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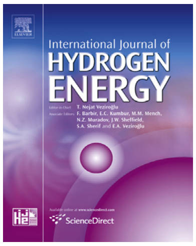

Characteristics of biomass gasification using chemical looping with iron ore as an oxygen carrier

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ABSTRACT

Experiments regarding to biomass gasification using chemical looping (BGCL) were carried out in a fluidized bed reactor under argon atmosphere. Iron ore (natural hematite) was used as an oxygen carrier in the study. Similar to steam, a performance of oxygen carrier which provided oxygen source for biomass gasification by acting as a gasifying medium was found. An optimum Fe_2O_3/C molar ratio of 0.23 was determined with the aim of obtaining maximum gas yield of 1.06 Nm^3/kg and gasification efficiency of 83.31%. The oxygen carrier was gradually deactivated with reduction time increasing, inhibiting the carbon and hydrogen in biomass from being converted into synthesis gas. The fraction of Fe^{2+} increased from 0 to 47.12% after reduction time of 45 min, which implied that active lattice oxygen of 49.75% was consumed. The oxygen carrier of fresh and reacted was analyzed by a series of characterization methods, such as X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Energy-dispersive X-ray spectroscopy (EDX).

1. Introduction

Synthesis gas, an important feedstock for the production of ammonia, methanol and other downstream products, can be produced from carbonaceous fuels such as oil, natural gas, coal and biomass [1–4]. Among these energy sources, biomass has the potential to be an interesting option due to its carbon neutral and renewable [5]. Synthesis gas is already obtained from biomass through gasification process, where biomass is partially oxidized into syngas and small amount of byproducts (i.e. tar and char) in a high temperature [6]. A large amount of pure oxygen is required as gasifying medium to obtain high quality gas in well-established biomass gasification process. The disadvantage of this process is that the introduction of air separation unit would increase the cost and make equipment facilities complicated. Biomass gasification using chemical looping (BGCL) can convert biomass into syngas without adding oxygen-enriched air as gasifying medium. BGCL process has the same basic principle as chemical looping combustion (CLC), with the main difference that target product in BGCL is synthesis gas rather than heat [7]. In the process of BGCL, biomass is firstly pyrolyzed at a high temperature, and then intermediate products of pyrolysis (e.g. H_2, CH_4, CO, tar and char) react with oxygen carrier particles. On the one hand, reduction reactions of oxygen carrier consume a part of pyrolysis products, promoting the process of biomass pyrolysis forward. On the other hand, the products of reduction reactions of oxygen carrier (i.e. CO_2 and H_2O) can act as gasifying

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medium enhancing the biomass and char gasification. In addition, the oxygen carrier particles play the roles of catalysts for decomposing and reforming the tarry materials, which are undesirable products in biomass gasification [8,9]. After biomass gasification, the reduced oxygen carrier recovers lattice oxygen to its original state in air atmosphere. These reactions occur sequentially and simultaneously during the reduction and oxidization of oxygen carrier particles. Thus, the final products of BGCL are determined by the combination of above mentioned reactions.

The oxygen carrier particles are used to transport oxygen from air to fuel via the recyclic redox reactions. Therefore, the performances of the oxygen carrier particles are crucial issues for BGCL process. Many important characteristics should be provided by oxygen carrier particles, such as high oxygen transport and reactivity, low cost and environmentally benign, high mechanical strength, resistant to agglomeration and attrition [10]. Some synthetic metal oxides, such as NiO, Fe_2O_3, CoO, CuO, and Mn_2O_3, some oxides of sulfate and perovskite have been intensively investigated as potential oxygen carriers for chemical looping scheme [11,12]. However, they presented respective disadvantages as summarized elsewhere [7,10].

Recently, natural iron ore has attracted significant interest due to its low cost and high melt point [13]. Leion et al. [14] investigated the CLC of different solid fuels (i.e. petroleum coke and coal) with iron ore (ilmenite) as the oxygen carrier in a fluidized bed reactor. The results indicated that the ilmenite presented comparable reactivity with synthetic oxygen carrier particles ($FeTiO_3$/Fe_2TiO_5). Xiao et al. [15] performed extensive investigation on iron ore as the oxygen carrier in the pressurized CLC of coal. The research results showed that elevated pressure improved the overall reaction rate of CLC of coal, and the reactivity of iron ore was notably enhanced with cycle numbers. The iron ore particles were further investigated in the continuous thermal CLC system with coal/biomass as fuels by Chalmers University of Technology [16–18] and Southeast University [19,20], respectively. Above mentioned researches indicate that iron ore particles as oxygen carriers are promising in CLC of solid fuels. High solid inventory (oxygen carrier particles) is required to obtain high concentration of CO_2 and heat in CLC of solid fuels. As the ratio of solid inventory to fuel is kept low, the partially oxidation process of solid fuel would occur with synthesis gas as the main target product. Until now, there are little open literatures to focus on using iron ore as an oxygen carrier for direct chemical looping conversion of biomass to generate synthesis gas. Hence, the investigation of BGCL for producing synthesis gas is an interesting issue and it can act as an innovation approach for biomass utilization.

The purpose of this study is to evaluate the effect reactivity performance of iron ore-based oxygen carrier on BGCL process. In the present work, contrast experiments regarding to the behavior of lattice oxygen in the hematite particles were firstly investigated. The influences of Fe_2O_3/C molar ratio and reduction time on BGCL were analyzed in terms of gas and solid products distribution. The characterization analyses of oxygen carrier particles were performed by several characterization methods such as X-ray diffraction (XRD), scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM–EDX).

2. Experimental

2.1. *Materials*

Sawdust of pine collected from Guangdong province (China) was used as fuel in the tests. The sample was crushed and sieved into particle with a size range of 250–425 μm, which was dried for 8 h at 105 °C before experiment. The ultimate analysis shows that the pine (air-dry basis) is composed of 48.85 wt.% carbon, 6.31 wt.% hydrogen, 0.05 wt.% nitrogen, 0.01 wt.% sulfur and 44.78 wt.% oxygen (by difference). The proximate analysis reveals 8.28 wt.% moisture, 84.75 wt.% volatile, 6.68 wt.% fixed carbon and 0.29 wt.% ash in the pine sample (air-dry basis). In addition, the lower heating value of the pine sample is 19.38 MJ/kg.

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 the experiments was selected from Australia. The elemental composition analysis shows that the hematite is composed of 0.024 wt.% sulfur, 90.73 wt.% Fe_2O_3, 6.78 wt.% SiO_2, 1.28 wt.% Al_2O_3, 0.13 wt.% CaO, 0.043 wt.% MgO, 0.027 wt.% Na_2O, 0.13 wt.% K_2O, 0.047 wt.% phosphorus. It can be seen that the hematite samples mainly consisted of 90 wt.% Fe_2O_3 approximately, with a little of other component.

2.2. *Material characterization*

The fresh and reacted oxygen carrier particles were analyzed by a series of characterization methods. An X-ray diffractometer (XRD, X'Pert Pro MPD) using Cu K_α radiation (40 kV, 40 mA) was used to analyze the crystal structure of fresh and reacted samples. The samples were scanned at a rate of 2°/min from $2\theta = 5°$ to 80° with a step of 0.02°. The surface morphology and characteristics of the samples were detected by scanning electron microscopy (SEM) on a Hitachi S4800 instruments. The element distribution on the surface of samples was analyzed by an energy-dispersive X-ray spectroscopy (EDX) system equipped with the SEM system.

2.3. *Fluidized-bed setup and procedure*

The gasification experiments were conducted in a bubbling fluidized bed reactor of quartz placed in a transparent furnace. The schematic layout of the laboratory setup is illustrated in Fig. 1. The reactor is with a length of 1000 mm and an inner diameter of 60 mm. A sample of oxygen carrier was loaded on a porous plate placed 300 mm from the bottom of the reactor and then heated in an inert atmosphere of argon to a desired reaction temperature. The bed temperature was measured 5 mm above the porous quartz plate using a K-type thermocouple. The static bed height was about 26 mm, while the bed height was about 40–60 mm when it was fluidized. During the reduction period, the fluidizing gas was argon (1500 L/h), which was introduced from the bottom of the reactor. After reaching the set temperature, biomass was continuously fed (by a screw feeder) from a hopper at the top of the reactor, where 200 L/h of argon was used as balance