



Methane dry reforming with microwave heating over carbon-based catalyst obtained by agriculture residues pyrolysis

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ABSTRACT

Contrary to conventional methane dry reforming on metallic catalyst using electric heating, dry reforming catalyzed by biomass-derived char with microwave heating was studied in this work. The results showed bio-char catalytic activity could be affected by raw material for char preparation, since it was greatly connected to the remained metal after char preparation. As a whole, cotton stalk char presented better activity than others. Bio-char with a particle size in 0.25–0.83 mm was suitable for being served as the catalyst. Supporting an appropriate additive on bio-char, particularly for Ni, was effective to improve bio-char catalytic ability. Original bio-char could only maintain its catalytic effect at an acceptable level in 70 min, due to an unavoidable carbon gasification reaction. Nevertheless, carbon gasification meanwhile generated part of CO production and it was a contributor to total syngas production. When applying original bio-char for the reforming reaction, the contribution of char-derived CO production to total syngas production was finally up to 10.2%. Deposited bio-char obtained from methane decomposition could be self-regenerated, when further using for dry reforming. No matter original bio-char or deposited bio-char was adopted, a noticeable decrease of H₂/CO ratio passed through the test. For example, the ratio achieved on original bio-char reduced from 0.88 to 0.71. Through carbon balance and direct weight measurement, it was obtained a loss by 8.3% was occurred on original bio-char after the test.

1. Introduction

Syngas which contains H₂ and CO is a critical intermediate for several industries, such as the manufacture of methanol and other commodity chemicals [1]. The most widely practiced production route of syngas is steam reforming [2,3]. However, the syngas produced from this method has a relatively high ratio and hence its downstream utilization is restricted to some extent. On the converse, CH₄ reforming by CO₂ can produce syngas with a moderate ratio of H₂ and CO. More importantly, this method can offer a desirable environmental benefits, since the most common greenhouse gas, i.e., CH₄ and CO₂ are consumed in a great manner. Therefore, this topic is really interesting and it has been recently studied as an alternative to conventional steam methane reforming [4–7]. For CH₄ reforming by CO₂, an appropriate catalyst is of great significance for the conversion of reactant gases and the yield of syngas production. Considering this fact, current efforts have been made to choose an effective catalyst. From the point of industrial application, a favorable catalyst for the reforming reaction

should include the following features: a good catalytic activity, a strong stability, an abundant resource and a low cost. Obviously, carbon-based catalysts, such as activated carbon, coal-char and bio-char completely meet the above standards, compared with metal-based catalysts [8–10]. In details, carbon-based catalysts are frequently served for CH₄ reforming by CO₂ via two methods: they are directly used as the catalyst and they are acted as the support to load a metal component by the means of mechanical mixing or impregnation [8–17]. Commonly, the later can present better performing on the reaction but its economic is lower than the former. In recent decades, numerous researchers conducted a systematical investigation on the performance of carbon-based catalyst on the reforming. Among these studies, Domínguez et al reported the mixture of activated carbon and Ni/Al₂O₃ could exhibit a promising activity on the reforming reaction, especially with the assistance of microwave [8]. The group also put forward a simple mechanism on this reaction, which was depicted as a combination of CH₄ decomposition reaction and CO₂ gasification reaction [11]. Zhang Guojie et al persisted the research on CH₄ reforming with CO₂, using

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coal-char or coal-char supported Ni or Co as the catalyst [7,12]. It could be concluded from their papers that coal char was available for acting as a desirable catalyst, owing to its relatively rich surface area and pore structure, the contained metal in the char and the oxygen-containing functional groups. They emphasized that the oxygen-containing functional groups exerted an obvious effect on the performance of coal-char [13]. Based on this finding, the semi-cokes oxidized by KMnO₄ or ammonia showed better activity [14]. Comparatively speaking, biomass-derived char utilized for CH₄ reforming with CO₂ was less involved in. Domínguez et al only discussed the effect of biomass char derived from coffee hull on the reforming of CH₄ with CO₂ [15]. Consequently, the detailed mechanism of bio-char on the reforming reaction is scarce and it needed a further exploration. Furthermore, agriculture residues is very abundant in China and pyrolysis is recognized as an efficient and value-added process for these biomass resources. During the process of pyrolysis, solid char is one of the three products and it even is dominant at the low temperature. Solid char itself is a good fuel but direct combustion can lead to a poor thermal utilization efficiency. From this point, using bio-char for the reforming reaction can provide an innovation method.

Microwave belongs to a electromagnetic wave with frequency range of 300 MHz–300 GHz, which is widely used for lignite drying, biomass pyrolysis as well as other processes [18–20]. Currently, methane microwave reforming as an alternative to conventional reforming has been paid a great attention to [8,10,11,15,21,22]. On the contrary to conventional heating, the main characteristic of microwave heating is that the material is directly heated by the radiation, thus reducing the thermal conductivity resistance. Compared to dry reforming with conventional heating, the reaction with microwave heating could achieve a better conversions and a greater syngas production under the similar conditions. Normally, hot spot effect was considered to be the main contributor to this [10,21]. With regard to hot spot effect, it was qualitatively analyzed by the author of Fidalgo et al [11]. During methane reforming experiment in our lab, the hot spot was also noticed. This phenomenon could be justified from two sides: One was spark was occasionally observed in the char bed during the reforming experiment, which was an indicator that hot spot was created in the bed. On the other side, it was found that the local temperature in the char bed soared to an extremely high level during the temperature measurement. Sometimes the detector of thermocouple was burnt out, which revealed a very high temperature was brought about and hence a considerable temperature gradient was formed. The internal mechanism of hot spot effect was needed to be further explored. The premise for bio-char served for microwave drying is its microwave absorbing capacity. However, the effect of different bio-char obtained from agriculture residues on CH₄–CO₂ reforming with assistance of microwave was rarely referred to in previous studies. Moreover, the feasibility of recycling bio-char for methane dry reforming with microwave heating was seldom investigated in previous studies.

In order to implement the dry reforming of methane aiming at valorizing CO₂ on a large scale, a reaction system with bio-char as a catalyst is quite interesting. In this work, bio-char derived from microwave-assisted pyrolysis of agriculture residues was applied for the

reforming reaction. Catalytic effect of bio-char on the reforming reaction was investigated from the point of raw material, the remained metal, particle size and different supported metals. A great attention was also paid to study the behavior of dry reforming reaction on original bio-char and deposited bio-char as well as perform a characterization on syngas production and bio-char mass changes.

2. Material and methods

2.1. Preparation and characterization of bio-char

The most common agriculture residues in China were chose for the preparation of bio-char, which were respectively cotton stalk (CK), wheat stalk (WK) and corn straw (CW). Before the initiation of pyrolysis, raw material was crushed and then screened to an average diameter of 2–4 mm. Afterward, 30 g of material was loaded on a porous plate that fixed inside a quartz reactor. The reactor had a geometric size of Ø40 × 200 mm and it was completely sealed to cut off the air. After the remained air was fully driven from the reactor, N₂ was still continuously fed into the reactor with a flow rate of 1 L/min during the experiment. Considering bio-char itself was not a good microwave absorber, a certain ratio (10 wt%) of biomass-derived char was mechanically mixed with the material. The next step was to place the reactor in the center of a commercial microwave oven, whose power was ranged from zero to 3 kW. More importantly, the microwave oven could realize an excellent temperature control, with the precision at ± 20 °C. The temperature control was mainly dependent on a high accurate temperature measurement and an immediate response of output microwave power. Through the preliminary experiments, it was determined that the temperature for bio-char preparation was controlled at 800 °C and the duration for each run was 20 min. Under these setting conditions, the volatile matters could be fully released. If the material was heated at a higher temperature or in a longer time, porous structure was shrunk and some active matters remained in bio-char might be escaped, thus cutting down bio-char activity.

Original char was handled by HCl picking to obtain demineralized bio-char. The detailed procedure of this method was reported in our recent published paper [3]. After this treatment, five additives (alkaline metal: Na and K; alkaline earth metal:Ca and Mg; transition metal:Ni) were respectively supported on the demineralized char by incipient wetness impregnation, according to a mass ratio of 1:10. The nitrate that included a kind of metal was used as the precursor, in which bio-char was adequately soaked. Thereafter, the impregnated char was dealt in turn with drying at 105 °C and calcination at 800 °C. Finally, a modified catalyst containing a certain metal species was obtained.

A series of measurement on bio-char was performed, which included proximate and ultimate analysis, textural characterization and inorganic composition of the ash in bio-char. Proximate and ultimate analysis on bio-char was respectively conducted at a TGA thermo-balance and in a Vario ELCHONS apparatus. BET properties of different bio-chars were characterized by means of N₂ adsorption-desorption isotherms at 77 K in a Micromeritics instrument ASAP 2020. Inorganic composition of the ashes was measured in a QUANT'X X-ray

Table 1
Proximate and ultimate analysis on bio-char.

Sample	Proximate analysis(air-dried basis)				Ultimate analysis(air-dried basis)			
	Moisture	Ash	Volatile	Fixed carbon	C	H	N	O ^a
CK	0.65	10.99	10.25	78.11	63.27	2.83	11.28	22.62
WK	0.78	11.36	11.27	76.59	61.33	3.01	12.03	23.63
CW	0.67	12.21	13.02	74.1	60.78	2.98	11.78	24.46
CK-H ₂ O	0.52	9.48	7.89	80.31	65.72	2.02	11.42	20.84
CK-HCl	0.46	7.82	10.35	81.37	66.87	1.56	10.59	20.98

^a Evaluated by difference.

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