



Full Length Article

Performance of bio-char and energy analysis on CH₄ combined reforming by CO₂ and H₂O into syngas production with assistance of microwave



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ABSTRACT

The reforming of methane by CO₂ and H₂O on biomass-derived char (bio-char) was run in a lab-scale microwave oven (2.45 GHz). Special attention was dedicated to the effect of bio-char and energy utilization for the reforming reaction. Through comparing CH₄ conversion from combined reforming and the weighted value of CH₄ conversion from two individual reaction: steam reforming and dry reforming, synergetic effect on CH₄ conversion was confirmed at 900 °C in combined reforming. This effect was attributed to less carbon consumption of bio-char in combined reforming and it was significantly influenced by the contained metal in bio-char. Alkaline metal and alkaline earth metal in bio-char were favorable for improving the conversion of CO₂ and CH₄, respectively. Through comparison, the mixture of demineralized bio-char and nickel-based catalyst was the most effective to promote combined reforming. Energy efficiency was related to temperature and it was maximized to be 49.2% at 800 °C. The changes of energy efficiency during the reforming process was similar to the variation of CH₄ conversion with time. Specific energy consumption for producing per m³ of syngas was 4.14 kWh, with a scale-up microwave-assisted combined reforming process as the model.

1. Introduction

Syngas (i.e., H₂ + CO) obtained from a variety of feed-stock can be used for Fischer–Tropsch process or other catalytical process to obtain different chemical products [1–3]. Syngas can also be served as an important source for hydrogen production, by means of water-gas shift reaction (CO + H₂O ↔ CO₂ + H₂). A conventional route to produce syngas is reforming of natural gas that contains 98% CH₄ [2–4]. Syngas can also be produced by reforming of bio-gas that is usually from anaerobic digestion or fermentation of biodegradable materials (biomass, municipal waste, etc). There are several methods for CH₄ reforming, such as partial oxidation (POM), steam reforming (SRM) and dry reforming (DRM) [2,5]. The last method has an environmentally benign, because it can realize effective utilization of both greenhouse gas (i.e., CH₄ and CO₂). Drying reforming is also potentially beneficial, since it can produce syngas with the lower ratio of H₂/CO and the syngas is suitable for synthesis of oxygenates. Considerable research with regard to dry reforming had been conducted on laboratory-scale or polite-scale device with conventional heating [6–8]. In general, previous studies concerned on the effect of main operating parameters such

as temperature, the composition of reactant gas and residence time on drying reforming reaction. Another focuses was to investigate catalytic ability and the deactivation of used catalyst during the reforming process. Normally, the catalysts employed for dry reforming are based on noble metal and transition metal, due to their fairly desirable catalytic performance. But both kinds of catalyst have significant limitations: the former is unsuitable for practical application, owing to its high cost and insufficient long term stability; the latter is prone to be deactivated by carbon deposition [6–8]. As an alternative, carbon-based material is characterized by low cost, significant catalytic effect, sulfur tolerance and excellent feasibility of reactivation, and hence it receives more interest in promoting the reforming reaction [9–11]. Carbon-based catalyst can be divided into two types [9–21]: One is directly originated from carbon materials, such as activated carbon, coal char and semi-cokes; The other is prepared by carbon material and metal component through impregnation method or mechanically mixing. Bio-char as the solid residues of biomass pyrolysis belongs to carbon material and it can present a desirable catalytic effect on methane dry reforming [22–23]. Catalytic performance of bio-char is mainly dependent on its pore-structure, oxygen-containing groups and the remained metal in ash. It

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must be noted that definition of a catalyst for carbon material is not correct since these materials are unavoidably consumed during the reforming reaction. Whereas, the oxidation reaction of carbon materials is considerably lower than the $\text{CH}_4\text{-CO}_2$ reaction in the reforming process. From this point, carbonaceous materials are defined as the catalyst in the literature [1,3–5]. In addition, the oxidation of carbon materials can also yield the positive effect on the reforming reaction, since it can regenerate some active sites and offer a certain amount of syngas production [22–23].

The ratio of H_2 and CO in syngas from dry reforming is often less than one, while synthesis of liquid hydrocarbons or methanol requires the ratio at about two [2]. For this reason, the content of H_2 in syngas production is needed to be enhanced. Combination of steam and dry reforming is regarded as a feasible method to increase H_2 concentration in syngas. Moreover, the ratio of H_2 and CO is easy to be controlled in combined reforming, by changing the feeding ratio of reactant gases. There is a few attention on combined reforming in the literature, whereby the effect of temperature and feed composition on the conversions was studied with metal-based catalyst [2]. In our recent work, bio-char was utilized to promote combined reforming in view of its excellent microwave absorbing feature and it had been demonstrated bio-char exhibited a favorable performance on the reforming reaction [22–23]. However, underlying information on bio-char activity in the reforming reaction was not considered. Therefore, the effect of demineralized bio-char as well as the mixture of demineralized bio-char and additive on combined reforming was addressed in this work.

Microwave is a kind of electromagnetic radiations in frequency range of 300 MHz–300 GHz and it belongs to non-ionizing radiations. Microwave can be transmitted, absorbed or reflected, in response to various materials. Microwave heating is featured by selectivity, penetrability, high efficiency and instantaneity. Compared to conventional heating, temperature gradient inside the sample is reduced under microwave heating and hence the higher heating rate can be achieved. From this point, microwave heating is efficient for wastes disposing and methane reforming reaction [22–27]. Currently, methane dry reforming with microwave heating had been widely studied [15–17,22–23]. In these studies, an intense attention was paid to the effect of various catalyst and different operating variables on catalyst stability, gas conversions and the ratio of H_2/CO . Combined reforming with assistance of bio-char and microwave irradiation was relatively scare. Further, the detailed energy analysis on combined reforming was little made. Accordingly, energy efficiency based on a lab-scale microwave-assisted setup and specific consumed energy for combined reforming in a pilot scale with microwave heating were evaluated in the paper.

In this paper, methane reforming with or without water was performed on a lab-scale microwave heating device, with bio-char as microwave absorbent and accelerator for the reforming reaction. To further obtain the effect of bio-char on reforming reaction, demineralized bio-char as well as mixed catalyst prepared by demineralized bio-char and additive were respectively used for the reforming reaction. Besides, energy analysis on combined reforming with microwave heating was emphasized to provide valuable information for optimization of the reforming process.

2. Experimental

2.1. Bio-char preparation and characterization

Bio-char (BC) was prepared by microwave-assisted pyrolysis of cotton stalk at 800°C . Before the initiation of pyrolysis, the material was firstly treated by washing and drying. After that, it screened to an average diameter of 2–4 mm. A series of characterization on bio-char, including proximate and ultimate analysis, BET analysis, metal content in the ash and the images of bio-char surface were performed, respectively on elemental analyzer (Vario ELCHNS), automatic proximate

Table 1
Proximate and ultimate results of cotton stalk.

Proximate analysis/wt% (air-dried basis)				Ultimate analysis/wt% (air-dried basis)				
M_{ad}	A_{ad}	V_{ad}	FC_{ad}	C_{ad}	H_{ad}	O_{ad}^*	N_{ad}	S_{ad}
7.5	4.7	70.2	17.6	43.51	6.23	36.38	1.52	0.16

Note: The content of oxygen is calculated by subtraction method in percentage of weight.

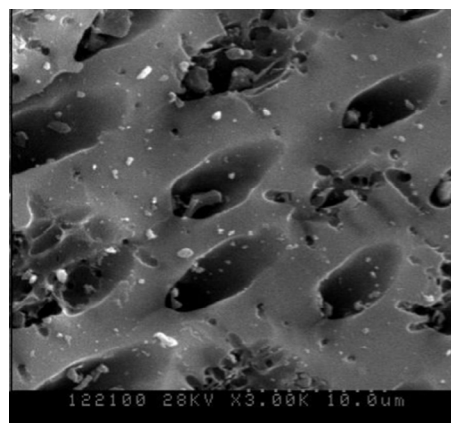


Fig. 1. SEM image of the prepared bio-char.

analyzer (SDTGA8000), micromeritics instrument (ASAP 2000), inductively coupled plasma atomic emission spectrometer (Optima 7300 V) and scanning electron microscopy (JSM-4800). The measured results of the prepared bio-char were summarized in Table 1. Among the dates, the volatile had a content of 70.2% and it was liable to be decomposed. Ash was mainly composed of different kinds of minerals. It was given in Fig. 1 that a certain amount of irregular pore structure was distributed on the surface of bio-char. The pore structure could provide the channel for the contact of reactant gases and bio-char. It was also found that some large pores were formed after the preparation of bio-char at 800°C . The explanation to this was that a large number of volatile was released at this temperature, and hence part of small pores was broken or merged into larger pores. It was lastly pointed that pore structure of the prepared bio-char was less significant than that of activated carbon. This also revealed that the performance of bio-char on the reforming reaction was less dependent on its pore properties in this paper.

A quartz reactor with a diameter of 40 mm and a height of 200 mm was employed for the experiment. An orifice plate was designed inside the reactor to be used as char bed, which was placed at the height of 40 mm from the bottom. Both ends of the reactor were sealed completely with two Teflon flanges. To ensure a good airproof performance, the flanges were pressed by long bolts. Microwave generator could alter the power in range of 0–3 kW at a constant frequency of 2.45 GHz. To ensure an inert atmosphere for pyrolysis, nitrogen was used as carrier gas and introduced into the reactor at a rate of 1 L/min for 10 min. Subsequently, nitrogen gas continued to feed the reactor and microwave oven was turned on. When the setting temperature was reached, biomass sample was put into the reactor and began to decompose. After the experiment was finished, the carrier gas kept purging until solid residues were cooled to ambient temperature. Then the residues were removed out of the reactor and weighed. Bio-char with an average size of 0.33–0.83 mm was adopted for the reforming experiment.

To obtain demineralized bio-char, washing treatment on fresh bio-char was carried out, respectively by distilled water or HCl solution with a concentration of 0.1 mol/L. At first, 20 g of bio-char was fully soaked in 500 mL of solution and evenly dissolved in the solution for 2 h. Temperature during this process was maintained at 80°C for

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