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Research article

Bio-oil heavy fraction for hydrogen production by iron-based oxygen carrier redox cycle

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ABSTRACT

Chemical looping hydrogen generation by the iron-based oxygen carrier redox cycle is promising thanks to its inherent CO_2 separation and low energy penalty. Bio-oil heavy fraction, characterized as the oil fraction of pyrolysis bio-oil and difficult to be upgraded for bio-fuel or chemicals production, was used as the feedstock to generate hydrogen for the hydrodeoxygenation process of aqueous phase of pyrolysis bio-oil. The result showed the successful generation of hydrogen by this process, but the undesired carbon formation on the iron-based oxygen carrier resulted in the low purity hydrogen. To avoid this, removal of deposited carbon by the introduction of steam vapor in the fuel reactor was proposed and evaluated. The result confirmed that the positive role of steam vapor played on the enhancement of hydrogen purity, over 99% of hydrogen concentration was obtained in the case of steam to oil ratio at 2.0. However, the hydrogen purity and hydrogen production were in a competing relationship and the hydrogen purity enhancement inevitably suppressed the hydrogen production after steam vapor addition. By taking account of the hydrodeoxygenation process of aqueous phase of pyrolysis bio-oil, the steam to oil ratio of 1.2 was preferred.

1. Introduction

Oil derived from biomass liquefaction reduces the dependence on fossil fuels and has stimulated worldwide interests in recent decades due to the abundant resources of biomass and its unique feature of nearly zero net carbon emission [1–3]. One of the promising technologies for high-quality oil production is the biomass flash pyrolysis combined with the subsequent hydrotreatment of aqueous phase oil, which features the achievements of high yields of specific and well-defined products and the avoidance of energy-intense distillation process [4–9]. However, two tough challenges should be overcome prior to its large-scale application. One is the large amount of hydrogen consumption in the hydrodeoxygenation process to lower the oxygen content in aqueous phase oil. Another is undesirable conversion of biomass to final oil product because the oil fraction of pyrolysis bio-oil, referred to as bio-oil heavy fraction, accounted for 35% of total crude oil and is difficult to be upgraded for bio-fuel or chemicals production [6,10]. Therefore, bio-oil heavy fraction as a feedstock to produce hydrogen for the aqueous phase hydrotreatment seems to be an ideal way to increase economic efficiency of the system.

With respect to the hydrogen production technologies, steam reforming is well established and preferred commercially due to the less technical complexity and high economic efficiency. However, the major drawbacks associated with this process are: additional heat supply to maintain the high reforming temperature, the large amount of CO_2 emission and the high capital costs associated with the hydrogen separation process and the involved post-purification units, particularly the fast deactivation of the catalysts resulted from the oil re-polymerization and the high costs for the catalysts regeneration and replacements when bio-oil was used as a feedstock [11]. In response to the energy penalty and the environmental concerns involved in the steam reforming, an alternative method for hydrogen production via the iron-based oxygen carrier (OC) redox cycle has been proposed and gained increased attention [12–17]. By transforming the lattice oxygen in OC to the fuel, chemical looping technology could achieve the instinct gas separation and maintain the system heat balance with less energy penalty and lower cost for CO_2 capture. The principle of this technology is shown in Fig. 1. In the fuel reactor (FR), the oil inert gasification (Eq. (R1)) and OC reduction (Eqs. (R2–R5)) are integrated and simultaneously occurred, giving rise to the oxygen-deficient OC and a gas mixture of CO_2 and H_2O if the reducing gas is fully converted.

Oil inert gasification:

$$\text{Bio-oil heavy fraction} \longrightarrow CO + CO_2 + H_2 + CH_4 + C_2^{+} + \text{coke.} \tag{R1}$$

OC reduction (CO and H_2 as the representative):

$$1.126\,Fe_2O_3 + CO \leftrightarrow 2.378\,Fe_{0.947}O + CO_2 \quad \Delta H^{\theta}_{1223K} = 6.538\ \text{kJ/mol}. \tag{R2}$$

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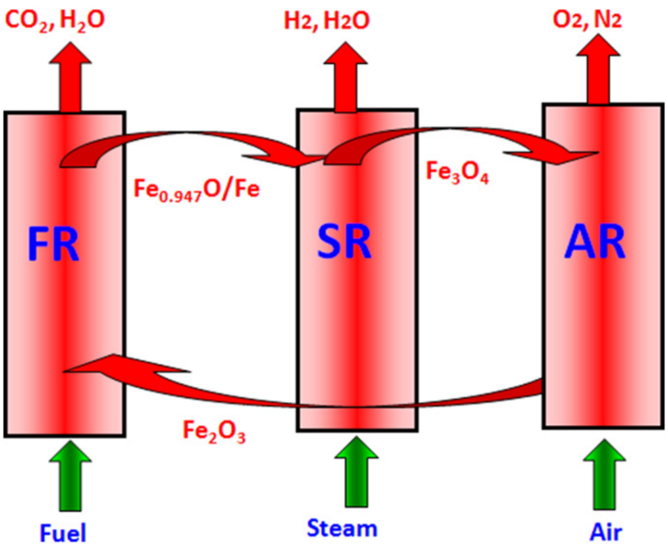

Fig. 1. The principle of the iron-based oxygen carrier redox cycle.

$$Fe_{0.947}O + CO \leftrightarrow 0.947\,Fe + CO_2 \quad \Delta H^{\theta}_{1223K} = \text{-}20.763\ \text{kJ/mol}. \tag{R3}$$

$$1.126\,Fe_2O_3 + H_2 \leftrightarrow 2.378\,Fe_{0.947}O + H_2O \quad \Delta H^{\theta}_{1223K} = 39.196\ \text{kJ/mol}. \tag{R4}$$

$$Fe_{0.947}O + H_2 \leftrightarrow 0.947\,Fe + H_2O \quad \Delta H^{\theta}_{1223K} = 13.724\ \text{kJ/mol}. \tag{R5}$$

In the steam reactor (SR), the oxygen-deficient OC is partially oxidized by steam vapor for water splitting with hydrogen production (Eqs. (R6 and R7)):

Steam oxidization:

$$3.807\,Fe_{0.947}O + H_2O \leftrightarrow 1.202\,Fe_3O_4 + H_2 \quad \Delta H^{\theta}_{1223K} = \text{-}68.277\ \text{kJ/mol}. \tag{R6}$$

$$3\,Fe + H_2O \leftrightarrow Fe_3O_4 + H_2 \quad \Delta H^{\theta}_{1223K} = \text{-}46.094\ \text{kJ/mol}. \tag{R7}$$

Subsequently, the OC is subject to a further air oxidation (Eq. (R8)) in the air reactor (AR), as shown in Fig. 1, to construct an autothermal system, although the fully oxidization of magnetite to hematite has no contribution to hydrogen production in SR.

Air oxidization:

$$4\,Fe_3O_4 + O_2 \longrightarrow 6\,Fe_2O_3 \quad \Delta H^{\theta}_{1223K} = \text{-}480.417\ \text{kJ/mol}. \tag{R8}$$

Overall, after experiencing water condensation and gas drying, hydrogen can be obtained in SR without further purification processes. Simultaneously, CO_2 is inherently centralized in FR, which provides more access to the carbon storage and utilization.

Currently, the process has been demonstrated using a variety of fuel [16,18–20], e.g. coal, CO and CH_4, etc. the results showed that the hydrogen can be produced successfully and the purity could reach over 95%. To make this process more attractive, Bleeker et al. [21,22] paid attention to the hydrogen production from the renewable energy carrier of bio-oil. However, this study identified the large amount of carbon deposition and the fast deactivation of OC. Although the iron oxide OC processes large source abundance and brings lower costs in the regeneration and replacement, the gas impurities released and polluted the hydrogen stream significantly (Eqs. (R9) and (R10)) [13,23]. Therefore, considering the feedstock liable to form carbon deposition in FR, the hydrogen purity would be a great concern. To the best of our knowledge, research work on enhancing the hydrogen purity in SR has not been noticed in the previous literatures. In this work, the aim is to inhibit the carbon deposition in the reduction period, and thus restraining the gas impurities. Using bio-oil heavy fraction as a feedstock, we conducted the chemical looping redox cycle to investigate the producing route of the hydrogen and the impurities. Then, we proposed a strategy of adding steam vapor in FR for the enhancement of hydrogen purity. By varying the reducing atmosphere in FR, the redox performance was evaluated and optimal steam to oil ratio was explored.

$$C + H_2O \leftrightarrow CO + H_2 \quad \Delta H^{\theta}_{1223K} = 135.639\ \text{kJ/mol}. \tag{R9}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^{\theta}_{1223K} = \text{-}32.658\ \text{kJ/mol}. \tag{R10}$$

2. Material and methods

2.1. Materials

The iron-based oxygen carrier performing the redox cycle was prepared by mechanical mixing method. Active compounds of Fe_2O_3 were dispersed on an inert support of Al_2O_3 with the Fe_2O_3 loadings of 60%. After the components mixing, the mixed sample was calcined at 1000 °C for 6 h in a fluidized bed reactor with air injection and then crushed and sieved to the size range of 0.1–0.2 mm.

The crude bio-oil was produced by Shandong Tairan Co. Ltd in a 1000-ton pilot-scale cotton stalks pyrolysis unit. Followed by the condensation of the pyrolysis gas, water was immediately added into the oil tank and aged several days for phase separation. After moving the supernatant aqueous fraction, the heavy fraction of bio-oil could be obtained. The ultimate analysis and water content of the oil are listed in Table 1.

2.2. Experimental setup and procedures

A fixed-bed reactor made of stainless steel with a total length of 950 mm and an inner diameter of 30 mm was used to perform the experiments. A porous distributor was installed at 450 mm from the bottom of the reactor to support the bed material. The heat needed in the experiments was provided by an electric furnace. The reaction temperature was monitored and controlled by two thermocouples, one (T_1) was located between the tube and the furnace and another (T_2) was inserted into the OC bed material. By adjusting T_1, the desired T_2 could be reached, that is also considered as the reaction temperature.

The flow rates of N_2 and air (99.99% purity) were measured by the mass flow controllers (MFC, Beijing Sevenstar Co. Ltd). The distilled water was introduced by a high performance liquid chromatography (HPLC) micro-pump (TBP1002, 0–10.0 mL/min, accuracy = 1%, Shanghai Tauto Biotech Co. Ltd) and evaporated by steam generator operated at a constant temperature of 250 °C. The inert N_2 was used to introduce the steam vapor smoothly and the inlet and outlet heat taps were kept at 250 °C. The schematic layout of the experimental setup is shown in Fig. 2.

Prior to each experiment, 40 g sand particles with a size range of 0.6–1.0 mm was placed on the porous distributor to avoid the large temperature fluctuation of the bed material and prevent the OC particles from falling through the distributor. A batch of 35 g OC particles was then loaded on the sand bed, after which the reactor was heated under the N_2 atmosphere. When the desired temperatures (from 850 °C to 1000 °C) reached and stabilized, a gas mixture of 200 ml/min inlet N_2 and 0–0.5 ml/min (water) steam vapor was introduced into the reactor, at the top of which the oil was fed at a constant rate of 0.25 g/min

Table 1
Ultimate analysis and water content of bio-oil heavy fraction (ad, wt.%).

C	H	O[a]	N	H_2O
57.18	6.75	35.65	0.42	18.54

ad: air dried basis.
[a] By difference.