PRODUCTION OF THE PERFLUOROPOLYETHER. I-OPTIMIZATION OF THE CHLORODIFLUORO METHANE PYROLYSIS REACTOR FOR THE SYNTHESIS OF THE TETRAFLUOROETHYLENE.

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INTRODUCTION

The thermal decomposition of chlorodifluoromethane (R-22) may be considered as the first stage of a most complex process leading to the synthesis of the perfluoropolyether (PFPE).

Park et al[1] studied this process for the first time. Their results were confirmed by other laboratories[2,3,4], including our own[5,6]. Basically, the R-22 conversion rises with temperature and contact time. The tetrafluoroethylene (TFE) yield rises with the R-22 conversion until it reaches a maximum, where subproducts yield starts to rise. However, the studied temperature and contact time were not consistent with commercial practice, and uncertainties in the obtained conversion convinced us of the need of futher study. This paper presents a preliminary study of the heat transfer inside the pyrolysis reactor in order to project a pilot or industrial scale reactor in the near future.

EXPERIMENTAL PROCEDURE

The schematic diagram of the R-22 pyrolysis unit is shown in figure 1. R-22 was pyrolyzed in quartz tubes of diferent inner diameters (Di) and lenghts (L) (tube a: Di=8mm, L = 400mm; tube b: Di = 2mm, L = 1000mm; tube c: Di = 2mm, L = 1960mm; tube d: Di = 2mm, L = 3600mm), with diferent contact time and temperature ranges. The pressure was maintened near atmosferic at the end of the tube. The pyrolysis products were first washed by passing through columns of water and potassium hydroxide aqueous solution to remove acids (HCl and HF), and them, they were dried by sulfuric acid and anhydrous calcium choride columns. Finally, they were purified by a distilation column 150 cm high and 21 mm in inner diameter, filled with helipack. These products were identified by GC-mass spectroscopy and the routine analysis was done with a gas chromatograph (GC) with a Porapak Q column.

RESULTS AND DISCUSSION

Figure II (a*, b) shows the results of the R-22 conversion as a

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function of temperature and contact time, for diferent lenghts and inner diameters of the reaction tube. Graphs a and b show the expected behaviour of R-22 conversion, i.e., the conversion increasing with temperature and contact time. However, comparing the 0,14s contact time line from graph b with the 1,43s contact time line from graph a, we see that the conversion made in the "case b" reaction tube (Di = 2mm, L = 1000 mm) is slightly higher than the one made in the "case a" reaction tube (Di = 8mm, L = 400mm), in spite of the "case a" contact time (1,43s) being 10 times longer than "case b" contact time (0,14s). This means that the heat transfer in tube b was 10 times better than in tube a, because the fluid velocity in tube a was very low, promoting a thermal laminar profile. In others words, the gas flowed in progressively lower temperatures from the inner surface to the center of the tube.

Figure III (c, d) shows that for longer tubes (tube c: L = 1960mm, tube d: L = 3600 mm) of the same diameter (Di = 2 mm), the conversion lines have the same shape and values. For example, the 0,29s contact time line from graph d almost overlaps the 0,16s contact time line from graph c. Graph d also shows the conversion decreasing with time. It was concluded, consequently, that the kinetic equilibrium was shifting from the reactions of R-22 decomposition to the reactions of R-22 synthesis, as showed below by the following set of equations describing the kinetic of the pyrolysis:

$$CHClF_2 \rightleftharpoons CF_2\cdot + HCl$$

$$2CF_2: \rightleftharpoons C_2F_4 \text{ (TFE)}$$

$$2C_2F_4 \rightleftharpoons C\text{-}C_4F_8$$

$$C_2F_4 + CF_2: \rightleftharpoons C_3F_6 \text{ (HFP)}$$

$$C_2F_4 + HCl \rightleftharpoons H(CF_2)_2Cl$$

and it is produced 2 series of "high boilers" with general molecular formula $H(CF_2)_nCl$ and C_nF_{2n}, but in very low concentration.

The R-22 conversion decreasing with contact time is unpublished and it is conflicting with a recent kinetic work[4]. This results, consequently, will be studied with more accurated temperature and contact time control and determination.

* the authors had showed this graph before [6].

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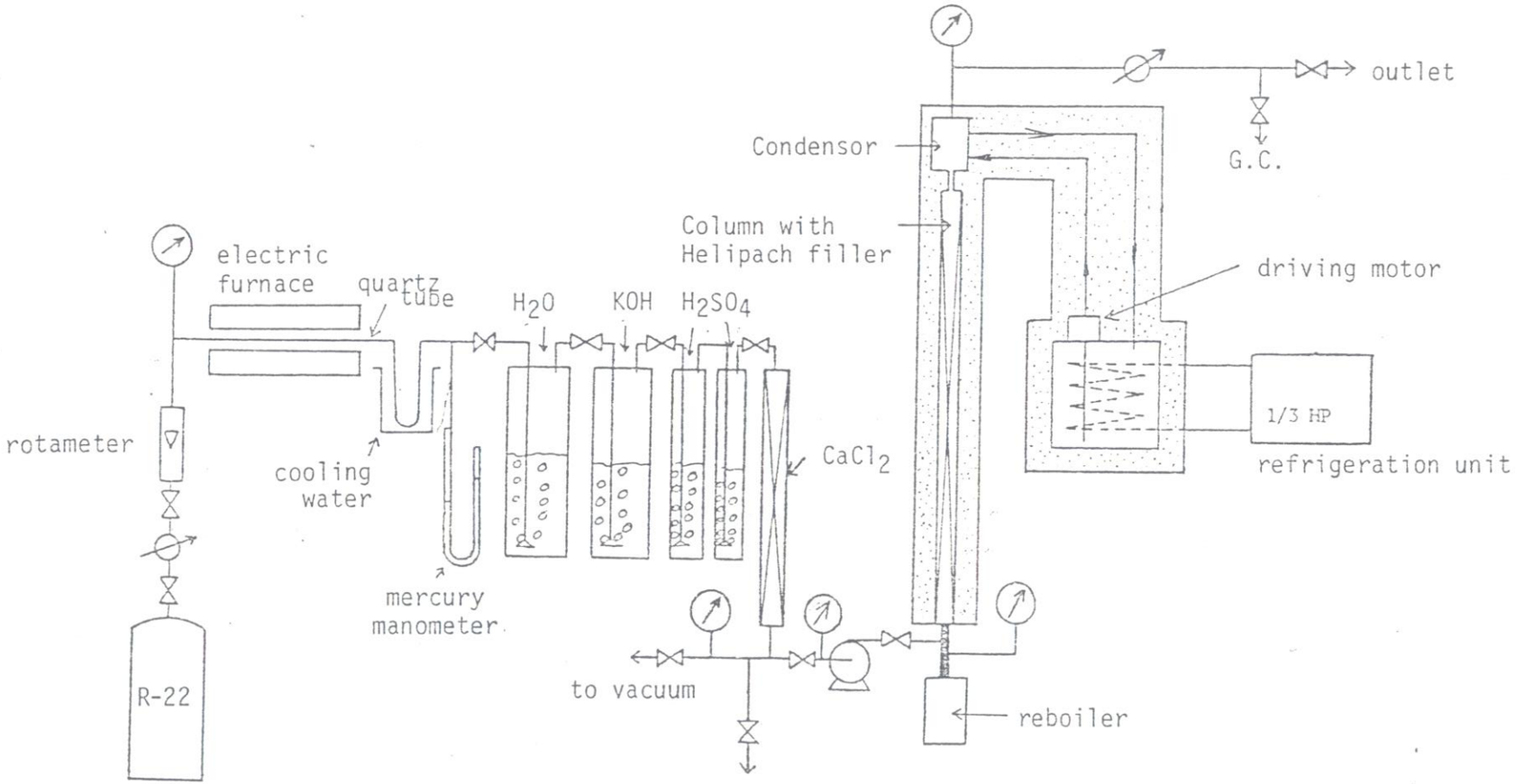
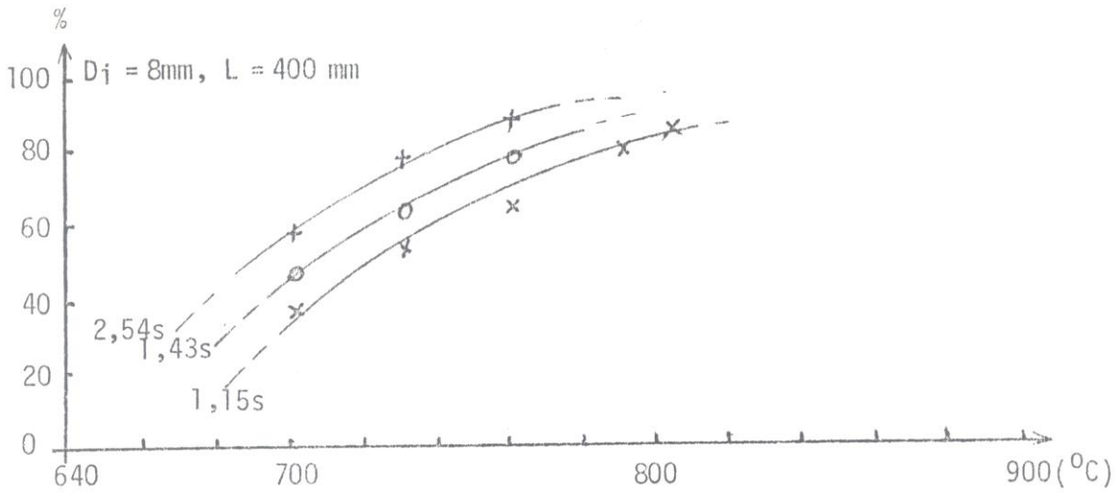
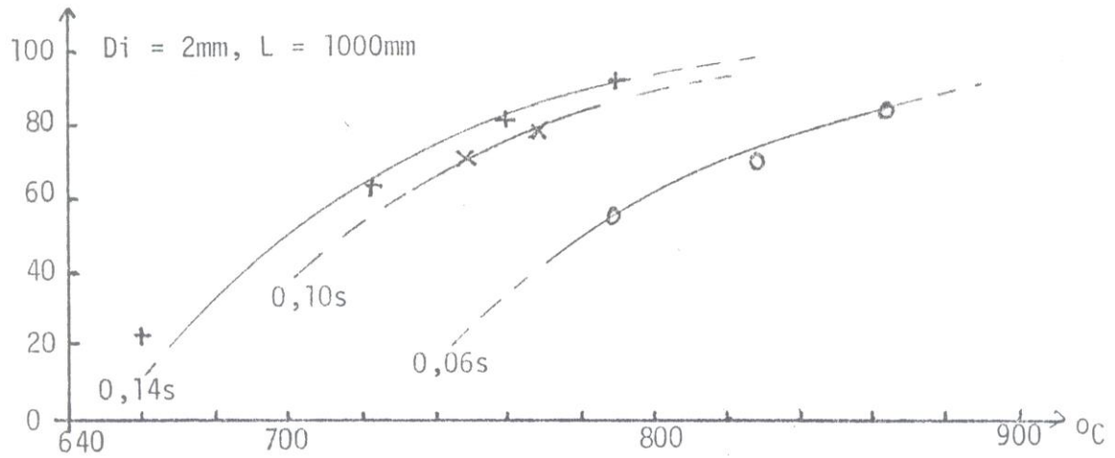
Figure I - Schematic diagram of pyrolysis unit.



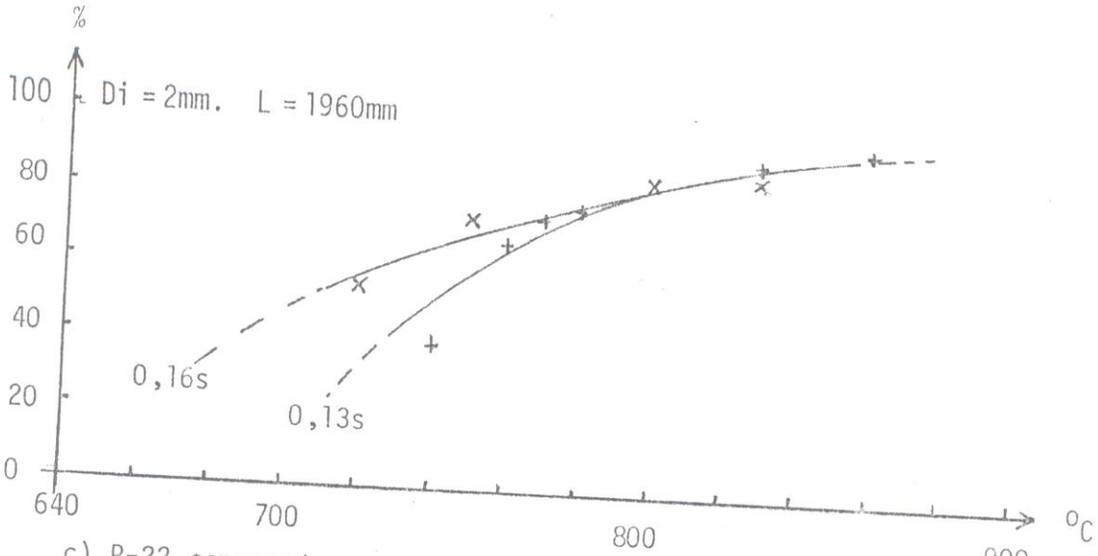


a) R-22 conversion vs. temperature for 1.15s. 1.43s and 2.54s contact time. Tube a: Di = 8mm, L = 400 mm.

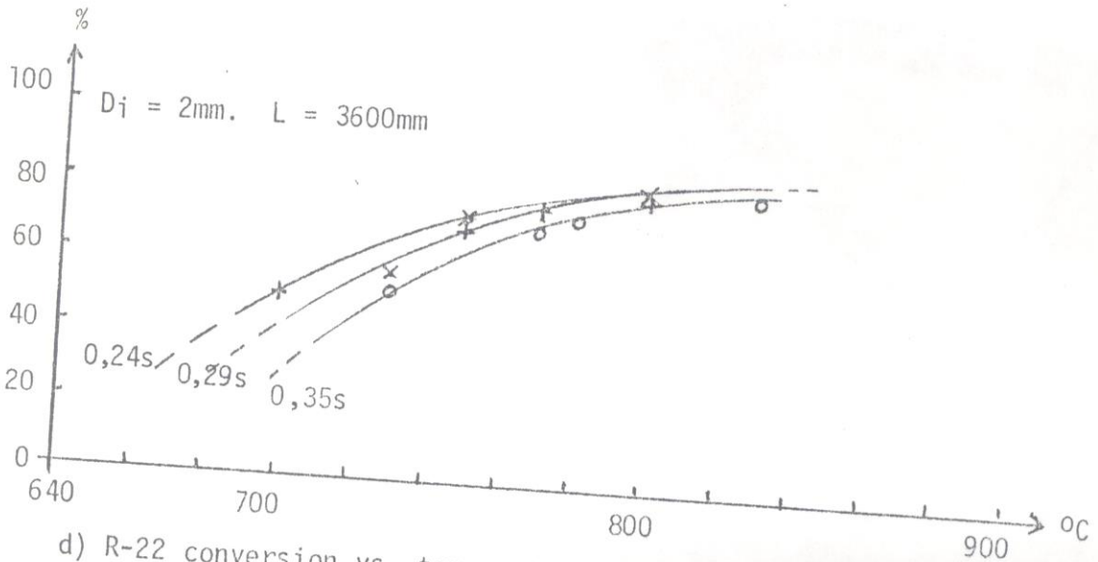


b) R-22 conversion vs. temperature for 0,06s, 0,10 and 0,14s contact time. Tube b: Di = 2mm, L = 1000mm

Figure II - Expected behaviour of R-22 conversion as a function of temperature and contact time.



c) R-22 conversion vs. temperature for 0,13 and 0,16s contact time. Tube c: Di = 2mm, L = 1960mm.



d) R-22 conversion vs. temperature for 0,24s, 0,29s and 0,35s contact time. Tube d: Di = 2mm, L = 3600mm.

Figure III - Anomalous behavior of R-22 conversion as a function of temperature and contact time.