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# PERFLUOROPOLYETHER PRODUCTION. II PRELIMINARY STUDY OF HEXAFLUOROPROPYLENE SYNTHESIS BY TETRAFLUOROETHYLENE PYROLYSIS.

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## INTRODUCTION

Perfluoropolyethers (PFPE) are a well-known class of fluids with excellent physical and chemical properties and high thermal stability. They can be considered as one hypothetic liquid polytetrafluoroethylene (PTFE).

Perfluoropolyethers fluids are used as working fluids for vacuum pumps (rotatory, turbo-molecular, vapour diffusion), as lubricants for compressors and valves. They can also be used in many other advanced technologies such as aerospace, nuclear, electrical-eletronic, sealed for life bearings and precision equipment. Yet, their high price (US$ 200,00 at US$ 800,00/kg, FOB) is a limiting factor for wider consumption.

The perfluoropolyether production process can be summarized by the following sequence of four complex steps:

1. hexafluoropropylene (HFP) monomer synthesis;
2. hexafluoropropylene photo-oxidation and subsequent photo-polymerization;
3. peroxide linking destruction and end acid groups elimination by direct fluorination;
4. analysis of intermediary and end products.

During this research, the first step of this process has been studied, that is, hexafluoropropylene monomer synthesis by tetrafluoroethylene (TFE) pyrolysis, which was obtained in our laboratory using chlorodifluoromethane (R-22) pyrolysis(1, 2).

Several authors studied tetrafluoroethylene pyrolysis using different experimental systems(3-6).

Nelson(4) describe the principal reactions of tetrafluoroethylene pyrolysis as follows:

$$C_2F_4 \rightleftharpoons 2 : CF_2 \qquad (1)$$

$$C_2F_4 + :CF_2 \rightleftharpoons C_3F_6 \qquad (2)$$

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Ten Eyck et al(5) say that the formation of hexafluoropropylene is not limited by the above reaction. They observed the formation of octafluorocyclobutane (OFCB) and other higher molecular weight perfluorocarbon compounds.

A more recent work(6) report the formation of solids polymers that may be plugging the unit.

Formation of these products as well as the formation of polymers were observed in the present research.

The principal advantage of this method relative to chlorodifluoromethane pyrolysis(1,2) is the azeotrope absence which makes the purification process easier.

The synthesis of hexafluoropropylene monomer was studied considering the variation of several parameters involved in the pyrolysis, that is: temperature, contact time, pressure and flow velocity, in order to improve the hexafluoropropylene yield. It was possible to obtain 99% pure hexafluoroethylene, by fractional distillation.

## EXPERIMENTAL PROCESS

Figure I shows the units for the hexafluoropropylene synthesis by tetrafluoroethylene pyrolysis and for the hexafluoropropylene purification.

Horizontal quartz tubular reactors were used preliminarly to obtain hexafluoropropylene by tetrafluoroethylene pyrolysis. The reactors have 7.8mm and 6.5mm inner diameters, both with 190mm lenght. The contact times of the gaseous reaction mixture were 2.40s and 0.35s, pressures of 0.12MPa and 0.13MPa and flow velocity of 250 cm/min and 169 cm/min respectively. Plugging problems were observed.

To increase the flow velocity into the reaction zone a new pyrolysis reactor was projected with the objetive to suppress the formation of solids polymers and to increase tetrafluoroethylene convertion with hexafluoropropylene higher yield.

It was constructed a stainless steel spiral reactor with 1.5mm of inner diameter and reaction zone of 1450mm length. The present pyrolysis was carried out at temperature of 600°C to 760°C, pressure of 0.12MPa and 0.13MPa and flow velocity of 14430 cm/min. The contact time of the gaseous reaction mixture was 0.6s. The reaction products were cooled at the output of reactor and sended straight through two mixed columns, the first one with dolomite and NaOH and the second with NaOH and $CaCl_2$ to remove humidity and avoid possible formation of $F_2$ and HF.

With the use of stainless steel reactor, unreacted tetrafluoroethylene, hexafluoropropylene, octofluorocyclobutane and minimum quantities of other perfluorocarbons were obtained. They were all identified by gas chromatography and mass spectroscopy.

After the pyrolysis, the reaction mixture was sended into a 1.5m long distillation column with inner diameter of 20.7mm, filled with "Helipak" packing at steady temperature of -30$^{o}$C at the top of the column and at room temperature at the bottom. In this condition pure tetrafluoroethylene was obtained at the top of the column. Hexafluoropropylene was separated from other perfluorocarbons maintaining the temperature of -20$^{o}$C at the top of the column and +10$^{o}$C at the bottom. Octafluorocyclobutane was removed maintaining the temperature of +20$^{o}$C at the top of the column and +40$^{o}$C at the bottom.

In this way it was possible to obtain 99% pure hexafluoroethylene. The purity of the monomers was checked by gas chromatography.

The chromatographic analysis were carried out in a gas chromatograph, model CG-500A, with a "Porapak Q" column, a thermal conductivity detector and superdried hydrogen as a carrier gas.

## RESULTS AND DISCUSSION

Former experiences made in quartz reactors with low flow velocity, showed a large formation of solids polymers, plugging the reaction unit and so discontinuing the pyrolysis.

Figure II (a, b, c, d, e) shows the chromatograms obtained by tetrafluoroethylene pyrolysis which show the percentage variations of unreacted tetrafluoroethylene and the percentage formation of hexafluoropropylene, octafluorocyclobutane and higher molecular weight perfluorocarbons during the pyrolysis at several temperatures, as follows: 600$^{o}$C (a), 700$^{o}$C (b), 740$^{o}$C(c), 750$^{o}$C (d) and 760$^{o}$C(e).

These experiences were made with a 1450mm length stainless steel reactor of 1.5mm inner diameter, contact time of 0.6s, 14430 cm/min of flow velocity and pressure of 0.12MPa and 0.13MPa.

In former pyrolysis experiences made with this reactor a large formation of solid polymer was observed at temperature of 600$^{o}$C with low formation of hexafluoropropylene and formation of octafluorocyclobutane as can be seen in Figure II (a). Consequently the follow experience was begun at 700$^{o}$C. In Figure II (b) the low convertion of tetrafluoroethylene in hexafluoropropylene was observed, but convertion in octofluorocyclobutane is similar in percentage to that of hexafluoropropylene formation. As the temperature was used over 700$^{o}$C (Figure II (c), (d), (e)), an increase of tetrafluoroethylene convertion was observed accompanied with a decrease in the octafluorocyclobutane formation and an increase in the hexafluoropropylene formation up to 85% of the last one at 760°C (Figure II (e)). At this temperature was also observed an increase in the higher molecular weight perfluorocarbons formation (Figure II (e)).

Table I shows tetrafluoroethylene convertion values and yield of hexafluoropropylene as a function of temperature.

TABLE I - Percentages of pyrolysis products formation, tetrafluoroethylene convertion and hexafluoropropylene yield at diferent temperatures. Contact time = 0.6s. Pressure=0.12MPa - 0.13MPa. Flow velocity=14430 cm/min.

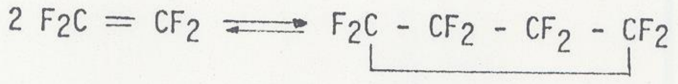
| TEMP. °C | HFP | TFE | OCFB | OTHER | TFE CONVERTION | HFP YIELD |
|---|---|---|---|---|---|---|
| 700 | 36 | 29 | 35 | - | 71 | 51 |
| 740 | 53 | 27 | 19 | 1 | 73 | 73 |
| 750 | 62 | 25 | 12 | 1 | 75 | 83 |
| 760 | 85 | 6 | 2 | 7 | 94 | 90 |

The convertion represents the quantity of tetrafluoroethylene pyrolysed in hexafluoropropylene and subproducts and the yield is the quantity of hexafluoropropylene formed from the converted tetrafluoroethylene.

According with Table I, it was observed that the pyrolysis of tetrafluoroethylene at 760°C gives a 94% convertion of TFE and a 90% yield of hexafluoropropylene.

At 800°C carbonizing problems were observed, preventing the obtaining of data at higher temperatures. These carbonizing phenomena were also observed by Ten Eyck et al(5).

The results obtained with this research show that the first reactions occuring during the tetrafluoroethylene pyrolysis are the formation of octafluorocyclobutane and oligomers of tetrafluoroethylene.



$$2\,F_2C = CF_2 \rightleftharpoons F_2C - CF_2 - CF_2 - CF_2 \qquad (3)$$

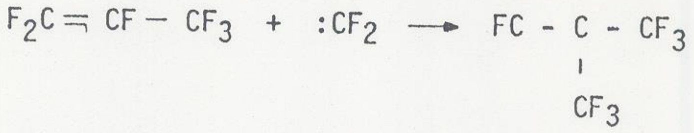
$$n\,(F_2C = CF_2) \rightleftharpoons -\!\!\left( CF_2 - CF_2 \right)\!\!-_{n} \qquad (4)$$

As the temperature rises, difluoromethylene radicals begin to appear as product of the tetrafluoroethylene decomposition (reaction (5)), reacting with another tetrafluoroethylene molecule and producing hexafluoropropylene in increasing amounts (reaction (6)).

$$F_2C = CF_2 \rightleftharpoons 2{:}CF_2 \qquad (5)$$

$$F_2C = CF_2 + {:}CF_2 \rightleftharpoons F_2C = CF - CF_2 \qquad (6)$$

However, the higher hexafluoropropylene production increase the formation of higher molecular weight subproducts, among them, the highly toxic perfluoroisobutene (PFIB) (reaction (7))



$$F_2C = CF - CF_3 + {:}CF_2 \longrightarrow FC - \underset{\substack{|\\ CF_3}}{C} - CF_3 \qquad (7)$$

These higher molecular weight subproducts are thermaly very stables contrarily to the oligomers formated at low temperatures, thus its production is favored by contact time.

Because of the experimental difficulties founded, it has not been possible to study the kinetic of the hexafluoropropylene formation.

Eventual modification of the process are in project, in order to make it more efficient, even though the recent results are good, with 94% of tetrafluoroethylene convertion and hexafluoropropylene yield of 90%.

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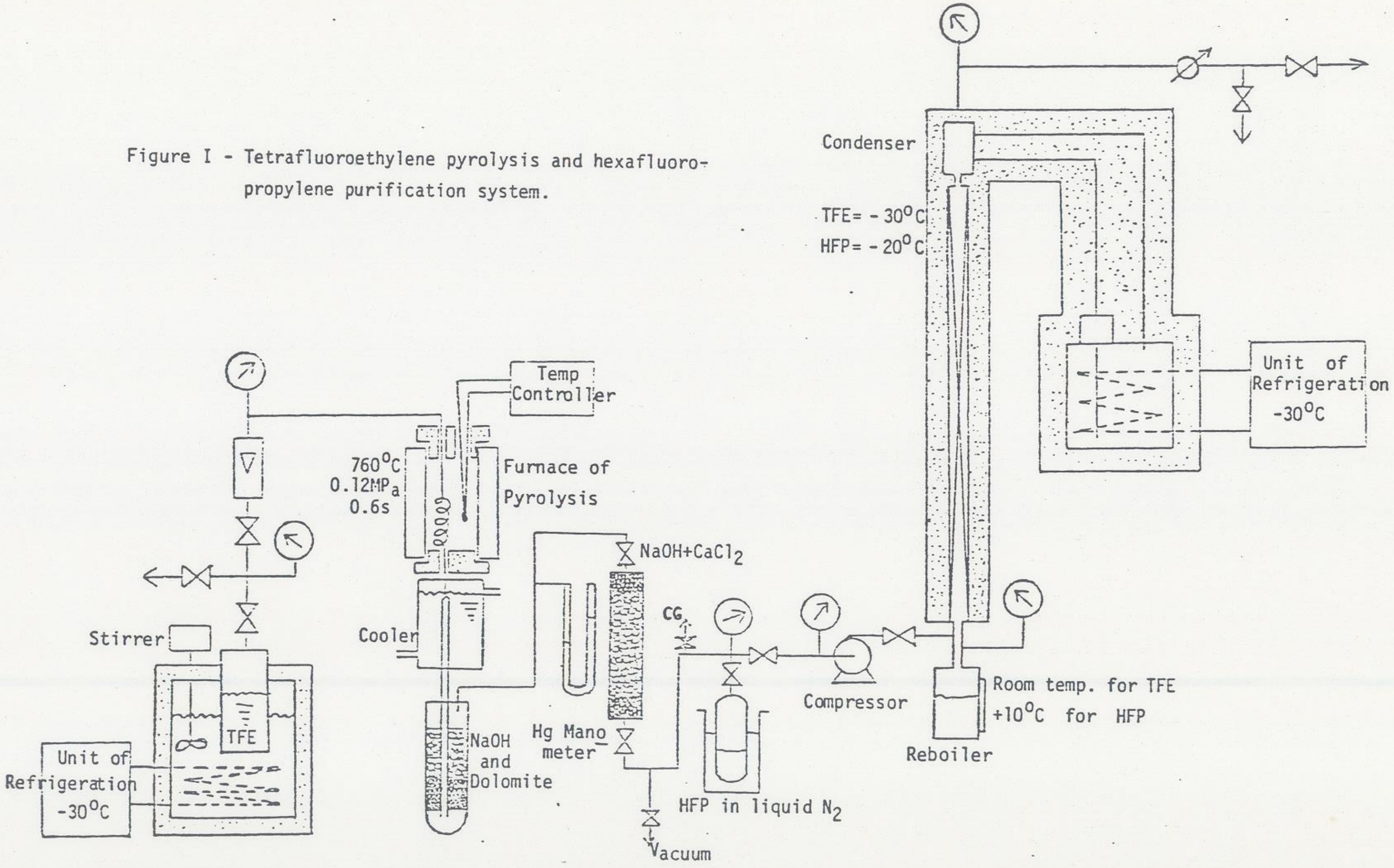
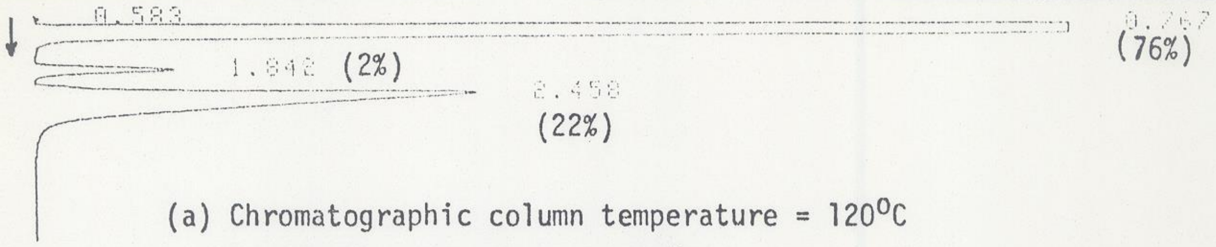
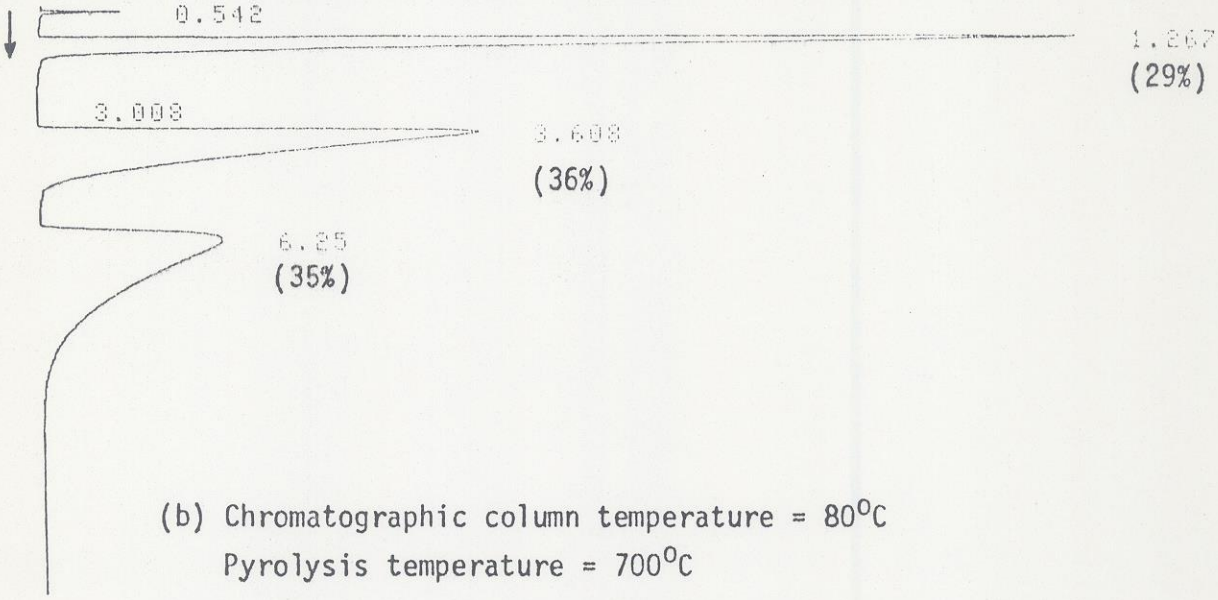


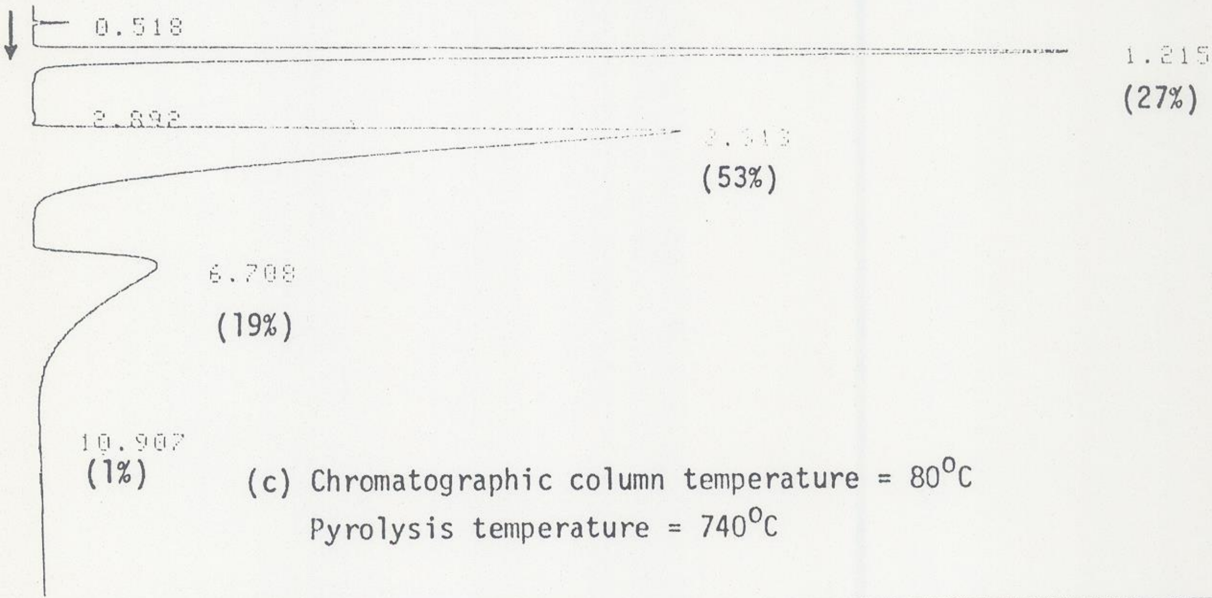
Figure I - Tetrafluoroethylene pyrolysis and hexafluoropropylene purification system.



(a) Chromatographic column temperature = 120°C
Pyrolysis temperature = 600°C.

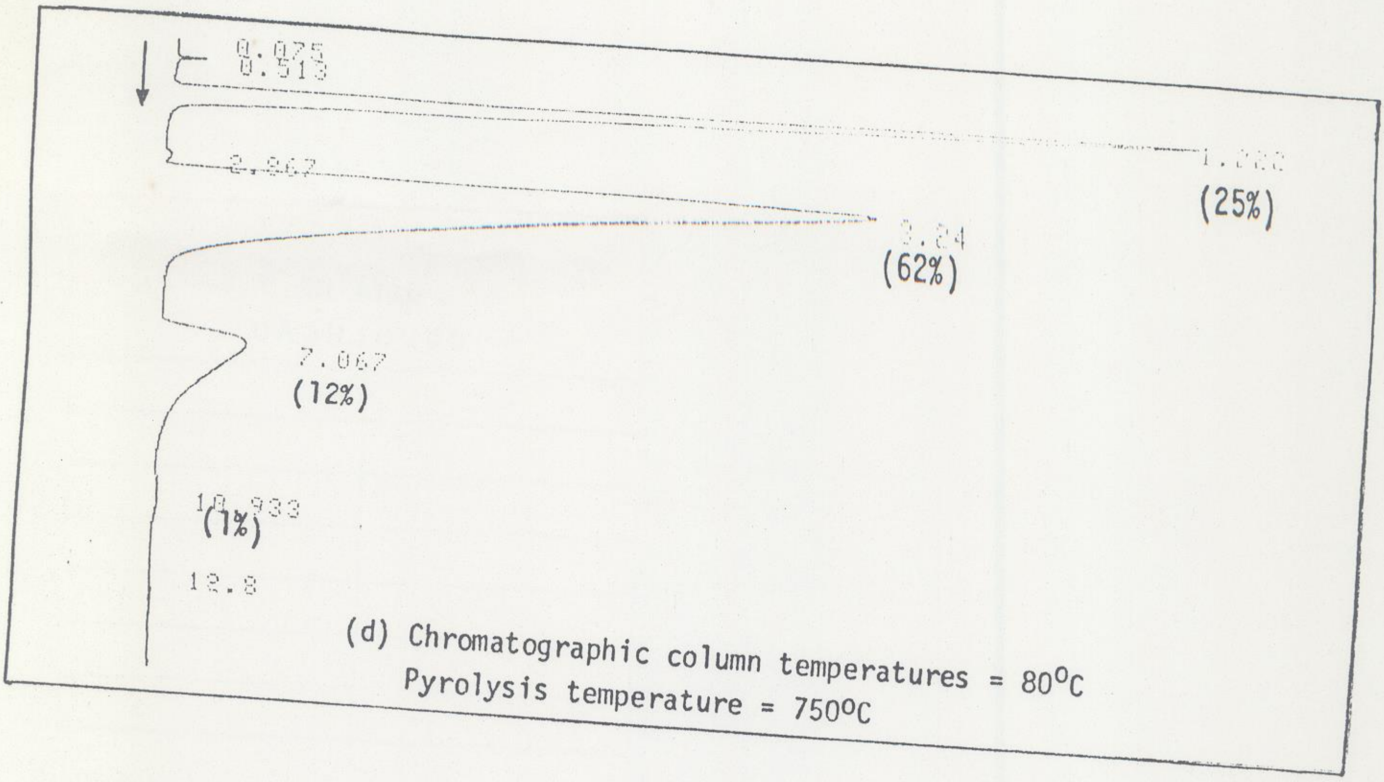


(b) Chromatographic column temperature = 80°C
Pyrolysis temperature = 700°C

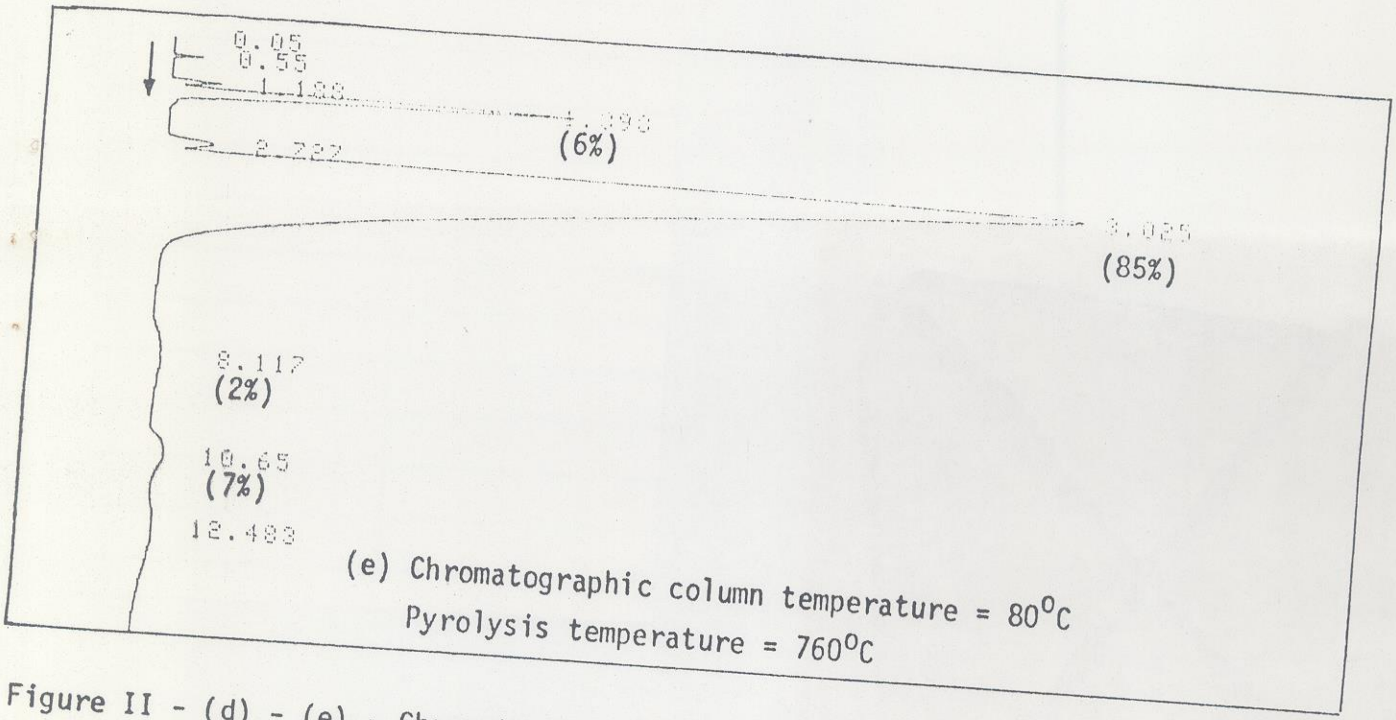


(c) Chromatographic column temperature = 80°C
Pyrolysis temperature = 740°C

Figure II - (a) - (b) - (c) - Chromatograms obtained in the tetrafluoroethylene pyrolysis at diferent temperatures.



(d) Chromatographic column temperatures = 80°C
Pyrolysis temperature = 750°C



(e) Chromatographic column temperature = 80°C
Pyrolysis temperature = 760°C

Figure II - (d) - (e) - Chromatograms obtained in the tetrafluoroethylene pyrolysis at diferent temperatures.