INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 3649–3656

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/he

Hydrogen-rich gas from catalytic steam gasification of eucalyptus using nickel-loaded Thai brown coal char catalyst

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ARTICLE INFO

Article history:
Received 3 October 2013
Received in revised form
17 December 2013
Accepted 24 December 2013
Available online 4 February 2014

Keywords:
Steam gasification
Catalyst
Fixed bed reactor
Eucalyptus

ABSTRACT

Hydrogen gas production from eucalyptus by catalytic steam gasification was carried out in an atmospheric pressure of two-stage fixed bed. The gasifier was operated with the temperature range of 500–650 °C and steam partial pressure of 16, 30 and 45 kPa; nickel-loaded Thai brown coal char was used as a catalyst. The yields and compositions of the gasification products depend on the operating conditions, especially, the reaction temperature and the steam. The yield of H_2 increased at elevated temperatures, from 26.94 to 46.68%, while that of CO dramatically decreased, from 70.21 to 37.71 mol%. The highest H_2 yield, 46.68%, was obtained at the final gasifying temperature of 650 °C. Eucalyptus catalytic steam gasification indicated that the maximum H_2/CO ratio reached 1.24 at the gasification temperature of 650 °C and the steam partial pressure of 30 kPa. It can be concluded that eucalyptus is appropriate for synthesis gas production from eucalyptus volatiles by catalytic steam gasification while using nickel-loaded brown coal char as a catalyst.

1. Introduction

At present, in the middle of growing concern about the depletion of fossil fuel reserves and the pollution caused by the continuously increasing energy demands, production and use of hydrogen would be most appropriate as hydrogen is an attractive alternative energy source. Hydrogen is currently derived from nonrenewable energy sources, but could, in principle, be generated from renewable resources such as biomass, as well. Generation of energy from renewable resources such as biomass is considered as one of the most plausible ways of serving energy resources for developing an efficient utilization technology, for example, combustion process, pyrolysis at high temperature, biomass gasification and co-gasification with coal. Thus, the gasification process is regarded as one of the most promising options for utilizing biomass. In particular, biomass gasification technology is considered as one of the best potential possibilities [1–3].

Using a catalyst in the biomass gasification process can increase the amount of biomass processed or decrease the size of the reactor as result of the enhancement in the reaction rate. Throughout the biomass gasification with air (partial oxidation) or steam at high temperatures, useful gaseous products, mainly consisting of hydrogen and carbon oxides, a small amount of methane, and other light hydrocarbons, are

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0360-3199/$ – see front matter
http://dx.doi.org/10.1016/j.ijhydene.2013.12.155

obtained. The gaseous products can be widely used in gas turbines for power generation, for chemical synthesis, in fuel cells and for oil upgrade. At the same time, tarry materials are simultaneously released during the biomass gasification, a phenomenon that always presents a serious impediment to the functioning of the biomass gasification system. It should be noted that Bridgwater mentioned that biomass-derived tar was very refractory and hard to crack just by putting it through thermal treatment alone [3].

Catalytic decomposition in the biomass conversion process is one of the promising ways to develop significantly higher efficient biomass conversion technology than non-catalytic methods. Nickel-based catalysts have proven to be very active in tar decomposition/cracking. For nickel catalyst development, brown coal containing O (acidic) functional groups presents ion-exchanging capacity with nickel and the ability to disperse the nickel within the coal matrix. The nickel species, ion-exchanged into brown coals, exerted a great influence on the steam gasification of brown coal and brown coal tar at low reaction temperatures of around 600 °C [4–7]. Also, compared to the conventionally supported catalysts, this special catalyst prepared using brown coal is cheap and can exhibit catalyst recovery as well. At the end of the service life, the catalyst can be disposed of simply by gasifying/burning the coal char, during which the energy value of the char support can be recovered. Also, the agglomerated nickel residues could be used as functional materials for powder metallurgy and battery development. Furthermore, a highly significant result that was ascertained was that carbon deposition on the nickel-loaded coal char could be remarkably prevented during the hydrocarbon cracking reaction [8–12]. The catalyst transforms liquid products (tars) into gas and modifies the gas composition, increasing H_2 and CO yields and decreasing CH_4 and C_2 yields [13]. Adegoroye et al. [14] studied the characterization of tars produced during the gasification of sewage sludge in a spouted bed reactor and reported that the quantity of tar formed during the gasification was low and that it did not show much variation with temperature within the range of 760–980 °C. Mogi et al. [15] developed an efficient biomass gasification process using Ni-loaded brown coal at low temperatures between 723 K and 823 K in a two-stage fixed bed reactor. Ni-loaded brown coal showed high activity for tar decompositions and their results illustrated that almost all of the tar materials were converted to light gases such as H_2, CO_2, and CH_4. Consequently, it can be seen that it is quite worthwhile to discuss the catalytic behavior of the nickel-loaded brown coal char during the biomass gasification.

According to our knowledge, the research on producing the synthesis gas, hydrogen gas and carbon monoxide gas, from catalytic steam gasification of eucalyptus using nickel-loaded brown coal char prepared from lignite mine of Thailand has not been done. In this study, eucalyptus pyrolysis and the gasification of the derived volatiles were conducted in a two-stage fixed bed reactor. The catalytic behavior of the nickel-loaded coal char on eucalyptus gasification was investigated at low temperatures ranging from 500 °C to 650 °C. The effects of the catalyst, temperature and steam on the products, gas compositions and H_2 + CO gas synthesis are discussed.

2. Experimental

2.1. Biomass

The original material, eucalyptus, was used as the sample for the gasification. Consistent with our previous researches and Luo et al. [16], the sample was pulverized with particle size between 0.25 and 0.45 mm. The average proximate, ultimate, gross calorific value and total sulfur examinations of eucalyptus were performed according to ASTM E 870-82, ASTM D3176, ASTM E711-87 and ASTM D3177, respectively. The results of the proximate and ultimate analyses of the sample, as well as the gross heating value and total sulfur, are given in Table 1. The ultimate analysis was conducted using a CHNS/O Analyzer, Perkin Elmer PE2400 Series II and the total sulfur analysis was done by the bomb calorimeter.

2.2. Catalyst

Nickel-loaded brown coal was prepared by the ion-exchange method using low sulfur-brown coal gained from the Mae Moh lignite mine of Thailand as a supporter (with particle size less than 0.25 mm). The analysis results and the gross heating value of the Mae Moh brown coal are shown in Table 1.

The preparation of nickel-loaded brown coal was done by mixing $NiCO_3.2Ni(OH)_2.4H_2O$ (Carlo Erba), $(NH_4)_2CO_3$ (Fluka), NH_4OH (Merck), and DI water together and then further mixing this with Mae Moh brown coal, with constant stirring speed of 400 rpm for 24 h at room temperature. The ion-exchanged coal was filtrated and washed repeatedly until no nickel ion was detected in the water. Thereafter, it was dried at 107 °C for 24 h, and the procedure for the preparation of nickel-loaded brown coal was complete.

The nickel-loaded brown coal was devolatilized in a flowing nitrogen atmosphere from the ambient temperature to the temperature of 650 °C and then was held for 1 h to produce

Table 1 – Proximate analysis, ultimate analysis, and heating value of eucalyptus and brown coal.

	Eucalyptus	Coal
Proximate analysis (wt%) (as received)		
Moisture	5.21	10.82
Volatile matter	78.66	43.90
Ash	3.53	22.40
Fixed carbon	12.60	22.88
Ultimate Analysis (wt%) (dry basic)		
Carbon	48.28	49.61
Hydrogen	6.65	2.55
Nitrogen	0.22	1.50
Oxygen	44.85	46.34
Total sulfur (wt%) (by calorimeter)	0.08	0.54
Heating value (cal/g)	4221	3737
Empirical formula (calculation)	$C H_{1.637}O_{0.696}$	$C H_{0.609}O_{0.700}$
Molar formula (calculation)	$C_{0.299}H_{0.490}O_{0.209}N_{0.0012}$	$C_{0.427}H_{0.261}O_{0.300}N_{0.0114}$