

Pyrolysis of PU/CFCs wastes

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Abstract

In the TGA experiments, the activation energy (25–30 kcal mol⁻¹) and preexponential constant ($\ln A = 34.6 \text{ h}^{-1}$) of the pyrolysis of PU/CFCs wastes were obtained. At least three discrete features at 328, 423, and 443 K are observed corresponding to desorption of CFC-141b from external, internal, and crosslink of the PU matrix, respectively. It indicates that pyrolysis of the PU polymer (at elevated temperatures) may not be effected by the presence of CFCs. In a single pass through the heated sodium oxalate bed (573 K) caused a nearly complete mineralization of CFC-141b. © 1998 Elsevier Science B.V.

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1. Introduction

In 1974, Molina and Rowland first reported that chlorofluorocarbons (CFCs) diffused into the stratosphere and broke down the ozone layer [1]. There is also a direct correlation between the increasing concentrations of CFCs in the atmosphere and the greenhouse effect [2]. Although CFCs as solvents and detergents have been highly restricted and replaced by hydrochlorofluorocarbons (HCFCs), CFCs still exist in the forms of refrigerants, heat-transfer media, propellants and various solvents in the electronic industry. Chlorofluorocarbons are among the most inert substances known. Many methods, such as incineration, catalytic decomposition and reaction with molten

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sodium, have been used to collect and dispose of the remaining stocks of CFCs [3–5]. These methods were reported to have technical or economical difficulties.

Polyurethane are produced originally from crude oil and can be thermally cracked into fuels or petrochemicals. However, pyrolysis of PU (polyurethane) wastes is complicated by the fact that the environmentally hazardous species, e.g. CFCs, are present and degradation of these macromolecules requires considerable amount of energy. Currently, no CFCs destruction facilities are now operating. Burdeniuc and Crabtree [6] note that the sodium oxalate reaction is very attractive for complete mineralization of CFCs in a noncorrosive operating condition. Thus, the main objective of the present work was to investigate the feasibility for mineralizing CFCs (using the sodium oxalate reaction) in the process of pyrolysis of PU wastes with product oils recycling. Degradation behavior of the PU polymer was also studied.

2. Experimental

A dual packed-bed reaction system was used to investigate the mineralization of CFCs released from pyrolysis of PU wastes. These reactors were enclosed in electrically heated jackets. Pyrolysis of PU wastes were conducted at 673–773 K in the flowing nitrogen (GHSV = 1000 h⁻¹). Vapors formed in the pyrolysis reactor passed through a packed bed of heated powdered sodium oxalate (Na₂C₂O₄) at 543–573 K. The condensates were then separated and collected in a knockout separator (300 ml). The noncondensable gases were sampled and analyzed by on-line FTIR spectroscopy and gas chromatography. Infrared spectra were recorded on a Digilab FTIR spectrometer (FTS-40) with fully computerized data storage and data handling capability. For all spectra reported, a 64-scan data accumulation was conducted at a resolution of 4 cm⁻¹. Preliminary kinetic parameters for pyrolysis of PU wastes were also calculated and measured using a thermal gravimetric analyzer (TGA). The TGA (model SDT 2960 and Thermal Analyst 2000, TA instruments) has a capability of determining weight loss and temperature difference simultaneously.

3. Results and discussion

The PU wastes represent a significant quantity of energy in terms of the energy consumed in processing petroleum. Recovery of part of this energy content in a form with the highest possible value, i.e. fuel gas and/or oil, would also reduce a growing environmental problem of these wastes. However, pyrolysis of PU wastes is relatively complicated by the fact that the environmentally hazardous species (e.g. CFCs) are released in the pyrolysis process. Thus, experiments were carried out to investigate the feasibility of the PU pyrolysis, and determined if destruction of the CFCs would be warranted.

Table 1
Kinetic parameters for pyrolysis of polyurethane

	E_a (kcal mol ⁻¹)	ln A (1 h ⁻¹)
PU/CFC-11 ^a	30.1	34.3
PU/HCFC-141b ^b	26.4	32.7
PU/CFCs	25.2	34.6
PU	25.0	28.9

^aCFC-11: trichlorofluoromethane (CCl₃F).

^bHCFC-141b: 1,1-dichloro-1-fluoroethane (CCl₂FCH₃), b indicates Cl and F atoms interacted with the same carbon atom.

Thermal degradation behaviors of the PU wastes were investigated. The derived kinetic parameters of the PU wastes obtained from the TGA experiments are summarized in Table 1. A single step process for thermal degradation of PU wastes were characterized with activation energy of 25–30 kcal mol⁻¹ and preexponential factor (ln A) of 34.6 h⁻¹, approximately. It seems that pyrolysis of the PU polymer (at elevated temperatures) may not be effected by the presence of CFCs. The CFC-11 (trichlorofluo-

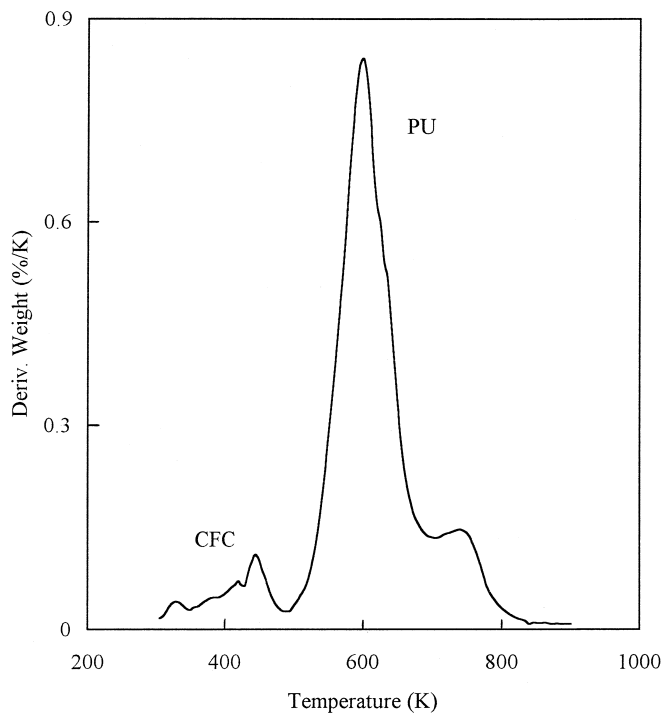


Fig. 1. Thermal gravimetric analysis of PU/HCFC-141b.

romethane, CCl_3F) and HCFC-141b (1,1-dichloro-1-fluoroethane, CCl_2FCH_3) are released in the very early stage of the temperature-programmed pyrolysis process (see Fig. 1). At least three discrete features at 328, 423, and 443 K are observed corresponding to desorption of CFC-141b from external, internal, and crosslink of the PU matrix, respectively. Note that it seems that pyrolysis of the PU polymer (at elevated temperatures) may not be effected by the presence of CFCs.

The chemical inertness of CFCs makes it very difficult to be destroyed effectively. Very few reactions of CFCs are known. It is generally believed that fluorides and chlorides can be abstracted by metal cations. Sodium oxalate seems a good choice [6]. In the early stage of the mineralization process, shown in Fig. 2, in a single pass through the sodium oxalate bed caused a nearly complete mineralization of CFC-141b. NaCl and NaF, that are not corrosive species, are formed in the residue. Note that as shown in Fig. 1, no tendency to give uncontrollable exotherms for mineralization of excessive CFC-141b is observed.

A pyrolysis temperature course for the sodium oxalate reaction with CFC-141b released from PU wastes is shown in Fig. 3. As expected, the reaction also produces CO_2 . It should be noted that any oxalate salt remaining can be further decomposed to the carbonate at elevated temperatures (> 623 K). After burning out the element carbon, the NaF, a common fluorine source, can be recycled. Moreover, when the temperature of the sodium oxalate bed is controlled at ~ 500 K to prevent excessive mineralization

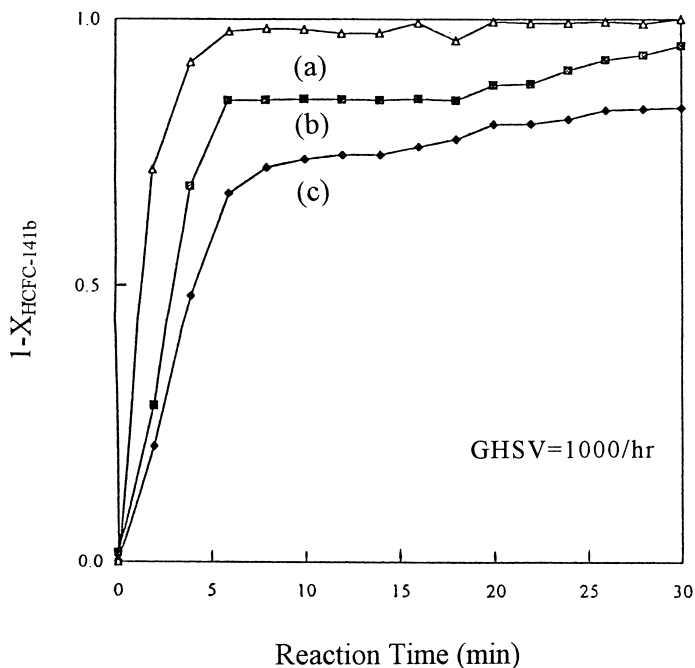


Fig. 2. Mineralization of HCFC-141b with $\text{Na}_2\text{C}_2\text{O}_4$ in a fixed-bed ($\text{GHSV} = 1000 \text{ h}^{-1}$) at (a) 543 K, (b) 563 K, and (c) 573 K.

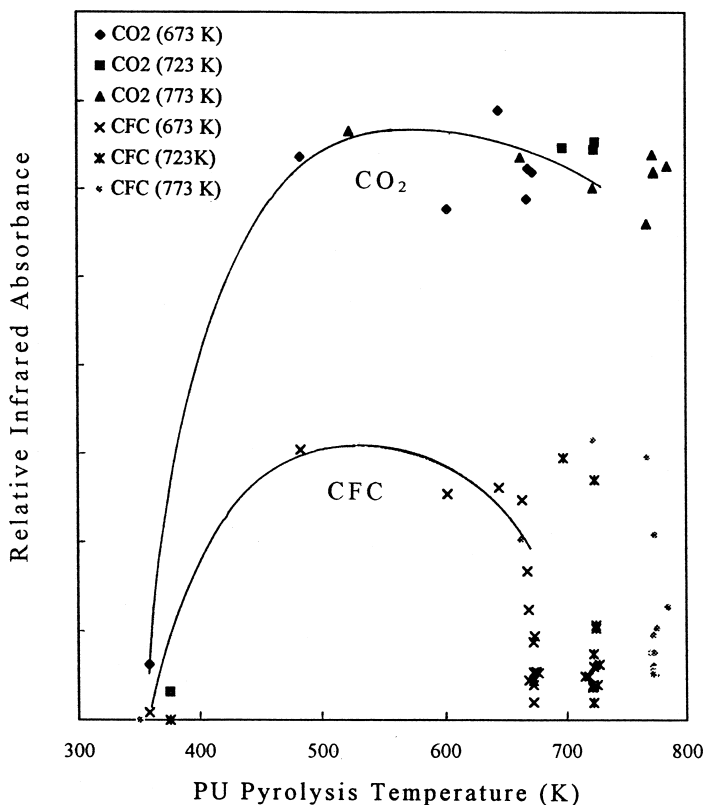


Fig. 3. Formation of CO₂ from mineralization of HCFC-141b released from PU pyrolysis.

(Fig. 3), defluorination is no longer complete [6]. Thus, a possible reaction path may be directed for CFCs selectively converted to less toxic HCFCs via the sodium oxalate reaction routes.

4. Conclusions

The derived activation energy (E_a) and preexponential constant ($\ln A$) of the pyrolysis of PU/CFCs wastes using the TGA technique are 25–30 kcal mol⁻¹ and 34.6 h⁻¹, respectively. The CFCs are released from the PU waste in the very early stage of the temperature-programmed pyrolysis process. However, the pyrolysis of the PU polymer may not be effected by the presence of CFCs. In a single pass through the heated sodium oxalate bed (563 K) caused a nearly complete mineralization of CFC-141b. The solid residue may be handled easily by elevating the reaction temperatures (> 623 K), the oxalate salt remaining can be further decomposed to the carbonate. NaF can be recycled. At 500 K, a possible reaction path may be directed for CFCs selectively converted to less toxic HCFCs via the sodium oxalate reaction routes.

Acknowledgements

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