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Dry and steam reforming of biomass pyrolysis gas for rich hydrogen gas

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ABSTRACT

Biomass pyrolysis gas (including H_2, CO, CH_4, CO_2, C_2H_4, C_2H_6 and etc.) reforming for hydrogen production over Ni/Fe/Ce/Al_2O_3 catalysts was presented in this study. This study investigated how the operating conditions, such as the calcinations temperature of catalysts, the reaction temperature, the gas hourly space velocity (GHSV) and the ratio of H_2O/C, affect the conversion of CH_4 and CO_2 and the selectivity of hydrogen from dry and steam reforming of pyrolysis gas. The experimental results indicated that, under the conditions: the reaction temperature of 600 °C, the GHSV of 900 h^{-1} and H_2O/C of 0.92, the reaction efficiency is the optimal. Especially, the concentration of H_2, CO, CH_4, CO_2, and C_2H_n (C_2H_4 and C_2H_6) were 36.80%, 10.48%, 9.61%, 42.62%, 0.49% respectively. The conversion of CH_4 and CO_2 reached 45.9% and 51.09%, respectively. There were all kinds of reactions during the processing of reforming of pyrolysis gas. And the main reactions changed with the operation condition. It was due to the promoting or inhibiting interaction among different constituents in the pyrolysis gas and the different activity of catalysts in the different operation condition.

1. Introduction

Pyrolysis gas, which is composed of H_2, CO, CH_4, CO_2, C_2H_4, C_2H_6 could be produced by pyrolysis of agricultural waste. At present, pyrolysis technology is widely used in field of biomass conversion. The bio-char, bio-oil and pyrolysis gas are the products of biomass pyrolysis. Bio-char could be effectively applied in preparing carbon fertilizers and active carbon. The bio-oil pyrolysis could be used as the raw material for preparing renewable fuel or refining chemical products. However, the pyrolysis gas is rarely investigated. And the pyrolysis gas got from biomass conventional pyrolysis (pyrolysis temperature is below 600 °C and the heating rate is between 0.1 and 1 °C/s), which accounts for about one third of agriculture waste in weight, could be used as the heat resource for biomass pyrolysis by combustion or applied in automotive internal combustion engines. Moreover, after catalytic reforming, the pyrolysis gas is suitable for hydrogen production or directly utilizing as the feedstock of fuel cell (see Fig. 1) [1–6].

At present, the steam reforming of natural gas or fossil fuels is the widespread technology for hydrogen production. However, in the long term, hydrogen produced from renewable sources or biomass derivatives is a more promising method, especially, for the biogas [7]. The use of waste organic materials as substrate for biogas production is environmentally friendly due to reduction of greenhouse gases and organic content in waste products [8]. Moreover, Herdin et al. [9] and Gruber et al. [10] had confirmed that, in comparison to CH_4, gas engines fuelled with H_2-rich gases had high efficiency

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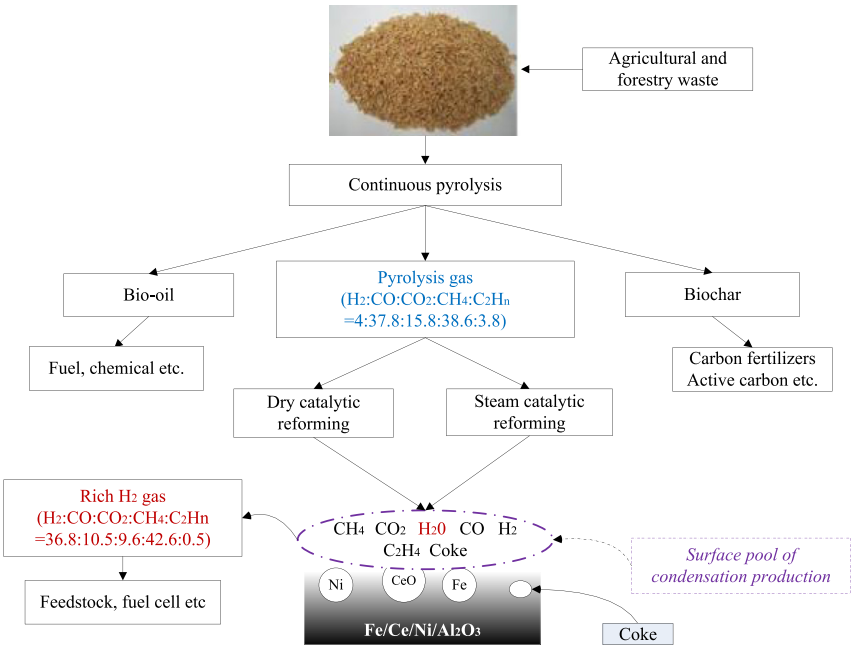

Fig. 1 – The utility of biomass pyrolysis products and the process of dry and steam reforming of biomass pyrolysis gas to H_2.

and low nitrogen oxide emissions. They also tested the gas with a high CO content but the effect was somewhat smaller [9]. Therefore, the reforming of biogas before combustion in gas engines seems to be advantageous.

It is well known that the Ni-based catalyst on Al_2O_3 support is widely used for steam reforming of biogas. It is cheap but high activity for both steam and dry reforming processes [10–12]. It is also used in industrial steam reforming applications [10–12]. Unfortunately, it has been found that Ni-based catalysts deactivate easily and quickly due to the coking and sintering problems.

Several researchers have reported that the ceria is a beneficial promoter for several chemical processes, such as reforming [13], CO oxidation [14,15], water gas shift reaction [16] and reduction of NO [17,18], due to its ability to oxygen capacity and excellent redox properties. Overall, the ceria plays a dominant role in improving the reaction efficiency in several processes by taking up oxygen under oxidizing conditions and releasing it under reducing ones [19].

Moreover, iron oxide is beneficial for H_2 production by taking the reaction [20–22]: $Fe_xO_{y-1} + H_2O \rightarrow Fe_xO_y + H_2$ and $(2n + m)Fe_xO_y + C_nH_{2m} \rightarrow (2n + m)Fe_xO_{y-1} + nCO_2 + mH_2O$. Matsuoka and Aupretre et al. [23,24] found that Fe supported on Al_2O_3 could promote the cracking of the coke on the iron oxide particles to increase H_2 yield. Besides, it also could boost the catalyst activity in the SRR (steam reform reaction: $CH_4 + 2H_2O = CO_2 + 4H_2$) to maximize the CH_4 conversion to hydrogen and selectivity towards the formation of CO_2 both in the SRR and in the water gas shift reaction (WGSR): $CO + H_2O \rightarrow CO_2 + H_2$.

In this study, pyrolysis gas is from the pyrolysis of rich husk at 500 °C and the content of H_2, CO, CH_4, CO_2, C_2H_4, C_2H_6 is 4%, 37.8%, 15.8%, 38.6%, 1.9%, 1.9%, respectively. At present, we prepared the Ni/Fe/Ce/Al_2O_3 catalysts and applied them in pyrolysis gas steam and dry reforming reactions (see Fig. 1). The aim of this work is to investigate the mutual influences of different compositions in the pyrolysis gas during several reaction processes and the productivities of hydrogen at different operating condition as well as to develop the effective Ni/Fe/Ce/Al_2O_3 catalysts in pyrolysis gas reforming processes for hydrogen rich production.

2. Experimental

2.1. Catalyst preparation

The Ni/Fe/Ce/γ-Al_2O_3 catalysts were prepared by impregnating γ-Al_2O_3 with aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 6H_2O$, stirring for 2 h at room temperature, followed by drying at 70 °C overnight. Then, the material was calcined in air for 3 h at designated temperatures that were 500, 550, 600 and 700 °C. The amount of Ni loading on the catalyst was controlled at Ni/Al = 0.07:1 (rate of atom mass). The rate of Ni/Fe/Ce/Al is 0.07:0.05:0.05:1 (rate of atom mass). The process of preparing Ni/CeO_2/γ-Al_2O_3 almost is the same with Ni/γ-Al_2O_3. The γ-Al_2O_3 carrier was purchased from Xinyu Chemical Packing Co., Ltd. The composition of γ-Al_2O_3 is $SiO_2 + Al_2O_3 < 5\%$, $Fe_2O_3 > 1\%$, γ-$Al_2O_3 > 93\%$. The diameter of particle is 3.6–4.7 mm, which is same with the one showed in our previous research.

2.2. Catalyst characterization

The Scanning electron microscopy (SEM) (Phillips XL30 Environmental) was used to investigate the surface morphology of the catalysts and the carbon deposited on the used catalysts. At a heating rate of 10 °C/min and a dry air flow rate of 3 cm^3 min^{-1}, the thermal analysis (TG) on the spent catalyst was carried out on a STA449CJupiter-Simultaneous TG-DSC