

PYROLYSIS KINETICS OF SPENT LOW-LEVEL RADIOACTIVE RESIN

RADIOACTIVE WASTE
MANAGEMENT
AND DISPOSAL

TECHNICAL NOTE

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KEYWORDS: LLRA resin, cation exchange resin, kinetic

Received April 23, 2001

Accepted for Publication November 18, 2001

Spent low-level radioactive (LLRA) cation ion exchange resins (consisting of base copolymers of styrene and divinyl benzene and sulfonic acid) are difficult to treat effectively by conventional cement-solidification methods. Pyrolysis of the spent LLRA resin has been recognized to be very effective in reducing the volume and mass of the waste. Experimentally, we found by the thermogravimetric analysis (TGA) method that the activation energy for the pyrolysis of an LLRA resin was 319.2 kJ/mol. The reaction order and pre-exponential factor were 0.61 and $1.1 \times 10^{20} \text{ s}^{-1}$, respectively. Note that during the pyrolysis, ~50% of the SO_4^{2-} species in the resin was decomposed to SO_2 at 673 to 873 K. At high temperatures (>873 K), most of the aromatics of the resin were also thermally cracked.

I. INTRODUCTION

Ion exchange resins are widely used in the filter-demineralization operation units of nuclear power plants to remove radioactive pollutants.^{1,2} Instead of regeneration, the spent cation exchange resins are stored in high-integrity containers. These resins generally consist of base copolymers of styrene and divinyl benzene (DVB) and sulfonic acid. Because of lack of a proper adhesion between the cement binder and the resin beads, treatments of the resin wastes by conventional cement-solidification methods were not very effective. Because of the long period of operation of nuclear power plants,

it is inevitable that expansion of the storage sites or reduction of the volume of wastes will be needed.

Pyrolysis has been found to be very useful in the reduction of the volume/mass of wastes with minimum gas emissions.³⁻⁸ Mason et al.⁸ also provided the pyrolysis/steam reforming technologies for volume and weight reduction and stabilization of low-level radioactive (LLRA) and mixed wastes. Thermogravimetric analysis (TGA) has been widely used to investigate the pyrolysis kinetics of polymers. Reaction kinetic parameters (such as activation energy, the pre-exponential factor, and reaction order) can be derived from the treatment of the TGA data by the classical laws of kinetics.⁹⁻¹⁹ Detailed descriptions of these methods have been given by Reich and Levi,¹⁵ Friedman,¹⁷ and Petrovic and Zavargo.¹⁸

The apparent activation energy of 60 to 200 kJ mol⁻¹ and maximum degradation rate of 0.0024 s⁻¹ (685 K) in the pyrolysis of polystyrene was determined by the TGA method.¹⁶ Anderson and Freeman¹³ found that the activation energies for the pyrolysis of polystyrene at the first ($T < 643 \text{ K}$) and second stages ($T > 643 \text{ K}$) were ~192 and 251 kJ/mol, respectively. Matsuda et al.^{20,21} found that the SO_4^{2-} species in the cation resin could increase the thermal stability of the polymers by forming sulfonyl bridges in the pyrolysis. However, pyrolysis kinetics of spent LLRA resins have seldom been reported in the literature. Thus, the objective of this work was to study the pyrolysis kinetics of LLRA exchange resin by the TGA method. Pyrolysis products were also monitored by on-line Fourier Transform Infrared (FTIR) spectroscopy.

II. EXPERIMENTAL

The resin sample was provided by the Taiwan nuclear power company. The physical and chemical properties of the

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TABLE I
Physical and Chemical Properties of the Powdex Resin

Combustibles (wt%)	42.0
Carbon	17.4
Hydrogen	2.6
Oxygen	17.0
Nitrogen	<0.01
Sulfur	5.0
Chlorine	<0.01
Moisture (wt%)	42.0
Ash (wt%)	16.0
Heating values (kcal/g)	50 to 85
Total capacity (milli-equivalent/g dry resin)	4.5
Thermal stability (K)	423
Surface area (m ² /g)	30 to 40
Porosity (%)	30 to 35
Particle size	20 to 50 mesh (wet)

resin^a are shown in Table I. The cation ion exchange resins were dried at 343 K to maintain water content of 5 to 10% before the TGA experiments. The resin consists of styrene-DVB copolymer and sulfonic acid groups. Pyrolysis kinetics of the resins were studied on a thermogravimetric analyzer.^b Product gases were analyzed by on-line FTIR spectroscopy. Infrared spectra were recorded on an FTIR spectrometer^c with fully computerized data storage and handling capability. For all spectra reported, a 64-scan data accumulation was conducted at a resolution of 4 cm⁻¹. The organic structure of the resin during pyrolysis was also studied by diffuse reflectance FTIR (DRIFT) spectroscopy. About 10 to 15 mg of the resin sample was used in the flowing nitrogen gas (30 ml/min) at elevated temperatures (303 to 723 K).

In the TGA experiments, the resins were heated from 303 to 1173 K at a heating rate of 4, 5, or 8 K/min in high-purity nitrogen (99.999%) at a flow rate of 100 ml/min. The calibration procedures for the TGA baseline and temperatures were performed once a month. Typically, 5 to 10 mg of sample and aluminum oxide (reference) were used in all TGA experiments.

III. RESULTS AND DISCUSSION

The pyrolysis kinetics for the LLRA resin with the characteristics of high moisture (42%), sulfur (5.0%), and ash (16.0%) are relatively complicated. In order to determine the structural changes during pyrolysis, infrared spectra of the resins pyrolyzed at 373 to 673 K were studied by in situ DRIFT spectroscopy. Figure 1 shows that pyrolysis of the resin was not very effective until 673 K. The organic structure of the resin was not perturbed significantly while dehydration was predominant at ~473 K (the infrared absorbance between 3200 and 3700 cm⁻¹ generally contributed to the moisture). A very small amount of aromatics in the resins was pyrolyzed at 473 to 673 K.

^aThe resin was manufactured by the Dow Chemical Company.

^bThe thermogravimetric analyzer was model SDT 2960 from TA Instruments.

^cThe FTIR spectrometer was model FTS 40.

In order to obtain global kinetic data, the resin was heated from 303 to 1173 K at a heating rate of 4, 5, or 8 K/min under flowing nitrogen (100 ml/min). The gaseous products were monitored by on-line FTIR spectroscopy. The resin was dehydrated at 378 K to reduce the possible steam reforming reactions involved in the pyrolysis process. A typical TGA curve obtained from the pyrolysis of the resin is shown in Fig. 2. The main degradation reactions of resins occurred at ~700 and 950 K.

Figure 3 shows the temperature dependence for the infrared absorbance of gases (alkanes, alkenes, and SO₂) yielded from the pyrolysis of the resin. We monitored the infrared features at 2800 to 3000, 1600 to 1700, and 1300 to 1400 cm⁻¹ as indicators of alkanes, alkenes, and SO₂, respectively. Figure 1 (by DRIFTS) shows a reduction of aliphatics in the resin upon raising the temperature to 673 K. Figure 3a also shows that the gaseous alkanes were generated in the period of pyrolysis of the resin at $T > 673$ K. The cross-linkings of the resin (consisting of base copolymers of styrene and DVB) might be, to some extent, cracked and yield gaseous alkanes as well as alkenes. About 50% of the SO₄²⁻ species was decomposed to SO₂ at 673 to 873 K. However, at high temperatures (> 873 K), the decomposition of aromatics in the resin occurred and yielded alkenes and alkanes. The sulfonyl bridges were decomposed with yields of SO₂ and CO. Matsuda et al.^{20,21} also reported a similar observation. The residue in the pyrolysis of the resin was ~30%.

Kinetic parameters (such as activation energy and the pre-exponential factor) for pyrolysis of the resins were numerically calculated from TGA weight loss data at different heating rates using the modified Freeman algorithm.¹⁷ Fine resins (300 mesh) were used in the kinetic studies to reduce ash layer diffusion control problems. The overall rate equation of the conversion factor can be expressed in the Arrhenius relation:

$$\frac{dx}{dt} = A \exp(-Ea/RT)(1-x)^n$$

and

$$x = \frac{w_0 - w}{w_0 - w_f}$$

where

t = time (s)

A = pre-exponential factor (s⁻¹)

Ea = activation energy (J/mol)

T = reaction temperature (K)

R = universal gas constant (8.314 J/mol·K)

w = mass of the sample at time t

w_0, w_f = initial and final (or residual) masses of the sample, respectively

x = conversions

n = reaction for the unreacted resin.

In Fig. 2, a maximum weight loss of the resin occurred at 700 K ($w/w_0 = 0.81$ to 0.73). The average activation energy

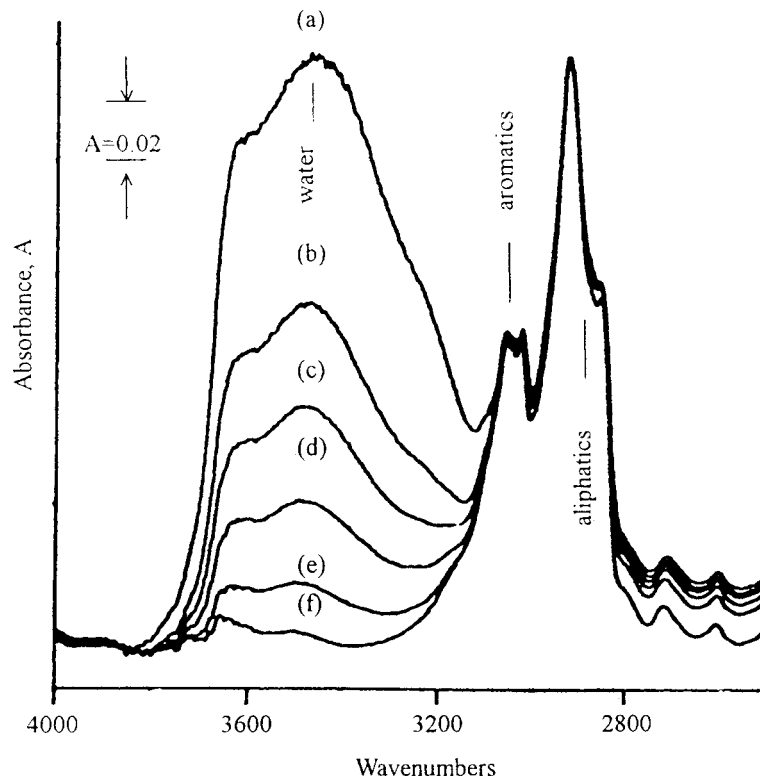


Fig. 1. DRIFT spectra of the resin during pyrolysis at (a) 373, (b) 473, (c) 523, (d) 573, (e) 623, and (f) 673 K.

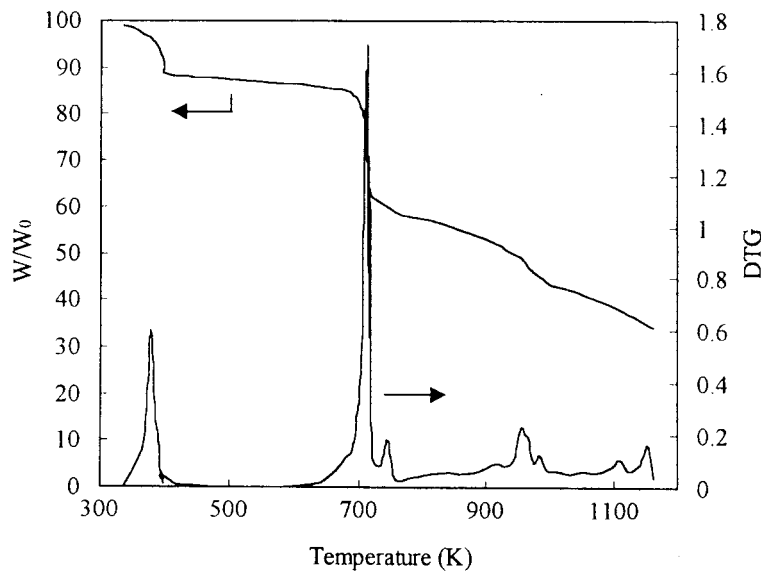


Fig. 2. TGA for pyrolysis of the resin.

(E_a) for pyrolysis of the resin was 319.2 kJ/mol. The reaction order and the pre-exponential factor for pyrolysis of resin were 0.61 and $1.1 \times 10^{20} \text{ s}^{-1}$, respectively. The overall kinetic equation can be expressed as $dx/dt = 1.1 \times 10^{20} \exp(-319200/RT)(1-x)^{0.61}$ (at 717 to 736 K). We also used the non-

parametric Mann-Whitney U test to compare differences between the experimental and predictable data. Figure 4 shows that the agreement [probability (p) = 0.95; coefficient of determination (r^2) = 0.99] between the experiment data and the fitting of the derived equation is quite good.

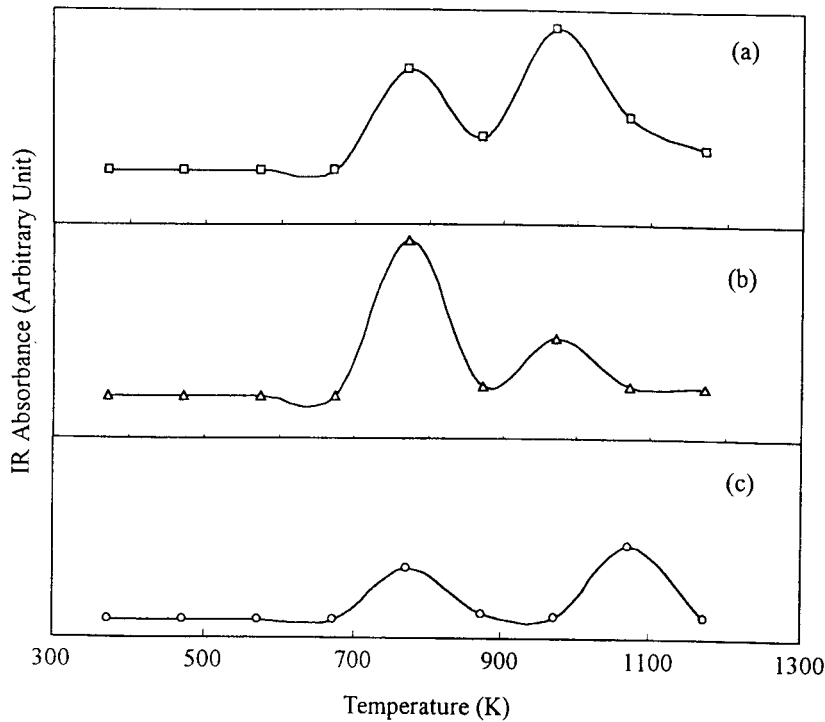


Fig. 3. Temperature dependence for the infrared absorbance of product gases (a) alkanes, (b) alkenes, and (c) SO₂ during the pyrolysis of the resin.

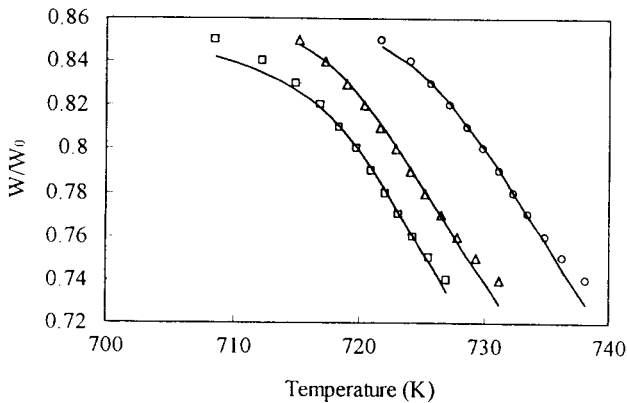


Fig. 4. The Arrhenius plots for pyrolysis of resin at a heating rate of □ 4, △ 5, and ○ 8 K/min. The solid line denotes the fitting of the pyrolysis kinetic equation [$dx/dt = 1.1 \times 10^{20} \exp(-319200/RT)(1-x)^{0.61}$].

IV. CONCLUSIONS

During the temperature programmed pyrolysis of the LLRA resins, the main decomposition reactions occurred at ~700 and 950 K. At 673 to 873 K, mainly alkanes and alkenes were yielded during pyrolysis. Some of the functional sulfonic acid groups were decomposed to SO₂. However, at higher temperature (>873 K), aromatics might involve cracking and form alkenes and alkanes. At 973 to 1273 K, the sulfonyl bridges

SO₄²⁻ species in the resin was decomposed to SO₂. The average activation energy for pyrolysis of the resin was 319.2 Kcal/mol. The overall kinetic equation can be expressed as $dx/dt = 1.1 \times 10^{20} \exp(-319200/RT)(1-x)^{0.61}$.

ACKNOWLEDGMENT

Financial support by the National Science Council, Taiwan, is gratefully acknowledged.

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