INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 37 (2012) 3177–3185

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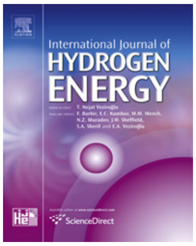

Hydrogen production by supercritical water gasification of biomass: Explore the way to maximum hydrogen yield and high carbon gasification efficiency

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ARTICLE INFO

Article history:
Received 11 October 2011
Received in revised form
9 November 2011
Accepted 13 November 2011
Available online 15 December 2011

Keywords:
Biomass gasification
Supercritical water
Maximum hydrogen yield
Orthogonal experimental design

ABSTRACT

Supercritical water gasification (SCWG) is a promising technology for wet biomass utilization. In this paper, orthogonal experimental design method, which can minimize the number of experiments compared with the full factorial experiments, was used to optimize the operation parameters of SCWG with a tubular reactor system. Using this method, the influences of the main parameters including pressure, temperature, residence time and solution concentration on biomass gasification were also investigated. Simultaneously, in order to further improve the gasification efficiency of biomass, acid hydrolysis pretreatment of feedstock, oxidizers addition and increasing reaction temperature were employed. Results from the experiments show that in the range of experimental parameters, the order of the effects of the factors on H_2 yield of corn cob gasification in SCW is temperature > pressure > feedstock concentration > residence time. Temperature and pressure have a significant and complicated effect on biomass gasification. Hydrogen yield increases by the acid hydrolysis pretreatment of feedstock, and oxidizer addition reduces the hydrogen yield but it promotes the increase in carbon gasification efficiency. Biomass feedstock with high concentration was gasified successfully at high reaction temperature.

1. Introduction

Energy from biomass may significantly contribute to the growing future demand for energy. Comparing with fossil fuel, biomass for hydrogen production can lead to near zero CO_2 emission [1]. As is well known, a large portion of biomass wastes is wet biomass in the earth [2]. However, wet biomass is not used as a promising feedstock for conventional thermochemical conversion process because the cost of drying the feed is too high [3]. Supercritical water gasification (SCWG) can circumvent this problem. The critical point of water is the temperature of 647.3 K and the pressure of 22.1 MPa. The theory of SCWG is based on a series of unique properties of water near the critical or supercritical thermodynamic state. Because the dielectric constant and the number of hydrogen bonds are lower, and hydrogen bonds' strength is weaker than those of ambient water, supercritical water (SCW) behaves like many organic solvents so that organic compounds and gases have complete miscibility with SCW. Therefore, SCW can provide homogeneous environment for chemical reaction, which reduce the mass transfer limitations of reaction [4]. Also, the value of ion product for liquid water near the

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doi:10.1016/j.ijhydene.2011.11.064

critical temperature is several orders of magnitude higher than that of ambient liquid water. Consequently, water at these conditions enjoys concentrations of H^+ and OH^- ions that are naturally higher than in ambient liquid water. As such, liquid water near the critical temperature is an effective medium for acid- and base-catalyzed reactions [5,6].

Some pioneering work has been done in SCWG by Modell from MIT [7,8]. He issued a patent and reported experiments involving the quick immersion of maple wood sawdust in SCW. The sawdust quickly decomposed to tars and some gas in the SCW without the formation of char [3]. So far, a number of scholars from different institutions have conducted a systematic theoretical and experimental study on SCWG of model compounds and real biomass [2,3,6,9–24]. However, how to achieve the complete gasification of biomass and obtain the maximum H_2 yield is still one of the key issues in SCWG. Antal et al. [11] used carbon-based catalysts for high concentration biomass gasification in SCW with the tubular reactor. The biomass was almost gasified completely with product gas of H_2 and CO_2, and the H_2 yield could be more than 100 g per kg dry biomass which closes to chemical equilibrium yield. However, they observed reactor plugging caused by the accumulation of chars and tars and occurring several hours after the feedstock injection. In our previous work [25], a SCW fluidized bed system was developed. The reactor plugging was avoided and continuous stability gasification was realized by this innovation and optimization of reactor structure. Some people obtained the rules and optimal operating conditions of the gasification process by a parameter study in order to high-yield hydrogen production [6,26]. Susanti et al. used a batch reactor with new material and large-volume to enable the gasification to be run at higher temperature and longer residence time, and obtained higher H_2 yield [26]. Some researchers try to study on the reaction mechanism and obtain the reaction pathway, which provides guidance for efficient hydrogen production [14,18,27–29]. Other researchers use different catalysts including metal oxide [30,31], metal [12,19,32–34], alkali [12,15,35] and activated carbon [3,11] to achieve complete gasification of biomass by low temperature SCWG. But so far, the results from these studies are not satisfactory.

This paper is aimed to explore the way to high efficiency biomass gasification and maximum H_2 yield. Firstly, the orthogonal experimental design method was used to optimize the operation parameters of corn cob gasification in SCW with a tubular reactor system. The optimum reaction parameters, and the influences of the main parameters including pressure, temperature, residence time and solution concentration on biomass gasification were gain. Secondly, acid hydrolysis pretreatment of feedstock, oxidizers addition and increasing reaction temperature were used to further improve the gasification efficiency of biomass.

2. Experimental

2.1. Materials

Real biomass feedstock (corn cob from Hubei, China) was used in this work. The continuous feeding of multiphase mixture of real biomass feedstock is a technical issue in SCWG. We made a gel by combining the sodium carboxymethylcellulose (CMC) and an amount of water. The real biomass suspended in the CMC gel which can flow at high pressure. CMC is a derivative of cellulose, which is the main component of biomass. It is cheap and usually used as emulsifier. It has the similar gasification characteristics of cellulose [15]. In this paper, CMC is not only the emulsifier but also the raw materials of SCWG. The CMC was purchased from Shanghai Shanpu Chemical Co., Ltd, and its mass fraction of C is 33.44wt%. Before real biomass was mixed into CMC gel, it was ground with plant mill to 40 mesh. Water was added, if necessary, to achieve the desired solids loading, then the mixture was continually stirred until it was homogeneous. $KMnO_4$ was used as the oxidant. Table 1 shows the results of elemental and proximate analyses of the biomass feedstock.

Table 1 – Elemental and proximate analysis of corn cob.

Elemental analysis (wt %)					Proximate analysis (wt %)			
C	H	N	S	O[a]	Moisture	Ash	Volatiles	Fixed carbon
43.24	5.28	0.44	0.08	41.02	7.04	2.90	72.67	17.39

a Difference.

2.2. Experimental apparatus

A schematic of the apparatus is shown in Fig. 1. Two kinds of reactor were used in this work. The reactor #1 is made of special alloy tube with 14 mm o.d., 6 mm i.d. and 650 mm length. The reactor #2 is made of Hastelloy C-276 tubing with 13.4 mm o.d., 7.7 mm i.d. and 650 mm length. The feedstock is fed into the reactor by the high-pressure pumps and two feed tanks. In the reactor, biomass feedstock is heated to the reactor temperature (All in this paper, temperature refers to the set-point temperature of reactor wall) with four electrical heaters, and gasified. After the gasification reaction, the effluent is cooled down to room temperature by a cooling water jacket at the exit of the reactor. A back-pressure regulator is used to decrease the exit pressure of product fluid to atmospheric pressure. Then, the effluent is transferred into a gas–liquid separator. The liquid phase is collected at the bottom of the phase separator, and the gas phase is passed to a wet gas flow meter to determine the volume of the formed gas mixture. Finally, gas samples are collected by a balloon. The detailed experimental process can refer to our previous work [6].

2.3. Analysis of gaseous and liquid product

The current work employs a Hewlett–Packard model 6890 gas chromatograph with thermal conductivity detectors. Gas analysis are accomplished with a Carbon-2000 capillary column (Φ0.53 mm × 25 m), heated at 333 K for 2 min, followed by a 30 K min^{-1} ramp to 423 K, and hold 2 min at 423 K. The carrier gas is helium and its flow rate is 10 ml min^{-1}. The