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Integrated carbon dioxide/sludge gasification using waste heat from hot slags: Syngas production and sulfur dioxide fixation

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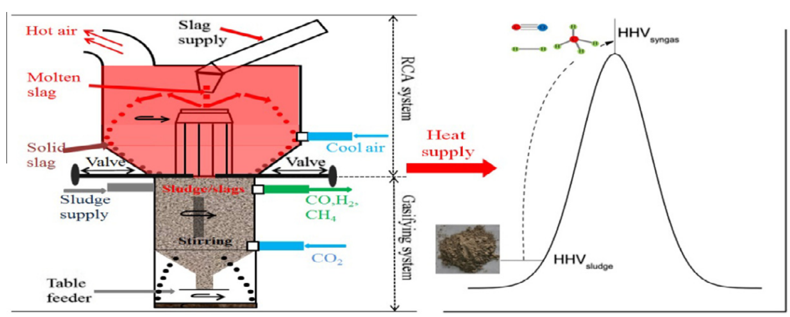
HIGHLIGHTS

- Integrated CO_2/sludge gasification was explored using the waste heat from slags.
- The characteristics and the mechanism of syngas release were identified.
- The hot slags acted as not only good heat carrier but also effective SO_2 fixation.
- A conceptual model of CO_2/sludge gasification with multi-system was designed.

GRAPHICAL ABSTRACT

Syngas production was achieved using an integrated method of CO_2/sludge gasification using hot slags from the steel industry. This method mainly involved a rotary cup atomizer (RCA) system and a gasifying system.



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ABSTRACT

The integrated CO_2/sludge gasification using the waste heat in hot slags, was explored with the aim of syngas production, waste heat recovery and sewage sludge disposal. The results demonstrated that hot slags presented multiple roles on sludge gasification, i.e., not only a good heat carrier (500–950 °C) but also an effective desulfurizer (800–900 °C). The total gas yields increased from 0.022 kg/kg_{sludge} at 500 °C to 0.422 kg/kg_{sludge} at 900 °C; meanwhile, the SO_2 concentration at 900 °C remarkably reduced from 164 ppm to 114 ppm by blast furnace slags (BFS) and 93 ppm by steel slags (SS), respectively. A three-stage reaction was clarified including volatile release, char transformation and fixed carbon using Gaussian fittings and the kinetic model was analyzed. Accordingly, a decline process using the integrated method was designed and the optimum slag/sludge ratio was deduced. These deciphered results appealed potential ways of reasonable disposal of sewage sludge and efficient recovery of waste heat from hot slags.

1. Introduction

Nowadays, numerous advanced routes have been exploited to foster clean and sustainable energy sources and reduce the energy consumption in traditional industrial sectors, which is significant not only for energy savings but also for greenhouse gas (GHG) reduction. Amongst the traditional sectors, the steel industry contributes to a large part of energy consumption and GHG emission. Currently, the energy consumption per ton crude steel in China is ~15% higher than the international advanced level (Li and Zhu, 2014) and it has been evaluated that the heat recovery from hot slags represents a great potential to reduce energy consumption

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in the steel industry (Barati et al., 2011; Zhang et al., 2013). The untapped molten slags at 1550–1650 °C, carry a high quality thermal energy, and blast furnace slags (BFS) and steel slags (SS) are two kinds of byproducts generated from iron and steel making processes, which account for more than 90% of the waste heat in slags (Barati et al., 2011). In China, the substantial waste heat of BFS and SS (200 million tons and 70 million tons in 2012) is more than the heat of 16 million tons of standard coal; however, the recovery ratio was less than 2% (Cai et al., 2007). Therefore, this study was motivated with the aim of heat recovery from BFS and SS.

The thermal conductivity is ranged from 1–3 $Wm^{-1}K^{-1}$ for solid slags to 0.1–0.3 $Wm^{-1}K^{-1}$ for liquid slags (Barati et al., 2011), which accounted for the fundamental constraint of heat extraction. To meet this challenge, we have analyzed the cooling path of BFS (Sun et al., 2014a) and proposed a multi-stage control method (Sun et al., 2014b), based on which a chemical method at temperatures lower than 950 °C was theoretically reasonable. Amongst the chemical methods, coal gasification and methane reforming have been extensively investigated recently. Li et al. (2012a, 2013) found that BFS acted as an active catalyst for CO_2/coal gasification at 1300–1400 °C because of a remarkable increase of the reactivity index. A series of studies (Maruoka et al., 2004; Purwanto and Akiyama, 2006; Shimada et al., 2000) on methane reforming using hot slags were performed and the catalytic effect was also identified at 700–1000 °C and the economic feasibility was evaluated. Recently, Nakano and Bennett (2014) made a pioneering effort to produce CO and H_2 by utilizing reaction between CO_2/H_2O, CaO-rich slags and V_2O_3-riched slags at 1405–1460 °C. Additionally, Malvoisin et al. (2013) even designed an emerging method to produce H_2 from water using the heat at 200–400 °C by means of the Fe_2O_3 formation from FeO in slags.

Meanwhile, more than 6.55 million tons of dry sewage sludge was discharged by urban wastewater treatment plant in China, the timely and effective disposal of which has been a severe environmental issue. Currently, pyrolysis and gasification of dry sewage sludge are considered as the waste-to-clean strategies and have been extensively studied. De Andres et al. (2011a) investigated the air–steam gasification of sludge at 750–850 °C using dolomite, olivine and alumina as catalysts and a syngas composed of CO, H_2, CH_4 and CO_2 was obtained. Roche et al. (2014) studied the air and air–steam sludge gasification and they found that dolomite enhanced the tar decomposition and increased the syngas yield at 800 °C. Nipattummakul et al. (2010) explored the evolutionary behavior of sludge–steam gasification at 700–1000 °C and discovered that sludge yielded more hydrogen than paper and food wastes. Recently, supercritical water gasification of sludge has been intensively investigated because of the high yield of hydrogen in spite of the accompanied operational difficulties (Acelas et al., 2014; Li et al., 2012b; Wilkinson et al., 2012). Besides, Liu et al. (2013) discovered that the calcium in lime-conditioned sludge encouraged the cleavages of C—C and C—H bonds and greatly improved the gaseous production.

These studies provided increasing possibilities of sludge disposal using novel routes. In views of heat recovery from slags, the waste heat could act as heat carrier for gasification and an integrated system was therefore designed. Although the advantageous role of the thermal energy in the slag is obvious, it is not known whether the presence of slag could exhibit a possible catalytic effect or even change the kinetic mechanism of sludge gasification, and therefore the present study was motivated. In this study, both BFS and SS were utilized to perform the sludge gasification; meanwhile, CO_2 was used as gasifying agent rather than steam from point of view of carbon capture and storage (CCS). Both the overall characteristics of the sludge gasification and the possible variation of reaction mechanism due to the hot slags were analyzed.

2. Methods

2.1. Sample preparations

The sewage sludge sample was supplied from a municipal wastewater treatment plant located in Beijing, China. The results of the proximate and ultimate analyses of the sludge samples are shown in Table 1 in addition with the chemical compositions of the BFS and SS collected from Shougang Corporation, China, analyzed by X-ray fluoroscopy (XRF, S4-Explorer, Bruker). The sludge and slag samples were dried in air at 105 °C for 24 h, crushed and ground to 300 meshes, and then thoroughly mixed using a ball mill. Three samples containing 0.05 g dry sludge were used to conduct the gasification, i.e., the dry sewage sludge (**S1**), the mixture of sludge and BFS with the mass ratio of 1:1 (**S2**), and the mixture of sludge and steel SS with the mass ratio of 1:1 (**S3**). In addition, the chemical composition of the sludge ashes were determined by XRF, as listed in Table 1.

2.2. Experimental apparatus and procedure

A series of isothermal gasification experiments were conducted using a fixed bed system, which was composed of a control part of gasifying agent, a tube furnace reactor, a gas condenser and purifier part and a gas analyzer (depicted in Supplemental Fig. S1). A quartz boat was used to hold the samples and placed into a quartz tube reactor, which was externally heated by an electric furnace. Pure CO_2 was used to perform the gasification and the flow rate was accurately controlled by a mass flow meter, i.e., 200 ml/min; the gasification temperature was selected as 500–950 °C, which was widely employed for sludge gasification (De Andres et al., 2011a; Nipattummakul et al., 2010; Roche et al., 2014). The tube reactor was first heated with the gasifying agent pumped into the system to fully expel the air inside and as the temperature reached the prescribed point, the quartz boat filled with samples was then placed on the right side of the tube for 20 min to stabilize the temperature and the atmosphere. Then the sample boat was rapidly

Table 1
Characteristics of sewage sludge, blast furnace slags and steel slags.

Dry sludge	Proximate analysis (%)				Ultimate analysis (%)					HHV (MJ/kg)
	Moisture 1.97	Volatile 36.53	Ash 54.34	Fixed carbon 9.13	C 22.11	H 3.37	O 22.92	N 4.97	S 1.07	9.35
Sludge ash (XRF)	SiO_2 34.44	Al_2O_3 18.14	CaO 13.77	P_2O_5 13.02	Fe_2O_3 8.01	MgO 5.69	Na_2O 2.43	K_2O 2.34	TiO_2 0.661	S 0.186
BFS (XRF)	CaO 37.88	SiO_2 34.61	MgO 15.62	Al_2O_3 8.56	S 0.92	Fe_2O_3 0.6	Na_2O 0.54	TiO_2 0.45	MnO 0.36	K_2O 0.26
SS (XRF)	CaO 41.98	Fe_2O_3 18.89	SiO_2 15.85	Al_2O_3 8.59	MgO 7.79	MnO 3.15	P_2O_5 1.19	TiO_2 1.17	V 0.453	S 0.283