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Investigation on model compound of biomass gasification tar cracking in microwave furnace: Comparative research

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HIGHLIGHTS

- A microwave catalytic cracking method of toluene was proposed.
- Char-supported Ni was employed as bifunctional catalyst.
- The energy conversion efficiency of microwave heating was calculated.
- Special attention was paid on hot spots and microwave plasma.

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ABSTRACT

Tar is a major concern for advancing biomass gasification in industrial application due to its risk to downstream pipes/equipment and tar-contaminated environmental issue. Meanwhile, tar also leads to energy loss. Thermal cracking with or without catalyst is a widely used method for removing tar during biomass gasification. Microwave thermal cracking is a lately developed method of removing tar and only a few literatures are available on its reaction parameters and catalytic effect. A microwave tube furnace was designed for investigating tar cracking in our lab. Toluene as biomass tar model compound was cracked under various operating conditions assisted by three different bed materials (SiC, biochar, and biochar-Ni). The results showed that microwave heating is effective for toluene cracking, and biochar can act as a bi-functional catalyst for toluene cracking. Toluene cracking rate reached 95.12% under reaction temperature of 800 °C, catalyst particle size of 40–60 meshes and Ni loading of 4 wt%. Hydrogen concentration was higher than 92 vol%. The mechanism of toluene cracking, effect of microwave and efficiency of energy conversion were also carefully discussed, and the applied potential of microwave tar cracking technology was proved.

1. Introduction

Gasification is a promising thermal conversion route for recovering energy from biomass and wastes. The high-quality gas produced from gasification can be subsequently used for gas supply and power generation as well as syngas [1]. But a major drawback of using biomass gasification in industrial scale is tar release. Tar can clog the downstream pipe and coke reforming, upgrading, Fischer-Tropsch synthesis, fuel cell catalysts, and foul other unit operations [2]. Tar is also an environmental hazard (toxic, and carcinogenic) and usually co-exists with water purification during biomass gasification. As a result, tar dry-removal by an efficient method should be indispensable for commercializing biomass gasification.

In general, tar removal can be categorized in two methods, depending on the location where tar is removal, either in gasifier itself (known as primary method) or outside of gasifier (known as secondary method). It is well known that complete removal of tar is not feasible without a second method [3]. Several secondary methods are well known for tar elimination, such as mechanical or physical methods, thermal cracking, plasma cracking, and catalytic cracking [4,5]. Among these methods, catalytic thermal cracking is considered as the most promising one in large-scale applications due to its fast reaction rate, high reliability and increasing syngas yield [6].

Many kinds of catalysts have been used for catalytic cracking of

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biomass gasification tar or its model compounds. These catalysts can be divided into the six categories, including nickel-based catalysts, non-nickel metal catalysts, alkali metal catalysts, basic catalysts, acid catalysts, and activated carbon catalysts [4]. Among of which, nickel-based catalysts have been extensively researched because of its high-efficiency in tar elimination and syngas reforming [7,8]. Zhang et al. [9] have used commercial steam reforming Ni-based catalysts (ICI46-1, Z409 and RZ409) to investigate catalytic destruction of tar in a fluidized bed biomass gasifier, and their study proved that Ni-based catalysts were very effective in eliminating heavy tar and hydrogen yield was also improved by 6–10%. However, Ni-based catalysts weren't applied industrially because of rapid deactivation from coking.

In order to improve biomass tar cracking performance as well as energy efficiency, the microwave heating technique, as an emerging method, seems promising [10]. Comparing with conventional heating methods where the heat is transferred from the surface towards the center of the material by conduction and radiation, the microwave heating can penetrate materials and deposit energy thus the heat can be produced throughout the volume of the materials rather than an external source, thereby leading to a lot of advantages such as ease of operation and maintenance, no need for feedstock grinding and energy saving [11]. Zhao et al. [12] conducted biomass microwave pyrolysis experiments and the lowest energy consumption as 0.371 kw (kg straw)$^{-1}$ was obtained. Arshad Adam Salema et al. [13] designed a microwave reactor and performed biomass briquette pyrolysis experiments which scaled up to kilograms. Furthermore, microwave heating exhibits some unique advantages for biomass tar cracking. Yuli Zhou [14] conducted experiments to cracking biomass model tar with microwave-induced electrical discharge and it was confirmed that microwave plasma and photo-catalytic effect gave birth to a high tar cracking efficiency. Besides, the interactions between microwave and absorbent also bring beneficial effects on endothermic chemical reactions such as accelerating chemical reactions and reducing activation energy [15,16]. It could save ordinary endothermic reaction time as high as 80% [17]. Beneroso et al. [18] proposed a two stages biomass microwave pyrolysis device to produce syngas and crack tar. Biomass char produced in pyrolysis step was circularly used as bed material to crack tar under microwave irradiation and the overall conversion rate of syngas could reach 54%. Xie et al. [19] developed a fast microwave-assisted catalytic biomass gasification system. Their experimental results showed that tar content in gaseous product was reduced from 15 wt% to 5.1 wt%.

However, not all materials can be heated up under microwave irradiation. Some materials will reflect or conduct microwave energy instead of adsorbing it and improving temperature themselves [20]. For this reason, it is very important to carefully choose suitable material that can absorb microwave and increase temperature rapidly. Normally, the inertness of silicon carbide (SiC) can play this role as microwave absorber. Zhao et al. [21] reported that when the microwave power reached 900 W, the heating rate of SiC was about 60 °C min^{-1}. Besides, recent studies reported that biomass pyrolytic carbon residue (biomass char) which has high electric conductivity and dielectric constants can also act as microwave absorber and improve reaction temperature [22]. Moreover, biomass char has been used as adsorbents or catalysts for tar removal due to its highly porous textural structure, activity of tar reaction, high resistance to coking and relatively low cost [23,24]. Biomass char loading with metal may further improve tar cracking efficiency as well as quality of syngas. However, very few experiments focused on combination of char-supported metallic catalysts and microwave heating method. Considering the synergistic action may occur on biomass char-supported metallic catalysts, and few experimental reports have been found on biomass char as a bi-functional catalyst to ex-situ crack tar under microwave heating. It seems very interesting to carry out investigating biomass char as a bi-functional catalyst for tar cracking under microwave.

In this study, we creatively employed char-supported Ni to act as a bi-functional catalyst which absorbed microwave and catalyzed the toluene cracking process. Through the special design of reactor and precise control of experimental conditions, toluene as model tar was thoroughly cracked. The cracking mechanism was investigated by comparable experiments with SiC and RHC. Meanwhile, special attention was paid on the effect of microwave phenomena (hot spots and microwave plasma) which were not deeply investigated before. The generation conditions and mechanism of microwave-carbon interaction were studied in detail. Furthermore, the energy consumption evaluation of microwave tar cracking was performed. By indirect measurement of energy conversion efficiency and conducting operation simulation in a biomass gasification plant, the applied potential of microwave tar elimination was proved.

2. Materials and methods

2.1. Materials

It is believed that small aromatics ring systems are more difficult to be destructed than bigger ones [25], so analytical grade toluene (Jiangtian Chemical Co., Ltd., Tianjin, China) which is the lightest alkyl-aromatic tar was used as model tar. SiC (16 meshes) employed in experiments was produced by Mingmaite company, Zhengzhou, China. Rice husk due to its wide distribution in China's rural areas was chosen as biomass feedstock. It was dried at 105 °C for 12 h and ground into small particle size. Rice husk char (RHC) was generated by pyrolyzing dried rice husk at 750 °C for 30 min in a tube furnace with nitrogen as inert sweep gas. Then RHC was sieved to different particle size at 20–40 meshes (0.83–0.38 mm), 40–60 meshes (0.25–0.38 mm), and 60–80 meshes (0.18–0.25 mm). Proximate and ultimate analysis (as received basis) of rice husk were conducted on thermogravimetric analyzer (SDT-Q600, DSC-TGA) and elemental analyzer (Vario Micro cube, Elementar), respectively. The results were listed in Table 1. Fixed carbon, Oxygen content were calculated by difference, and low heating value was calculated by empirical formula (1) and (2) [26].

$$\mathrm{HHV\ (MJ\ kg^{-1})} = 33.5 \times \mathrm{C} + 142.3 \times \mathrm{H} - 15.4 \times \mathrm{O} - 14.5 \times \mathrm{N} \quad (1)$$

$$\mathrm{LHV\ (MJ\ kg^{-1})} = \mathrm{HHV} - 2.44(9 \times \mathrm{H}) \quad (2)$$

where C, H, O, N is carbon, hydrogen, oxygen and nitrogen mass percentage obtained by ultimate analysis.

Char-supported Ni catalysts (RHC-Ni) were prepared by incipient wetness impregnation. RHC was incipient wet-impregnated with different concentration gradient of Ni using $Ni(NO_3)_2{\cdot}6H_2O$ as precursors, followed by drying at 105 °C for 12 h. Then RHC containing metal species was calcined in a microwave pyrolysis reactor for 20 min at 800 °C in an inert gas atmosphere. The prepared catalysts were noted as RHC-χ Ni, where χ represents percentage of Ni content in aqueous solution divided by the mass of RHC (χ = 2, 4, 6, 8 wt%).

Table 1
Proximate and ultimate analysis of rice husk.

Proximate analysis (wt.%, dry basis)			Low heating value LHV (MJ kg^{-1})		
Volatile	Ash	Fixed carbon[a]			
67.35	18.16	14.49	13.05		
Ultimate analysis (wt.%, dry basis)					
C	H	O[a]	N	S	Cl
38.45	5.08	37.83	0.15	0.23	0.10

[a] Calculated by differences.