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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, CaSO4, CoO, Fe2O3, Mn3O4, and FeTiO3, 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, Fe2O3, and FeTiO3), 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.

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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 of dioxin.
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 CO2 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 CO2 and steam, which can be condensed into pure CO2.

\[(4m + n)\text{MeO} + 2C_mH_n \rightarrow (4m + n)\text{Me} + 2m\text{CO}_2 + n\text{H}_2\text{O}\]  (1)

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

\[2\text{Me} + \text{O}_2 \rightarrow 2\text{MeO}\]  (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 CO2 without dilution by N2 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 CO2 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.
on the solid surface. Vogg et al. (1987) proposed a reaction mechanism in which the formation of dioxin in the post combustion zone occurs in the following order: (a) the fuel containing abundant chlorine releases HCl during incineration; (b) HCl is oxidized to Cl₂ through the Deacon reaction, catalyzed by CuCl₂; (c) the hydrogen on the aromatic ring of phenols produced in incineration is substituted by Cl₂; and (d) the chlorinated precursor is catalytically oxidized to dioxin. The mechanism was verified by Gullett et al. (1990a,b, 1992).

De novo synthesis is the mechanism in which residual carbon bonds with hydrogen, oxygen, chlorine, and other atoms through gasification, deconstruction, and reorganization, and is gradually converted to dioxin precursors and dioxin. Vogg et al. (1987) first discovered that dioxin is formed by the conversion of residual carbon in fly ash and proposed a two-step mechanism to explain the formation of halogenated organic compounds. First, halogenation occurs on the carbon surface, which includes a mechanism of ligand transfer catalyzed by Cu⁺⁺ or Fe³⁺. Second, the macromolecular carbon structure is ruptured because of oxidation, which is also catalyzed by Cu⁺⁺ or Fe³⁺. Precursor synthesis and de novo synthesis are summarized in Fig. 2 (Tuppurainen et al., 1998).

The chlorination of the benzene ring by Cl₂ is an essential step in both precursor synthesis and de novo synthesis (Fig. 2). The chlorine elements in solid waste exist in the form of HCl in the gas phase during thermo-chemical treatment (Julien et al., 1996; Kanters et al., 1996; Pasek et al., 1996; Wang et al., 1999). Therefore, HCl must be oxidized to Cl₂, which is called the Deacon reaction (Gullett et al., 1992; Vogg et al., 1987), to participate in the formation of dioxin. As the production of dioxin decreases when the Deacon reaction is inhibited, the Deacon reaction can be used as an indicator of dioxin formation. Notably, the formation of dioxin is also affected by other kinetic factors, such as the catalytic action of metal ions. However, the impact is very complicated and still not fully understood, meanwhile, the catalytic effect of metal ions on the Deacon reaction will not affect its thermodynamic equilibrium. Therefore, these kinetic factors are not considered in the paper.

1.2. Chemical looping combustion

The basic concept of CLC for CO₂ production was presented by Lewis and Gilliland in the 1950s (Lewis et al., 1951; Lewis and Gilliland, 1954). Afterwards, Ritcher and Knoche (Richter and Knoche, 1983) proposed a two-step reaction between metal oxide and fuel to replace the traditional one-step combustion to reduce the irreversible entropy increase in combustion. These concepts are the prototype of CLC. However, only in 1987 was the concept of CLC formally proposed by Ishida et al. (Ishida et al., 1987). Then, in 1994, CLC was first applied to CCS (Ishida and Jin, 1994). Lyngfelt et al. (Lyngfelt et al., 2001) initially assessed the technical and economical feasibility of CLC operated in a fluidized bed reactor in 2001, which indicated that CLC was feasible. Since then, CLC has rapidly developed.

Studies on CLC mainly focus on the oxygen carrier, reactor, process development, and simulation. The oxygen transfer in CLC is dependent on the oxygen carrier; thus, the oxygen carrier is crucial to CLC. The oxygen carrier is required to possess high reactivity and excellent mechanical and material properties (Adánez et al., 2012). Currently, more than 700 oxygen carriers based on the metals Ni, Co, Fe, Cu, Mn, and other active metals (Adánez et al., 2012; Lyngfelt et al., 2008) have been studied for CLC. Oxygen carriers are studied to improve their performance (Adánez et al., 2006a; Adánez et al., 2012; Gayán et al., 2011), obtain their kinetic parameters (Go et al., 2008; Monazam et al., 2012, 2013), and explore their reaction mechanisms (Galinsky et al., 2013; Li et al., 2011a,b). A recognized reaction mechanism of the oxygen carrier is lattice oxygen transfer, which has been confirmed by experiments (Li et al., 2011a; Sun et al., 2012). As lattice oxygen participates in the oxygen carrier reaction rather than molecular oxygen, restricting the formation of dioxin when pyrolysis gas is combusted by the oxygen carrier is possible. This will be further discussed in the following parts.

CLC occurs in reactors. There are three main types of CLC reactors: fluidized bed reactor (Johansson et al., 2006; Kronberger et al., 2004; Linderholm et al., 2008; Lyngfelt et al., 2001; Mattisson et al., 2007), moving bed reactor (Jukkola et al., 2003; Li et al., 2010a,b; Sridhar et al., 2012; Zhou et al., 2013), and packed bed reactor (Hua et al., 2014; Noorman et al., 2007, 2010, 2011a,b,c). The fluidized bed reactor is the most widely

Fig. 2 – Schematic diagram of dioxin formation routes.
used reactor type in CLC. To improve the conversion of the oxygen carrier in the fluidized bed reactor, the moving bed reactor has been applied to CLC, which achieves a favorable effect (Li et al., 2010b). In the fluidized bed reactor and moving bed reactor, a high-temperature oxygen carrier is transported among different reactors. This approach increases the operative difficulty of the reactor and the requirements for the mechanical properties of the oxygen carrier. To deal with these drawbacks, Noorman et al. (2007) proposed the concept of a dynamically operated packed bed reactor. In this concept, the oxygen carrier remains stationary in the reactor, and by switching the gas, the oxygen carrier is alternately exposed to oxidizing and reducing atmospheres to realize CLC. The pros and cons of these reactors are summarized in detail by Zhao (2012). The gas-solid contact mode in the fluidized bed reactor is considered in the thermodynamic simulation in this paper.

As CLC was proposed as a new means of energy conversion, its process development has attracted research attention. The process development of CLC mainly has two aspects. The first one is the evolution of CLC, which includes chemical looping gasification (Fan et al., 2008; Li et al., 2009, 2010a,b), the carbonation–calcination reaction process (Fan, 2011; Wang et al., 2010), chemical looping reforming (Rydén et al., 2006; Zafar et al., 2005), and chemical looping with oxygen uncoupling (Leion et al., 2009; Mattisson et al., 2009a,b), etc. (Fan, 2011). The other aspect is the coupling of CLC with other processes. For example, the CLC process has been integrated with a power plant to maximize net efficiency (Naqvi and Bolland, 2007; Wolf and Yan, 2005; Yu et al., 2003), and CLC was combined with methane-steam reforming to achieve heat integration (Rydén and Lyngfelt, 2006).

With the development of computer technology, simulation has gained increasing importance in the research. Simulation can help in the design, optimization, and scale-up of the CLC process (Adanex et al., 2012). Simulation of CLC mostly involves the fluid dynamics of the reactor (Abad et al., 2010; Kolbitsch et al., 2009), reaction scheme (Adánez et al., 2006b; Adanez et al., 2012), reaction kinetics (changing grain size model (García-Labiano et al., 2005; Georgakis et al., 1979), shrinking core model (Ishida et al., 1996), nucleation and nuclei growth models (Hossain and de Lasa, 2007), residence time distribution in the reactor (Abad et al., 2007), and process simulation (Ishida and Jin, 1994; Ishida et al., 1987; Richter and Knoche, 1983; Xiang et al., 2008). Commercial software is always used in simulation. The Advanced System for Process Engineering (ASPEN Plus®) is widely applied to the simulation of CLC because of its comprehensive physical and thermodynamic property data banks and mature modules (Abanades et al., 2010; Li et al., 2010a,b; Xiang et al., 2008, 2010). In the current paper, ASPEN Plus® is used to execute the simulation calculation of thermodynamic equilibrium.

### 1.3. Research framework

In this paper, we attempt to illustrate that CLC is a low-dioxin energy conversion system, based on thermodynamic simulation. As dioxin comprises up to 210 types of compounds (McKay, 2002) and the thermodynamic data for dioxin are absent, the formation of dioxin is indicated by the Deacon reaction, which is the necessary step in dioxin synthesis. That is to say, less Cl₂ means less dioxin, which is the basic idea of this study. The research framework is presented in Fig. 3.

Based on the Gibbs free energy minimization principle, the generation of dioxin is estimated by the equilibrium Cl₂ amount of the Deacon reaction. The effect of the oxygen carrier and process condition on pyrolysis gas CLC is studied based on the thermodynamic equilibrium. Notably, all reactions are assumed to reach equilibrium to provide an extreme case of the Deacon reaction. However, in real cases thermodynamic equilibrium is not reached, and the small deviation due to not reaching equilibrium is not within the scope of this paper.

### 2. Methodology

#### 2.1. Pyrolysis gas and excess oxygen coefficient

The composition of pyrolysis gas changes with the pyrolysis of different solid wastes in different technological conditions. Therefore, the typical composition of pyrolysis gas, which is 16.6% H₂, 15.9% CH₄, 30.4% CO, 31.7% CO₂, 2.2% C₂H₄, 3.1% C₂H₆, and 0.1% HCl, is adopted here (Jiang, 2005; Wu et al., 1998). Notably, the concentration of HCl is selected as the average value of the typical range.

![Fig. 3 – Schematic diagram of the research framework. K_p is the equilibrium partial pressure ratio of Cl₂ and HCl in a typical condition at 900 °C, 1 atm, the excess oxygen coefficient R_o = 2.](image-url)
To ensure complete combustion of pyrolysis gas, sufficient oxygen is required from the perspective of the chemical reaction. The amount of oxygen is represented by the excess oxygen coefficient, \( R_o \).

\[
R_o = \frac{O_{\text{act}}}{O_{\text{the}}} \tag{3}
\]

where, \( O_{\text{the}} \) is the theoretical oxygen demand, i.e., the quantity of oxygen needed to complete the entire combustion of pyrolysis gas, and \( O_{\text{act}} \) is the actual amount of oxygen. In the conventional combustion of pyrolysis gas, the excess oxygen coefficient is 1.7–2.5 (Jiang, 2005). Therefore, the maximum value of the excess oxygen coefficient, \( R_o \), is set to 3.

### 2.2. Simulation specification

ASPEN Plus® is used to calculate the thermodynamic equilibrium. The comprehensive physical and thermodynamic property data banks and mature modules embedded in the ASPEN Plus® make the software appropriate for equilibrium composition simulation. The RGIBBS module, which is based on the Gibbs free energy minimization principle, is used to determine the equilibrium composition of the Deacon reaction. The key parameters are listed in Table 1. The physical property data and methods were verified by HSC® chemistry.

### 3. Results and discussion

#### 3.1. Effect of oxygen carrier

Research on oxygen carriers mainly focuses on iron, nickel, copper, cobalt, manganese-based oxygen carriers, CaSO₄, and ilmenite. Iron, copper, cobalt, and nickel have a variety of oxides in different valences, and Fe₂O₃, NiO, CuO, Mn₃O₄, and CoO are widely used as oxygen carriers (Li et al., 2009). At 900 °C and 1 atm, the equilibrium condition for pyrolysis gas reacting with the seven kinds of oxygen carriers under various excess oxygen coefficients is obtained. The equilibrium of pyrolysis gas reacting with air is also presented as a reference. The results are illustrated in Fig. 4. The possible reactions of HCl with oxygen carriers (metal oxides) are presented in two ways: (a) the Deacon reaction produces Cl₂; and (b) the double decomposition reaction generates metal chlorides. The Deacon reaction is preferred in the simulation condition.

**Fig. 4 – Amount of Cl₂ in various equilibrium conditions.**

The activity order of the Deacon reaction is air > CuO > NiO > CaSO₄ > CoO > Fe₂O₃ > Mn₃O₄ > FeTiO₃ (Fig. 4). Pyrolysis gas combusted by air produces the maximum amount of Cl₂, which is the reason for dioxin formation in the pyrolysis gas direct combustion. The amount of Cl₂ increases with the excess oxygen coefficient. However, when \( R_o > 1.5 \), the amount of Cl₂ remains relatively constant. This finding indicates that the equilibrium of the Deacon reaction is not affected by molecular oxygen when oxygen is sufficient. CuO reacting with pyrolysis gas generates the maximum amount of Cl₂ among the seven kinds of oxygen carriers. Notably, the amount of Cl₂ can reach 35% of that in the air case when \( R_o > 2.5 \). The reason for this phenomenon is that CuO can undergo the following reaction to release molecular oxygen.

\[
4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2 \tag{4}
\]

The release of molecular oxygen makes CuO similar to air when reacting with pyrolysis gas, and the release mechanism is the basis of chemical looping with oxygen uncoupling (Mattisson et al., 2009b).

NiO reacting with pyrolysis gas releases the maximum amount of Cl₂ among oxygen carriers with lattice oxygen oxidization, which indicates that the thermodynamics of NiO in the pyrolysis gas oxidization reaction is beneficial to the Deacon reaction. The amount of Cl₂ in the CaSO₄ case is slightly less than that in NiO case. The amount of Cl₂ during pyrolysis gas combustion by CoO is less than that in NiO and CaSO₄ cases. However, the three cases show similar tendencies, in which the amount of Cl₂ initially increases and then remains constant with \( R_o \). The amount of Cl₂ in Fe₂O₃ and Mn₃O₄ cases is relatively small and slowly increases with \( R_o \). FeTiO₃ (ilmenite) reacting with pyrolysis gas generates the minimum amount of Cl₂, and the amount of Cl₂ keeps steady with \( R_o \). From the abovementioned results, the activity of the Deacon reaction oxidized by lattice oxygen is less than that by

### Table 1 – Key parameters of the simulation.

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<td>Calculation algorism</td>
<td>Sequential modular</td>
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<tr>
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</table>
molecular oxygen. Therefore, lattice oxygen shows a lower activity than molecular oxygen in dioxin formation.

Moreover, when \( R_o > 1 \), the amount of \( Cl_2 \) in NiO, CaSO_4, CoO, and FeTiO_3 cases almost remains constant, but the amount of \( Cl_2 \) in CuO, Fe_2O_3, and Mn_3O_4 cases increases with \( R_o \). The reason for this phenomenon is that the reduction of CuO, Fe_2O_3, and Mn_3O_4 involves multiple stages, and the proportion of high-valence oxides with superior thermodynamic properties increases with \( R_o \), which leads to the increased amount of \( Cl_2 \). Conversely, the reduction of NiO, CaSO_4, CoO, and FeTiO_3 only contains one stage; thus, the equilibrium composition of the system is not affected by \( R_o \).

CuO is a typical oxygen carrier applied to chemical looping with oxygen uncoupling (Mattisson et al., 2009b). NiO is widely used in CLC (Linderholm et al., 2008). Fe_2O_3 is the most common oxygen carrier in chemical looping gasification (Li et al., 2009b). FeTiO_3 has emerged as a new oxygen carrier (Bao et al., 2013) that reacts with pyrolysis gas and releases a minimum amount of \( Cl_2 \). The following discussions are based on these four oxygen carriers.

### 3.2. Effect of temperature

Temperature is a vital parameter that determines the thermodynamic equilibrium. The influence of temperature on the Deacon reaction of the four representative oxygen carriers at 1 atm and \( R_o = 2 \) is presented in Fig. 5. The air case is shown for reference.

As shown in Fig. 5, in the range of 700–1100 °C, the activity order of the Deacon reaction is air > CuO > NiO > Fe_2O_3 > FeTiO_3, which corresponds to Fig. 4. For NiO, Fe_2O_3, and FeTiO_3, an increase in the amount of \( Cl_2 \) as a function of temperature was observed. The reason for this phenomenon is that the reaction between \( HCl \) and the three oxygen carriers is endothermic, as shown in the following:

\[
MeO_x + 2(x-y)HCl \rightarrow MeO_y + (x-y)Cl_2 + (x-y)H_2O, x > y, \Delta H > 0
\]  
(5)

where \( MeO_x \) represents NiO, Fe_2O_3, and FeTiO_3, and \( MeO_y \) indicates the reduced oxides, such as \( Ni, Fe_3O_4, FeO, Fe, \) and \( Fe + TiO_2 \). The reaction heats (\( \Delta H \)) of all reactions involved in general formula (5) were obtained from HSC® Chemistry, and the results are shown as Eqs. (6)–(10).

\[
\begin{align*}
NiO + 2HCl & \rightarrow Ni + Cl_2 + H_2O, \quad \Delta H = 176.7-174.1\,kJ/mol at 700-1100°C \\
3Fe_2O_3 + 2HCl & \rightarrow 2Fe_3O_4 + Cl_2 + H_2O, \quad \Delta H = 188.5-183.6\,kJ/mol at 700-1100°C \\
Fe_3O_4 + 2HCl & \rightarrow 3FeO + Cl_2 + H_2O, \quad \Delta H = 234.0-233.9\,kJ/mol at 700-1100°C \\
FeO + 2HCl & \rightarrow Fe + Cl_2 + H_2O, \quad \Delta H = 205.3-205.2\,kJ/mol at 700-1100°C \\
FeTiO_3 + 2HCl & \rightarrow Fe + TiO_2 + Cl_2 + H_2O, \quad \Delta H = 323.4-278.0\,kJ/mol at 700-1100°C \\
O_2 + 4HCl & \rightarrow 2Cl_2 + 2H_2O, \quad \Delta H = -118.0-119.4\,kJ/mol at 700-1100°C
\end{align*}
\]  
(6–11)

Eq. (5) is endothermic and is favorable at high temperature. Moreover, the amount of \( Cl_2 \) in the post-combustion zone increases with temperature, which leads to increased dioxin. For NiO, Fe_2O_3, and FeTiO_3, low temperature is good for the inhibition of dioxin. However, reactivity is low and carbon is formed at low temperature. Therefore, the optimal temperature should represent a tradeoff among these issues.

For CuO, a decrease in the amount of \( Cl_2 \) with temperature was observed, similar to the air case. This result reveals that the CuO and air cases have a similar reaction mechanism, which is molecular oxygen oxidation. Moreover, the Deacon reaction oxidized by molecular oxygen, as shown in Eq. (11), is exothermic, which proves the previous hypothesis. As mentioned previously, the optimal temperature for the CuO case should also make compromises among dioxin formation, material, and cost.

### 3.3. Effect of pressure

In a reaction with a changeable gas stoichiometric coefficient, the equilibrium composition is also affected by pressure aside from temperature. The effect of pressure on the Deacon reaction of the four representative oxygen carriers at 900 °C and \( R_o = 2 \) is shown in Fig. 6. The air case is also presented for reference.
In the range of 0.1–10 atm, the activity order of the Deacon reaction is air > CuO > NiO > Fe₂O₃ > FeTiO₃, which is in accordance with Fig. 4. For NiO, Fe₂O₃, and FeTiO₃, the amount of Cl₂ nearly remains constant with increasing pressure (Fig. 6). This result indicates that the gas stoichiometric coefficient of reaction, which is the formation of Cl₂ oxidized by NiO, Fe₂O₃, and FeTiO₃, is unchangeable. The Deacon reaction oxidized by these three oxygen carriers is described in the Kröger–Vink notation (Murugan et al., 2011):

\[
2\text{HCl} + O^X_0 \rightarrow \text{H}_2\text{O} + \text{Cl}_2 + V_0
\]  

where, \(O^X_0\) is lattice oxygen and \(V_0\) is oxygen vacancy. This equation is the formula for the Deacon reaction in which lattice oxygen is involved. As lattice oxygen and oxygen vacancy both exist in the solid phase, the gas stoichiometric coefficient of the reaction remains constant. Therefore, the amount of Cl₂ produced is not affected by pressure, similar to Fig. 6, which indirectly demonstrates the lattice oxygen oxidation mechanism (Galinsky et al., 2013; Li et al., 2011a,b; Murugan et al., 2011).

However, CuO shows a different phenomenon compared with the other three oxygen carriers. That is, the amount of Cl₂ distinctly increases with pressure. This result denotes that the gas stoichiometric coefficient of the reaction oxidized by CuO decreases. As presented in Eqs. (11) and (12), the gas stoichiometric coefficient of molecular oxygen involved in the Deacon reaction decreases; and the gas stoichiometric coefficient of lattice oxygen involved in the Deacon reaction is unchangeable. Therefore, molecular oxygen oxidation is the mechanism of the Deacon reaction oxidized by CuO. This is also demonstrated by the amount of Cl₂ in the CuO and air cases, which show similar tendencies with pressure.

3.4. Effect of gas composition

To avoid the need for a pyrolysis device and the complexity of real pyrolysis gas compositions, simulated gas, such as pure CO (Bao et al., 2013) and a mixture of CO and H₂ (Sridhar et al., 2012; Tong et al., 2013), is widely used as fuel in studies of CLC. Comparing simulated gas and pyrolysis gas is essential to determine the experimental scheme of the Deacon reaction or dioxin formation. The effect of the pyrolysis gas composition on the Deacon reaction can be obtained from this comparison. Four gases with different compositions (Table 2) are discussed in this section. Simulated gas IV is used to demonstrate the proposed hypothesis, which is discussed later.

The composition of other components in pyrolysis gas (III) is shown in Section 2.1.

3.5. Effect of tar

The pyrolysis of solid waste generates tar, whose maximum mass fraction can reach up to 0.1 of pyrolysis gas (Jiang, 2005). The requirements of different processes determine whether tar is removed. As CLC can handle tar (Luo et al., 2013), tar can remain in the pyrolysis gas in the pyrolysis-CLC process. In this section, toluene is applied as a tar model compound for thermodynamic calculation because the composition of tar is complex and changes with the pyrolysis conditions and solid waste (Tang et al., 2012; Tao et al., 2013). The effect of tar on the Deacon reaction of the four typical oxygen carriers at 900 °C and 1 atm is shown in Fig. 8.

As presented in Fig. 8, for each oxygen carrier, the addition of tar can slightly suppress the Deacon reaction and reduce the amount of Cl₂. The tendency that the amount of Cl₂ changes with \(R_o\) is the same. The effect of added tar on the amount of Cl₂ is insignificant.

<table>
<thead>
<tr>
<th>Gas component (symbol)</th>
<th>CO (I)</th>
<th>CO + H₂ (II)</th>
<th>Pyrolysis gas (III)</th>
<th>CO + H₂O (IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.999</td>
<td>0.666</td>
<td>0.304</td>
<td>0.666</td>
</tr>
<tr>
<td>H₂</td>
<td>–</td>
<td>0.333</td>
<td>0.166</td>
<td>–</td>
</tr>
<tr>
<td>H₂O</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.333</td>
</tr>
<tr>
<td>HCl</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
</tbody>
</table>

The composition of other components in pyrolysis gas (III) is shown in Section 2.1.
3.6. Prediction of dioxin reduction

The effects of various factors on the Deacon reaction have been discussed above. Dioxin reduction is predicted by adopting the process shown in Fig. 1 to deal with solid waste. Dioxin reduction of the four oxygen carriers at 900 °C and 1 atm with typical pyrolysis gas and no tar is predicted. The main assumptions are as follows: (a) dioxin formation during pyrolysis of solid waste is insignificant; (b) the chlorine element in solid waste exists in the form of HCl in pyrolysis gas; (c) the reduction ratio of Cl2 produced by the Deacon reaction is the reduction ratio of dioxin; and (d) dioxin
reduction is predicted on the basis of thermodynamic equilibrium. Dioxin reduction in China, Europe, the United States, and Japan is predicted, and the results are presented in Fig. 9.

The column in Fig. 9 represents the dioxin production per year reported in the literature (Gao, 2009). The solid symbol in Fig. 9 denotes the predicted dioxin production when the pyrolysis-CLC process is applied to dispose solid waste. The open star in Fig. 9 is the proportion of dioxin produced during solid waste incineration in the total dioxin production, and it is expressed as sw/tot. The dioxin production during solid waste incineration can be substantially reduced by using pyrolysis-CLC (Fig. 9). For NiO, Fe₂O₃, and FeTiO₃, the dioxin produced by solid waste incineration is almost reduced to zero, and for CuO, the dioxin generated by solid waste incineration also decreases to an extremely low level. The total dioxin production is decreased when the solid waste is disposed by the pyrolysis-CLC. The reduction of total dioxin is more conspicuous when the proportion (sw/tot) is large (Fig. 9).

4. Conclusions

The potential application of chemical looping combustion in dioxin inhibition based on the thermodynamic equilibrium of the Deacon reaction is investigated in this paper. The thermodynamic analysis shows that the Cl₂ amount of the Deacon reaction oxidized by seven oxygen carriers is lower than that by air. For the four typical oxygen carriers, the influences of temperature, pressure, gas composition, and tar on the Deacon reaction are discussed in detail. The results indicate that the activity of lattice molecular oxygen. The change in dioxin production is predicted when the pyrolysis-CLC process is applied to dispose solid waste. The result reveals that the predicted reduction of total dioxin production is obvious in China, Europe, the United States, and Japan.

From the perspective of thermodynamic equilibrium, chemical looping combustion can inhibit dioxin formation. It is a promising technology that can be applied for the clean disposal of solid waste.

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REFERENCES


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