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Thermogravimetric characteristics and combustion emissions of rubbers and polyvinyl chloride in N_2/O_2 and CO_2/O_2 atmospheres

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HIGHLIGHTS

- Understanding the rubber and plastic combustion in CO_2/O_2 is novel.
- Combustion characteristics between different materials were compared.
- Replacement of N_2 by CO_2 decreased the reactivity of the samples.
- Effects of heating time, temperature, atmosphere on emissions were studied.
- Replacement of N_2 by CO_2 reduced NO_x or SO_2 emissions at some temperatures.

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ABSTRACT

The thermogravimetric characteristics of tire rubber (TR), rubber mattress (RM) and polyvinyl chloride (PVC), representing the rubber and plastic materials of municipal solid waste (MSW) were compared under $80N_2/20O_2$ and $80CO_2/20O_2$ atmospheres. Replacement of N_2 by CO_2 reduced the weight loss rate of most peaks below 600 °C, postponed the location of the peaks above 600 °C, and resulted in less complete burnout, which indicated the combustion in CO_2/O_2 atmosphere decreased the reactivity of the samples. The emissions of TR, RM and PVC combustion in a tube reactor were analyzed by a flue gas analyzer. The concentrations of CO, H_2, SO_2 and NO_x all increased initially and decreased afterwards along with the heating time. During 800–1000 °C, NO_x and SO_2 emissions of all samples increased by the temperature, and decreased by the replacement of N_2 by CO_2. In both atmospheres, the subsequence of the NO_x emission was TR > RM > PVC, and the subsequence of the SO_2 emission was TR > PVC > RM. The effects of temperature and atmosphere on the CO and H_2 emissions of two rubbers were different from those of PVC.

1. Introduction

Due to the issues like low weight, durability, energy efficiency, design flexibility and low cost, plastic and rubber are widely employed in a broad variety of consumer products [1]. The worldwide demand for plastic and rubber products is growing, especially in developing countries [2]. Plastic and rubber are both major components of municipal solid waste (MSW), and appropriate treatment of such products contributes significantly to establishing good waste management practices [3]. Thermal treatments such as incineration and pyrolysis are important alternatives to the widespread disposal of plastic and rubber waste in landfills [4].

The industrial feasibility of CO_2 capture is now fairly well established [5]. Oxy-fuel combustion, which utilizes a CO_2/O_2 mixture as the oxidizer instead of air, is a promising technique to address the problem of CO_2 emissions [6]. The principal advantage of oxy-combustion is that it increases significantly the partial pressure of CO_2 in the exhaust gases [5]. Although the coal oxy-fuel combustion technology has been studied in a number of investigations [7–9], little research has been accomplished on the oxy-fuel combustion characteristics of other solid waste, such as plastic and rubber waste.

The aim of this work is to provide a relatively comprehensive laboratory study on the oxy-fuel combustion characteristics of plastic and rubber. Kinetic data for combustion stages were determined by thermogravimetric analysis (TGA), and CO, H_2, SO_2 and NO_x emissions were studied using a lab-scale electrically heated tube furnace.

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2. Materials and methods

2.1. Materials

Materials tested included wiring duct mainly made of polyvinyl chloride (PVC), tire rubber (TR) and rubber mattress (RM). In this paper, the PVC represented the plastic as it is an important part of the plastic fraction contained in MSW [10], and 38–66% of the chlorine content of MSW originated from PVC. The presence of PVC in MSW influences the quantity of chlorine in the raw gas and the corresponding effluents from gas treatment systems [4]. PVC also influences the heavy metal content in the MSW [4]. The rubber was represented by a commonly used tire rubber (TR) and a rubber mattress (RM). TR is basically a mixture of two or more polymers, carbon black, inorganic compounds (calcium carbonate, silica, etc.) and organic substances (plasticizers, lubricants, antioxidants, vulcanization agents, etc.) [11].

The experimental materials were pulverized by DFY-300 pulverizer (Wenling Linda Machinery Co., Ltd., Zhejiang Province, China), and then passed through a sieve with a mesh size of 178 μm. The samples were dried at 105 °C for 3–4 h and stored in desiccators.

The materials' ultimate and proximate analyses are shown in Table 1. Vario EL-II chons elemental analyzer was used to determine carbon, hydrogen, nitrogen, sulfur content. The electronic balance was used for the proximate analysis. The ultimate analysis and proximate analysis are based on ASTM D5373-2008 criterion and GB212-91 criterion respectively. The chlorine content was tested based on IC(EN 14582-2007 addenda A) criterion in China National Analytical Center, Guangzhou. As Table 1 shown, the chlorine concentration in rubber mattress and PVC was high, especially in PVC. They released HCl and dioxins, namely polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs). The emissions of HCl and dioxins of rubber mattress and PVC is a problem deserving of thorough study, but this problem is beyond the scope of this paper, because of the restriction of the used flue gas analyzer.

2.2. Thermogravimetric analysis (TGA)

The thermal behaviors were studied using a NETZSCH STA 409 PC Luxx simultaneous thermal analyzer (Bavaria, Germany). The experimental analyzer has been described in detail in the previous paper [12]. Combustion in $80N_2/20O_2$ and $80CO_2/20O_2$ atmospheres was performed in the temperatures varying from 100 to 1000 °C at the heating rates of 10, 20 and 40 °C/min. The flow rate of the mixed gas was 1.67×10^{-6} m^3/s (100 ml/min), and the initial weight of the sample for TGA was 6 ± 0.5 mg. All the experiments were replicated to determine the reproducibility, and the repeated experiments were all highly correlated.

2.3. Kinetic theory

The NETZSCH-TA4-Kinetic2 software was used to study kinetic mechanism by using *n*th order reaction model. The independent parallel reactions model was chosen. In this model, the materials consisted of several components, each of which was assumed to decompose independently. The kinetic model in Section 2.3 has been described in detail in the previous paper [12,13]. Different calculated curves were obtained by choosing different reaction parameters of the fitting model. The correlation coefficient was the index for the correlation degree between the calculated and experimental weight loss curves. The parameters were optimized so that the correlation coefficient was the closest to 1.

The correlation coefficient is defined as:

$$CorrCoeff = \sqrt{1 - \frac{SAQ}{\sum_{i=1}^{N} w_{YO_i}2 - \left(\sum_{i=1}^{N} w_{YO_i}\right)^2 / N}} \quad (1)$$

where *SAQ* is the sum of least squares

$$SAQ = \sum_{i=1}^{N} (w_{YO_i} - w_{YR_i})^2 \quad (2)$$

w_{YO_i} is the weight of the calculated curve obtained by the fitting model at point *i*; w_{YR_i} is the real weight of experimental curve at point *i*; *i* ranged from 1 to number of measurement points *N*.

2.4. Flue gas analysis

The flue gas experiments were performed in a horizontal quartz tubular electrical reactor. The experimental apparatus have been described in detail in the previous paper [14]. Combustion experiments were conducted at six different temperatures (500, 600, 700, 800, 900 and 1000 °C) in $80N_2/20O_2$ and $80CO_2/20O_2$ atmospheres. The flow rate of the mixed gas was 1.67×10^{-5} m^3/s (1 L/min). When the furnace was heated to a desired temperature, 0.1 ± 0.001 g samples were loaded into a sample holder and then the sample holder was inserted into the above reactor. The residence time at the designed temperature was 600 s (10 min). The composition of exhaust gases was determined using a TESTO 350-Pro flue gas analyzer (Lenzkirch, Germany). This instrument was calibrated periodically by injecting standard gases. The flue gas emissions were reported in the commonly used unit of ppmv (part-permillion by volume).

3. Results and discussion

3.1. Weight loss in thermogravimetric experiment

The obtained DTG (weight loss rate) curves for TR, RM and PVC combustion at the heating rate of 20 °C/min in N_2/O_2 and CO_2/O_2 atmospheres were presented in Fig. 1. Table 2 showed the characteristic parameters obtained during combustion of three materials in N_2/O_2 and CO_2/O_2 atmospheres.

Under both atmospheres, RM began to lose its weight at around 277 °C, and the first two peaks of DTG curves were located around 305 °C and 430 °C respectively. Although the type of atmosphere had no significant effect on the ignition temperature and location of the first two peaks, replacement of N_2 by CO_2 decreased the maximal weight loss rate ($R_{max} = MAX(R_1, R_2, R_3, R_4)$) of RM from 12.9%/min to 11.6%/min. The third peak corresponding to char combustion in CO_2/O_2 atmosphere was much earlier than that in N_2/O_2 atmosphere by about 80 °C. For the peak above 600 °C (the

Table 1
Ultimate and proximate analysis of PVC, TR and RM (on air dried basis).

Materials	Ultimate analysis (wt%)						Proximate analysis (wt%)			
	C	H	O	N	S	Cl	Moisture	Volatile matter	Fixed carbon	Ash
Plastic wiring duct (PVC)	34.6	4.4	11.6	0.4	2.6	29.8	0.2	65	18.4	16.4
Rubber mattress (RM)	28.6	2.3	20.6	0.5	1.5	7.6	1.1	54.9	6.2	37.8
Tire rubber (TR)	27.1	4.6	13.5	0.7	2.4	0.1	1.5	60.9	7.5	30.1