Bioresource Technology 267 (2018) 333–340

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Microwave-assisted in-situ elimination of primary tars over biochar: Low temperature behaviours and mechanistic insights

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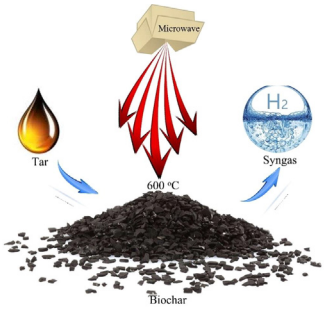
GRAPHICAL ABSTRACT

94.03% tar removal efficiency, 50.5 vol% H_2 and 94.5 vol% syngas content are attributed to hot spots and active AAEMs over biochar catalysts at 600 °C under microwave heating.



ARTICLE INFO

Keywords:
Primary tars
Microwave
Biochar
AAEMs
Hot spots

ABSTRACT

An efficient method for microwave-assisted low temperature catalytic elimination of primary tars using cheap biochar as catalyst has been developed along with H_2 rich syngas production. Tar removal efficiency reached 94.03% after 8 min reaction at 600 °C, while the concentration of H_2 and syngas was up to 50.5 vol% and 94.5 vol% respectively, which were significantly comparable to conventional technologies at 700–900 °C. The FT-IR, ICP and EDX results indicated that the biochar surface contained O-containing functional groups and 12.6 wt% uniformly dispersed alkali and alkaline earth metals (AAEMs) in the carbon skeleton. The low temperature behaviours were attributed to the hot spots, which were induced by the increased dielectric properties of biochar and decentralized AAEMs under microwave heating. Possible reaction mechanism for the elimination of primary tars over biochar catalysts were discussed based on this experimental study.

1. Introduction

Biomass is gaining more attention as a renewable resource to partly substitute fossil fuels with the demand of sustainable development. Pyrolysis and gasification of biomass are regarded as promising thermal technologies to produce bio-based chemicals, fuels and syngas (Devi et al., 2003; Park et al., 2016). During the gasification process, biomass was firstly pyrolyzed into char, primary tar (volatiles or vapors) and non-condensable gases. Undesired primary tars were referred to as a group of organic compounds with large molecular weights (Font Palma,

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https://doi.org/10.1016/j.biortech.2018.07.071
Received 28 May 2018; Received in revised form 12 July 2018; Accepted 13 July 2018

2013; Guan et al., 2016), and could generate heavier tars by polymerization at higher temperature. These tars can adhere easily to turbines and pipes, causing mechanical corrosion or catalysts inactivation if left to condense; therefore, it is essential to eliminate tars during a thermochemical process (Gilbert et al., 2009).

To eliminate primary tars, the physical, thermal and catalytic technologies have been developed, among them, catalytic removal is a promising technology to convert tars to syngas with the aid of metal and non-metal catalysts (Adrados et al., 2013; Park et al., 2016; Wang et al., 2011). Biochar catalyst presents cheap and green advantages to directly reform primary tars into syngas without regeneration after deactivation (Devi et al., 2003; Shen, 2015; Shen and Yoshikawa, 2013). Simultaneously, biochar contains active metals such as Na, Ca, K and Fe, which is in favor of cracking tars over biochar surface (Feng et al., 2016; Kastner et al., 2015). Extensive research efforts have showed that biochar could provide a high removal efficiency of phenol and naphthalene, which was related to the O-containing functional groups and dispersed alkali and alkaline earth metals (AAEMs) in the carbon skeleton (Abu El-Rub et al., 2008; Bhandari et al., 2014; Feng et al., 2016; Guan et al., 2016; Kastner et al., 2015; Min et al., 2011a,b; Wang et al., 2014). Abu El-Rub et al. have compared the ability of biochar and different catalysts for tar conversion under 700–900 °C. The biochar was equivalent to the Ni-based catalysts for cracking of phenol and naphthalene, and it obtained the highest naphthalene conversion among the cheap catalysts (Abu El-Rub et al., 2008; Park et al., 2016). Bhandari et al. have explored the catalytic performances of biochar and the removal efficiency was 69–92% for toluene in a fixed bed reactor at 700–800 °C (Bhandari et al., 2014; Guan et al., 2016). Min et al. have found that AAEMs could be served as active points, where AAEMs dispersed in biochar matrix can promote the condensation of hydrocarbons in volatile phase to form coke, so as to convert tar to small molecules (Min et al., 2011a,b; Wang et al., 2014). Feng et al. found that the earth metal species (K and Ca) were converted to K^+ and/or Ca^{2+} cations which combined with activated tar fragments in the gas phase through de-alkylation and de-polymerization of model tar compounds, and more O-containing functional groups were formed on K-loaded biochar than Ca-loaded and H-form biochar (Feng et al., 2016). Typical model compounds (phenol and naphthalene) have been used to reveal the mechanism of tar elimination over biochar catalyst, and a series of studies showed the main process were cracking, deposition, dehydrogenation to form coke, and then coke gasification to produce gases products (Fuentes-Cano et al., 2013; Hosokai et al., 2008; Hosokai et al., 2011; Sueyasu et al., 2011). In fact, the elimination of tars from real biomass feedstocks is of great importance to explore the whole process with current demand.

Meanwhile, effective elimination of tars was performed at temperatures between 800 and 1000 °C in an atmosphere of steam and CO_2 with high energy consumption (Abu El-Rub et al., 2008; Al-Rahbi et al., 2016; Borges et al., 2014). To reduce the reaction temperature, new approaches such as microwave heating (MH) was exploited to realize selective, rapid, and volumetric heating, and enhance the heat and mass transfer compared with conventional heating (CH) (Huang et al., 2016; Luo et al., 2018). Compared with CH processes where heat is transferred from the surface to the center of the material through conduction driven by temperature gradients, MH can provide uniform internal heating at the molecular level by direct conversion of the electromagnetic energy into heat. The temperature reduction induced by MH in pyrolysis and gasification reactions has also been proved in previous studies (Bermúdez et al., 2014; Luo et al., 2017; Xiao et al., 2015). Bermúdez et al. have developed the microwave-assisted pyrolysis (MAP) of macroalgae for syngas production and found the content of H_2 was 57 vol% at 600 °C with MH, which was higher than that of CH at 800 °C (33 vol%). The metal oxides in macroalgae could result in arcing effects under microwave irradiation, which was observed as a pseudo-catalytic effect to improve the gas and H_2 yields (Bermúdez et al., 2014). Our precious work about the MAP of sawdust showed that the temperature could be reduced to 400 °C without obvious liquid yield decrease compared with CH at 500–650 °C (Luo et al., 2017). Meanwhile, compared with CH, the initial decomposition temperatures of biomass components using MH were reduced by 50–100 °C and the fastest weight loss regions were shifted to lower temperatures, which was due to the generation of microwave hot spots within biomass (Luo et al., 2018). With AAEMs, the gasification of biochar with MH was performed at 700 °C, which provided a similar result to that obtained at 1000 °C by CH (Xiao et al., 2015). In fact, there are few reports concerned with the low temperature behaviors and corresponding reaction mechanism of tars conversion over biochar catalyst with MH.

Here, the elimination of primary tars over biochar and generation of H_2-rich syngas at low temperatures were investigated using MH. A microwave fixed bed reactor was applied to explore the low temperature elimination of rice straw derived primary tars when it passed through a hot biochar particle bed at 500–600 °C. Furthermore, FT-IR, ICP and EDX were applied to characterize the O-containing functional groups and AAEMs distribution in the carbon skeleton. Dielectric properties of biochar were measured within the main pyrolysis temperature range to reveal the generation of hot spots. Combined AAEMs catalytic performance and microwave hot spots were applied to explore low temperature behaviors and possible tar elimination mechanism, which could provide a better knowledge of design and scale-up of portable microwave plants suitable for industrial application.

2. Material and methods

2.1. Materials

Rice straw used in the experiment was obtained from the countryside of Chongming District, Shanghai, China. It was naturally dried and sieved to 10–20 mesh before use. The main characteristics of rice straw were listed in Table 1. The proximate analysis was carried out according to the ASTM standards (Hu et al., 2015; Luo et al., 2017) and elemental analysis was tested by the Thermo Scientific Flash 2000 analyzer with a dry basis.

Fresh biochar (FB) and used biochar (UB) served as catalysts to reveal the catalytic effect and stability. The biochar was prepared by microwave-assisted pyrolysis of the raw rice straw in N_2 at 600 °C in a fixed bed reactor with a holding time of 30 min. Before using as catalysts, the obtained biochar samples were dried at 105 °C for 4 h.

2.2. Experiment procedures

The pyrolysis of rice straw and tar reforming was performed in a microwave-assisted fixed bed reactor, which consisted of a microwave oven (SYNOTHERM Corporation, Changsha, China) and a quartz tube reactor, as shown in Fig. 1. The maximum power of the microwave was 1400 W at the frequency of 2.45 GHz. The output power can be continuously changed (20–1400 W) to obtain the programed temperature rising detected and controlled by the infrared thermometer (−25 to 900 °C), which was calibrated with thermocouples in advance. A cylindrical insulating brick was placed in the middle of the oven. The detailed composition of the microwave equipment were described in our previous work (Luo et al., 2018). A quartz reactor with inlet and

Table 1
Characteristics of rice straw.

Proximate analysis (wet basis, wt%)		Elemental analysis (dry basis, wt%)	
Moisture content	10.88	C	41.22
Ash content	10.93	H	5.56
Volatiles	64.73	N	0.92
Fixed carbon	13.46	O[a]	52.30

[a] Calculated by difference.