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Design of a continuous gas-phase process for the production of hexafluoropropene oxide

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ABSTRACT

The partial oxidation of hexafluoropropene (HFP) yields 2,2,3-trifluoro-3-trifluoromethyl oxirane (commonly known as hexafluoropropene oxide, HFPO), a highly reactive and versatile fluorochemical intermediate that is used in the manufacture of various high-performance organofluorine products. Most industrial methods of HFPO preparation involve the high-pressure liquid-phase oxidation of HFP in the presence of chemical oxidizers and solvents. Processes that employ molecular oxygen as the oxidizing agent generally have a lower environmental impact. In this study, the design and analysis of a 500 tpa continuous gas-phase process for the epoxidation of HFP with molecular oxygen was carried out. A modular coil-type reactor fabricated from drawn copper tubing is proposed to attain residence times up to 120 s which are required for acceptable levels of HFP conversion (70%) and HFPO yield (40%). The HFPO product is separated from the residual HFP through a novel sequence of CO_2 gas stripping and conventional distillation steps. A final product having a purity of 99.8 mol% is obtained. The recovered HFP, which has a purity of 99.2 mol%, is subsequently recycled. The process unit operates at a HFP recycle ratio of 0.39.

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1. Introduction

The synthesis of HFPO on a commercial scale is usually achieved using a batch or semi-batch liquid-phase process that is carried out at low temperature employing chemical solvents and oxidizing agents such as hydrogen peroxide (Millauer et al., 1985; Furin, 2006). Over the years several modifications to the process have been made, including the addition of phase transfer catalysts and the use of different solvents and oxidizers, resulting in improved selectivity towards the epoxide product (Ikeda et al., 1990). The gas-phase synthesis of HFPO has certain advantages over the conventional liquid-phase process. It is generally safer, cleaner and more amenable to scale-up. However, the propensity of the epoxide to decompose at the temperatures required for initiation of the reaction have rendered this route relatively unexplored.

Initial investigations of the gas-phase non-catalytic oxidation of HFP were focused on the photo-initiated reaction occurring at room temperature. In one of the earliest reported studies, Saunders and Heicklen (1965) investigated the gas-phase reaction of oxygen atoms with HFP at 297 K in a cylindrical Pyrex cell. The oxygen atoms were generated by in situ mercury-photosensitized decomposition of N_2O. The major advantages for this method of generating oxygen atoms were that the only oxygen specie produced was atomic oxygen having a triplet electronic spin state and that N_2O was non-reactive with this specie and most radicals. Appreciable amounts of CO_2, COF_2 and CF_3COF were formed, together with small quantities of C_4F_8 (as perfluorinated methyl-cylcopropane) and a C_5 fluorocarbon, which was most likely perfluoro-1,2-dimethylcyclopropane. Heicklen and Knight (1965) studied the same system at 486 K. They found that CO_2, COF_2, CF_3COF, C_2F_4 and C_4F_8 were produced when the reaction was carried out in the presence of molecular oxygen.

Sianessi et al. (1973) carried out some exploratory work on the high temperature gas-phase oxidation of HFP with molecular oxygen. The reactions were carried out at atmospheric pressure. Apart from some acid fluorides (40% COF_2, 37% CF_3COF) and oligomeric products (5%), the experiments yielded no HFPO, with the temperature well beyond the decomposition temperature of the epoxide.

The photo-initiated gas-phase oxidation of HFP was also studied by Kuricheva et al. (1999), between 680 and 840 K. The reaction was initiated using a CO_2 IR laser source and was carried out batch-wise in a 12 or 24 cm^3 glass reactor equipped with BaF_2 windows for spectrophotometric analysis. At the conditions that were employed, only deeper

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Nomenclature

Symbols

A	Pre-exponential factor $cm^3 mol^{-1} s^{-1}$ or s^{-1}
A_c	Tube cross-sectional area m^2
C_{pi}	Heat capacity of species i $J mol^{-1} K^{-1}$
d_c	Coil diameter m
De	Deans number
d_t	Tube diameter m
E_a	Activation energy $J mol^{-1}$
f_c	Friction factor for coil
f_s	Friction factor for straight tube
F_i	Molar flowrate of species i $mol s^{-1}$
ΔH_r	Enthalpy of reaction $J mol^{-1}$
L	Tube length m
N	Number of tubes
Nu	Nusselt number
N_{tubes}	Number of tubes
P	Pressure bar
Pr	Prandtl number
r	Reaction rate $mol cm^{-3} s^{-1}$
r_t	Tube radius m
R_e	Reynolds number
R_i	Net rate of change of species i $mol cm^{-3} s^{-1}$
S	Scale-up factor
T	Reactor temperature K
T_f	Feed temperature K
u	Velocity $m s^{-1}$
U	Overall heat transfer coefficient $W m^{-2} K^{-1}$
z	Incremental length m
ρ	Density $kg m^{-3}$

oxidation products such as COF_2 and CF_3COF were formed together with trace amounts of C_2F_4 and C_4F_8.

Trifluoromethyl hypofluorite was used as a chemical initiator for the gas-phase oxidation of HFP with molecular oxygen at 303, 313 and 323.4 K (dos Santos Afonso et al., 2000). The use of chemical initiators, instead of ultraviolet light, for the oxidation of fluoro-olefins can result in better control over the structure and relative molecular mass of the perfluoropolyethers that are formed (Romano et al., 2003). The major products included COF_2, CF_3COF and $CF_3OCF_2OCF_3COF$. Small amounts of CF_3OCF_2COF were also formed. Under the temperatures that were studied, no HFPO was formed.

An important recent investigation of the gas-phase epoxidation of HFP was conducted by Romano and Czarnowski (2004). The thermal gas-phase reaction between NO_2 and HFP was carried out using a 270 cm^3 quartz bulb reactor at temperatures of 413.1, 421.0 and 432.8 K. Only four compounds were observed in the work of Romano and Czarnowski (2004) viz., NO, HFPO, $CF_3CFNO_2CF_2NO$ and $CF_3COCF_2NO_2$. A HFPO yield of 63–89% was obtained.

No other significant study on the subject was carried out until the South African Nuclear Energy Corporation began investigations into the gas-phase synthesis during the latter part of the last decade.

It was found that higher pressures (30 bar) and lower temperatures (373–473 K) favoured the formation of oligomeric products (>60%), although some unquantified levels of HFPO were also observed in the gas products. Reactions carried out in ½ in. and ¼ in. stainless steel or copper tubes were sometimes found to proceed explosively, clear evidence of thermal excursions and a radical-based reaction mechanism.

The benefits of using capillary-type reactors in continuous flow oxidation processes has been suitably highlighted in the review by Gemoets et al. (2016). The technology offers enhanced heat and mass transfer, safe handling of hazardous oxidants and greater potential for scale-up. The synthesis of satisfactory quantities of HFPO was eventually accomplished by the authors using a 115 m long, small diameter (1/8 in.) copper tube in the form of a coil, operating within a narrow temperature range of 463–493 K and at a relatively low pressure of 4.5 bar (Lokhat et al., 2014). In fact, this was shown to be the lowest pressure at which appreciable amounts of HFPO were formed. Using surface response methodology and experimental data generated using a laboratory scale apparatus, optimal operating conditions were identified for the non-catalytic process which gave a maximum HFPO selectivity of 60% and a yield of 40% (Lokhat et al., 2014). In this study, the design and analysis of a 500 tpa continuous gas-phase process for the production of HFPO was carried out. The design was based on available laboratory data. The sensitivity of reactant and product exit stream concentrations to operating conditions were also analysed.

2. Reaction chemistry and kinetics

Several preliminary experiments were conducted using the high residence time flow-through apparatus constructed from small diameter copper tubing. At atmospheric pressure the reaction was found to require an initiation temperature well beyond the decomposition temperature of HFPO and the only products were acid fluorides (Lokhat et al., 2014). It was clear that thermal initiation alone was not sufficient for a usable process. In the literature almost all early work on the oxidation of HFP was conducted at very low temperatures (Shapovalov et al., 1984). It was found that the reaction mechanism is the same at low and intermediate temperatures, first an oligomer is formed and then gas phase products are obtained from the interaction of HFP and oxygen with the active oligomer (Shapovalov et al., 1984). The presence of the oligomer was a critical requirement. Literature evidence also showed that higher pressures favoured the formation of the oligomer and the walls of the reactor can catalyse its formation (Kartsov et al., 1978). Copper is a good hydrocarbon oligomerisation catalyst, so the small diameter copper tube was used to lay down a layer of oligomer that then functions as an activator for the epoxidation of HFP. Silver was also considered, due to its activity for epoxidation of HFP (Huang et al., 2006), but was ruled out due to the high cost. By combining the thermal and chemical initiation routes, a suitable process was developed for the production of HFPO.

The reaction is proposed to take place in two stages. First HFP and oxygen interact with the clean copper surface to form an oligomeric product. The oligomer is deposited on the inner surface of the reactor tube (cf. Fig. 1). This reaction proceeds via a surface redox mechanism involving copper oxides, i.e. it is catalysed by the surface of the reactor. The rate of oligomer formation gradually decreases as the inner surface is coated with the oligomeric film. In the second stage the gas-phase oxygen and oligomer combine to form an oxygen containing adduct which gives HFPO after interaction with HFP. The total oxidation of HFP also yields the acid fluoride byproducts COF_2 and CF_3COF whilst the thermal decomposition of HFPO further broadens the product distribution.

A simplified steady state reaction model comprising eight reactions was proposed based on this mechanism (Lokhat et al., 2016). The complete mechanism is shown in Fig. 2. Concentration based equilibrium constants were calculated using thermochemical data. Analysis of the results showed that only the HFPO decomposition reaction exhibits significant reversibility within the temperature range of 463–493 K (Lokhat et al., 2015). Rate data generated using the laboratory scale apparatus were used to identify the rate parameters in the model using non-constrained least squares minimisation (c.f. Table 1).

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