



Coproduction of clean syngas and iron from woody biomass and natural goethite ore

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ABSTRACT

Conversion of biomass into clean syngas was studied considering application of low-grade iron ore to reforming of tar. Chipped cedar with moisture content of 0.1–10.1 wt% was continuously pyrolysed at 550 °C, and the nascent volatiles were subjected to reforming at 690–800 °C in a bed of mesoporous hematite derived from a type of natural goethite. The yield of heavy tar (b.p. > 350 °C) decreased from 18.8 to less than 0.01 wt% during the reforming mainly by its oxidation by the ore and conversion into coke. The hematite was reduced completely to magnetite and further but incompletely to wustite. The formation of iron was inhibited by high CO₂/CO and H₂O/H₂ ratios of the gas phase. The coke-loaded magnetite/wustite mixture was, however, an excellent precursor of iron. Reheating the spent ore up to 800 °C in the absence of the volatiles reduced the magnetite/wustite to wustite/iron obeying direct and indirect reduction mechanisms. Repeated cycles of such reheating and reforming converted the volatiles and ore into syngas with a total tar concentration as low as 10 mg Nm⁻³-dry and coke-loaded iron, respectively. Contribution of the steam reforming with iron–wustite redox cycles became more important as the reforming–reheating cycles were repeated.

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1. Introduction

Pyrolysis is the primary step of biomass gasification, and formation of condensable organic product, which is generally termed tar, is therefore inevitable. Complete conversion of tar into a major portion of the gaseous product, in particular, that inside the reactor system has been a most important engineering subject [1–3] since it can greatly enhance the process efficiency and reduce the implementation/operating cost of the gasification. Direct use of product gas as a fuel for internal combustion engines is generally requested to reduce residual concentration of tar (except for light aromatic hydrocarbons such as benzene and alkylbenzenes) to a level below 50–100 mg Nm⁻³ on a steam-free basis [1]. Such a concentration corresponds to a mass yield around 0.01 wt%-dry-feedstock, though the volume of the product gas depends on gasifying agents. In application of product gas to Fischer–Tropsch (FT) synthesis, naphthalene concentration should be below 10–20 mg Nm⁻³, while this process is normally tolerant to benzene and toluene [4].

It is known for complete or nearly complete conversion of the tar that non-catalytic reforming is needed to be operated at temperature as high as 1200 °C and therefore consumption of much O₂ or air, which is associated with a great heat penalty [5]. Partial

oxidation of a mixed vapour of tar and lighter gases such as CO and H₂ at temperature as low as 800 °C results in preferential consumption of the latter and formation of refractory aromatics from the formers [1,6]. Catalytic reforming of the tar has been studied by a number of researchers. Performances of a number of Ni–Al₂O₃ catalysts with and without promoters and other types of synthesised catalysts, for example, have been investigated [3,7–9]. However, there still remain subjects to overcome problems of catalyst deactivation [10,11]. There have also been operating problems arisen from particulate matters such as ash, soot and char. As reviewed comprehensively by Yung et al. [10], most of previous studies on steam reforming of volatiles from biomass, specific light hydrocarbons or light aromatics over Ni-based catalysts and others employed steam-to-carbon molar ratios, S/C, of 0.5–5. Such high S/C, which is impractical in consideration of heat demand of gasification and its thermal efficiency, suggests difficulty in preventing the catalysts from being deactivated by coking with limited supply of steam and/or oxygen.

Another option of the tar reforming is to employ a catalyst or catalyst-like solid that can be used as material or fuel even after the loss of activity. An example is tar reforming over charcoal that is produced by the pyrolysis of biomass simultaneously with the volatiles to be reformed [12–14]. It has been demonstrated that tar vapour undergoes very fast thermochemical deposition onto micropore surface of the charcoal and then the deposited carbon

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(i.e., coke) is gasified with steam together with the original carbon of the charcoal at 750–900 °C [13]. Coke gasification slower than coke formation leads to loss of micropores and then deactivation of the charcoal, but the resulting charcoal is a product that can be used in another way. Not only charcoal but also tar-derived coke can accelerate its decomposition [15,16].

The present authors propose simultaneous production of clean gas and carbon-loaded iron or iron oxide from biomass and low-grade natural iron ores, respectively. The low-grade iron ores such as limonite and goethite (FeOOH) have hardly been employed in steel production mainly due to necessity of endothermic dehydration to form hematite (Fe₂O₃). At the expense of this, the resulting hematite is a mesoporous solid having specific surface area even as high as 70 m² g⁻¹ [17,18]. Hata et al. [17] exposed hematite that had been prepared from a natural goethite to vapour of nascent volatiles from the pyrolysis of pine sawdust at 500 °C. The hematite was reduced to magnetite during the exposure while the tar was deposited leaving carbon into mesopores with a concentration up to 4 wt% of the resulting ore. Heating this carbon-loaded magnetite in an inert atmosphere up to 900 °C further reduced the ore mainly by direct reduction, i.e., reduction by the solid carbon, producing ore with an O/Fe atomic ratio of 0.81. Such a ratio resulted from limited loading of carbon into/onto the ore. In other words, the ore could be fully reduced if more carbon were loaded. Catalytic performance of iron oxide toward reforming of tar from biomass has been demonstrated by Uddin et al. [19] and Nordgreen et al. [20], and they suggested the importance of specific surface area and oxidation state for the activity.

In the present work, nascent volatiles from the pyrolysis of woody biomass (moisture content; 0.1–10 wt%), which contained tar with concentration above 1000 g Nm⁻³, were subjected to reforming at 690–800 °C over mesoporous hematite derived from a natural goethite without either of external supply of steam or oxygen. The main purpose of this work was to investigate the followings:

- Characteristics of simultaneous progress of (a) reduction of the ore, (b) oxidation of the volatiles, (c) consumption of steam by steam reforming and water–gas shift reaction, and (d) carbon deposition into/onto the ore
- Conditions necessary for formation of iron
- Conditions necessary for reducing the tar concentration to a level below 100 mg Nm⁻³

2. Experimental

2.1. Material

Chipped Japanese cedar was used as the biomass feedstock. Chips were rectangular in shape with an average size of 10 × 10 × 2 mm. The chemical composition of the feedstock, estimated on dry basis by elemental analysis, was found to be: 50.9 wt% C, 6.1 wt% H, 42.5 wt% O, <0.05 wt% N, <0.01 wt% S, 0.5 wt% ash. The moisture content was within a range of 7.6–9.6 wt%-wet, which was measured for each run of pyrolysis/reforming. It was subjected to the pyrolysis with or without pre-drying in air at 100 °C for 6 h. A type of natural goethite ore was pulverised to sizes from 1.2 to 2.4 mm and heated in air at 500 °C for complete dehydration. The resulting ore was a mixture of hematite (α-Fe₂O₃) and gangue with contents of 89.2 and 10.8 wt%, respectively. The contents of Fe and O as hematite were 62.4 and 26.8 wt%, respectively, of the dehydrated ore. The specific BET surface area and average pore size of the dehydrated ore were 40 m² g⁻¹ and 4.0 nm, respectively. Commercially available natural silica sand (particle size; 1.2–2.4 mm) was employed as a material reference to the dehydrated ore.

2.2. Pyrolysis and reforming

Fig. 1 shows a schematic diagram of the apparatus that was used for the pyrolysis/reforming under atmospheric pressure. The reactor consisted of the horizontal screw-conveyer pyrolyser and vertical reformer with inner diameters of 50 and 54 mm, respectively. The biomass was fed into the pyrolyser at a constant rate of 260–270 g-wet h⁻¹, while N₂ was supplied from the hopper and also from the char collector at a total flow rate of 2.25 NL min⁻¹. The temperature of the pyrolyser, which was defined as that inside the hollow shaft of the screw, distributed over a range from 300 to 550 °C along with the pyrolyser axis. From this temperature distribution and the average moving rate of chips in the axial direction, 3.2 mm s⁻¹, the average heating rate of chips was estimated to be 5.3 °C s⁻¹. The solid product, char, dropped into the collector and it was cooled to ambient temperature, while the volatiles were introduced into the reformer together with N₂ via a connector tube that was heated at 500 °C. Reheating in another reactor up to 800 °C of the char recovered from the collector demonstrated that the tar evolution from the biomass had been completed in the pyrolyser.

The reformer consisted of a fixed bed of fresh dehydrated ore or spent ore from a previous reforming run. Table 1 summarises the experimental conditions for ten different runs. In a run of R1–R7, the fresh ore was charged into the reformer so that the fixed bed was formed with an initial height of 40, 100 or 180–190 mm. The sections 1–5 with equivalent lengths of ca. 40 mm were defined because of temperature variation along with the reformer axis. The temperatures at the top of the section 1 and bottom of the section 5 were 690 and 745 °C, respectively. R1 and R8–R10 were runs in series. After the reformer was cooled down to ambient temperature in R1, the spent ore was taken out of the reformer avoiding mixing of particles in the axial direction and divided into five portions with roughly equivalent masses. A certain amount of particles was sampled from each portion for analyses such as X-ray diffractometry (XRD) and carbon quantification. The rests of the five portions were then recharged into the reformer without changing the original arrangement of them. In R8, the recharged ore was heated in N₂ flowing at a rate of 0.3 NL min⁻¹ up to the reforming temperature before starting the pyrolysis, in other words, before its exposure to the flow of volatiles from the pyrolysis. R9 and R10 were performed in the same manner as mentioned above. The initial height/volume of recharged ore bed decreased with the run number. This was due to not only the sampling but also increase in the bulk density of the ore, which was arisen from the increase in the true density due to net progress of the reduction, i.e., loss of oxygen and also from loss of pores.

2.3. Analyses of reforming products

As seen in Fig. 1, the stream of the reforming products was introduced into the train of liquid condensers with the aerosol filter for capturing aerosol particles of a portion of tar so that light liquids were condensed completely. Non-condensable gases that had passed through the condensers were analysed on-line with a portable TCD gas chromatograph (GC) and also collected in gasbags for analyses with general TCD and FID GCs. The heaviest portion of condensables was deposited between the reformer and the aerosol filter. Such deposit was recovered completely by washing the tubes with acetone or tetrahydrofuran. In the present study, collection and quantification of condensable material were thus performed as thoroughly as possible. The condensable organic products were classified into three groups: monoaromatic hydrocarbons (MAHs; benzene, toluene, xylenes and styrene), light tar consisting of aromatics with boiling point temperatures below 350 °C, and heavy

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