Integration of biomass/steam gasification with heat recovery from hot slags: Thermodynamic characteristics

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ABSTRACT

Herein the thermodynamics of an emerging strategy, biomass/steam gasification integrated with heat recovery from hot slags, were systematically investigated following the principle of minimum Gibbs free energy to simultaneously deal with the issues of biomass disposal in agricultural sector and heat recovery in steel industry. Not only the syngas yields but also the influence of slags were identified including blast furnace slags (BFS) and steel slags (SS). The results demonstrated that, from viewpoint of maximization of H_2 production and higher heating value (HHV) of syngas, the optimum gasification temperatures for biomass and sludge were 1000 °C and 1100 °C, respectively. Compared to BFS, SS remarkably increased the H_2 production and syngas HHV at lower temperatures; while for polluted gas releases including NH_3, NO and NO_2, BFS showed more prominent influence. The present results thus provided significant clues for syngas yield optimization and pollution mitigation toward application of this novel route.

Introduction

Nowadays with the continuous development in China, there is an increasing consideration of energy saving and emission reduction in the traditional industry, especially the iron and steel industry, as an energy intensive and carbon intensive industry. Because of the substantial production and the high carbon-intensity of the products (pig iron and crude steel), implementing low carbon technologies into the steel industry is quite urgent, although a series of advanced technologies have been introduced such as the continuous casting [1,2]. In the context of global cooperation to curb the global warming, China has promised that its carbon emission would peak in 2030 [3,4], which would provide great pressure on the improvement of energy efficiency and reduction of the carbon-intensity in the steel industry.

Amongst the possible technological routes, heat recovery from high temperature slags is believed to represent the last great potential for energy saving in the steel industry [5,6]. In 2014, the output of pig iron and crude steel in China were 712 Mt (million tons) and 823 Mt [7], respectively, and accordingly, the blast furnace slags (BFS) and steel slags (SS) discharged during the ironmaking and steelmaking processes were ~213 Mt and ~123 Mt, respectively. These slags, tapped 1450–1650 °C, carried a large amount of high grade energy of 5.2×10^{14} J, corresponding to ~18 Mt standard coals, accounting for a great heat resource. However, the recovery ratio of this thermal heat was quite low as ~2% [8], leading to a large energy waste due to the fundamental constraints such as low thermal conductivity and strong crystallization trend of the slags [5,6,9].

To recover the high grade waste heat from these slags, numerous technologies have been developed recently, which could be overall categorized into two main types, i.e., physical methods and chemical methods. Physical methods were mainly focused on the development of granulation technologies of the slags such as rotary cup atomizer (RCA) [10], rotary cylinder atomizer (RCLA) [11] and spinning disk atomizer (SDA) [12]. Compared to physical methods, chemical methods provided great advantages such as production of high value syngas composed of CO, H_2 and CH_4 and integration of various industrial systems [6,9]. Therefore a series of chemical methods have been exploited during the past decade including methane reforming reaction, coal gasification as well as biomass gasification.

Matsuura et al. reported the generation of H_2 gas by reaction between FeO in steel slags and water vapor [13] and Nakano et al. performed a reaction to convert CO_2 and H_2O gas into CO and H_2 using a mixture of molten CaO-rich metallurgical slags and V_2O_3-rich gasifier slags in the agents of CO_2 and steam, respectively [14]. Li et al. experimentally investigated the kinetics of coal gasification reaction using the waste heat from BFS under CO_2 agent and found that the BFS acted as a good catalyst on coal gasification [15,16] and recently Duan et al. [17,18] calculated the thermodynamics of coal/steam gasification in the presence of BFS. Compared to primary coal, biomass was a natural carbon-neutral, the gasification of which is generally an important approach of syngas production for the chemical engineering industry [19,20]. Additionally, biomass was a quite abundant resource in China, the production of which was ~803 million tons in 2009 [20]. In this case, utilization of biomass gasification to recover the slag waste heat has been proposed recently [21,22], which provided new potential in the family of heat recovery technologies. Meanwhile, sewage sludge, regarded as a special biomass, has been increasingly discharged due to the continuous urbanization in China, the disposal of which has been a severe environmental problem. Gasification reaction was an effective route for sludge treatment and we have performed a series of studies on sludge gasification integrated with heat recovery from hot slags [23–25].

Despite of the foregoing researches, the systematically investigation on the thermodynamics of biomass gasification was quite limited, and thus the present study was motivated. Given the agents using for biomass gasification, steam was assumed to be employed in this study for the purpose of enhancement of H_2 production [26,27]. Furthermore, to extend the research area, on one hand, not only the conventional biomass but also a particular type, sewage sludge, were used in study; on the other hand, as for the clarification of the influence of the hot slags, both BFS and SS were analyzed. The clarification of the basic thermodynamic principles of this emerging route could provide significant theoretical guidance, not only for the reasonable design of an experimental process but also for the further scale-up application of the novel route in the future.

Methodology

Determination of the chemical compositions of the biomass and hot slags

Since the main objective was to clarify the theoretical syngas yields and polluted gas releases during biomass gasification integrated with slag heat recovery, thus the first step should be the determination of the chemical compositions of the biomass and hot slags. With respects to this, the ultimate analysis results of the biomass and sludge in the previous studies and reviews [28,29] including the analysis results in our own studies [21,23] were mainly referred to, as detailed in Table 1. While for the hot slags, chemical compositions reported in the previous reviews and studies [5,6] measured by X-ray fluorescence (XRF) technique were mainly considered including the researches of the present authors [21,23], as detailed in Table 2. In addition, it should be pointed out that the chemical composition of the biomass was similar to those of wheat straw reported in the previous studies [21,28,29].

As for the conventional biomass, the chemical compositions were simplified so that only C, H and O elements were considered and for the sewage sludge, N elements was also taken into account to clarify of the releases of N-related polluted gases due to its relatively high content. On the other hand, in convenience of syngas calculation, the mole contents of these elements in the raw materials were deduced based on the mass contents obtained and thus the reactive organics in the biomass and sludge could be derived as $CH_{1.47}O_{0.70}$ and $CH_{1.54}O_{0.43}N_{0.12}$, respectively. Furthermore, to confirm the complete gasification of the biomass, it was assumed that the mass ratio of the organics in biomass (or sludge) to the hot slags was 1.0 since the heat capacity of hot slags was around 1.15 kJ kg^{-1} K^{-1} [5,24] and accordingly the mass and moles of the hot slags used in the gasification could be calculated in addition to the moles of the particular oxides in the slags.

Basic reactions associated with biomass gasification

After determining the chemical compositions of biomass, the main reactions during gasification process, especially those

Table 1 – Chemical compositions (wt. %) of the biomass and sludge employed.			
Conventional biomass	C	H	O
	45%	5.5%	42%
Sewage sludge	C	H	O	N
	35%	4.5%	20%	5%