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Promoting effect of various biomass ashes on the steam gasification of low-rank coal

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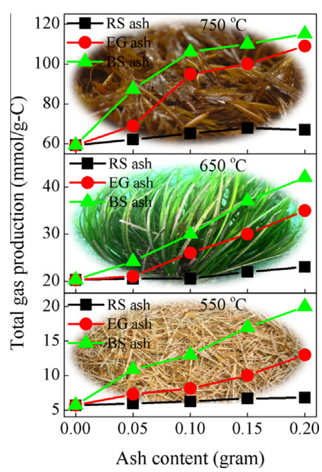
HIGHLIGHTS

- Biomass ash was utilized to promote gasification of low rank coal.
- Promoting effect of biomass ash highly depended on AAEM content in the ash.
- Stability of the ash could be improved by maintaining AAEM amount in the ash.
- Different biomass ash could have completely different catalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Application of biomass ash as a catalyst to improve gasification rate is a promising way for the effective utilization of waste ash as well as for the reduction of cost. Investigation on the catalytic activity of biomass ash to the gasification of low rank coal was performed in details in the present study. Ashes from 3 kinds of biomass, i.e. brown seaweed/BS, eel grass/EG, and rice straw/RS, were separately mixed with coal sample and gasified in a fixed bed downdraft reactor using steam as the gasifying agent. BS and EG ashes enhanced the gas production rate greater than RS ash. Higher catalytic activity of BS or EG ash was mainly attributed to the higher content of alkali and alkaline earth metal (AAEM) and lower content of silica in it. Higher content of silica in the RS ash was identified to have inhibiting effect for the steam gasification of coal. Stable catalytic activity was remained when the amount of AAEM in the regenerated ash was maintained as that of the original one.

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1. Introduction

Gasification is a thermochemical conversion process in which solid carbonaceous materials such as coal and biomass are converted into syngas. Recently, gasification process has been intensively studied to produce syngas from alternative and renewable fuel such as woody biomass and agricultural residues [1–5]. Gasification is also considered as an effective way to utilize coal cleanly. Despite the serious environmental problem by burning coal, coal is still widely used and becomes the main energy sources in the world due to its low-cost. It shared about 29.9% of global primary energy consumption in 2012 in which China, USA and India shared approximately 50.2%, 11.7% and 8.0%, respectively [6]. The main purposes to develop the coal gasification technology are to increase the conversion efficiency [7–11] and to utilize low-rank coal effectively [12–16].

Utilization of catalyst to increase the gasification rate is an attractive option. It can either increase the coal conversion rate at certain temperature or decrease gasification temperature but maintain the high conversion rate [17,18]. Furthermore, the use of catalyst can reduce the tar formation [19,20]. Sutton et al. [21] summarized the fundamental criteria for the selection of catalyst for the gasification. The selected catalyst should be able to remove tar effectively, to reform methane well, and to obtain the intended syngas ratio. Furthermore, the catalyst should not be easily deactivated, or can be easily regenerated, and has low cost. Some catalysts such as nickel based catalysts were found to be able to increase the hydrogen production, and result in a high H_2/CO ratio [22]. Some natural minerals such as olivine [23], calcite [24], and dolomite [25] were also found to be suitable for the gasification. Alkali and alkaline earth metal (AAEM) species have been extensively applied for the coal gasification due to their high catalytic activity and low cost [26–31]. Mitsuoka et al. [26] investigated the catalytic effect of K and Ca on the CO_2 gasification of Japanese cypress char and the result confirmed that the additions of K and Ca effectively enhanced the reactivity of char. K and Ca species were also found to improve the reactivity of coal char [27]. Zhang et al. [29] successfully utilized low cost AAEM precursors such as soda ash and slaked lime for promoting the pyrolysis of coal char. In fact, almost all biomass contain AAEM species. However, different biomass contains different contents of AAEM. Biomass with high content of AAEM was found to be able to improve the gasification performance when it was co-gasified with coal [32–37] or with other biomass containing low concentration of AAEM [38]. It is found that some components of AAEM in the biomass were easily volatilized and resulting in the increase in the reactivity of the coal [36,37]. When biomass is burnt, most of AAEM species could still remain in its ash. The cost will be considerably reduced if biomass ash can be used as the catalyst. Biomass ash was found to be able to promote the biodiesel production rate due to its alkalinity [39–42]. Ash was also reported to have good catalytic activity for other reactions such as ethanol dehydrogenation [43] and partial oxidation of methanol [44]. Lahijani et al. [45] successfully used the ash from palm empty fruit bunch to enhance CO_2 gasification of palm shell char. However, only limited number of studies focused on the direct utilization of biomass ash for promoting coal gasification rate. In the present study, various biomass ashes were prepared at different calcination temperatures and used for the gasification of low-rank coal. The effects of the ash compositions and ash addition amount in the coal sample on the gasification rate were investigated in details. To understand the effect of AAEM contents in the ash on the catalytic activity, simulated catalysts, i.e., K/CaO and K/SiO_2 with different K loading amounts, were prepared and used for the coal gasification. The stability and reusability of the ash as the catalyst were also examined in order to provide more information for the application biomass ash as a catalyst in a practical gasification process.

2. Materials and methods

2.1. Feedstock and ash preparation

Adaro coal (Indonesian brown coal) is a kind of low rank coal. Proximate analysis result based on ASTM S3172-75 and ultimate analysis result based on elemental analyzer (Vario EL cube elemental analyzer) for it are shown in Table 1. It was ground and sieved to particle size of 1–2.8 mm and dried in the oven at 105 °C overnight prior to use. The remaining moisture content was measured by using moisture content analyzer (MX50, AND, Japan).

Three kinds of biomass (rice straw, eel grass/*Zostera caespitosa*, and brown seaweed/*Sargassum horneri*) collected from Aomori Prefecture, Japan were chosen as the ash sources since they contained high content of ash as shown in Table 2. Ash contents of rice straw (RS), eel grass (EG), and brown seaweed (BS) were 14, 6.6, and 13.5 wt% in dry base, respectively. In order to investigate the effect of calcination temperature on the ash catalytic activity, various ashes were prepared by calcination of biomass at 600, 800, and 1000 °C for 2 h, respectively. Metal content in the ash was measured by using X-ray fluorescence (XRF) analysis (Energy Dispersive X-ray spectrometer, EDX-800HS, Shimadzu).

To understand the effect of AAEM content in the ash on the catalytic activity, two simulating catalysts, i.e., K/CaO and K/SiO_2, were prepared by incipient wetness impregnation method. Herein, Mg was assumed to have the similar effect as Ca since they have similar chemical properties as they are belonged to the same group. CaO support was obtained by calcining scallop shell at 1000 °C while SiO_2 was provided by Saint-Gobain Norpro, US. X ray diffraction analysis (XRD) showed that almost pure CaO phase was obtained from the calcination of scallop shell at 1000 °C. Catalyst support was soaked into the KNO_3 (Wako, Japan) solution at certain concentration so that the as-prepared catalysts would have the similar potassium composition as those in biomass ash (30 wt%-K/CaO for BS ash and 50 wt%-K/SiO_2 for RS ash). The slurry was then dried overnight in the oven and calcined at 650 °C for 3 h.

2.2. Gasification experiments

Steam gasification experiment was conducted in a fixed bed reactor. Schematic illustration of the experimental setup can be

Table 1
Proximate and ultimate analysis of Adaro coal sample.

Proximate analysis (wt%-dry)			Ultimate analysis (wt%-daf)[a]			
Ash	Volatile matter	Fixed carbon[b]	C	H	O[b]	N
2.1	47.8	50.1	70.0	4.9	24.7	0.4

[a] Dry ash-free.
[b] By difference.

Table 2
Proximate analysis of brown seaweed, eel grass, and rice straw.

Biomass	Proximate analysis (wt%-dry)		
	Ash	Volatile matter	Fixed carbon[b]
Brown seaweed	13.5	52.8	33.7
Rice straw	14.0	52.0	34.0
Eel grass[a]	6.6	53.8	39.6

[a] Based on thermogravimetry analysis.
[b] By difference.