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Chemical looping combustion: A new low-dioxin energy conversion technology

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ABSTRACT

Dioxin production is a worldwide concern because of its persistence and carcinogenic, teratogenic, and mutagenic effects. The pyrolysis-chemical looping combustion process of disposing solid waste is an alternative to traditional solid waste incineration developed to reduce the dioxin production. Based on the equilibrium composition of the Deacon reaction, pyrolysis gas oxidized by seven common oxygen carriers, namely, CuO, NiO, $CaSO_4$, CoO, Fe_2O_3, Mn_3O_4, and $FeTiO_3$, is studied and compared with the pyrolysis gas directly combusted by air. The result shows that the activity of the Deacon reaction for oxygen carriers is lower than that for air. For four typical oxygen carriers (CuO, NiO, Fe_2O_3, and $FeTiO_3$), the influences of temperature, pressure, gas composition, and tar on the Deacon reaction are discussed in detail. According to these simulation results, the dioxin production in China, Europe, the United States, and Japan is predicted for solid waste disposal by the pyrolysis-chemical looping combustion process. Thermodynamic analysis results in this paper show that chemical looping combustion can reduce dioxin production in the disposal of solid waste.

Introduction

Persistent organic pollutants (POPs) with persistence, bio-accumulation, long-range transport, and bio-toxic properties have been a major focus of the international community. To protect human health and the environment from POPs, more than 90 countries and regional economic integration organizations signed the Stockholm Convention on POPs (Stockholm Convention) on May 23, 2001, which addressed the elimination, reduction, and control of POPs (UNEP, 2001).

Dioxin is one of the initial 12 POPs included in the Stockholm Convention. Dioxin is carcinogenic, teratogenic, and mutagenic to humans and wildlife, and it affects reproduction and interferes with the endocrine system. Therefore, dioxin is called the "century poison" (Kogevinas, 2001). Dioxin pollution has caused concern to both governments and people around the world and has become a hotspot in different environment fields.

Solid waste incineration is the main source of dioxin emission, as listed in Annex C of the Stockholm Convention, and it accounts for a large proportion in the generation of dioxin (Quaß et al., 2004). Therefore, the reduction of dioxin produced by solid waste incineration is an important means to reduce dioxin emission. Pyrolysis is unfavorable for the formation of dioxin because of lack of oxygen; thus, it is an alternative process to dispose of solid waste to reduce dioxin emission (Addink and Olie, 1995; Malkow, 2004; Miyagoshi et al., 2004; Pekárek et al., 2001; Xie et al., 2009). Although dioxin is not formed during pyrolysis, pyrolysis gas contains abundant dioxin precursors. Therefore, preventing the formation of dioxin in pyrolysis gas treatment processes is a key issue. Chemical looping combustion (CLC) may inhibit the formation

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of dioxin during the combustion of pyrolysis gas because CLC is mainly a lattice oxygen combustion strategy.

CLC is a new technology in energy conversion. It is an attractive technology because of its high energy conversion efficiency and intrinsic CO_2 separation properties. The principle of CLC is that traditional combustion, in which fuel is combusted by directly contacting with air, is separated into two reactors, namely, a fuel reactor and air reactor, by means of an oxygen carrier (Lyngfelt et al., 2001). In the fuel reactor, the oxygen carrier, MeO (Me denotes as metal), is reduced by fuel. In turn, the fuel is oxidized to CO_2 and steam, which can be condensed into pure CO_2.

$$(4m+n)\mathrm{MeO} + 2\mathrm{C}_m\mathrm{H}_n \rightarrow (4m+n)\mathrm{Me} + 2m\mathrm{CO}_2 + n\mathrm{H}_2\mathrm{O} \quad (1)$$

In the air reactor, the reduced oxygen carrier, Me, is re-oxidized to its original oxidation state by air.

$$2\mathrm{Me} + \mathrm{O}_2 \rightarrow 2\mathrm{MeO} \quad (2)$$

In CLC, the oxygen carrier is alternately oxidized and reduced to provide the oxygen needed to convert fuel. As the direct contact between fuel and air is avoided, sequestration-ready CO_2 without dilution by N_2 is obtained. Therefore, CLC is considered a next-generation carbon capture and storage (CCS) technology (Figueroa et al., 2008; Zhao et al., 2013).

At present, the solid waste pyrolysis-chemical looping combustion (pyrolysis-CLC) process can be proposed as an alternative to solid waste incineration to prevent the formation of dioxin in the disposal of solid waste. In this process, solid waste is initially pyrolyzed, and then pyrolysis gas is used as the CLC fuel. Fig. 1 shows the schematic diagram of the solid waste pyrolysis-CLC process. In the pyrolysis reactor, solid waste is pyrolyzed under anaerobic conditions to obtain the pyrolysis gas. Pyrolysis gas is used as the CLC fuel, which carries out the capture of CO_2 during energy conversion. The pyrolysis-CLC process is attractive because it restrains the formation of dioxin and realizes carbon management. The pyrolysis of solid waste can control dioxin production, as has been extensively illustrated in the literature (Addink and Olie, 1995; Malkow, 2004; Miyagoshi et al., 2004; Pekárek et al., 2001; Xie et al., 2009). Therefore, the formation of dioxin in pyrolysis gas CLC is mainly discussed here.

In this paper, the dioxin formation mechanism and chemical looping combustion are initially reviewed to briefly explain the research idea. Then, the effects of oxygen carrier, excess oxygen coefficient, temperature, pressure, gas composition, and tar on dioxin, which is formed in pyrolysis gas CLC, are determined by thermodynamic simulation. Lastly, dioxin generation in China, Europe, the United States, and Japan, using the solid waste pyrolysis-CLC process as a substitute for solid waste incineration, is predicted according to the results of the thermodynamic calculation. Notably, given the difficulty in measuring dioxin in laboratory-scale CLC equipment, this paper is only based on thermodynamic analysis to investigate the application of CLC in dioxin inhibition. Kinetic factors, such as the catalytic action of metal ions, are not considered.

1. Literature review and research framework

1.1. Formation mechanism of dioxin

Olie (1977) first discovered dioxin in the flue gas and ash discharged from solid waste incineration plants in Amsterdam. Since then, considerable in-depth research on the formation mechanism of dioxin during incineration has been widely conducted. However, because of the vast number of dioxin isomers, complex reaction mechanism, massive number of factors, and limited monitoring methods, the formation mechanism of dioxin remains unclear. At present, the widely accepted formation mechanisms of dioxin include direct release, pyrosynthesis, precursor synthesis, and *de novo* synthesis (Fiedler, 1998; Hutzinger et al., 1985; Stanmore, 2002, 2004). In these mechanisms, direct release and pyrosynthesis are secondary, and precursor synthesis and *de novo* synthesis are primary (Huang and Buskens, 1999; Shaub and Tsang, 1983).

Precursor synthesis is the mechanism in which a precursor undergoes a catalytic chlorination reaction to generate dioxin

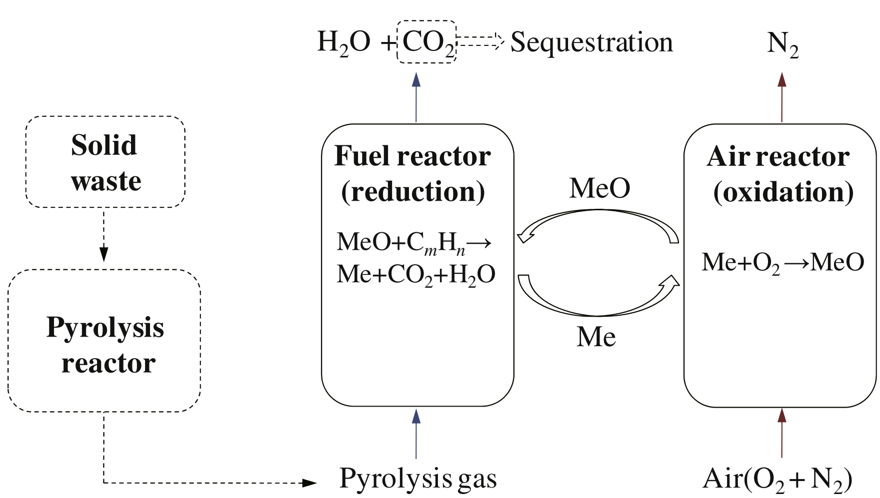

Fig. 1 – Schematic diagram of the solid waste pyrolysis-chemical looping combustion process.