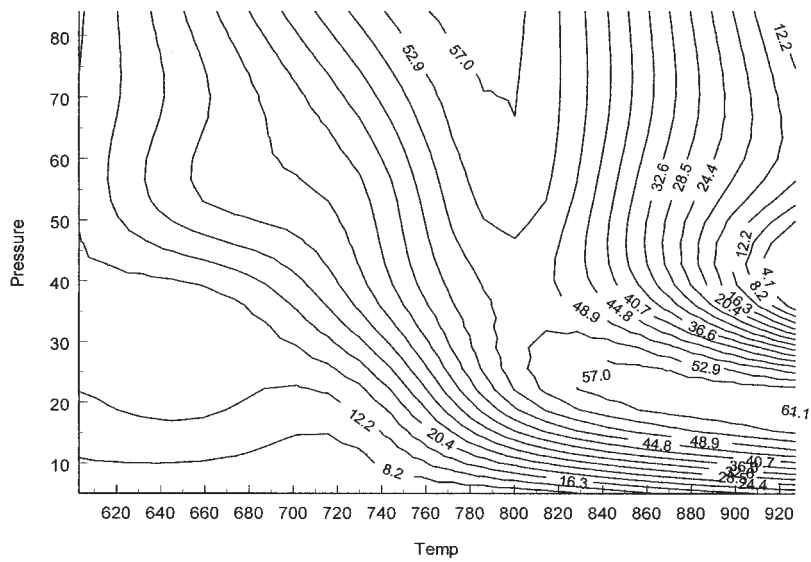
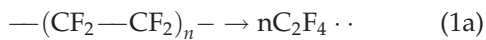


Figure 6 Concentration of HFP obtained as a function of temperature and pressure.

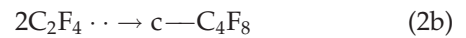
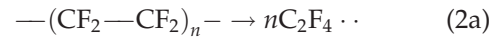
nism the higher temperature range (700–930°C). No clear cutoff point between the two mechanisms exists. Whether the one mechanism dominates the other is determined by the temperature and pressure where the reaction takes place. The first mechanism is limited to a temperature of 620 < T < 700°C and pressures of 10–80 kPa. The proposed reaction mechanism at a temperature of < 700°C is as follows.

Reaction mechanism at low-temperature range (mechanism 1):

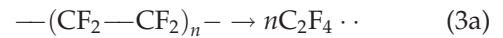
1. Random chain scission and TFE formation:



2. Random chain scission and OFCB formation



3. Random chain scission and HFP formation



In this scheme, PTFE converts directly into a TFE intermediate radical via sublimation. This intermediate

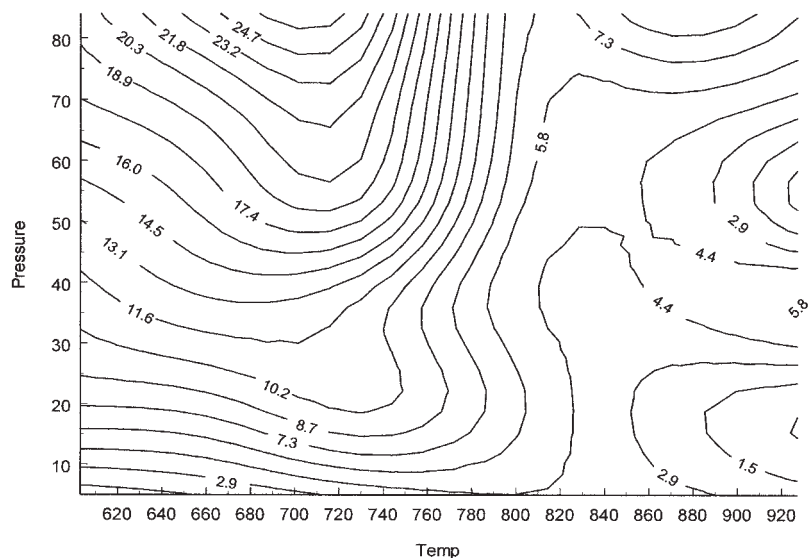


Figure 7 Concentration of OFCB obtained as a function of temperature and pressure.

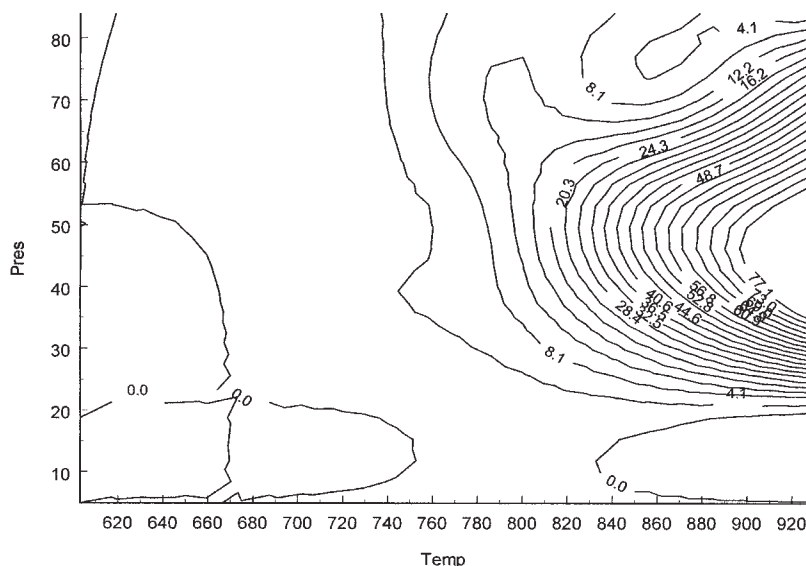


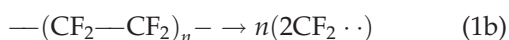
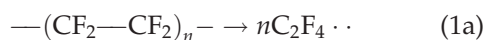
Figure 8 Concentration of C_2F_6 obtained as a function of temperature and pressure.

radical can, under low pressures, form TFE selectively. The formation of HFP and OFCB is minimized by the low pressure because of a low radical concentration. At higher pressures, however, the radical concentration becomes sufficient to promote the formation of HFP and OFCB. The HFP reaction will yield a $CF_2\cdot\cdot$ radical. Combination of two of these $CF_2\cdot\cdot$ radicals will form additional TFE molecule to add to the total TFE concentration that was formed. This simplified scheme was experimentally confirmed because of the high selectivity of TFE formation when PTFE was depolymerized at 10 kPa. At higher pressures, HFP and OFCB were formed, but the TFE formation reaction dominated.

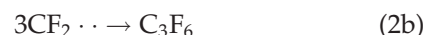
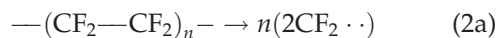
The next proposed reaction mechanism, at $T > 700^\circ C$, is more complex because the mechanism makes use of highly reactive intermediate products ($F\cdot$ and $CF_2\cdot\cdot$). Product formation occurs on the surface of the quench probe where these intermediate species combines according to the following set of equations. The simplified reaction mechanism is presented as follows. (The first mechanism forms the basis of the second mechanism.)

Reaction mechanism at high-temperature range (mechanism 2):

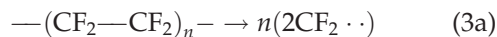
1. HFE formation via $F\cdot$ radicals



2. HFP formation via $CF_2\cdot\cdot$ radicals



3. OFCB formation via $CF_2\cdot\cdot$ radicals



This mechanism takes place at temperatures of $>700^\circ C$. At these temperatures, enough energy is supplied to the PTFE to crack the polymer further into the smallest molecule possible ($CF_2\cdot\cdot$). At temperatures of 800 and $900^\circ C$, enough energy is supplied to break the C—F bond to form $F\cdot$ and consequently, HFE could be formed in significant amounts. This product composition is also temperature and pressure dependent. Other compounds like the other C_4F_8 isomers also start to form, but in very small concentrations. Even higher pressure than atmospheric pressure is needed to optimize for longer-chain products (HFP, OFCB).

CONCLUSION

A 2-kg h^{-1} continuous PTFE depolymerization laboratory system was successfully developed. The product composition is dependent on the pressure and temperature at which the reaction takes place. The optimum TFE yield was obtained at $600^\circ C$ and 5 kPa. Different ratios of the main products (TFE, HFP, and OFCB) as a function of temperature and pressure were obtained. From these experimental data, it is possible to predict

TABLE III
Maximum Yields Achieved and Their
Experimental Conditions

	Concentration (mol %)	Temperature (°C)	Pressure (kPa)
TFE	94	600	5
HFP	61	800	82
OFCB	22	600	84
HFE	77	920	55

maximum yields of HFE, TFE, HFP, and OFCB at reduced pressures and within a temperature range of 600–900°C. In a continuously running system, this may be valuable information. If a certain product mix is required, the operating parameters can be changed while in operation, to accomplish this. Local maxima of the different products were identified and are presented in Table III.

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