Investigation on hydrogen production by catalytic steam reforming of maize stalk fast pyrolysis bio-oil

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ABSTRACT

Hydrogen production via catalytic steam reforming of maize stalk fast pyrolysis bio-oil over the nickel/alumina supported catalysts promoted with cerium was studied using a laboratory scale fixed bed coupled with Fourier transform infrared spectroscopy/thermal conductivity detection analysis (FTIR/TCD). The effects of nickel loading, reaction temperature, water to carbon molar ratio (WCMR) and bio-oil weight hourly space velocity (W_bHSV) on hydrogen production were investigated. The highest hydrogen yield of 71.4% was obtained over the 14.9%Ni-2.0%Ce/A1$_2$O$_3$ catalyst under the reforming conditions of temperature = 900 °C, WCMR = 6 and W_bHSV = 12 h^{-1}. Increasing reaction temperature from 600 to 900 °C resulted in the significant increase of hydrogen yield. The hydrogen yield was significantly enhanced by increasing the WCMR from 1 to 3, whereas it increased slightly by further increasing WCMR. The hydrogen yield decreased with the increase of W_bHSV. Meanwhile, the coke deposition percentage changed little with increasing W_bHSV up to 12 h^{-1} and then it increased by 4.5% with the further increase of W_bHSV from 12 to 24 h^{-1}.

Introduction

Nowadays, there is a growing interest in the utilization of hydrogen as an environmentally friendly and efficient energy carrier for power generation coupled with fuel cell systems. Moreover, hydrogen is an important chemical raw material and widely used in the chemical, fertilizer, food, petrochemical and metallurgical industries [1]. Currently hydrogen is mainly produced by catalytic steam reforming of fossil fuels such as coal, natural gas, naphtha and heavy oils [2]. Considering both the growing shortage of fossil fuels and the worsening of ecological environment, hydrogen production from bio-oil produced by fast pyrolysis of biomass as a renewable energy source has attracted more and more attention all over the world.

The bio-oil catalytic steam reforming technology for hydrogen production has the following advantages: (1) The biomass fast pyrolysis technology for bio-oil production has been extensively studied and made great progress in the past

twenty years, which provides technical support for the effective mass production of bio-oil; (2) The liquid bio oil has significantly higher energy density and is much easier to collect, store and transport than solid biomass, which solve the problems of the large-scale collection, storage and transportation of biomass raw materials; (3) This technology gives hydrogen–rich gas and high value-added by-products, which can improve the economy of the entire process. Therefore, the bio-oil catalytic steam reforming technology is one of the most promising approaches to produce hydrogen from biomass on an industrial scale.

At present, the research progress in bio-oil catalytic steam reforming for hydrogen generation remains very slow. This is mainly attributed to the complexity of biomass pyrolysis oil composition. The existing most studies have focused on catalytic steam reforming of bio-oil aqueous fraction [3–6] and model compounds such as acetic acid [7], acetone [8], acetol [9], butanol [9], ethylene glycol [10] and m-cresol [11] over different catalysts. It is worth noting that the energy yield decreases when bio-oil aqueous fraction is catalytically reformed by the steam, due to the requirement of the primary separation process [12]. With respect to this issue, hydrogen production from crude bio-oil is a viable option.

However, the studies on steam reforming of bio-oil itself for hydrogen generation are very limited and the existing studies have mainly focused on hydrogen production via steam reforming of bio-oil itself in a two-step process. Kan et al. [13] investigated catalytic steam reforming of corn stalk pyrolysis bio-oil over the NiCuZnAl catalyst in the gasification-reforming dual beds. The maximum hydrogen yield of 81.4% with carbon conversion of 87.6% was achieved through the integrative gasification-reforming process. Wu et al. [14] studied catalytic steam reforming of sawdust pyrolysis bio-oil for hydrogen production in a two-stage fixed bed reactor system. They chose dolomite in the first steam reforming stage for the conversion of bio-oil and Ni/MgO in the second stage for the conversion of methane to increase the hydrogen purity and yield. Davidian et al. [15] employed a sequential catalytic cracking/reforming process for hydrogen generation from beech wood pyrolysis oil over the Ni/Al_2O_3 and $Ni–K/La_2O_3–Al_2O_3$ catalysts and obtained a hydrogen-rich gas mixture in which the hydrogen concentration was 45–50%. Domine et al. [16] studied hydrogen production from biomass-derived oil over monolithic platinum- and rhodium-based catalysts using steam reforming and sequential cracking processes. They reported that the highest hydrogen yield was 70% with the Pt catalyst at 780 °C and an S/C ratio of 10. To the best of our knowledge, few studies have been performed on the catalytic steam reforming of crude bio-oil in a one-stage process for hydrogen production, particularly for maize stalk fast pyrolysis bio-oil.

In the present study, hydrogen production via catalytic steam reforming of maize stalk fast pyrolysis bio-oil over the nickel/alumina supported catalysts promoted with cerium was studied using a laboratory scale fixed bed coupled with Fourier transform infrared spectroscopy/thermal conductivity detection analysis (FTIR/TCD). The effect of various influential parameters such as nickel loading, reaction temperature, water to carbon molar ratio (WCMR) and bio-oil weight hourly space velocity (W_bHSV) on the hydrogen production were also analyzed herein.

Experimental

Bio-oil feedstock

The bio-oil used in this work was obtained by fast pyrolysis of maize stalk in a fluidized-bed biomass fast pyrolysis liquefaction plant located in Shandong Research Center of Engineering & Technology for Clean Energy (Zibo, China). The pyrolysis of maize stalk was performed at 540–550 °C with a heating rate of about 10^3 °C/s for a residence time of less than 2 s. The elemental composition of bio-oil was analyzed using a Euro EA3000 elemental analyzer. The water content of bio-oil was determined by the Karl–Fischer method [17] using Metrohm-870 KF Titrino plus Karl–Fischer titrator. Before the measurement, a Karl–Fischer reagent (Hydranal Composite 5) was used as a titrant and standardized with deionized distilled water. The calorific value was obtained using an IKA C2000 automatic isoperibol calorimeter. The pH value was measured by a PHS-2F digital pH meter. Prior to the measurement, the instrument was calibrated with a liquid calibration standard of pH 7. The density of bio-oil was measured using a density measurement bottle. The gas chromatography/mass spectrometry (GC/MS) analysis of bio-oil was conducted using an Agilent 6890/5973N Gas Chromatograph–Mass Spectrometer.

Catalysts preparation and characterization

Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and aluminum oxide (γ-Al_2O_3) were purchased from Sinopharm Chemical Reagent Co., Ltd. A series of $Ni–Ce/Al_2O_3$ catalysts with different nickel loadings were prepared by co-impregnation using the aqueous solution of nickel nitrate and cerium nitrate supported on alumina. The γ-Al_2O_3 was first pretreated at 650 °C for 6 h and then crushed to 60–80 mesh. Known amounts of $Ni(NO_3)_2 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in deionised water and the pretreated γ-Al_2O_3 was added to the solution. The obtained slurry was continuously stirred at room temperature for 3 h, then dried at 110 °C for 48 h in a drying oven and subsequently calcined at 600 °C for 4 h in a muffle furnace. The metallic element contents in the prepared catalysts were measured by the inductively coupled plasma atomic emission spectroscopy (ICP/AES) using a TraceScan AdvantageTM equipment (Thermo Jarrell Ash Corporation). Four catalysts were obtained: 5.1%Ni -2.0%Ce/Al_2O_3, 10.3%Ni-2.0%Ce/Al_2O_3, 14.9%Ni-2.0%Ce/Al_2O_3 and 20.4%Ni-2.0%Ce/Al_2O_3, which were labeled as NiCe-1, NiCe-2, NiCe-3 and NiCe-4, respectively.

The Brunauer–Emmett–Teller (BET) surface area and pore structural characteristics of the catalysts were evaluated by using a Micromeritics TriStar 3000 gas absorption analyzer. Before the nitrogen physisorption experiments, the samples were preheated according to the method provided by the literature [18]. The catalyst crystallographic structure was determined by X-ray diffraction (XRD). The XRD patterns were obtained using a Bruker AXS D8 Advance X-Ray Diffractometer with Cu Kα radiation of wavelength 0.154 nm at 40 kV and 35 mA. The data were recorded from a start angle of 10° to an end angle of 70°.