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Dechlorination of organochloride waste mixture by microwave irradiation before forming solid recovered fuel

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ABSTRACT

In order to form a modified solid recovered fuel (SRF) with low chlorine content, high calorific value and well combustion performance, low temperature microwave irradiation was applied to remove the chlorine of the organochloride waste mixture before they were mixed to form SRF. The optimizing conditions of final temperature, microwave absorbents and heating rate were also detected to obtain high dechlorination ratio and high ratio of hydrogen chloride (HCl) to volatiles. In the temperature range of 220–300 °C, 280 °C would be chose as the optimal low microwave modified temperature concerning at which the dechlorination ratio was high and ratio of HCl to volatiles was relatively high as well; The use of microwave absorbents of graphite and silicon carbide (SiC) had a pronounced effect on the dechlorination of organochloride waste mixture, and the dechlorination ratio was increased significantly which could be reached to 87%, almost 20% higher than absorbent absent sample; The heating rate should set be not too fast nor too slow, and there was no big difference between the heating rate of 13 °C/min and 15 °C/min; The content of Cl of modified SRF is dramatically decreased and reaches to a low level 0.328%. Hence, the modified SRF can be ascended from the third class to the second class according to the Finland chlorine Classes I-III. Moreover, the combustibility of modified SRF was substantial improved compared to the traditional SRF. The low heating value was almost 20.56 MJ/kg which is close to the LHV of lignite coal and bituminous coal in China, and it increased by 60% over that of traditional SRF. Removing chlorine of organochloride waste mixture before they are mixed with other kinds of combustible waste to form a modified SRF which is expected to be an alternative fuel for combustion in the future.

1. Introduction

Despite increasing attention for waste prevention and sustainability, total municipal solid waste (MSW) generation in China has increased from 148.56 million tons in 2003 to 163.95 million tons in 2011 and it is undergoing an annual 1.3% increasing according to the statistic of National Bureau of Statistics of China (National Bureau of Statistics of China, 2013). Currently, the total capacity of untreated MSW has reached 7 billion tons, nearly two-thirds of China's cities are being surrounded by the MSW (Zhao et al., 2016). We are looking forward to an alternative treatment since the ability of landfill to handle waste is limited and it will cause pollutions to air, water, soil, plant and humans. Although reuse and recycling are preferred, energy recovery which is the process of converting energy to heat and/or electricity starting from waste will be the key aspects of waste management (US EPA, 2011; Jeong et al., 2015; Chen et al., 2016; Lombardi et al., 2015; Rada, 2014; Zhao et al., 2016). According to the garbage disposal statistical analysis in China, landfill and incineration treatment of MSW respectively accounted for 60.7% and 26.8% in 2013 (MSW Disposal Specialized Committee of Chinese Environmental Protection Industry Association, 2015). Moreover, incineration shows a good prospect in China (Fu et al., 2015).

Nevertheless, directly incineration is prone to lead to variable or even unstable operation condition due to the heterogeneous characteristics of MSW which contains various materials. MSW derived fuel is known as solid recovered fuel (SRF) which is considered more homogeneous and less contaminated fuel and processed from the combustible in MSW, composing of waste plastic package and other ignitable stuffs such as food waste, textiles and wood (Wagland et al., 2011; Paolo and Paola, 2015; Rada and Ragazzi, 2014; Kruger et al., 2014; Rada and Andreottola, 2012). A wide range of wastes are processed to SRF/refuse derive fuel (RDF) in

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recent years in China. These wastes include plastics and paper/card from commercial and industrial activities (packaging waste or rejects from manufacturing), waste tyres, biomass resource (straw, untreated waste wood, dried sewage sludge), waste textiles, residues from car dismantling operations (automotive shredder residues – ASR) and hazardous industrial wastes with high calorific value, for example, waste oils, industrial sludge, impregnated sawdust and spent solvents. The pre-treatments of MSW to form SRF by shredding, magnetic separation, trammel screening, air classification, drying and molding help producing a fuel. It is easier to be stored, handled and transported with higher heating value, more homogeneous physical and chemical compositions. Moreover, less pollutant will be released during combustion (Kagiya, 1996; European Commission, 2003).

However, the acidic flue gases mainly of hydrogen chloride (HCl) which is released during municipal waste burning will cause corrosion on the wall of the metal equipment. The existence of HCl may also induce the formation of highly toxic substances, like dioxins and furans, causing severe environmental pollution. Song (Song et al., 2009) and Hietanen (Hietanen, 2000) have claimed that HCl is considered to be released from two parts: one is released from the chlorinated organic materials mostly are polyvinyl chloride (PVC), chlorinated polyethylene (CPE), and polyvinyl dichloride (PVDC) daily plastic products; another is transformed from inorganic chlorine NaCl. Currently, one way to minimize HCl emission during SRF combustion is mainly by adding some calcium compound such as CaO or $Ca(OH)_2$ to form $CaCl_2$ in the fly ash when burned (Chiang et al., 2008). However, in order to avoid dioxins the burning temperature is set to be above 800 °C at which $CaCl_2$ will be decomposed. Moreover, according to thermodynamic theory, when the calcium compounds are directly introduced into a fluidized bed MSW incinerator at 800 °C with a water content of 10%, it cannot be expected to reduce the concentration of HCl to a low level (Lopez et al., 2011; Abbasian et al., 1993; Gui et al., 2001). Another way is to select and remove the part of chlorinated organic waste, but it will lead to high calorific value loss simultaneously which is not cost-effective.

Nowadays, most researches about SRF utilization are about the combustion, pyrolysis or gasification characteristics of SRF (Agon et al., 2016; Wagland et al., 2011.), while how to modify the SRF physical and chemical properties before SRF forming was rarely explored. The objective of the present work is to elucidate the possibility of remove the chlorine of the organochloride waste mixture by microwave irradiation to form a modified refuse derived fuel with low chlorine content, high calorific value and well combustion performance. The optimizing conditions of final dechlorination temperature, microwave absorbents and heating rate are also detected to obtain high dechlorination ratio and high ratio of HCl to volatiles. It is considered to provide fundamental knowledge for industrialization of the low temperature microwave irradiation dechlorination of organic chlorinated waste mixture to form modified SRF.

2. Material and methods

2.1. Materials preparation

Organochloride waste mixture consists of PVC waste, PVDC waste and CPE waste which were obtained from a plastic product plant (Wuxi, Jiangsu). For experimental purpose, they were cut into small pieces with a size of about 5 mm × 5 mm and homogenously mixed. The samples comprised 70% PVC, 20% PVDC and 10% CPE by weight (w/w). The ultimate analysis (C/H/N) was carried out via Vario Macro cube, Elementar (Germany). In addition, the total content of Cl was analyzed by AI card mixture method (ISO 587-1997) and S was measured by an infrared sulfur analyzer (5E-IRS II). The low heating value (LHV) analysis of the chlorinated organic wastes and samples were measured by calorimeter (SDACM4000, Hunan). The main characteristics of the chlorinated organic wastes are listed in Table 1.

2.2. Experimental apparatus

A laboratory microwave furnace (M7, from Changsha Synotherm Co., Ltd.), with a power of 3 kW at a frequency of 2.45 GHz, was applied to remove chlorine of the organochloride waste mixture, as shown in Fig. 1(a). It consists of the microwave generator, the applicator and the power monitor. In addition, the power monitor installed between the microwave generator and the applicator in the experimental bench, and the input voltage change of the microwave generator can manage microwave power in the experiment. The experimental samples were put into a glass round bottom flask which was bolted in the middle of the furnace via an insulation bucket. The thermocouple was positioned under the bottom of the flask and through the bucket for the measurement of the sample temperatures in the experiment. Furthermore, the samples were partially decomposed after heated and reach to a certain temperature, and the released gases were absorbed by the absorbent, as shown in Fig. 1(b).

In order to enhance the dechlorination action of the organochloride waste mixture in the experiment, the effects of final temperature, microwave absorbents and heating rate on the dechlorination ratio of organochloride waste mixture were studied, respectively. In the experiment, samples of 50 g organochloride waste mixture were placed in the flask in a batch-type operation under different operation conditions: (a) 9 °C/min (800 W), no microwave absorbent added, heated to the final temperature 220 °C, 240 °C, 260 °C, 280 °C and 300 °C by the microwave irradiation respectively; (b) 9 °C/min (800 W), 280 °C, being added of silicon carbide (SiC) and graphite as microwave absorbents which are with a bulk size of 10 mm × 10 mm (supplied by Xinghua City Feihua Stone Factory in Jiangsu), covering the external bottom of the flask. The ratio of microwave absorbent to samples is 1:2; (c) 280 °C, no microwave absorbent added, heated by different heating rates of 4 °C/min, 9 °C/min, 13 °C/min and 15 °C/min which were linked with the microwave power input of 400 W, 800 W, 1200 W and 1400 W.

2.3. Analytical methods

Released HCl was absorbed by the excess sodium hydroxide (NaOH) in the experiment and analyzed via silver nitrate titration method. Where the pH of the absorption liquid was adjusted to the value ranges from 6.5 to 10.5, and the chlorine anion (Cl^-) was titrated with standard aqueous solution of silver nitrate ($AgNO_3$) at the ambient temperature 25 °C and the pressure 101,325 Pa ($Ag^+(aq) + Cl^-(aq) \rightarrow AgCl\ (s)$). 1 ml potassium chromate solution was added into the absorption liquid, which acted as the indicator in the titrated experiment. It was not stopped titrating until a brick red precipitate occurred in the bottom of the bottle, which caused by reaction of the excess silver cation (Ag^+) and chromate anion (CrO_4^{2-}).

In order to interpret the results of the dechlorination of the organochloride waste mixture, the dechlorination ratio is introduced in this study. It represented by the ratio of removed chlorine and the total original chlorine. The dechlorination ratio (α) is defined as follow:

$$\alpha = \frac{(m_0 \times c_0 - m_r \times c_r)}{m_0 \times c_0} \times 100\% \quad (1)$$

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