

Polytetrafluoroethylene 의 열분해

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The Pyrolysis of Polytetrafluoroethylene

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요 약. Scrap teflon 으로부터 tetrafluoroethylene 을 회수하기 위하여 Teflon 을 온도와 압력등을 변 화시키면서 열분해를 시도하였다. teflon 은 내열성이 강하나 360°C에서 장시간 유지하면 상압에서 도 약간의 열분해가 일어난다. 얻어진 결과에 의하면 일반적으로 감압하에서 온도를 증가시키면 tetrafluoroethylene 의 수득률이 상승하는 것을 알수 있었다. 동분말을 사용하여 teflon 의 분해를 시 도하였으나, 현저한 변화를 볼수 없었다.

ABSTRACT. Although teflon(PTFE) is quite stable at the normal fabricaion temperature of 330 to 360°C, it does undergo pyrolysis if it is maintained at temperature above 360°C for extended periods of time. The extent and rate of this pyrolysis increases as the temperature is raised and pressure is reduced. The pyrolysis was also carried out in the presence of copper, no significant change was observed.

INTRODUCTION

The pyrolysis of teflon(PTFE) was first carried out by Benning *et al.*¹ at a temperature range of 500°C to 700°C under atmospheric pressures. They first isolated and identified tetrafluoroethylene, in 25 % yield along with hexafluoropropane¹, octafluorocyclobutane² and other higher fluorinated products. Later, Lewis³ improved the yield by carrying out the pyrolysis under reduced pressures. As Lewis and Naylor⁴ obtained the products of pyrolysis of teflon(PTFE) at temperatures from 600 to 700°C and pressures between 5 and 760 mmHg. These consisted of C₂F₄, C₄F₈, and C₄F₈ in yields as high as

97 % in varying quantities depending on conditions. Using a variation of the above procedures, English workers⁵ obtained higher yields of the homologues of tetrafluoroethylene.

It is generally believed that the products formed by the polymerization of tetrafluoroethylene was straight chains terminated by as yet unidentified end groups. If such is the case, one might expect the products of the thermal cracking to have structural characteristics similar to those of the compounds obtained from the thermal cracking of high molecular weight straight-chain hydrocarbons. This prediction would lead to the conclusion that the low molecular weight products formed should consist of straight- and branched-

chain, saturated and unsaturated compounds along with carbon tetrafluoride. A broad range of molecular weights in the products would be expected. Actually, however, the products obtained by pyrolysis of polytetrafluoroethylene were of low molecular weight.

EXPERIMENTAL

A weighed amount of scrap Teflon (usually 5g) was placed in the Inconel tube and placed in proper position with the plunger in the hot zone when the desired temperature and pressure was attained. The rate of decomposition was visually observed with the mercury bubble counter. The effluent gases from the Inconel tube were condensed in a series of tared traps cooled successively in baths of dryice-acetone and liquid nitrogen (see Fig. 1). Nearly all of the degradation products were trapped in the liquid nitrogen traps. After each run, any extraneous air (N_2, O_2) condensed in the liquid nitrogen traps was pumped out and IR and VPC studies were made on the combined pyrolyzate. For VPC determination, a 10 ft. Kel-F-Oil column was used at room temperature on an Aerograph instrument.

By incorporating an evacuated gas collector

and an IR-cell in the system at the end of the sampling line (Fig. 1), it was quite simple to collect uniform samples very readily and quickly. After completion of a pyrolysis run, the system was once again completely evacuated. The valves to both the gas collector and IR-cell were then closed: the collector traps taken out of their cooling baths and allowed to reach room temperature. The initial gas sample had to be adjusted to produce an adequate positive pressure to insure complete mixing and evaporation of the condensates. After this procedure, samples were taken for analysis. The percentage given for the relative amounts of the various fluorocarbons present are in volume percents and are the average of three to four runs for each type of scrap Teflon.

PYROLYSIS PROCEDURE

The pyrolysis runs were carried out under a variety of conditions. The pressure was varied from 5 mmHg. pressure to atmospheric (627 mm Hg.). The degradation was tested over a range of 600~800 °C. Both an Inconel and a copper-lined pyrolysis tube were used to determine the catalytic effect of copper, if any. Materials ranging from 5~20 g were pyrolyzed in order to

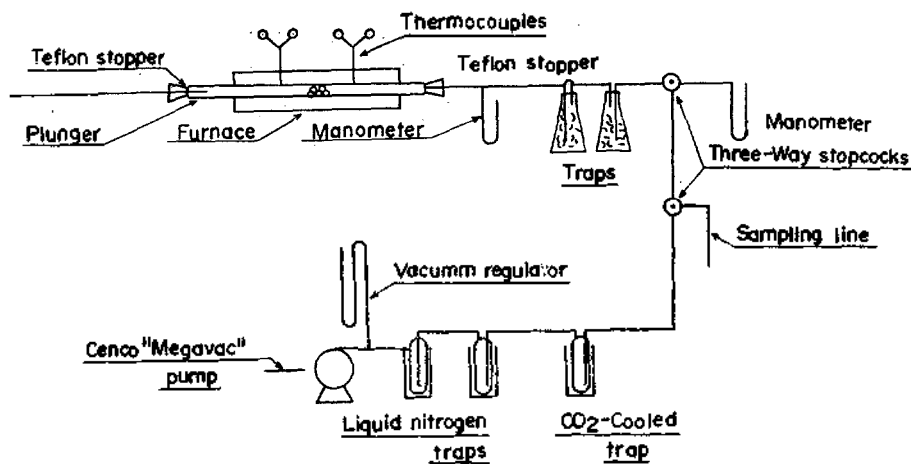


Fig. 1. Apparatus for the pyrolysis of polytetrafluoroethylene.

check the effects produced by the presence of a large excess of scrap polytetrafluoroethylene.

The experimental portion of this study was carried out in an apparatus shown in Fig. 1.

The various Teflon samples were compressed into pellets and inserted into the center of the pyrolysis tube by means of the plunger. The plunger was then withdrawn back to the Teflon plug. This was done to insure uniform heat transfer to the scrap pellets. The mercury bubbler was used to visually determine when the degradation was complete.

The time required for the completion of a unit pyrolysis experiment varied, depending on the size of the sample, pressure and temperature. In general a 10 g sample, under a pressure of 100 mm and at 700°C required about 11~12 minutes to be completely pyrolyzed.

The first step of this study consisted of numerous runs on the different types of scrap Teflon in order to check the material balance. A good material balance was obtained with all of the different types of scrap.

The infrared spectra give a qualitative indication as to what substances were present in the pyrolyzate.

The clean Teflon turnings (d) were chosen at the start, to carry out a large portion of our preliminary studies since it yielded the least amount of residue. Accumulation of these pyrolysis products served as the basis for the isolation and definite identification of the pyrolyzates.

The conditions selected for this accumulation were 600°C and 100 mmHg. pressure since VPC analysis had shown that the yield of C_2F_4 was optimum at this temperature and pressure.

In order to have a standard for use on the VPC and IR, C_2F_4 was specially prepared from the debromination of $C_2F_4Br_2$.

In Tables 1, 2 and 3 are summarized the results of our pyrolytic studies.

As can be seen in Table 2, the yield of TFE is not as dependent on temperature as on pressure. For example, at 5 mm, the difference in TFE yield at 600 and 700° is only 2%, which is well within experimental and mechanical error. However, comparing the TFE percentage at 5 mm and 627 mm at 700°, there is a difference of 41%. Also, it may be noted that at 627 mm and 700° a significant amount of cyclic C_4F_8 and higher boiling perfluoro compounds re formed, which are absent at 5 mm.

On the other hand, as the temperature was increased from 600 to 750° at 627 mm, the percentage yields of TFE steadily increased from 32 to 64% and at 800°, charring was evident.

At 600°, 100 mm, a 20 g. sample was used to study the effects of the presence of unpyrolyzed material in the pyrolysis tube. A sample was collected before the entire pellet could be pyrolyzed. The resulting percentage of TFE was 94. This if compared with results obtained

Table 1. Clean sintered teflon inconel pyrolysis tube. Avg. sample Wt. 5 g, pressures in mmHg.

		5 mm	100 mm	200 mm	627 mm
600°	I	95	92	81	32
	II	5	8	13	26
	III	—	—	6	42
	IV	—	—	—	—
650°	I				47
	II				29
	III				24
	IV				—
700°	I	93	83	76	52
	II	7	13	16	24
	III	—	4	8	18
	IV	—	—	—	5
750°	I				64
	II				28
	III				8
	IV				—

Legend: I = $CF_2=CF_2$, II = $CF_3CF=CF_2$, III = cyclic C_4F_8 , IV = Higher boiling perfluoro compounds

on a 5 g sample (see *Table 1*) shows no apparent deviation.

Effect of Copper in the Pyrolyzate Distribution. It was at first thought that the presence of copper in the pyrolysis tube and had a positive catalytic effect in increasing the yield of C_2F_4 when the furnace temperature of 600° was used. This error was due to a bad sampling technique. However, at $700^\circ C$ and at 200 mm.

Table 2. Clean sintered teflon copper-lined pyrolysis tube.

Avg. wt. sample 5 g.

		100 mm	200 mm
600°	I	65	
	II	20	
	III	15(very slow)	
	IV	—	
700°	I	90	90
	II	9	6
	III	1	4
	IV	—	—

Legend: same as in *Table 1*.

Table 3. Inconel pyrolysis tube.

Avg. sample wt. 5 g, Constant pressure 100 mm.

		Glass filled	Rulon A	Unsintered colored	oily
600°	I	98.5	96	97	97
	II	1.5	4	3	3
	III	—	—	—	—
	IV	—	—	—	—
650°	I	98.5	99	98.5	95
	II	1.5	1	1.5	5
	III	—	—	—	—
	IV	—	—	—	—
700°	I	91	93	89	93
	II	7	6	9	6
	III	2	1	2	1
	IV	—	—	—	—

Legend: same as in *Table 1*.

With this experimental error, the different types of scrap teflon gave the same results.

pressure (see *Table 2*), copper did seem to increase the yield of C_2F_4 , 76 % to 90 %. This data should be checked thoroughly. If our data is correct, it would permit us to carry the degradation of PTFE as a higher pressure without much loss in C_2F_4 yield.

Effect of Nitrogen. The effect of nitrogen as a bleed gas was also studied. Nitrogen was passed through the entire pyrolysis system at the rate of 70 ml/min. This was one at 700~627 mm. The following results were observed: C_2F_4 -34 %, C_3F_6 -41 %, C_4F_8 -20 % and 5 % higher boiling perfluoro compounds. If compared with results obtained under the same conditions in the air, it is seen that the TFE yield is sharply decreased by using the nitrogen flow technique. The C_3F_6 was correspondingly increased by this procedure and the percentage of higher boilers remained unchanged.

Table 1 contains the pyrolysis percentages of several Teflon varieties.

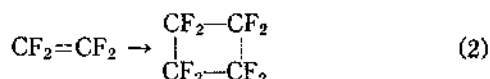
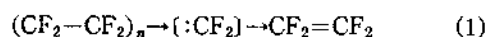
RESULTS and DISCUSSION

The present study was initiated to obtain data for the optimum reaction (temperature contact time, catalysts, etc.) for obtaining maximum yields of tetrafluoroethylene and the effect of impurities present in the scrap polytetrafluoroethylene on the yield of tetrafluoroethylene.

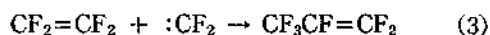
The pyrolysis studies were carried out on various types of scrap polytetrafluoroethylene to test their suitability in a regenerative process in order to obtain maximum yields of tetrafluoroethylene. The following polytetrafluoroethylene varieties were included in this study: a) Glass-filled polytetrafluoroethylene turnings, b) oily polytetrafluoroethylene screw-machine turnings (both unwashed and washed with acetone), c) unsintered tape paste extrusion, d) sintered, clean teflon turnings and e) Rulon A.

The pyrolysis of the various samples of "sc-

rap" teflon was carried out successfully and yields of 95~97 % were attained at 600~700 °C at 5 mmHg pressure. Yields of 92~94 % were obtained under similar reaction temperatures at 100 mmHg pressure. This suggests that tetrafluoroethylene^{6,7} decomposed to yield difluorocarbenes. These difluorocarbene fragments couple to form tetrafluoroethylene which in turn dimerized to octafluorocyclobutane:



Hexafluoropropene can also form via insertion of difluorocarbene to tetrafluoroethylene.



Thus when polytetrafluoroethylene is pyrolyzed in a hot tube, reactions 1, 2 and 3 occurs simultaneously.

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