A novel integrated process for hydrogen production from biomass

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ABSTRACT

A novel process, which integrated with biomass pyrolysis, gas–solid simultaneous gasification and catalytic reforming processes, was utilized to produce hydrogen. The effects of gasification temperature and reforming temperature on hydrogen yield and carbon conversion efficiency were investigated. The results showed that both higher gasification temperature and reforming temperature led to higher hydrogen yield and carbon conversion efficiency. Compared with the two-stage pyrolysis-catalytic reforming process, hydrogen yield and carbon conversion efficiency were greatly increased from 43.58 to 75.96 g H_2/kg biomass and 66.18%–82.20% in the integrated process.

1. Introduction

Recently, the global warming effects and the depletion of fossil fuel issues have been drawn more and more attentions around the world. In order to find a viable solution, researchers have made a lot of efforts in the development of renewable energy [1–4]. Hydrogen is a promising energy to replace fossil energy and plays an important role in future energy systems, since its combustion only generates water [5–7]. Currently, most of hydrogen is generated from natural gas and fossil fuels via steam reforming and coal gasification, which is considered as unsustainable due to low conversion efficiency and significant CO_2 emission [8–11]. Biomass as a kind of renewable energy has more advantages and less impact to environment than fossil fuels [12], which can be transformed into hydrogen with CO_2 neutral and low sulfur content [13,14].

So, biomass has been considered as one of the most probable source for hydrogen production. This is driving research towards the hydrogen production from biomass [15]. Thermo-chemical conversion is the most commonly biomass conversion method to produce hydrogen [16]. Among these conversion processes, the two-stage pyrolysis-catalytic reforming process has been extensively used for the hydrogen production from biomass [17–19], because that the tar produced by pyrolysis under the lower temperature can be converted easier compared with that of produced by gasification [20]. Bio-char, as a byproduct of the two-stage process, was

usually used for combustion to provide heat [21,22]. However, the high alkali content in the bio-char which may cause agglomeration and corrosion problems in the combustion [23—25]. If the bio-char could be used for hydrogen production, the hydrogen yield and total carbon conversion efficiency of the process will be increased simultaneously.

In this study, the bio-char was utilized for hydrogen production through a gas—solid simultaneous gasification process which was integrated into the two-stage pyrolysis-catalytic reforming process. The objective of this study was to evaluate the integrated process on hydrogen production and carbon conversion efficiency.

2. Experimental and methods

2.1. Materials

Sawdust obtained from a local timber mill was employed as the feedstock in this study. The particle size of the sawdust is between 0.18 and 0.25 mm. The ultimate and proximate analysis of the sawdust are reported in Table 1. The heating media used in the fluidized bed reactor is silica sand with a mean particle size of 0.15—0.18 mm.

2.2. Catalyst

In this paper, commercial catalyst NiO/MgO (7.2 wt.% NiO) was used produced by Wuxi QiangYa refractory material Co., Ltd. NiO/MgO was first crushed and sieved to a particle size range of 0.15—0.18 mm. The catalyst was treated in H_2 flow at 500 °C for 10 h prior to use.

2.3. Apparatus and procedures

A schematic flow sheet is shown in Fig. 1. The experimental reactor system consist of three stages, a first stage fluidized bed pyrolysis reactor where pyrolysis of the sawdust occurred, a second stage entrained flow gasification reactor where gas—solid simultaneous gasification occurred, the products (gas and solid) exiting the entrained flow gasification reactor passed through a cyclone separator for separating the ash, and then the products were introduced into the third stage fixed bed catalytic steam reforming reactor. After left the reforming reactor, the products passed through a condenser. The gas products were condensed and sampled for quantitative analysis with GC.

The fluidized bed reactor was 700 mm long × 100 mm diameter, constructed of stainless steel and heated by an heating wire to a fixed pyrolysis temperature of 600 °C. The second stage entrained flow gasification reactor and the third stage fixed bed catalytic steam reforming reactor were two same stainless steel tubes (1000.0 mm long and 150 mm i.d.). K-type thermocouples were used to measure the temperatures of the reactor. Steam of 600 °C generated in a steam generator was employed as fluidizing agent, and the steam flow rate was controlled with a water pump. When the system approached the desired temperature, the biomass was fed into the fluidized bed pyrolysis reactor by a continuous feeding system composed of a screw feeder and a variable speed motor. Meanwhile, the steam was injected into the fluidized bed pyrolysis reactor. All experiments were carried out at atmospheric pressure. Each experiment was carried out three times in order to determine the repeatability of each experiment and the reliability of the system, at the same conditions.

2.4. Product analysis

Non-condensable gases composed of H_2, CO, CO_2 and CH_4 were collected in sample bags for gas composition analysis. The gas product was analyzed by gas chromatography Agilent Technologies 6820. A temperature program started from 50 °C to 230 °C at a heating rate 50 °C/min while Argon as carrier gas flowed at 40 ml/min through a 3 m-long column. The sample was analyzed in the thermal conductivity detector (TCD) at the temperature of 230 °C. The column was HP-5MS (30 m × 0.25 m × 0.25 μm).

2.5. Data analysis

The low heat value (LHV) of dry gas can be expressed by Eq. (1) [26]:

$$LHV(MJ/Nm^3) = (H_2 \times 107.98 + CO \times 126.36 + CH_4 \times 358.18)/1000 \tag{1}$$

where, H_2, CO and CH_4 are the molar percentages of the obtained gas.

The carbon conversion can be defined as Eq. (2):

$$X_C(\%) = \left[(n_{CO} + n_{CH_4} + n_{CO_2})/n_C^0 \right] \times 100\% \tag{2}$$

In Eq. (2), n_{CO}, n_{CH_4} and n_{CO_2} are the number of moles of CO, CH_4 and CO_2 obtained and n_C^0 is the number of mole of carbon in the biomass.

3. Results and discussion

3.1. Effect of gasification temperature

The results of the integrated process for hydrogen production at various gasification temperatures were obtained at the pyrolysis temperature of 600 °C, gasification temperature increasing from 700 °C to 850 °C at 50 °C increments, reforming temperature of 850 °C, S/B (steam to biomass ratio) of 3 and WHSV (biomass to catalyst ratio) of 1.

Table 1 — Ultimate analysis and proximate analysis of the sawdust.[a]						
Ultimate analysis (wt.%)				Proximate analysis (wt.%)		
C	H	O[b]	N	Volatile matter	Fixed carbon	Ash
53.42	5.97	40.48	0.13	78.96	19.78	1.26

[a] Dry basis.
[b] By difference.