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Synthesis gas production from biomass gasification using steam coupling with natural hematite as oxygen carrier

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ABSTRACT

Biomass gasification using lattice oxygen (BGLO) of natural hematite coupling with steam was conducted in a fluidized bed reactor. The presence of hematite particles evidently facilitated to biomass gasification. Comparing with biomass steam gasification (BSG), carbon conversion and gas yield increased by 7.47% and 11.02%, respectively, and tar content lowered by 51.53%, in BGLO with an S/B of 0.85 at 800 °C. In this case, 62.30% of the lattice oxygen in the hematite particles was consumed in the biomass gasification. The reaction temperature, steam-to-biomass ratio (S/B) and reaction time on the performance of hematite particles were extensively investigated, in terms of gas distribution, heating value, yield and carbon conversion. With the reaction temperature increasing from 750 to 850 °C, the gas yield increased from1.12 to 1.53Nm^3/kg, and carbon conversion increased from 77.21% to 95.49%. An optimal S/B ratio of 0.85 was obtained in order to maximize the carbon conversion and gas yield of BGLO. At this ratio, the gas yield reached 1.41Nm^3/kg with carbon conversion of 92.98%. The gas concentration was gradually close to that of BSG at the end stage of BGLO due to the active lattice oxygen was depleted with the proceeding of reactions.

1. Introduction

Renewable energy is of growing importance with respect to global issues of fossil fuel depletion and greenhouse gas emissions. Biomass is a unique renewable resource which can be used for producing gas, liquid and solid fuels [1]. It is considered carbon neutral during biomass utilizing, because the amount of carbon released is equivalent to that it absorbed during its life time [2]. Therefore, the use of biomass as energy has shown a great application potential in mitigation of greenhouse gas emissions. Among biomass energy utilization technologies, gasification is considered as one of the promising technologies due to it gives high quality synthesis gas and low production cost. Biomass gasification is a thermo-chemical conversion process of partial oxidation which converts biomass into gases (such as H_2, CO, CO_2, CH_4 and volatile hydrocarbons), small amount of tar and char particles [3]. The gaseous product (so called “bio-syngas”) is widely used in power generation, heat supply and liquid fuel synthesis.

A large amount of oxygen-rich air or high temperature steam is required as gasifying agent in traditional biomass gasification technology, which results in high cost and complex process for producing pure oxygen. In contrast, biomass gasification using lattice oxygen (BGLO), based on the chemical looping combustion (CLC) [4,5] is an innovative gasification technique, where biomass can be converted into synthesis gas using lattice oxygen of oxygen carrier instead of molecular oxygen in the air. The product desired is synthesis gas rather than heat (produced by CLC) because of insufficient lattice oxygen in the BGLO. Hence, it is very crucial that the ratio of oxygen carrier to fuel should be kept low to prevent the fuel from becoming fully oxidized to CO_2 and H_2O [6]. In comparison to traditional biomass gasification technologies, BGLO has a major advantage for saving the cost of pure oxygen production and catalyzing tar cracking by using oxygen carrier [1,7–9].

Most of the research on partial oxidization of fuels using lattice oxygen has been focused on gaseous fuels, such as methane, because of the fine contact between gas and solid particle phases [10–12]. However, it would be highly advantageous if the technique could be applied for solid fuels, which are more abundant than natural gas. Recently, a number of literature were published about using lattice oxygen to partially oxidize solid fuels, such as coal [13], biomass [14] and plastics [15] to obtain synthesis gas or hydrogen. Acharya et al. studied the partial oxidization of biomass for hydrogen-enriched gas production and carbon dioxide capture with CaO as sorbent and obtained syngas with 71 vol. % of hydrogen

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as well as without CO_2 emission employing fluidized bed technology [16]. Matsuoka et al. investigated steam reforming of woody biomass with iron oxide-impregnated porous alumina as oxygen carriers and obtained substantial amount of H_2 by cracking of the coke on the iron oxide in a fluidized bed reactor [17]. Nevertheless, there is little of work to investigate biomass direct chemical looping conversion for generating synthesis gas with oxygen carriers of cheap and environmentally friendly. Currently, only He et al. in our research group have confirmed the feasibility of the BGLO with natural hematite as oxygen carriers in inert atmosphere (argon) by fluidized bed reactor and obtained synthesis gas with a gas yield of 0.95 N m^3/kg biomass and low heating value (LHV) of 12.47 MJ/N m^3 at 800 °C [18].

BGLO in steam atmosphere was investigated in this study, aiming to improving the biomass conversion efficiency and getting a suitable H_2/CO ratio. In the present work, thermodynamics performance of BGLO was analyzed. And the mass loss of hematite sample under argon atmosphere was studied through thermogravimetric experiment. BGLO with natural hematite as oxygen carrier was experimentally investigated in a lab-scale bubbling fluidized bed reactor using argon as fluidizing gas and steam as gasifying agent. The effects of the different operating conditions on biomass gasification were examined.

2. Thermodynamics analysis

In comparison to traditional biomass gasification, the process of BGLO is more complicated due to the presence of oxygen carrier. Biomass gasification and oxygen carrier reduction with biomass syngas were occurred simultaneously in BGLO. The major reactions involved in the biomass gasification are shown as follows:

$$\text{Water gas}: \quad C + H_2O(g) \rightarrow H_2 + CO \quad \Delta H_{923.15} = 131.7\text{kJ/mol} \tag{1}$$

$$\text{Water} - \text{gas shift}: \quad CO + H_2O(g) \rightarrow H_2 + CO_2 \quad \Delta H_{923.15} = -35.7\text{kJ/mol} \tag{2}$$

$$\text{Steam reforming}: \quad CH_4 + H_2O(g) \rightarrow 3H_2 + CO \quad \Delta H_{923.15} = 223.7\text{kJ/mol} \tag{3}$$

$$\text{Boudouard}: \quad C + CO_2 \rightarrow 2CO \quad \Delta H_{923.15} = 171.3\text{kJ/mol} \tag{4}$$

When Fe_2O_3 is used as oxygen carrier, the major reactions between biomass syngas and oxygen carrier are shown as below [19]:

$$H_2 + Fe_2O_3 \rightarrow H_2O + 2FeO \quad \Delta H_{923.15} = 32.438\text{kJ/mol} \tag{5}$$

$$CH_4 + 12Fe_2O_3 \rightarrow 2H_2O + CO_2 + 8Fe_3O_4 \quad \Delta H_{923.15} = 43.039\text{kJ/mol} \tag{6}$$

$$CH_4 + Fe_2O_3 \rightarrow 2H_2 + CO + 2FeO \quad \Delta H_{923.15} = 317.871\text{kJ/mol} \tag{7}$$

$$CO + Fe_2O_3 \rightarrow CO_2 + 2FeO \quad \Delta H_{923.15} = -3.217\text{kJ/mol} \tag{8}$$

Obviously, the reduction of hematite by gas intermediates would accelerate the process of biomass gasification. In addition, the tar would be decomposed to small molecular weight gases in the presence of iron oxide as follows [20]:

$$\text{tar} \rightarrow H_2 + CO + \text{hydrocarbon} \quad \Delta H > 0 \tag{9}$$

Hence, the final products of BGLO are determined by the interaction of a couple of above mentioned reactions.

Thermodynamics of chemical reactions is important for understanding of the reaction mechanism, the product component and the design of technical parameters. The reactions of biomass gasification and iron oxide reduction are dominated by both prevailing chemical thermodynamics and reaction kinetics [21]. Fig. 1 shows the chemical equilibrium constant (LogK) of reactions (1)–(8) calculated by HSC Outokumpu chemistry 5.1 as a function of temperature. It can be observed that LogK changes of biomass gasification are more than those of Fe_2O_3 reduction with biomass syngas within the temperature range from 650 to 900 °C. It implied that biomass gasification was easily influenced by temperature in BGLO. Additionally, some previous literature [22,23] reported that the coal gasification is the rate-controlling step in the CLC of coal. Similarly, it can be inferred that reaction rate of BGLO is determined by biomass gasification. It is well known that higher temperature favors the proceeding of biomass gasification. Hence, it can be concluded that BGLO is thermodynamically favored at higher temperatures. A reasonable reaction temperature is very important for enhancing the biomass conversion efficiency. To obtain higher biomass conversion efficiency, the reaction temperature should be maintained at 700–850 °C [24], which also can sustain the process of iron oxide reduction.

3. Experimental

3.1. Materials

Sawdust of pine selected from Guangdong province (China) was used as fuel in the tests. The sample was crushed and sieved into particles with a size range of 250–425 μm, which was dried for 8 h at 105 °C before experiment. The ultimate analysis of the pine (air-dry basis) was 49.85 wt.% carbon, 6.31 wt.% hydrogen, 0.05 wt.% nitrogen, 0.18 wt.% sulfur and 43.61wt.% oxygen (by difference). Its lower heating value was 18.52 MJ/kg. The proximate analysis of the pine (air-dry basis) was 8.39 wt.% moisture, 84.31 wt.% volatile, 6.88 wt.% fixed carbon and 0.42 wt.% ash.

Natural hematite mainly exists in the mineral form of iron oxide (Fe_2O_3), which crystallizes in the rhombohedral system, and it has the same crystal structure as ilmenite ($FeTiO_3$) and corundum. The hematite with particle sizes between 180 and 250 μm used in these experiments was supplied by Guangdong Iron & Steel Group Co. Ltd. The elemental composition analysis of the hematite was 0.03 wt.%

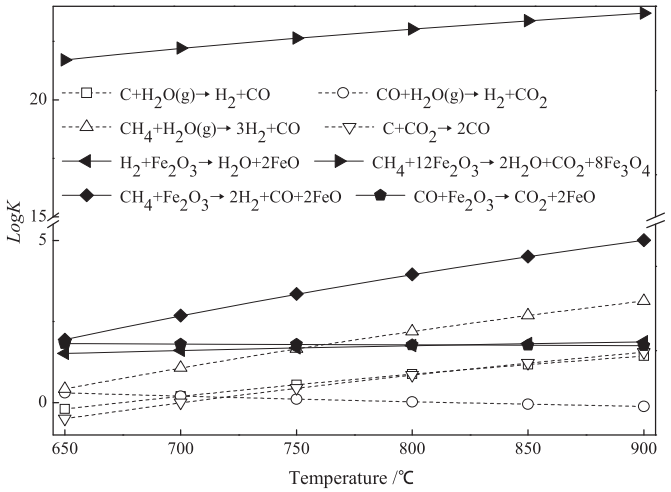

Fig. 1. Chemical equilibrium constant of both biomass steam gasification and reductions of iron oxide with syngas.