



Nitrogenous emissions from the catalytic pyrolysis of waste rigid polyurethane foam



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ABSTRACT

In this paper, we focus on the release of nitrogenous species from waste rigid polyurethane foam (WRPUF) during thermal conversion. Pyrolysis of WRPUF was experimentally studied to determine the effects of four operational parameters, temperature, particle size, sweeping gas flow rate and catalyst supplied, on the partitioning of the fuel nitrogen among nitrogen species. Experiments were performed using a bench-scale fixed-bed reactor and the important findings of this research include the following. (1) Five nitrogen-containing species, N₂, NH₃, HCN, NO₂ and NO, were found in gas-phase product and N₂ is dominant. (2) Tar N is retained as heterocyclic compounds, nitrile, or amine functional groups bonded to aromatic rings, and 4-[(4-aminophenyl)methyl]aniline is the main nitrogen-containing compound. (3) CaO has a good performance on increasing N₂ production and decreasing NO_x precursors. (4) The sweeping gas (Ar) flow rate and catalyst supplied were the most important parameters on affecting the N-containing species release. Whatever gaseous nitrogen, tar N or char N, they were significantly affected by sweeping gas flow rate, catalyst supplied or their interaction.

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1. Introduction

Polyurethanes are derived from oil and therefore possess a recoverable energy value that, in some cases, is comparable to coal and slightly less than that of fuel oil. Waste-to-energy and other thermal processing activities involving gasification, pyrolysis, and two-stage combustion (removing problematic components in a first stage) can reduce the volume of solid waste as well as our dependence on fossil fuels [1].

Rigid polyurethane foams, one of the most common polyurethanes, are used as encapsulants to isolate and support thermally sensitive components within weapon systems [2]. Worldwide, more and more attention is being focused on their recycling due to on-going changes in both regulatory and environmental issues. A pyrolysis process is an attractive technology to convert solid waste to gaseous products, which can be used in power generation. Several research groups have studied the pyrolysis process of polyurethane [3–5]. One main drawback of this technology is the high content of nitrogen in WRPUF (5–8%, 1.8–150 times higher than that in common biomass feedstocks [6]) as the fuel-bound nitrogen (fuel N) reacts during the thermochemical conversion to

form various toxic products e.g. ammonia (NH₃), hydrogen cyanide (HCN), NO_x and some liquid organic nitrogenated compounds (tar N) [7]. NH₃ and HCN are considered as NO_x precursors [8–10], and NO_x are contributors to photochemical smog and acid rain. Among all species in gas-phase evolved from fuel N during WRPUF pyrolysis, N₂ is the only desirable species. N₂ is environmentally friendly product, while others are contaminants and should be minimized.

Therefore, special attention should be dedicated to understand the formation and distribution of nitrogen-containing products in order to minimize the content of NH₃, HCN, and tar N in volatile nitrogen (vol N), and maximize N₂ yield. It is thus important to scrutinize the evolution of all of the main nitrogen-containing products to check if a given decrease in the amount of one of them could produce an increase of the above-mentioned contaminant compounds. To our best knowledge, no research has been reported on nitrogen emission during the pyrolysis of WRPUF. There is some research on nitrogen emission in pyrolysis of biomass (and coal), and there are some similarities between the products from thermal degradation of biomass and polyurethane. Zhou and co-workers [6] investigated the effects of operational parameters and nitrogen content of six biomass feedstocks on the partitioning of fuel-bound nitrogen among nitrogenous gas species (N₂, NH₃, and HCN) and the nitrogen remained in char. And some researchers studied the production of aromatic nitrogen-containing compounds included in tar from different biomass feedstocks and peat [7,11,12].

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Table 1
Proximate and ultimate analyses of WRPUF.

Proximate analysis (wt%)			Ultimate analysis (wt%)				
Moisture	Volatiles	Fixed carbon	Ash	C	H	N	O (by difference)
3.0	83.9	11.9	1.2	66.3	8.6	4.7	20.4

Meanwhile, other researchers focused on testing/developing catalytic materials able to catalyze the decomposition of tar N, HCN and NH₃ into N₂ [13–15]. All of these works have shown that there are many factors that influence the production and distribution of the nitrogen-containing products.

Taking into account the nitrogen contained in the main gas, liquid, and solid nitrogen-containing products, our present work is to investigate the nitrogen evolution during the pyrolysis of WRPUF and study the influence of selected variables, such as temperature, particle size, sweeping gas flow rate and catalyst supplied.

2. Experimental

2.1. Materials and chemicals

WRPUF was obtained from Shanghai Senlan Environmental Protection Science & Technology Co. Ltd. Ultimate analyses of WRPUF was analyzed by CHNS analyzer. Proximate analyses of WRPUF was analyzed by the method of ISO5068:1983(E), ISO562:1981(E) and ISO1171:1981(E). The analysis data were shown in Table 1. From Table 1, it can be seen that content of volatiles matter is 83.9%, while fixed carbon is 11.9%, which indicate that WRPUF is extremely flammable, with high calorific value. The samples were crushed and sieved to provide two kinds of feed sample size: one ranging from 2.80 mm to 4.75 mm, the other from 0.00 mm to 1.18 mm.

Four Catalysts (purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were of analytical grade and were crushed into powder before used in each experimental test: an alkaline earth metal oxide (CaO), an alkaline earth metal carbonate (CaCO₃) and two alkaline earth metal hydroxide (NaOH and Ca(OH)₂).

2.2. Bench-scale facility

All of the experiments performed in this work were carried out at atmospheric pressure in a bench-scale updraft fixed-bed reactor system which consists of air-blower, tubular fixed-bed reactor, feeding device, electric heater, temperature controller, char collector, condenser and liquid product collector. The system, as indicated in Fig. 1, was heated by an electric furnace and has a maximum operating temperature of 1200 °C. The reactor was made of 316 stainless tubing, 1.95 m long with an i.d. of 0.10 m. The reactor is coupled to a gas cleaning system, which is composed by two ice-water condensers connected in series to separate tar from noncondensable gas.

2.3. Recovery and quantification of nitrogen compounds

The quantification of the nitrogen-containing products obtained during the pyrolysis process was carried out as follows.

- (1) Nitrogen contained in char was measured using a CHNS analyzer (EA 3000, Euro Vektor Ltd.).
- (2) N₂ was analyzed by 3 m 5A Molecular Sieve column (GC9800, Shanghai Kechuang Chromatograph Instrument Co., Ltd., TCD detector, argon as carrier gas, flow rate was 40 ml/min, column temperature was kept at 120 °C for 15 min), and identified by comparison with standard substances.

- (3) The concentration of NO and NO₂ were measured by chemiluminescence NO–NO₂–NO_x analyzer (42i-TL, High Level, Thermo Electron Corporation).

- (4) The contents of NH₃ and HCN in the gas were determined by measuring the retained amounts in absorbing solutions. The NH₃ sampling train consisted of four impingers arranged in series. The second and third bubblers were filled with 40 mL of deionized water used to trap ammonia. The remaining two impingers were kept empty: the first one was connected in reverse orientation for preventing reverse gas flow, and the last one was placed in an ice-water bath in order to remove remaining moisture. The arrangement of the HCN sampling train was exactly the same as that described above for NH₃. In this case, the HCN was retained in two impingers filled with 40 ml of 0.1 M NaOH. The overall volume flow during each sampling campaign was measured by means of volume flow meters. NH₄⁺ and CN⁻ absorbed in solutions were then quantified with a Dionex 500 ion chromatograph equipped using an ED 40 electrochemical detector. The quantification of NH₃ was carried out with electrical conductivity detection following separation in a Dionex CS12 column with 0.02 M CH₃SO₃H as eluent. HCN was quantified with amperometric detection using a silver electrode following separation in a Dionex AS7 column with an aqueous solution of 0.1 M NaOH, 0.7 M CH₃COONa and 0.5% H₂NCH₂CH₂NH₂ as eluent.

- (5) Nitrogen-containing species in tar were detected following a GC/MS analytical method in an Agilent 7890 gas chromatograph, coupled to an Agilent 5957C MS Engine with an ion source of electron impact at 70 eV. A sample of the mixture formed by tar, water, and 2-propanol was dried using anhydrous sodium sulfate and filtered, and then injected into the gas chromatograph under splitless conditions. The gas chromatograph was fitted with a 30 m × 320 μm capillary column (HP-5 MS) coated with a 0.25 μm film of 5% phenylmethylsiloxane. Helium was employed as a carrier gas at a constant flow of 0.19 m s⁻¹. An initial oven temperature of 50 °C and a ramp rate of 4 °C min⁻¹ were implemented to reach a final column temperature of 250 °C. This temperature was maintained for 10 min. The injector and detector temperatures were 250 and 275 °C, respectively. Data were collected in the full-scan mode with mass to charge (*m/z*) ratios from 10 to 400 and a solvent delay of 1 min was used. The chromatographic peaks were identified from the NIST mass spectral data library. The applied method is based on a semiquantitative analysis assuming the same response factor (1.0) for all species detected. It must be remarked that the adopted procedure to measure N-tar is only suitable for comparative purposes.

2.4. Experimental design

A series of parallel experiments with different common catalysts were conducted to find the best catalyst to have minimum amount of NH₃, HCN, and N-tar in vol N, and preferably maximum amount of N₂ yield. The detailed conditions are as follows: temperature is 1000 °C, particle size is 2.80–4.75 mm, sweeping gas is argon and the flow rate is 240 L/h, catalyst supplied is 10 wt%. Afterwards, the influence of experimental conditions was studied experimentally using a factorial design, which is suitable for studying the influence of the experimental variables and also the influence of their interactions [16,17]. In terms of experimental design, the experimental variables studied are called factors and the results obtained are called response variables. The chosen factors are shown in Table 2.

In the present study, a full two level factorial design was selected. This means that 2^{*n*} runs were conducted, where *n* indicates the number of factors studied. For four factors considered, this design involves sixteen experiments. Four replicates in the center

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