



TG-FTIR study on urea-formaldehyde resin residue during pyrolysis and combustion

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ABSTRACT

The pyrolysis and combustion characteristics of urea-formaldehyde resin (UFR) residue were investigated by using thermogravimetric analysis, coupled with Fourier transform infrared spectroscopy (TG-FTIR). It is indicated that the pyrolysis process can be subdivided into three stages: drying the sample, fast thermal decomposition and further cracking process. The total weight loss of 90 wt.% at 950 °C is found in pyrolysis, while 74 wt.% of the original mass lost in the second stage is between 195 °C and 430 °C. The emissions of carbon dioxide, isocyanic acid, ammonia, hydrocyanic acid and carbon monoxide are identified in UFR residue pyrolysis, moreover, isocyanic acid emitted at low temperature is found as the most important nitrogen-containing gaseous product in UFR residue pyrolysis, and there is a large amount of hydrocyanic acid emitted at high temperature. The similar TG and emission characteristics as the first two stages during pyrolysis are found in UFR residue combustion at low temperature. The combustion process almost finishes at 600 °C; moreover, carbon dioxide and water are identified as the main gaseous products at high temperature. It is indicated that the UFR residue should be pyrolyzed at low temperature to remove the initial nitrogen, and the gaseous products during pyrolysis should be burnt in high temperature furnace under oxygen-rich conditions for pollutant controlling.

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1. Introduction

Hazardous wastes must be disposed in safe manner because of their adverse and chronic effects on environment. The toxicity and hazardous nature of organic hazardous wastes can be destroyed by thermal disposal, and incineration has been well recognized as the most available technology for thermal disposal of hazardous wastes [1], but a large amount of pollutant emission will be caused by waste incineration [2,3], and the cost for flue gas purification is high in order to satisfy the discharge standard for modern incinerators. The hazardous waste management in China has been strengthened in the last two decades [4]. The generation of industrial hazardous waste (IHW) reached 10.84 million tons in 2006, of which 52.2 wt.% was recycled and 26.7 wt.% was securely disposed, while the rest part of the total IHW in China was stored for further disposal. Organic resin residue was identified as hazardous waste in the latest China's National Catalogue of Hazardous Wastes enacted in 2008. A large amount of urea-formaldehyde resin (UFR) residues are generated in China, and it is necessary to safely dispose these wastes.

The difference between pyrolysis and combustion for organic compounds was investigated previously [5], and pyrolysis products

from organic wastes can be used as fuel and chemical materials, which is free of hazardous metals and chlorine content [6], therefore, pyrolysis is an alternative treatment technology for organic hazardous wastes. Temperature is the most important parameter for thermal degradation [7–9], and 550 °C is enough for organic matter pyrolysis [10–12], furthermore, most of mass loss occurs in 200–500 °C [13–15]. The pyrolysis process of organic matters can be subdivided into several stages: moisture evaporation at low temperature; degradation of organic structures (for most materials, this temperature range constitutes up to 95 wt.% of total degradation [16,17]); further cracking process of the residues [18,19] and higher temperature degradation of inorganic materials [20]. Most of gaseous products are emitted in the second stage. The studies of Girods et al. [21,22] show that 70 wt.% of the initial nitrogen in urea-formaldehyde can be removed during low temperature pyrolysis. The composition of the pyrolysis gas from organic wastes is rich in light hydrocarbons, H₂O, CO₂ and CO [10,11,19], and the content of CO₂ decreases with temperature, while the emission trends of other species varied on the reverse direction [23]. The interaction between different materials during pyrolysis is still unclear, and thermal decomposition can also be effected by other factors such as pretreatments, activators and pressure [8,24–26]. So it is necessary to study the thermal characteristics of single hazardous waste only.

The two-stage thermal treatment of pyrolysis-combustion technology is successfully applied to a disposal center for hazardous

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Table 1
Ultimate and proximate analysis of the UFR residue sample.

	Concentration (wt.%)
<i>Ultimate analysis</i>	
C	31.74
H	4.12
O	27.94
N	36.1
S	0.1
<i>Proximate analysis</i>	
Moisture	2.35
Ash	0.42
Volatiles	96.11
Fixed carbon	1.12
Higher heating value (MJ kg ⁻¹)	16.5

wastes in Zhejiang, China. After pyrolyzed in the first furnace at low temperature, the gaseous products of the wastes are introduced into the second furnace for high temperature combustion. The emission characteristics of pyrolysis gas from organic wastes therefore have the crucial effect on the combustion process in the secondary combustion chamber.

A large amount of UFR residues is generated in China every year, and most of them are kept in storage or disposed blended with other hazardous wastes, which cause severe pollution or potential safety hazard for environment. With increasing number of disposal centers for hazardous wastes being built in China at present, it is necessary to study the thermal characteristics of these hazardous wastes to gain the optimal operational parameter for thermal disposal. The pyrolysis characteristics and the gas evolution of UFR residue were investigated by using TG-FTIR. Nitrogen is used as the carrier gas during pyrolysis, and the weight loss with temperature is recorded automatically. The combustion characteristics at air atmosphere are also studied, because incineration is the most important technology for organic waste disposal currently, and the difference between pyrolysis and combustion for UFR residue is analyzed in this paper.

2. Experiments

2.1. Material

UFR residue used in this study is a chemical-waste originated from an organic resin factory in Zhejiang, China. After being dried in an oven at 105 °C for 3 h, the original materials were crushed and pulverized into a size of lower than 0.2 mm for further analysis. Preliminary analysis (moisture, ash, volatile content and fixed carbon of UFR residue sample) and detailed analysis of the combustible fraction (in weight-by-weight percentage) are shown in Table 1. About 10 mg sample material was used in TG-FTIR analysis.

2.2. Method

A Nicolet Nexus 670 spectrometer and a Mettler Toledo TGA/SDTA851^e thermo analyzer are coupled by a Thermo-Nicolet TGA special connector. The stainless steel transfer pipe and gas cell (20 cm optical path length) were heated at 180 °C, to minimize secondary reactions. Nitrogen was used as carrier gas because of its inertia with a flow rate of 60 ml min⁻¹ during pyrolysis; the air was used as oxidant during combustion at the same flow rate. A medium-sized alumina crucible of 70 μl was used as a sample container.

In our study for the pyrolysis and combustion of other organic wastes at different heating rates of 10, 30 and 50 °C min⁻¹, it was found that the intensity of the thermal decomposition and the emission of gaseous products were slowed down at lower heating rates,

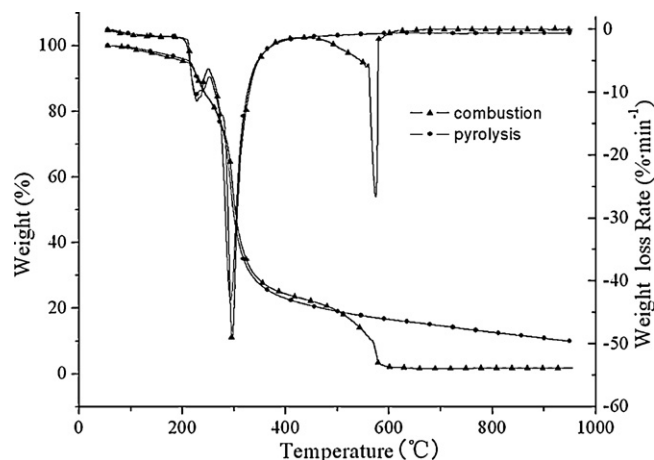


Fig. 1. TG/DTG profiles for the pyrolysis and combustion of UFR residue.

but the similar components of gaseous products and evolution with temperature at different heating rates were observed in those studies. So the heating rate of 30 °C min⁻¹ was adopted for thermal decomposition of UFR residue, with a final temperature of 950 °C starting from 50 °C. Resolution in FTIR was set at 4 cm⁻¹, spectrum scan frequency at 20 times per minute, and the spectral region at 4000–400 cm⁻¹.

3. Results and discussion

3.1. TG data analysis

The TG/DTG profiles for UFR residue as a function of temperature at the heating rate of 30 °C min⁻¹ during pyrolysis and combustion are shown in Fig. 1. The pyrolysis process can be subdivided into three stages based on the DTG profile. The first stage is a weight loss for drying the sample (below 195 °C). Surface moisture and inherent moisture are emitted in this stage, while few mass lost in this stage because of the low moisture content of UFR residue. The second stage is fast thermal decomposition for UFR residue between 195 °C and 430 °C; most of the weight loss (about 74 wt.% of the total weight of original samples) occurs in this stage. There are two peaks of the DTG curve (weight loss rate) in this stage: the maximum weight loss rate occurred at 294 °C, while the temperature at secondary peak is 225 °C. For organic wastes, the bond rupture is the primary cause for mass loss in thermal degradation, so there are two crucial reactions of bond ruptures at low temperature, and the second one is foremost for UFR residue thermal degradation. The last stage in UFR residue pyrolysis is further cracking process of the residues in a wide temperature range, from 430 °C to the end of this experiment (950 °C); about 10 wt.% of the total weight loss at a lower rate in this stage, and the total weight loss of 90 wt.% was discovered at 950 °C during pyrolysis. It was shown that 450 °C is enough for pyrolysis disposal of this waste, while the solid products in pyrolysis can be used as raw material for some industries, but incineration is the simplest and reasonable method to dispose those solid products.

The similar characteristics as pyrolysis during UFR residue combustion at low temperature are confirmed in this experiment, the DTG curves of pyrolysis and combustion perfectly coincide at low temperature stage, and 73 wt.% of the total weight lost at the temperature ranges between 195 °C and 430 °C. The complete combustion of solid product finished quickly around 600 °C, which is quite different from the pyrolysis process. The combustion of the UFR residue almost finishes after the weight loss peak between 500 °C and 600 °C, and about 20 wt.% of the original sample weight

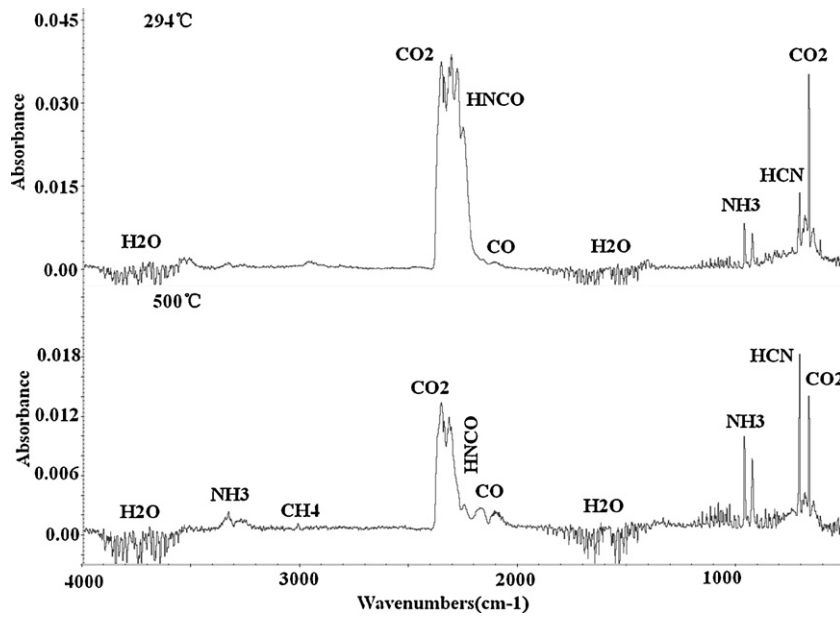


Fig. 2. FTIR spectrogram for gaseous products during UFR residue pyrolysis at 294 °C and 500 °C.

lost in this stage. The total weight loss of 99 wt.% is discovered at 950 °C in UFR residue combustion. There are no other solid products except ash content for UFR residue combustion at high temperature in oxidizing atmosphere. The comprehensive analysis for combustion and pyrolysis shows that almost all the solid products generated from UFR residue pyrolysis can be burnt at high temperature, and 650 °C is enough for complete combustion of UFR residue. It is indicated that the characteristics of UFR residue combustion are quite different from the pyrolysis at high temperature, furthermore, the comparability for pyrolysis and combustion of UFR residue agrees the characteristics of other organic matters in previous studies.

3.2. Kinetic parameters of pyrolysis and combustion of UFR residue

The kinetics of pyrolysis and combustion was largely described by first order Arrhenius law [27]. In this paper, it is assumed that the process of combustion was subdivided into two steps (low and high temperature), while only one step for the pyrolysis process at low temperature, and each step was governed by first order Arrhenius law. The mass loss fraction is defined as

$$\alpha = \frac{M_{s0} - M_s}{M_{s0} - M_{s\infty}} \quad (1)$$

where M_{s0} is initial mass, M_s is the mass during thermal degradation process, $M_{s\infty}$ is the final mass when experiment finished.

The kinetics of pyrolysis and combustion could be described as

$$\frac{d\alpha}{dT} = kf(\alpha) \quad (2)$$

where k is constant of reaction rate, T is thermodynamic temperature (K), $f(\alpha)$ is the differential form of kinetic mechanism function,

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (2a)$$

$$f(\alpha) = 1 - \alpha \quad (2b)$$

where R is universal gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), E is activation energy, A is a pre-exponential factor,

Eq. (2a) could be written as

$$\frac{d\alpha}{f(\alpha)} = \frac{k}{\beta} dT \quad (3)$$

where β is heating rate,

An integration function of Eq. (3) is shown below

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

Eq. (4) is integrated by using Coats–Redfern method [28]:

$$\ln \frac{g(\alpha)}{T^2} = \ln \left\{ \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] \right\} - \frac{E}{RT} \quad (5a)$$

where

$$g(\alpha) = -\ln(1 - \alpha) \quad (5b)$$

where $g(\alpha)$ is the kinetic mechanism function in integral form.

As the term of $2RT/E$ can be neglected since it is much less than 1, Eq. (5a) could be simplified as

$$\ln \frac{g(\alpha)}{T^2} = \ln \left(\frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (6)$$

The term of $\ln(g(\alpha)/T^2)$ varies linearly with $1/T$ at a slope $-E/R$. Meanwhile, the intercept of the line with y -axis is related to the

Table 2

Activation energy and Arrhenius pre-exponential factors from the pyrolysis and combustion of UFR residue.

Series	Temperature range (°C)	Activation energy (kJ mol ⁻¹)	Pre-exponential factor	R ²
(1) Pyrolysis at low temperature stage	195–430	47.3	6.48E+00	0.967
(2) Combustion at low temperature stage	195–430	44.6	2.97E+00	0.961
(3) Combustion at high temperature stage	465–595	96.2	1.38E+03	0.927

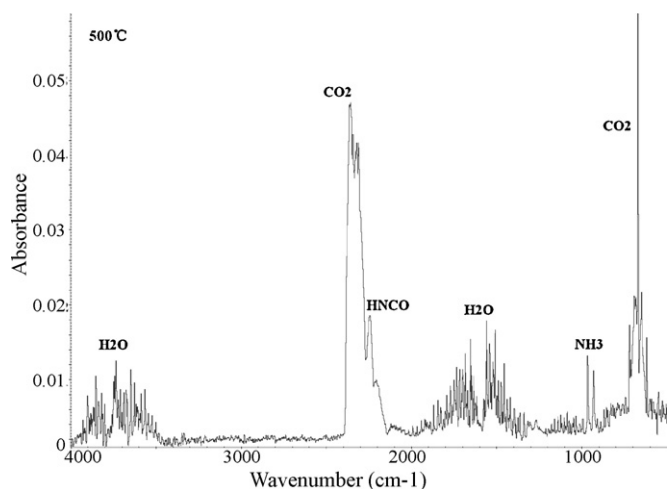


Fig. 3. FTIR spectrogram of combustion gaseous products emitted from UFR residue at 500 °C.

pre-exponential factor A . Both the activation energy E and pre-exponential factor A can be determined by the slope and intercept of the line.

Table 2 presents the activation energies E and the Arrhenius pre-exponential factors A for each step during UFR residue pyrolysis and combustion. It is observed that the activation energy in the second step for fixed carbon combustion is larger than the first step for volatile material combustion, and the activation energy of the first step during combustion is little more than that of the pyrolysis' first step. It is concluded that the thermal decomposition of UFR residue is accelerated by oxygen, which agrees well with the previous study of Font et al. [5].

3.3. Infrared spectrum analysis of gaseous products and pollutants

The gaseous products from TG analysis were detected on-line by using Fourier transform infrared spectroscopy (FTIR). The temperature dependence of intensity agrees well with the temperature dependence of DTG curve, and the intensity of gas emission reaches its maximum at 294 °C, which is the same temperature of the maximum loss rate during pyrolysis and combustion.

The spectrograms at 294 °C (the maximum point of the DTG curve) and 500 °C in UFR residues pyrolysis are shown in Fig. 2. The main compounds emitted at 294 °C are identified as carbon dioxide (CO₂), isocyanic acid (HNCO), ammonia (NH₃), hydrocyanic acid (HCN) and carbon monoxide (CO). HNCO and NH₃ are emitted as the main nitrogen-containing gaseous products during UFR residue pyrolysis at 294 °C, which agrees with the results of Girods et al. [21,22]. It is also found that the emission of HCN gradually takes the place of HNCO and NH₃ as the main nitrogen-containing component with the increasing temperature, and the intensity of HCN emission reaches its peak at 500 °C (as shown in Fig. 2). The main gaseous products at 500 °C are CO₂, HNCO, NH₃, CO and HCN, accompanied with a little methane (CH₄).

The emission characteristics in UFR residue combustion are also investigated by using TG-FTIR for comparison with pyrolysis. Furthermore, it is found that the gaseous products at 294 °C during combustion are similar with the pyrolysis gas at this temperature. It is indicated that the oxygen has a poor oxidizing property at low temperature. The difference between the emission characteristics of the two experiment condition at high temperature is observed in this study. The FTIR spectrum for combustion products evolving from UFR residues at 500 °C is shown in Fig. 3. CO₂ and H₂O are identified as the main combustion gaseous products, which is

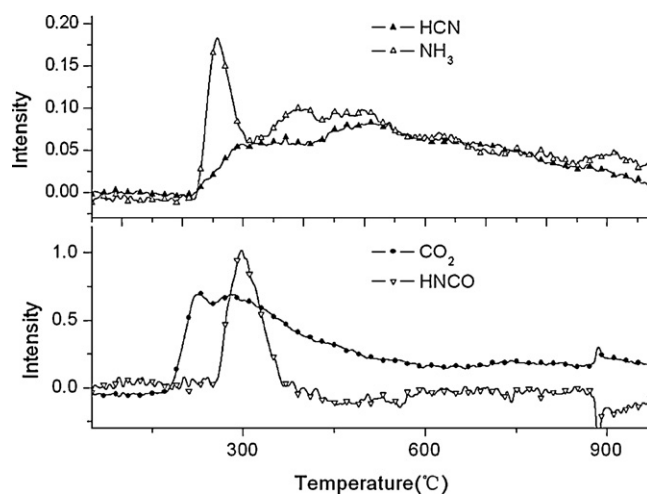


Fig. 4. Evolution of gaseous products with temperature during pyrolysis.

caused by the oxidation of decomposition product, such as HNCO and HCN, from UFR residue at high temperature, as shown in Eqs. (7) and (8).



The small quantities of NH₃ and HNCO are also detected at 500 °C during combustion, which is the result of the short residence time for combustion. The emission of HCN, which is toxic for environment, is almost completely prevented in high temperature combustion, and emission of NH₃ is also reduced. It is concluded that the high temperature at oxidized atmosphere is necessary for pollutant controlling in disposal of UFR residue.

The evolutions of absorption intensity with temperature for HNCO, NH₃, HCN and CO₂ during pyrolysis are shown in Fig. 4. The temperature evolution of CO and CH₄ is not analyzed in this paper because of their small quantity. The emission of NH₃ and HCN starts at the same temperature as shown in Fig. 4. HNCO is continuously emitted from 200 °C to 600 °C during pyrolysis, and most of HNCO is emitted in 250–400 °C. After a strong peak around 300 °C, the intensity of HNCO emission decreased continuously till the end of experiment. The maximum intensities of HNCO and NH₃ in FTIR spectrum agree well with the maximum weight loss rate of DTG profile. As shown in Fig. 4, of all the nitrogen-containing pyrolysis gas (include HNCO, NH₃ and hydrogen cyanide), HNCO has the maximum intense absorption identified by FTIR. It is concluded that HNCO is the most important nitrogen-containing gaseous product in UFR residue pyrolysis, and the most of thermal removal of nitrogen species from UFR residue occurs at low temperature, because the most of HNCO emits between 250 °C and 400 °C. The maximum emission of NH₃ occurs around 300 °C and decreases slowly after the secondary peak around 500 °C. Most of NH₃ and HNCO are emitted in a narrow temperature range, which is very different from the emission characteristics of HCN and CO₂.

HCN is found as the main nitrogen-containing gaseous product at high temperature in pyrolysis of UFR residue, furthermore HCN is emitted in a wide temperature range from 280 °C to 900 °C and reaches its peak at 500 °C. Further investigation is needed to clarify the mechanism of UFR residue thermal degradation, and the control measurement is necessary for HCN emission reduction during thermal disposal because of the toxicity of HCN to human beings. It is indicated that nitrogen-containing structures in UFR residues are cracked before 300 °C, the most of them emit as HNCO and NH₃ at low temperature, the others emit as HCN at higher temperature. It is appropriate that UFR residue should be pyrolyzed at low

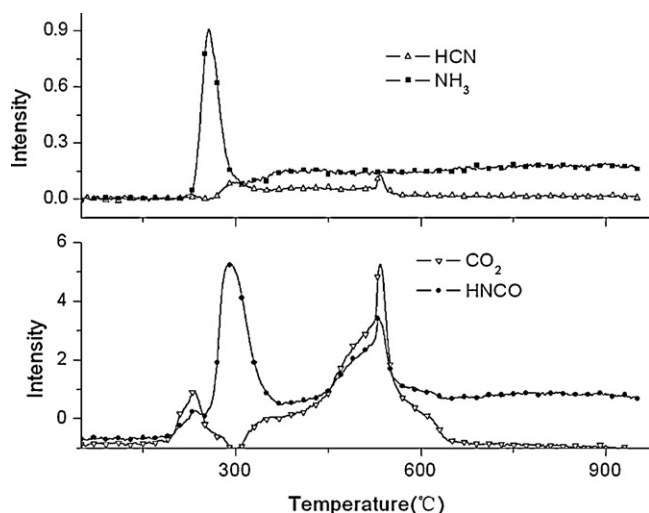


Fig. 5. Evolution of gaseous products with temperature during combustion.

temperature to remove the initial nitrogen [22], and the gaseous products during pyrolysis should be burned in a high temperature furnace under oxygen-rich conditions, so the poisonous gases such as HCN and HNCO can be oxidized, destroyed and detoxified. Because there is no oxidant in inert atmosphere, the emission of CO₂ (as shown in Fig. 4) during pyrolysis is induced by the decomposition of the original materials. The emission of CO₂ increased sharply before reaching its maximum intensity around 300 °C, and finished at 600 °C.

The evolving characteristics of absorption intensity with temperature for the gaseous products in UFR residue combustion are also analyzed and shown in Fig. 5. The emission characteristics of HNCO and NH₃ at low temperature combustion are similar to the characteristics of the pyrolysis process, and the poor oxidizability of oxygen at low temperature is confirmed. There is a peak for the HNCO emission around 570 °C in combustion, but the emission of HNCO occurs in a more narrow temperature range than the pyrolysis process does. Though the gaseous products can be oxidized by oxygen at high temperature, the cause of the second peak of the HNCO emission during combustion is still unclear. The emission of NH₃ at high temperature is also reduced by the oxidized atmosphere, and there is no other visible peak for NH₃ emission above 300 °C. Two inconspicuous peaks for HCN emission around 300 °C and 570 °C are found during combustion (Fig. 5), which is the big difference between the two experiment conditions. It is indicated that the further decomposition of UFR residue has a great effect on the emission of the nitrogen-containing gaseous products. Furthermore, high temperature and sufficient oxygen concentrations are necessary for the safe disposal of urea-formaldehyde resin residue during thermal treatment.

4. Conclusion

A large amount of UFR residue is generated in China every year, the pyrolysis and combustion characteristics and gas evolutions of these wastes were investigated by using TG-FTIR. The total weight loss of 90 wt.% occurs at 950 °C during pyrolysis of UFR residue. The pyrolysis process can be subdivided into three stages: drying the sample; fast thermal decomposition; further cracking process of the residue. The similar characteristics of pyrolysis and combustion at low temperature are confirmed in this study. The kinetics analysis of pyrolysis and combustion shows that the thermal degradation of UFR residue can be accelerated by oxygen atmosphere.

It was found that original nitrogen in UFR residue emitted as HNCO and NH₃ at low temperature, while HCN prevailed at high temperature during pyrolysis. The poisonous gases emitted from UFR residue during thermal decomposition such as HCN and HNCO can be oxidized and detoxified in oxidizing atmosphere at high temperature. The temperature evolutions of pyrolysis products show that HNCO is the most important nitrogen-containing product and HCN is found as the main nitrogen-containing gaseous product at high temperature. Furthermore, most of the thermal removal of nitrogen species from UFR residue occurs at low temperature, and the oxidizability of oxygen is found poor at low temperature in UFR residue combustion. It is recommended that UFR residue should be pyrolyzed at low temperature, and the gaseous products during pyrolysis should be fed into a high temperature furnace under oxygen-rich conditions.

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References

- [1] S.C. Saxena, C.K. Jotshi, Management and combustion of hazardous wastes, *Prog. Energy. Combust.* 22 (1996) 401–425.
- [2] B. Mithat, K. Aykan, A. Savas, Partitioning characteristics of targeted heavy metals in IZAYDAS hazardous waste incinerator, *J. Hazard. Mater.* B99 (2003) 89–105.
- [3] R. Addink, E.R. Altwicker, Formation of polychlorinated dibenzo-p-dioxins and dibenzofurans on secondary combustor/boiler ash from a rotary kiln burning hazardous waste, *J. Hazard. Mater.* B114 (2004) 53–57.
- [4] H.B. Duan, Q.F. Huang, Q. Wang, B.Y. Zhou, J.H. Li, Hazardous waste generation and management in China: a review, *J. Hazard. Mater.* 158 (2008) 221–227.
- [5] R. Font, A. Fullana, J. Conesa, Kinetic models for the pyrolysis and combustion of two types of sewage sludge, *J. Anal. Appl. Pyrol.* 74 (2005) 429–438.
- [6] E.S. Park, B.S. Kang, J.S. Kim, Recovery of oils with high calorific value and low contaminant content by pyrolysis of digested and dried sewage sludge containing polymer flocculants, *Energy Fuel* 22 (2008) 1335–1340.
- [7] B. Dou, S. Park, S. Lim, T.U. Yu, J. Hwang, Pyrolysis characteristics of refuse derived fuel in a pilot-scale unit, *Energy Fuel* 21 (2007) 3730–3734.
- [8] J.M. Encinar, F.J. Beltran, A. Ramiro, J.F. Gonzalez, Pyrolysis/gasification of agricultural residues by carbon dioxide in the presence of different additives: influence of variables, *Fuel Process Technol.* 55 (1998) 219–233.
- [9] K.E. Harfi, A. Mokhlisse, M.B. Chanaa, Yields and composition of oil obtained by isothermal pyrolysis of the Moroccan (Tarfaya) oil shales with steam or nitrogen as carrier gas, *J. Anal. Appl. Pyrol.* 56 (2000) 207–218.
- [10] C.Y. Chang, J.L. Shie, J.P. Lin, C.H. Wu, D.J. Lee, C.F. Chang, Major products obtained from the pyrolysis of oil sludge, *Energy Fuel* 14 (2000) 1176–1183.
- [11] I. de Marco, M.F. Laresgoiti, M.A. Cabrero, A. Torres, M.J. Chomon, B. Caballero, Pyrolysis of scrap tyres, *Fuel Process Technol.* 72 (2001) 9–22.
- [12] I. de Marco, B.M. Caballero, M.A. Cabrero, M.F. Laresgoiti, A. Torres, M.J. Chomón, Recycling of automobile shredder residues by means of pyrolysis, *J. Anal. Appl. Pyrol.* 79 (2007) 403–408.
- [13] H.P. Yang, R. Yan, T. Chin, et al., Thermogravimetric analysis-Fourier transform infrared analysis of palm oil waste pyrolysis, *Energy Fuel* 18 (2004) 1814–1821.
- [14] J.G. Liu, X.M. Jiang, L.S. Zhou, X.X. Han, Z.G. Cui, Pyrolysis treatment of oil sludge and model-free kinetics analysis, *J. Hazard. Mater.* 161 (2009) 1208–1215.
- [15] H.J. Park, Y.K. Park, J.I. Dong, J.S. Kim, J.K. Jeon, S.S. Kim, J. Kim, B. Song, J. Park, K.J. Lee, Pyrolysis characteristics of oriental white oak: kinetic study and fast pyrolysis in a fluidized bed with an improved reaction system, *Fuel Process Technol.* 90 (2009) 186–195.
- [16] F. Travis, H. Mohammad, W. Bruce, et al., Pyrolysis behavior and kinetics of biomass derived materials, *J. Anal. Appl. Pyrol.* 62 (2002) 331–349.
- [17] W. Song, J.G. Liu, Y.F. Nie, Pyrolysis properties of oil sludge, *J. Fuel Chem. Technol.* 36 (2008) 286–290 (in Chinese).
- [18] S.B. Ma, J. Lu, J.S. Gao, Study of the low temperature pyrolysis of PVC, *Energy Fuel* 16 (2002) 338–342.

- [19] J.L. Shie, Y.H. Chen, C.Y. Chang, et al., Thermal pyrolysis of poly (vinyl alcohol) and its major products, *Energy Fuel* 16 (2002) 109–118.
- [20] K. Tamer, Y. Jale, Y. Mithat, B. Henning, Characterisation of products from pyrolysis of waste sludges, *Fuel* 85 (2006) 1498–1508.
- [21] P. Girods, A. Dufour, Y. Rogaume, C. Rogaume, A. Zoulalian, Pyrolysis of wood waste containing urea-formaldehyde and melamine-formaldehyde resins, *J. Anal. Appl. Pyrol.* 81 (2008) 113–120.
- [22] P. Girods, A. Dufour, Y. Rogaume, C. Rogaume, A. Zoulalian, Thermal removal of nitrogen species from wood waste containing urea formaldehyde and melamine formaldehyde resins, *J. Hazard. Mater.* 159 (2008) 210–221.
- [23] M. Meng, H.Q. Hu, Q.M. Zhang, et al., Pyrolysis behaviors of Tumuji oil Sand by thermogravimetry(TG) and in a fixed bed reactor, *Energy Fuels* 21 (2007) 2245–2249.
- [24] E. Jakab, M. Blazso, O. Faix, Thermal decomposition of mixtures of vinyl polymers and lignocellulosic materials, *J. Anal. Appl. Pyrol.* 58–59 (2001) 49–62.
- [25] P. Alvarez, R. Santamaria, C. Blanco, M. Granda, Thermal degradation of lignocellulosic materials treated with several acids, *J. Anal. Appl. Pyrol.* 74 (2005) 337–343.
- [26] H.P. Chen, Z.W. Luo, H.P. Yang, F.D. Ju, S.H. Zhang, Pressurized pyrolysis and gasification of Chinese typical coal samples, *Energy Fuel* 22 (2008) 1136–1141.
- [27] J. Rath, G. Staudinger, Cracking reactions of tar from pyrolysis of spruce wood, *Fuel* 80 (2001) 1379–1389.
- [28] R.Z. Hu, *Thermal Analysis Kinetics*, Science Press of China, Beijing, 2001, 28–29.