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The production of hydrogen-rich gas by wet sludge pyrolysis using waste heat from blast-furnace slag

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ABSTRACT

Blast furnace (BF) slag, a byproduct of steelmaking industry, contains a large amount of sensible heat and is composed of some metal oxides, which exhibits preferable catalytic performance in improving tar cracking and C_nH_m reforming. This paper presents a heat recovery system from the heat of BF slag, which generates hydrogen-rich gas via the endothermic reactions of sludge pyrolysis. The effects of various parameters including the slag temperature, the mass ratio of slag to sludge (B/S), particle size and feed moisture on product yields and gas characteristics were evaluated separately. It was found that the pyrolysis products distribution was significantly influenced by the BF slag temperature. The differences resulting from varying B/S practically disappear as higher temperature heat carrier is approached. The optimum feed moisture was in favour of sludge pyrolysis by getting char and tar participate in gasification reactions, improving gas yield and quality. BF slag as catalyst can greatly increase H_2 and CO contents of gas by improving tar degradation and reforming of biogas (CO_2 and CH_4). Decreasing the slag particles size was helpful to sludge primary pyrolysis to produce more light gases, less char and condensate, while its effects on gas compositions was not evident.

1. Introduction

Sewage sludge is a waste product obtained from the domestic and industrial wastewater treatment plants. Sewage sludge commonly contains pathogens, heavy metals, poly-chlorinated biphenyls and dioxin and inevitably releases out odor, which therefore threatens the environmental security. Consequently, it is impressive to process the sludge to make it harmless [1,2]. Due to the high loading of organic matters and combustible components, the sludge has high energy development and utilization value. It will facilitate significant energy conservation, if the energy is recovered and translated into liquid or gas fuel easy to store and transport.

Despite the traditional incineration technology has the maximal capacity for sludge reduction, it will produce serious flue gas secondary pollution. In contrast, the sludge pyrolysis technology takes full advantage of calorific value of the sludge with higher energy utilization efficiency and lower cost, and is thus regarded as a suitable and promising technology [3,4]. In addition, it not only recovers energy from sewage sludge in the form of combustible gas, but also realizes the harmless and reducing treatment of sludge (preventing it from the toxic organic compounds, fixing the heavy metals in the resulting solid ash). In pyrolysis processes, some key endothermic reactions consume large amount of energy, which is normally sustained by the combustion of fossil fuel [5,6]. In consideration of this, it is an unreasonable and uneconomical strategy using fossil as the energy source.

Blast furnace slag, a byproduct of iron and steel production, usually discharged at high temperature (1200–1600 °C) [7], is dissipated into the atmosphere by water granulation, which gives rise to serious environmental problems (e.g., steam, polluted water, and hydrogen sulfide). Thus, several attempts have been made to enable energy conservation of waste heat of BF slag [8–10]. Specifically, the slag granulation method can produce fine slag particles less than 10 mm in diameter. According to the energy theory, high temperature waste heat should be used as a high temperature heat source [11]. Therefore, if waste heat is combined with the desired endothermic reaction, it will facilitate significant energy conservation. Recently, many researchers have been focusing on a new heat recovery system that uses an endothermic reaction instead of

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sensible heat. For instance, Zhao et al. [12] studied the combustible gas production from municipal solid waste using hot BF slag as heat carrier. Purwanto et al. [13] reported a hydrogen production process from biogas (CO_2 and CH_4) using hot waste heat from BF slag. Nobuhiro Maruoka [14] developed a new heat recovery system of hot wastes generated by molten slag. The results proved that the waste heat from molten slag could supply the energy for hydrogen production. In general, this method is attractive because it facilitates the direct recovery of waste heat without any decrease in its existing temperature. It is noted that sludge pyrolysis using hot BF slag as heat carrier and catalyst has never been referred to and lacks a comprehensive study. Furthermore, in the previous studies [11–14], the tests referring to using BF slag as heat carrier were mainly conducted in a fixed-bed reactor, in which the BF slag was packed together and kept still during reaction process. It was unfavorable for the heat and mass transfer during reactions.

In the present work, a continuous hydrogen-rich gas production system was designed. This system does not only recover the heat from molten slag in the form of combustible gas, but also realizes the resourceful, harmless and reducing treatment of sludge. A series of tests were carried out, and the optimal operation parameters (e.g., the temperature of BF slag, the feed moisture, the mass ratio of BF slag to sludge and the particle size of BF slag, etc.) affecting pyrolysis product distribution were investigated in the lab-scale testing facility. Also the evaluation of catalytic actives of BF slag in improving tar cracking and reforming was conducted. The aim is to understand the feasibility of realizing the waste heat recovery from BF slag and the production of hydrogen-rich gas by using the endothermic reaction of sludge pyrolysis. In a word, this study was helpful to the recycling of the sensible heat of BF slag, and to the converting of low-grade liquid BF slag waste heat to bio-energy.

2. Experiment and methods

2.1. Materials

The BF slag was obtained from Qingdao Iron & Steel Company, China. The mineral phases of BF slag was analyzed by powder X-ray diffractometry (XRD), using an X'Pert Pro XRD (Philips, PANalytical B.V., Netherlands) The compositions are as follows: 33.7% of SiO_2, 15.0% of Al_2O_3, 42.2% of CaO, 6.6% of MgO by weight as well as some minor iron, sulphur, titanium, manganese, and phosphor oxides. The density of BF slag is 1325 kg/m^3.

Sewage sludge was collected from a waste water treatment plant in Qingdao. The size of sewage sludge is 3.0 cm–4.0 cm on sieving before pyrolysis. Ultimate analysis of the sewage sludge samples was obtained with a CHNS/O analyzer (Vario Micro cube, Elementar). Such analysis gives the weight percent of carbon, hydrogen, nitrogen, and sulphur in the samples simultaneously, and the weight percent of oxygen is determined by difference. ATA Instruments system (TGA 2000, Las Navas) was used to obtain proximate analysis of the sample (that is, moisture, volatile matter, fixed carbon, and ash content of the material).The proximate and ultimate analysis of sludge powder are shown in Table 1.

2.2. Experimental apparatus and procedure

The schematic lab-scale configuration is illustrated in Fig. 1. The system, mainly composed of packing bed reactor and rotary reactor, integrated the functions of heat recovery from BF slag and sludge pyrolysis. In the packing bed, molten slag was firstly granulated using a rotary-cup granulator and then a packed bed made up of granulated slag was generated under the granulator. The high temperature granulated slag particle was used as the cracking catalyst of pyrolysis gas containing tar. They cooled as they passed through the pyrolysis gas and then further cooled in the rotary reactor by a heat exchange with sludge, both of which provided the rapid cooling for the formation of glassy slag product. In the rotary reactor, the recovered heat is supplied to the sludge which is the heat recovery medium and then changed into chemical energy through the endothermic reaction.

Table 1
Proximate analysis and elemental analysis of seweage sludge.

Proximate analysis/wd %		Ultimate analysis/ wd %	
Higher heating value (MJ/kg)	16875.50	C	45.17
Moisture content	6.20	H	3.78
Volatile matter	41.33	O	9.63
Fixed carbon	14.47	N	2.87
Ash	33.45	S	18.4

The rotary reactor was made of stainless steel and surrounded by an insulation layer outside. The effective length of the reactor was 1800 mm with an outside diameter (OD) of 219 mm. The mixture of hot BF slag and sludge showed a helical flow under the function of helical vane. The gas containing tar generated from rotary reactor is subsequently introduced into the packed bed, in which the tar and C_nH_m was decomposed, and then converted into hydrogen and carbon monoxide in the help of BF slag as a catalyst.

All tests were performed at the normal atmospheric pressure. The sludge was loaded in a feedstock hopper, which was fitted with an air-tight closure system. During the tests, the sludge was continuously fed into the rotary reactor by a screw feeder with feeding rate of 100 g min^{-1}. Purified nitrogen at a constant flow rate of 10 L min^{-1} was used as the carrier gas to provide an inert atmosphere for pyrolysis and to remove any gaseous and condensable products that evolved. To ensure the reliability of test data, each experiment was repeated three times, and the results were in good agreement. The data reported in this paper are average values of three times. When the system was stably operated, the fuel gas was sampled and analyzed. The gas compositions were analyzed by a gas chromatograph (Micro-GC 3000A, Agilent) with TCD and FID detectors. The gas volumetric production was measured online using a gas meter. A spray tower was used as cooling units for gas cooling and bio-oil capture. The mass of oil was obtained as the difference in masses of the condensers before and after test. The cooled granulated slag and char were collected and weighed at the end of each experiment.

2.3. Methods of data processing

The dry gas yield (Nm^3 kg^{-1}) is calculated by,

$$Y = V_g/M \tag{1}$$

Where, M is the feeding rate (kg min^{-1}) of sludge samples, and Vg represents the product gas flow rate (Nm^3 min^{-1}).

The tar production X (mg/Nm^3) is calculated by,

$$X = m/Y \tag{2}$$

Where, m is the tar yield (mg kg^{-1}), and Y is the dry gas yield (Nm^3 kg^{-1}).

Steam decomposition η (%) is calculated by,

$$\eta = \frac{1000Y(H_2\% + 2\times CH_4\% + 2\times C_2H_4\% + 3\times C_2H_6\%)\times 18/22.4}{W} \times 100 \tag{3}$$