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Chemical looping gasification of biomass char using iron ore as an oxygen carrier

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ARTICLE INFO

Article history:
Received 21 May 2016
Received in revised form
6 July 2016
Accepted 12 July 2016
Available online 7 August 2016

Keywords:
Biomass char
Chemical looping gasification (CLG)
Iron ore
Oxygen carrier
Cyclic performance

ABSTRACT

Chemical looping gasification (CLG), employing the oxygen carriers to replace the gasification agents for solid fuels gasification, is viewed as a promising gasification technology thanks to its low cost for producing high quality synthesis gas. In the present work, natural iron ore is applied as an oxygen carrier for CLG of biomass char in a fixed-bed reactor. The Redox reactions between biomass char and iron ore can occur even under inert atmosphere, but the char conversion is low due to inadequate contact of solid–solid phases, resulting in a low reaction rate. In order to improve the char conversion rate, mixture of steam and iron ore is used as gasification agent in the CLG of biomass char. An optimal mass ratio of oxygen carrier to biomass char and a suitable amount of steam addition are determined. It is observed that biomass char gasification with the mixture of iron ore and steam increases the carbon conversion by 80%, and attains three times gas yield as much as the char gasification with individual iron ore. The cyclic performance of iron ore is also discussed. The carbon conversion and gas yield shows a mild downtrend with the increase of cycle numbers due to a slight decrease of specific surface area of oxygen carrier, caused by the thermal sintering and ash deposition. However, iron ore still maintains a satisfactory reactivity after 20 cycles (~52 h), indicating that it is a good oxygen carrier candidate for char gasification.

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http://dx.doi.org/10.1016/j.ijhydene.2016.07.089
0360-3199/

Introduction

It is very necessary to develop renewable energy under the double pressure of the exhaustion of fossil fuels and seriousness of environmental pollution. Biomass energy is the most abundant renewable resource on earth, which is the world's fourth largest energy and plays an important role in the whole energy system [1,2]. Additionally, it is considered carbon neutral during the process of biomass utilization, where the released carbon in the utilization process is equivalent to the absorbed carbon through the photosynthesis in its lifetime [3,4]. Hence, the development and utilization of biomass energy has an extremely important positive significance to alleviate the energy crisis and the environment issue. Biomass gasification, which converts biomass to synthesis gas in the presence of gasification agent, is one of the most important technologies for biomass utilization [5]. The conventional biomass gasification technologies are mainly involved in biomass air gasification, oxygen-enriched gasification, steam gasification and oxygen-enriched-air and steam co-gasification [6]. However, there are some apparent disadvantages for these conventional technologies, such as the N_2 dilute, the high cost for oxygen production, and strong endothermic with steam gasification agent [6–9]. Under this background, a novel gasification technology is proposed for biomass thermo-chemical conversion, which is named chemical looping gasification (CLG) technology [10–13]. The process of CLG, derived from the chemical looping combustion (CLC) concept, is realized through the oxygen carrier particles continuously circulating between the reduction atmosphere and oxidation atmosphere. The targets are heat and high concentration CO_2 in CLC process because of excess oxygen carrier but the main product of CLG is synthesis gas through controlling the ratio of oxygen carrier to fuel at a low value [14–16]. Generally, there are some potential advantages for biomass CLG [17,18]. The circulation of oxygen carrier can provide continuous oxygen source for biomass gasification, thus the pure oxygen production is not required and then the cost is saved. The required heat in the conventional gasification is supplied by carbon combustion but the oxygen carrier can also act as a heat source for biomass gasification in the CLG process, thus more carbon is converted to synthesis gas rather than CO_2. Some oxygen carriers (e.g. Fe, Ni), especially their reduction products are good catalysts for tar cracking [19–21]. Besides, the N_2 dilute is avoided because the fuel is not directly exposed to air. Hence, the high quality synthesis gas (high calorific value and low tar content) with a low production cost can be obtained using CLG for biomass conversion.

Oxygen carrier development is viewed as one of key issues for chemical looping technology. The single transition-metal oxides were reported in the literatures as the main oxygen carriers [22,23]. Among these oxygen carriers, the iron based oxygen carrier is considered as a promising candidate because of its good stability at high temperature, low cost, non-toxic in nature and environmental friendly [22,24]. A high coal conversion of 90% and CO_2 purity of 99.5% were obtained in a 25-kW_{th} subpilot unit of 200 h continuous operation with iron-based oxygen carrier [25]. Recently, the natural iron ore oxygen carrier is given more attentions due to its satisfactory reactivity, more abundant sources and lower cost [26–28]. The research groups from Chalmers university of technology (Sweden) and Southeast University (China) extensively investigated the CLC of solid fuels (e.g. coal, petroleum coke and biomass) using iron ore oxygen carrier in the different pilot plants, respectively [29–34]. The iron ore particles showed good reactivity in the continuous running test and a high concentration of CO_2 (>95%) was captured. Using ilmenite as an oxygen carrier, the world's largest metal oxide CLC pilot plant of 1 MW_{th} was demonstrated [35]. The CLG of biomass was conducted with natural hematite as an oxygen carrier in our research group [10,16,17]. The biomass fuel can be efficiently converted into synthesis gas even in the absence of gasification agents. The carbon conversion of 82.23% and gas yield of 1.06 Nm^3/kg were achieved and the crude synthesis gas with the lower heating value of ~14 MJ/Nm^3 and tar content of 6.49 g/Nm^3 were obtained.

The pathway of biomass CLG can be described as shown in Fig. 1. The devolatilization firstly occurs and biomass is pyrolyzed into gas (pyrolysis gas), liquid (tar) and solid (char) three-phase products, and then a series of Redox reactions occur when the oxygen carrier particles contact with the three-phase products. Thus, biomass is converted to synthesis gas and the oxygen carrier is reduced in parallel. After that, the reduction oxygen carrier is re-oxidized into its initial state under air atmosphere, and then it again contacts with pyrolysis products to begin the next cycle. The pyrolysis gas (reducing gas, e.g. H_2, CO, CH_4 et al.) can easily react with oxygen carrier particles because of their Redox properties and good gas–solid contact. It is well known that the reduced products of transitional metal oxides (e.g. Fe_2O_3, NiO et al.) are good catalysts for biomass tar cracking. Hence, the liquid products of biomass pyrolysis (tar), can be catalytically cracked by oxygen carrier particles during the gasification process. In the absence of gas-phase oxygen, the solid product (char), is difficult to react with oxygen carrier particles due to inadequate contact between the two. Generally, the char accounts for 20%–30% of biomass pyrolysis products [10], thus it is very significant to enhance the char conversion achieving biomass gasification efficiently. Additionally, there is little work reports biomass char conversion using oxygen carrier particles.

Hence, the enhancement of reaction rate of char gasification is more interesting and challenging work during the biomass CLG. The gasification of biomass char using iron ore as an oxygen carrier was also investigated in our previous work. The solid–solid reactions of char with iron ore can occur in the absence of gasification agents but it required a high temperature (>1200 °C) [36]. Under inert atmosphere, the carbon conversion of char was low (~55%) even if the NiO-modified (10 wt.% NiO content) iron ore was used an oxygen carrier at high temperature (~1200 °C) [18]. Additionally, the thermodynamic analysis and TG experiments qualitatively described that the introduction of gasification agents (H_2O or CO_2) can evidently improve the char conversion at a relative low temperature (~850 °C) [36]. Nonetheless, the specific reactivity of char with iron ore, especially the cyclic performance of iron ore particles was not mentioned in the previous work. In order to improve the char conversion as far as