

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



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ABSTRACT

The granulation for molten slag produces a large amount of sensible and recoverable heat. In this paper, a system was proposed to simultaneously produce glassy slag and reuse the heat for production of hydrogen-rich gas via biomass catalytic pyrolysis. A variety of parameters, including slag temperature, mass ratio of slag to biomass (S/B), particles size, and rotor speed, were evaluated for their effects on pyrolysis product yields and gas characteristics. The catalytic activity of blast-furnace (BF) slag for improving tar cracking was also addressed. The conditions of 1000 °C of slag temperature and 0.6 of S/B achieved a complete pyrolysis of biomass. When the S/B value increased to 0.8, a lower slag temperature (700 °C) can afford a complete pyrolysis of biomass. The maximum gas yield was gained at a rotor speed of 16 rpm/min, when slag particles in reactor showed a “cascading” movement. BF slag exhibited a catalytic activity in tar cracking and C_nH_m reforming during biomass pyrolysis process. Furthermore, decreasing the slag particle size favored to produce more light gases, and less char and condensate. However, the effect of slag particle size became not evident in the subsequent catalytic reforming process.

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1. Introduction

Being an environmentally friendly resource, Hydrogen is considered as an alternative source of energy due to the environmentally friendly feature, and its demand is expected to surpass that of fossil fuels. Catalytic gasification of biomass is a promising method to produce hydrogen. However, key reactions in gasification processes need large amount of energy due to the endothermic nature [1,2]. It is unreasonable and uneconomical if the energy was provided by using the fossil energy. Waste heat is an alternative energy source for the gasification processes, which facilitates energy conservation.

The production of iron and steel is an energy-intensive process. The ever-increasing emphasis on the efficient use of energy promotes new ways to reduce the required energy for making iron and steel, which can be achieved by recovering and utilizing the waste heat in existed processes.

The sensible heat in molten slag is a promising source of waste heat with a temperature of over 1400 °C, accounting for 2–3% of the

energy consumption in crude steel production. Especially for the blast furnace (BF), the liquid BF slag is usually discharged at high temperature (1200–1600 °C) [3], and the emitted sensible heat is dissipated into the atmosphere. Approximately 80% of pig iron in the world is manufactured using BF ironmaking technology, and in China, the number reaches approximately 90%. Reutilization of waste heat in liquid slag has been a great opportunity to lower the energy requirement for metal production.

One of the most promising ways of recovering heat from liquid BF slag is the dry centrifugal granulation process [4,5], in which the liquid slag is granulated and then cooled rapidly to produce a glassy slag. Due to high temperature (as the time of granulation is short, and the temperature falls by only about 100–200 °C), the glassy slag becomes an ideal waste heat resource and can be used as the heat carrier in endothermic reactions. Zhao et al. [6] studied the combustible gas production from municipal solid waste (MSW) using hot BF slag as heat carrier in a fixed-bed reactor. The results showed that BF slag acted as both catalyst and heat carrier, and promoted the gasification reactivity of MSW. Purwanto et al. [7] reported a hydrogen production process from biogas (CO_2 and CH_4) using hot BF slag as heat carrier. The results proved that the waste heat from molten slag could supply the energy for hydrogen

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production. Nobuhiro Maruoka [8,9] developed a new heat recovery system of hot wastes generated from molten slag. The waste heat generated by the graduation was first stored using a phase-change material, and then supplied to an endothermic methane–steam reforming reaction as a heat source.

Although several attempts have been made to utilize the energy from liquid BF slag, there has not been efficient and feasible technology and reactor for the heat recovery till now. The main defects include:

- 1) In terms of reactor type, the experimental apparatus was usually fixed-bed reactor and the operation process was intermittent [6,7]. BF slag and biomass were packed together in the reactor and kept still during reaction process, which was unfavorable for the heat and mass transfer.
- 2) In terms of reaction scheme, the roles of BF slag as heat carrier and catalyst were simultaneously played in the same reactor [6], and the catalytic reactions was affected due to carbon deposition (from biomass pyrolysis) in the surface of BF particle.
- 3) In terms of regulation of reaction conditions, the regulation (such as temperature, atmosphere and time, etc.) was difficult to quickly achieve at the same time for both the pyrolysis of biomass and catalytic reforming of tar.

In the present work, a continuous-operation hydrogen-rich gas production system was designed (as shown in Fig. 1). The pyrolysis of biomass and the catalytic cracking of pyrolysis product were conducted in a rotary reactor and a granulation reactor, respectively. This system not only recovered the heat from the liquid BF slag in the form of combustible gas, but also produced a commercially useful glassy slag product (used as thermal insulation material or cement additives, etc.). This will achieve the recycling and conversion of the sensible heat of BF slag to bio-energy.

The motion states of BF slag in rotary pyrolysis reactor, catalytic activity of BF slag in tar cracking, and the influences of the mass ratio of BF slag to biomass, the temperature and particle size of BF slag on biomass pyrolysis product yields and gas characteristics were comprehensively studied. The objectives of this work are to

Table 1

Particle size distribution of biomass powder.

Particle size/mm	<0.075	0.075–0.15	0.15–0.3	0.3–0.7	0.7–1.4	>1.4
wt%	33.4	27.05	19.25	10.69	4.02	5.59

Table 2

Proximate analysis and elemental analysis.

Proximate analysis/wt%		Ultimate analysis/wt%	
Higher heating value (MJ/kg)	19.37	C	49.42
Moisture content	8.61	H	7.82
Volatile matter	76.50	O	42.49
Fixed carbon	14.41	N	0.12
Ash	1.02	S	0.06

investigate the reliability of hydrogen-rich gas production by catalytic pyrolysis of biomass using hot BF slag as thermal media and catalyst, and to optimize the operation parameters.

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 SiO₂, 15.0% of Al₂O₃, 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/m³.

The raw biomass materials, pine sawdust, were collected in Qingdao City, China, and were crushed by a self-designed crushing process [10]. Ultimate analysis of the biomass samples was obtained with a CHNS/O analyzer (Vario Micro cube, Elementar). Such analysis gives the weight percent of carbon, hydrogen, oxygen, 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 MSW samples (that is, moisture, volatile matter, fixed carbon, and ash content of the material). The particle size distribution and proximate and ultimate analysis of biomass powder are shown in Tables 1 and 2, respectively.

2.2. Experimental apparatus and procedure

The schematic lab-scale configuration is illustrated in Fig. 2a. The system integrated the functions of heat recovery from BF slag and biomass catalytic pyrolysis. It was mainly composed of a granulation reactor (for the granulation of liquid slag and the catalytic reforming of biomass gas containing tar) and a rotary pyrolysis reactor (for the flash pyrolysis of biomass using granulated slag as heat carrier).

The granulator can produce particles with a relatively narrow size range, which can be controlled by varying either the rotary-cup speed or the cooling agent flow. The particles cooled as they passed through the pyrolysis gas and then further cooled in the rotary pyrolysis reactor by heat exchange with biomass, both of which provided the rapid cooling condition for the formation of glassy slag product. The granulation reactor has a uniform temperature distribution, so that the temperature of testing point 1 (located in the middle of granulation reactor) can approximately reflect the reactor temperature.

The rotary pyrolysis reactor was made of stainless steel and

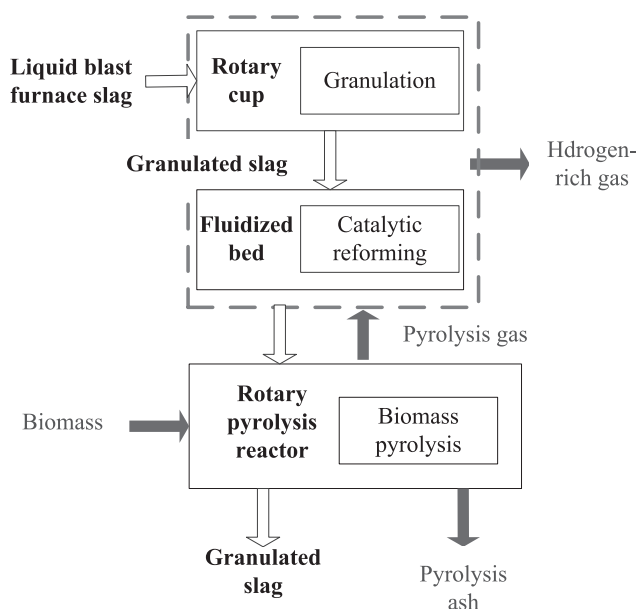


Fig. 1. Flowchart of the production of hydrogen-rich gas by catalytic pyrolysis of biomass using waste heat from blast-furnace slag.

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