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Inhibition of C—Cl formation during the combustion of MSW gasification syngas: An experimental study on the synergism and competition between oxidation and chlorination

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ABSTRACT

For the safe disposal of MSW, a four-step gasification-combustion conversion process is proposed in this work, consisting of material gasification, ash melting, syngas conversion and combustion. Based on the control method of dioxin in gasification process which has been studied previously, experiments of tar chlorination process under oxidative atmospheres were carried out in a homogeneous flow reaction system, using benzene as the tar model compound, to find a way for the inhibition of C—Cl formation during the syngas combustion process. Results indicated that Cl_2 reacts with benzene more easily than O_2 under low temperatures, and has a positive effect on both oxidative cracking and polymerization. For chlorination reactions, high temperature enhances the chlorination degree and leads to the formation of perchlorinated hydrocarbons, but also promotes the rupture of the weak C—Cl bonds. With the rise of temperature, hexachlorobenzene became the major product, the amounts of all chlorinated hydrocarbons decreased rapidly, and the conversion direction depended on the amount of O_2. O_2 generally promotes the formation of hydrogen chloride, and inhibits the chlorination of hydrocarbons. At a temperature above 900 °C, the total amount of chlorinated hydrocarbons was very low under oxidative atmospheres, even only with a equivalence ratio of 0.2. However, during the oxidation process under low temperatures, C—Cl can also be formed on cyclopentadienyl and 1,3-butadienyl radicals, whose chlorination products were observed. The synergistic and competitive effects between oxidation and chlorination are concluded and the major benzene conversion pathways are summarized according to the products detected.

1. Introduction

For the sake of MSW (Municipal Solid Waste) disposal, incineration has been rapidly developed and widely applied in China. However, dioxin formed during the process can hardly be avoided, leading to difficulties in site selection and increasing the operating costs significantly (Fukuda et al., 2003; McKay, 2002; Mukherjee et al., 2016). The heterogeneous combustion mode inhibits the complete oxidation of the materials, providing chlorinated hydrocarbons including dioxin precursors for gas-phase (Altarawneh et al., 2009; Shaub and Tsang, 1983) and heterogeneous catalytic (Ballschmiter et al., 1988; Lomnicki and Dellinger, 2003) formation of dioxins. To promote the oxidation reactions, a high ratio of air to fuel is demanded, which is in favor for both Deacon reaction (Deacon, 1875) and de novo synthesis (Altarawneh et al., 2009; Iino et al., 1999). On the other hand, the high amount of excess air also has a negative effect on the conversion efficiency of MSW. Moreover, the char bed with low thickness is weak in fly ash control, which provides suitable heterogeneous catalytic surface for dioxin formation in the low temperature zone (Ballschmiter et al., 1988; Iino et al., 1999; Lomnicki and Dellinger, 2003).

In view of these issues, gasification, an oxygen-lean thermo-conversion process, has been studied (Zhang, 2015), which is thought to be a complete and competitive technological alternative to incineration for the energetic valorization of the MSW (Panepinto et al., 2015). During gasification, the oxidative atmosphere can be avoided, the fly ash is well controlled by the fixed bed, and the complete oxidative conversion of MSW is easier to achieve under the gas-phase condition when the gasifier is coupled with a combustion chamber.

Plasma is often introduced into the gasification process for the treatment of harmful products, but the huge energy consumption has become the major obstacle to practical use. Thus, in order to find a low-cost way for dioxin control, the formation and rupture

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[1] The first two authors contribute to this work equally.

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of C—Cl bond, the characteristic structure of dioxins, has been experimentally investigated in the previous work (Zhang et al., 2015). H_2 has been found to have the ability of transferring Cl atoms into stable hydrogen chloride, from both the C—Cl contained molecules and the active chlorine species like Cl_2 and Cl radical that have the potential to form C—Cl. Then, a ‘homogeneous conversion’ process was proposed (Zhang et al., 2015) in which a reaction space with designed temperature and residence time was manually created above the bed and C—Cl was inhibited by the homogeneous reactions between chlorinated hydrocarbons and the abundant H_2 (Mandl et al., 2010; Yin et al., 2016) contained in the syngas itself. Through the HCl-targeted transfer of chlorine, dioxin formation was restrained.

Based on that, in this work, a four-step gasification-combustion conversion process is proposed for the safe disposal of MSW, as shown in Fig. 1. MSW will first enter an updraft gasifier and be converted into syngas. During gasification, organic chlorides are mainly released into the gas phase in the form of Cl·, Cl_2, HCl and C—Cl due to the weak C—Cl bond (Castro et al., 2012; Yin et al., 2016), while inorganic chlorides are more likely to remain in the solid phase due to the temperature dependency of their vapour pressures (Takasuga et al., 2000). The syngas then enters the ‘homogeneous conversion’ zone, where all chlorine species are transferred into hydrogen chloride according to the experimental results mentioned above. And thanks to the ‘homogeneous conversion’, plasma torch is only applied in ash treatment and has the ash vitrified into an inert state, which substantially improves the economy of the MSW conversion process.

After homogeneous conversion, the syngas will be oxidized and heat will be released in the combustion zone. Compared to the heterogeneous condition, the complete oxidative conversion is easier to realize in gas phase, and the O_2 can be supplied more accurately. Also, due to the barrier effect of the char bed in an updraft gasifier, fly ash can hardly enter the combustion zone, preventing the dioxin formation from low-temperature heterogeneous catalytic reactions. However, hydrogen chloride, the main speciation of chlorine in the syngas after homogeneous conversion, will be oxidized by O_2, O and OH radicals under high temperatures, leading to the regeneration of active chlorine species (Gullett et al., 2000; Perez-Ramirez et al., 2011). Senior et al. (2000) have reported a 1% conversion of HCl to Cl_2 in the reaction with O_2 at 1200 K, and Wikström et al. (2003) also found the presence of both Cl_2 and Cl radicals at 1273 K using HCl and air as reactants with a HCl conversion rate of nearly 6.75%.

These regenerated active chlorine species can compete with oxygen in the reactions with hydrocarbons in the syngas, and C—Cl may have the chance to be reformed. Considering the fact that tar occupies a certain proportion in the syngas, chlorobenzenes and chlorophenols may exist in the chlorination products, which are important precursors of dioxins and need to be strictly controlled (Altarawneh et al., 2009). A satisfactory combustion process should consist of a complete oxidation of the hydrocarbons in the syngas and the inhibition of the rechlorination by active chlorine species. The competition between oxidation and chlorination is affected by the amounts of both oxygen and chlorine. In practical application, the chlorine content is usually determined by raw material, while the amount of oxygen can be easily controlled by adjusting the flow rate of air and is thought to be the major way of controlling the competitive reactions. Moreover, Procaccini et al. (2003) pointed out the significant impact of temperature on the competition, chlorination reactions are dominant under low temperatures and oxidation reactions are strengthened with the rise of temperature.

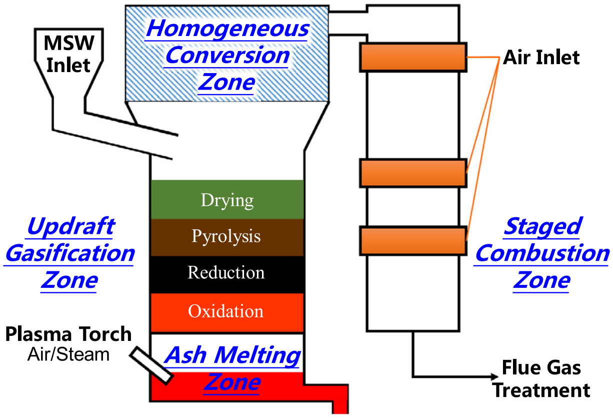

Fig. 1. Sketch map of the concept of a four-step MSW Gasification-Combustion Conversion Process.

Thus, in the present work, experiments on the chlorination of tar compounds under oxidative atmospheres will be carried out in a homogeneous flow reaction system, to reveal the effects of oxygen amount and temperature on the competitive reactions, built the conversion pathways of tar compound and obtain the reaction conditions suitable for the formation of C—Cl bonds, providing fundamental data for the prevention of C—Cl formation during the syngas combustion process.

2. Experimental methods

2.1. Reactants

Benzene has the basic molecular structure of aromatic hydrocarbons, and thus was chosen as the model compound for the tar component in syngas. It is in the liquid phase under room temperature, and was stored in an automatic liquid injector. During the experiments, benzene was injected into a gas mixer with a constant flow rate, and the mixer was electrically heated and kept at 150 °C. By adjusting the moving speed of the pushing rod of the injector, the concentration of benzene at the inlet of the reactor was controlled at 3000 ppm.

Cl_2, a common active speciation of element chlorine that can be readily converted into Cl radicals during thermochemical conversion processes (Gullett et al., 2000), was used as the chlorine source of chlorination reactions. Its flow rate was set according to the amount of benzene, keeping the ratio of carbon and H atoms to Cl atoms at 1:1 to ensure the amount of Cl_2 was enough for the complete chlorination of hydrocarbons.

The flow rate of O_2 was also set according to the amount of benzene, in order to sequentially provide the oxidative atmosphere with an equivalence ratio (ER) of 0.0–1.0, and investigate the effect of O_2 amount on benzene conversion process. N_2 was used as the balance gas.

Cl_2, O_2 and N_2 were all supplied by high-pressure gas cylinders. The flow rates were controlled by mass flowmeters (CS200D, Sevenstar) and adjusted according to the reaction temperature to maintain the residence time at 1.0 s.

2.2. Experimental rig

As shown in Fig. 2, the homogeneous flow reaction system consisted of a flow reactor, a gas preheater and a gas mixture. The reactants from the gas cylinders went through the mass flowmeters, the one-way valves, and then entered the gas mixer kept at 150 °C, together with benzene from the liquid injector. Subsequently, the mixture entered a ceramic tube with an inner diameter of 7.6 mm, which consisted of a preheated zone at 200 °C and a reaction zone at the temperature manually set. For

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