

Temperature and pressure effects on the product distribution of PTFE pyrolysis by means of qualitative, in-line FTIR analysis



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ABSTRACT

The results of the depolymerisation of PTFE under steady operating conditions in a semi-automated, continuous depolymerisation system are presented. The influence of temperature and pressure on the selectivity of the three main products of depolymerisation (tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and octafluorocyclobutane (OFCB)) was investigated via qualitative in-line FTIR analysis. No carrier gas was used, with the PTFE feed rate and experimental run time kept constant. The temperature and pressure ranges investigated were: 650 °C–750 °C and <10 kPa–40 kPa. The optimum operating conditions to maximise the three main products were determined using response surface methodology following a three-level face centered composite design. A TFE mole fraction of 0.95 and higher was achieved at operating conditions of ± 675 °C and <10 kPa. HFP mole fractions of 0.19 and higher were achieved within the operating range of 744 °C–750 °C and 32 kPa up to 40 kPa. At operating conditions of 750 °C and 40 kPa, OFCB fractions of 0.5–0.55 were achieved. The OFCB and HFP mole fractions achieved differed from those previously mentioned in the literature. Analysis of the determined product specific kinetics indicates that the predominant HFP production pathway at low residence times (<3 s) is via the reaction of TFE with difluorocarbenes. At higher residence times the dominant reaction pathway is the dissociation OFCB.

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1. Introduction

Fluoropolymers are important synthetic materials in science and industry and are used to meet a variety of severe specifications required by modern engineering. The most important of all of the industrial fluoropolymers is polytetrafluoroethylene (PTFE) due to its wide range of unique and extraordinary characteristics. Due to the non-melt-processability of PTFE resin, a large amount of waste is generated annually, most of which is either incinerated, landfilled or ground up and ram extruded to produce lower quality tubes and profiles [1,2]. These destructive or re-use methods pose economic and environmental issues, particularly when considering the evolution of extremely toxic gases (eg perfluoroisobutylene (PFIB)) during the incineration of PTFE. In recent years, methods of PTFE recycling have been investigated, with the main focus on the thermal decomposition of PTFE. This process produces high-value

monomers, which include tetrafluoroethylene (TFE), hexafluoropropylene (HFP) and octafluorocyclobutane (OFCB) [3]. Due to the transport and handling restrictions and difficulties of TFE, it has become commercially unavailable, leading to the requirement of safe, on-site production methods [4]. Since TFE is produced during the decomposition of PTFE, waste PTFE can in principle be used to produce new, high molecular weight PTFE in a multi-unit operation process.

The effects of temperature and pressure on the product distribution achieved during continuous PTFE depolymerisation have been reported numerous times in the literature [1,2,5–7]. Even though the overall effects of these two variables seem to stay the same, experimental results achieved at the University of Pretoria indicate that the exact distribution of the three main products (TFE, HFP, and OFCB) appear to be system specific. Meissner [6] and van der Walt [2] performed in-depth studies into the temperature and pressure effects on the product distribution and recommended the optimum operating conditions to optimise the three main products (TFE, HFP, and OFCB).

The main aim of this investigation was to determine the

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temperature and pressure effects on the selectivity of TFE, HFP, and OFCB for this particular system. If PTFE depolymerisation were to be used as a recycle method it would be beneficial to determine the operating conditions that would favour the production of single and two component systems. Since there is a small difference in the relative volatilities of HFP and OFCB, it would be advantageous to produce two component systems of TFE with either HFP or OFCB maximised. These operating conditions were determined statistically via a qualitative in-line FTIR analysis method developed in-house. The product specific kinetics of the system were also determined to achieve an in-depth analysis of the depolymerisation process.

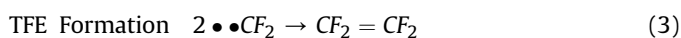
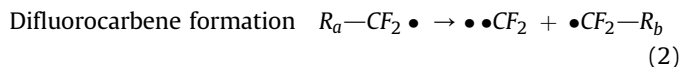
2. Depolymerisation mechanism

The mechanism of PTFE depolymerisation has been of interest since its discovery. Lewis [3] first proposed the unzipping or free-radical chain mechanism. Morisaki [8] proposed an elaborate PTFE depolymerisation mechanism which includes the formation pathways of most of the common depolymerisation products. Meissner [6] proposed a similar mechanism. In both Morisaki [8] and Meissner's [6] mechanisms, two HFP formation reactions were proposed. According to Meissner [6], the decomposition of OFCB is the most likely HFP production pathway. According to van der Walt [2], another depolymerisation mechanism may be present at high temperatures (700 °C–900 °C), which involves the polymer chain randomly breaking into fragments. From the literature cited, it can be concluded that the process of PTFE depolymerisation may occur via two possible mechanisms which are temperature dependent. The depolymerisation process can be divided up into five steps: Initiation, primary product formation, secondary and tertiary reaction steps and finally the recombination step. The main proposed mechanisms for each step is summarised below, including all of the possible pathways of product formation.

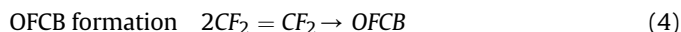
1. Initiation



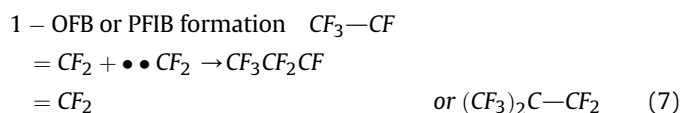
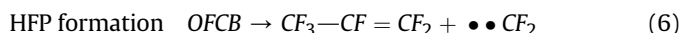
2. Primary product formation



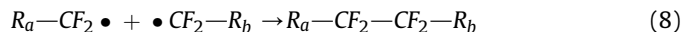
3. Secondary product formation



4. Tertiary product formation



5. Recombination step



3. Experimental

3.1. Raw material

Teflon® PTFE 807N was procured from DuPont (now known as Chemours) to be used as raw material for this investigation. The general material properties for Teflon® PTFE 807N are listed in Table 1.

3.2. Apparatus and operation

PTFE depolymerisation was achieved in the semi-automated depolymerisation system depicted in Fig. 1. The system was remotely controlled and monitored by software written in National Instruments™ LabVIEW Full Development Suite 2015. The system consists of a stainless steel pipe reactor 381 mm in length, with an internal diameter of 77.92 mm. The reactor was flanged using a Viton seal. In the top flange, a one-inch bore pipe connected the reactor to a ball valve and another one-inch bore pipe connected the ball valve to a screw feeder. The screw was operated using a reversible, geared AC induction motor. A variable frequency drive (VFD) was used to control the motor speed. The reactor was heated using a resistive furnace. The reactor temperature was monitored at three places; one thermocouple at the bottom of the reactor, one thermocouple halfway up the reactor and the last thermocouple was inserted in the reactor outlet tube. Glass wool was inserted in the reactor outlet to prevent any debris from entering the rest of the system. The product gas evolved during depolymerisation was pumped to a holding cylinder using a diaphragm pump. The system pressure during operation was controlled manually by restricting the product gas flow using valve V5.

No carrier gas was used. The Teflon® PTFE 807N feed rate was kept constant at 11 g min⁻¹ (±0.31 g min⁻¹) by setting the VFD frequency to 30 Hz. The experimental run time was 15 min. The first 5 min was used to pressurise the system and to allow the system to reach steady state.

3.3. Experimental design

The influence of temperature and pressure on the selectivity of TFE, HFP, and OFCB, was investigated using Response Surface Methodology (RSM) with temperature and pressure selected as input variables following a Face Centered Composite (CCF) design (NIST/SEMATECH, 2012). Meissner [6] and van der Walt [2] confirm that the response surface for each of the depolymerisation products is anything but linear. To incorporate this finding, a three-level full factorial design was followed. All of the experimental points were repeated twice to determine the stability of the system. The three level values for each of the two factors are indicated in Table 2. In total 27 experiments were performed.

Table 1
DuPont Teflon® PTFE 807N physical properties (DuPont, sa).

Average particle diameter	µm	600
Standard specific gravity		2.156
Bulk density	g · cm ⁻³	0.95
Melting peaks		
Initial	°C	344
Second	°C	327

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