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Microwave-assisted gasification of rice straw pyrolytic biochar promoted by alkali and alkaline earth metals

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ABSTRACT

A novel microwave assisted gasification technique was developed whereby pyrolytic biochar obtained from rice straw was used as the feedstock. The conversion efficiencies and gas composition obtained at 800 °C by conventional heating method were similar to that obtained at 550 °C by microwave-assisted gasification. At 550 °C using microwave heating, the $CO + H_2$ yields were over 90 vol.% and H_2 content was 60 vol.%. The effects of alkali and alkaline earth metals (AAEM) on microwave-assisted gasification activity of biochar were also investigated. The results indicated that 5% K_2CO_3 and 5% KOH increased the carbon conversion efficiency from 74.39% to 79.95% and 85.04%, respectively, but CO_2 content increased remarkably. $Ca(OH)_2$ was a suitable gasification catalyst and excellent CO_2 absorber. 10% $Ca(OH)_2$ reduced CO_2 percentage from 21.92 vol.% to 10.83 vol.% and shortened reaction time from 90 to 60 min. Based on the AAEM catalytic mechanisms and microwave heating function, the intermediate C(O) and dipole rotation of materials molecules played a crucial role in the microwave-assisted gasification of biochar. This study proves that microwave heating coupled with the addition of AAEM result in low-temperature microwave-assisted gasification of biochar.

1. Introduction

The increase in energy demand and depletion of fossil fuels has created considerable interest in the utilization of renewable energy. Among all the renewable energy sources, biomass is regarded as one of the best alternatives since it is one of the largest primary energy resources [1]. Therefore, considerable attention has been paid to biomass which is non-polluting since its use results in zero net emission of CO_2 and can be thus converted to clean fuels. Biochar, as a product of biomass pyrolysis, has low moisture content, high carbon content and is nonperishable. It can be used as a feedstock for combustion, gasification, amending soil and preparing activated carbon [2]. Biochar has promising applications in the production of synthesis gas (H2 + CO) through gasification, which can then be converted to liquid chemicals by Fischer–Tropsch technology. There are a series of studies which focused on biochar gasification using conventional heating model [3–5]. Pattanotai et al. [6–8]found that char gasification rate was controlled by the diffusion process and kinetics parameters of gasification when CO_2 and steam were present. At the same time, the effective catalytic property of alkali salts on the char gasification was investigated. Song and Kim [9] indicated that the catalytic activity of salts was in the order of $K_2CO_3 > Na_2CO_3$ almost-equal-to $FeSO_4 > K_2SO_4 > Fe(NO_3)_3$. Despite lots of efforts in the gasification technology, there are still some difficulties to overcome, such as high temperature, long residence time, low conversion or low-grade gas composition.

Microwave technology has drawn attention in academic and industrial fields for excellent thermal characteristics. Examples of the advantages associated with microwave processing include: rapid, selective and uniform heating, decreased sintering temperature, and improved physical and mechanical properties [10]. Microwave heating has been used in pyrolysis of biomass for obtaining hydrogen-rich fuel gas [11] and improving dry reforming of methane in the presence of char [12,13]. 99% CO_2 conversion was achieved during CO_2 gasification of oil palm shell char at 900 °C [14], and syngas with over 60 vol.% H_2 content was obtained by 5 kW microwave heating [15]. As an excellent microwave absorbing material, biochar in favor of gasification reaction and can avoid problems of conventional heating processes.

As the main constituents of biochar ash, alkali and alkaline earth metals (AAEM) serve as effective catalysts in conventional

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gasification reaction. It was reported that Ca showed a high activity in the steam gasification of coal-char and K acted as the main inherent catalyst for the gasification process [16–18]. Huang et al. [19] found that catalytic efficiency of metal additions is in the sequence of K > Na > Ca in CO_2 gasification. However, all the previous studies were carried out using conversional heating systems. There are very few studies which focused on AAEM effects on gasification of biochar through microwave heating.

In this paper, the microwave heating was applied in the steam gasification process of biochar. Conventional and microwave-assisted gasification methods were compared. Gas composition and conversion efficiency were investigated based on the different operating conditions. More importantly, we attempted to uncover the low-temperature gasification properties at 550 °C by microwave heating, as well as the AAEM influence on gasification reactivity and gas composition during the steam gasification. The AAEM catalytic mechanisms and microwave heating function were further explored.

2. Experimental

2.1. Preparation of samples

Rice straw obtained from countryside of Chongming District, Shanghai, China was used as the raw materials. The rice straw was pulverized to particle size 0.38–0.83 mm and then dried in oven at 105 °C for 24 h. Biochar samples were obtained from microwave-assisted pyrolysis of rice straw at 500 °C with a holding time of 30 min. The obtained biochar samples were dried at 105 °C for 4 h for further analysis and subsequent gasification experiments. In order to explore the effects of AAEM, activated carbon (AC) was chosen as reference substance and was obtained from Sinopharm Chemical Reagent Co., Ltd. For comparison purposes, AC was also heated at 500 °C for 30 min under N_2. Biochar and AC were individually physically mixed with AAEM additions. Table 1 shows the properties of the rice straw, biochar and activated carbon.

2.2. Steam gasification of biochar

Fig. 1 shows the schematic diagram of the microwave-assisted gasification apparatus. In a typical experiment, about 3.0 g of biochar (dry basis), was put into the quartz tube with perforated bottom and plugged between quartz wool at both ends. Circulated cooling water was started and N_2 (40 mL/min/3 g biochar) was introduced at the top of the reactor. The microwave apparatus was turned on and the biochar was heated to the set temperature. The intrinsic temperature of the biochar bed was measured and controlled by an infrared thermometer placed inside of microwave furnace. After desired temperature was reached, pre-gasified distilled water (0.1 mL/min/3 g biochar) was fed into the reactor for gasification reaction. The reaction was deemed completed when the desired temperature dropped rapidly, indicating that the residual biochar was not enough to support the gasification reaction. The gaseous product was cooled, dried, collected and analyzed by Gas Chromatography (GC). For the conventional gasification experiments, an electrical furnace was used at 700–1000 °C with the same set-up.

Table 1
The ultimate and proximate analysis of rice straw, biochar and activated carbon samples.

	Rice straw	Biochar	Activated carbon
Proximate analysis, dry basis (%)			
Volatile matter	75.61	9.71	3.39
Ash	10.93	36.44	3.06
Fixed carbon (by difference)	13.46	53.85	93.55
Ultimate analysis, dry basis (%)			
Carbon	41.22	52.04	89.54
Hydrogen	5.56	0.76	1.28
Nitrogen	0.92	0.68	0.07
Sulfur	0.06	0.05	0.00

The gas compositions were analyzed using a micro gas chromatograph (Inficon 3000 Micro GC gas analyzer) equipped with a TCD detector and two columns connected in series. The first column was a Polt U and the second was a molecular sieve. The second column was by-passed by a valve for the analysis of CO_2. The detector was calibrated with the standard gas mixture before use. The carrier gas was Ar and the inlet temperature was 80 °C. The Polt U and the molecular sieve temperature were 50 °C and 80 °C, respectively.

2.3. Biochar's property and data analysis

The proximate analysis of rice straw and biochar were performed according to the standards of densified biofuel (NY/T 1881.1-2010) and coal (GB/T 212-2008), respectively. The rice straw and biochar samples were also subjected to ultimate analysis using an organic elemental analyzer (Thermo Flash 2000). The

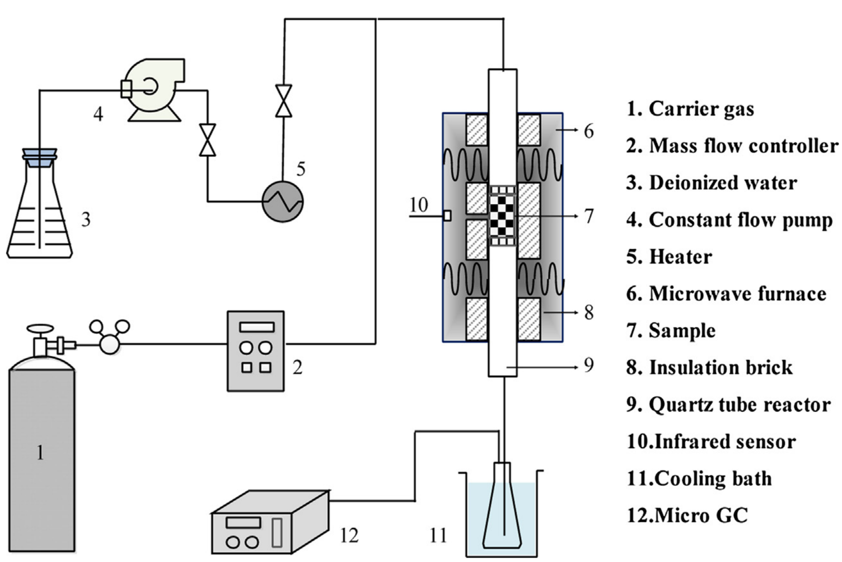

Fig. 1. Schematic diagram of the microwave-assisted gasification apparatus.