Steam gasification of iron-loaded biochar and subbituminous coal mixture

Lingbo Shen*, Kenji Murakami

Department of Engineering in Applied Chemistry, Faculty of Engineering and Resource Science, Akita University, 1-1 Tegata gakuen-machi, Akita city, Akita010-8502, Japan

Abstract:
This study aims to investigate the effect of the addition of the iron-loaded biomass pyrolysate (Fe-biochar) on the steam gasification of Indonesian Adaro sub-bituminous coal. The amount of hydrogen evolved from the steam gasification of the mixture of Fe-biochar and Adaro coal at 800°C for 60 min was much higher than that from the steam gasification of iron-loaded Adaro coal. From the result that the specific reaction rate did not decrease during the steam gasification of the mixture of Fe-biochar and Adaro coal, the iron catalyst on the biochar was found to be relatively stable in the steam gasification. The activity of iron catalyst was discussed by the differences in the chemical form and the crystallite size of iron catalyst.

Keywords: *biomass; subbituminous coal; steam gasification; iron catalyst*

**Corresponding author. Tel.: +81-18-889-2431, Fax: +81-18-837-0404*
E-mail address:bobo198743@yahoo.co.jp

1. Introduction

The effective utilization of low-rank coal is one of the hottest topics in these years. Steam gasification of low-rank coal is expected to produce valuable gases such as hydrogen and carbon monoxide. These gases can be used as resources for chemical raw materials as well as energy. However, when Adaro subbituminous coal, Indonesia, without catalyst was gasified with steam below 900°C, our previous study showed that not so much hydrogen was produced. Moreover, the iron catalyst had only a little effect on the hydrogen production. This is because the iron catalyst does not exist in an active form on the surface of coal after pyrolysis. On the other hand, Sergio and Mirella (2011) reported that the iron catalyst was very effective for the hydrogen production in the steam gasification of woody biomass. We also showed that the cementite, Fe_3C, produced during pyrolysis had a high activity for the hydrogen production in the steam gasification of wood (Murakami et al., 2011). Accordingly, it is very interesting to gasify the mixture of the Adaro coal and the biochar with Fe_3C. The purpose of this study is to investigate the effect of the addition of iron-loaded biochar on the steam gasification of Adaro coal at 800°C.

2. Experimental

2.1 Samples

Japanese cedar (hereafter referred to as SG) (C: 46.9 wt%, H: 5.8 wt%, N: 0.1 wt%, O (diff.): 47.1 wt%, Ash: 0.3 wt %) was used as woody biomass. This biomass was ground below 250 μm. Adaro coal from Indonesia (hereafter referred to as AD) (C: 67.8 wt%, H: 5.1 wt%, N: 0.44 wt%, S: 0.14 wt%, O (diff.): 26.5 wt%, Ash: 2.5 wt%) was used as coal sample and ground between 150-250 μm.

2.2 Iron catalyst loading

A weighed amount of SG (10 g) or AD (10 g) were immersed in 200 ml of aqueous solution containing $FeCl_2$ and the suspension was stirred at 40°C for 1 h under vacuum by using a rotary evaporator. Then the water was evaporated at 60°C for 1 h. The impregnated samples were dried at 110°C for 1 h before use. The iron catalyst loadings were determined by ICP (Seiko Instruments, SPS5510) to be 6.8 wt% in SG and 6.7 wt% in AD.

2.3 Pyrolysis and gasification

Fig. 1 shows the fixed bed reactor which is used for pyrolysis and gasification. The iron-loaded biochar was produced by the pyrolysis of 6.8 wt% of Fe-loaded SG at 800°C for 10 min.

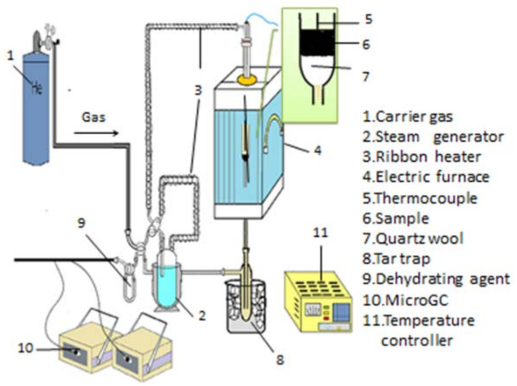

Fig. 1 Fixed bed reactor for pyrolysis and steam gasification.

Table 1 Samples used in the steam gasification

Samples	Fe loading, wt%
AD	—
3.2Fe-AD	3.2
6.7Fe-AD	6.7
6.8Fe-SG	6.8
1.8Fe-SG/AD	1.8
3.5Fe-SG/AD	3.5

The samples in Table 1 were used in the steam gasification experiment. In this table, the 1.8Fe-SG/AD and 3.5Fe-SG/AD samples mean that AD and 6.8Fe-SG char were mixed in the weight ratio of 10:1 and 10:2, respectively. At first, the sample is heated from room temperature to 800°C at the heating rate of 300°C/min under the helium flow in the vertical fixed-bed type reactor and held for 10 min. Then the 50 vol% of steam/He was introduced into the reactor and the sample was gasified at 800°C for 60 min. The gases (H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6) produced during steam gasification were determined by on-line Micro GC. The chemical form of Fe catalyst after pyrolysis and gasification was evaluated by XRD. The crystallite size of iron catalyst is caclculated by Sherrer equation.

$$L = \frac{K\lambda}{\beta \cos\theta} \quad (1),$$

where L is the crystallite size [nm], λ is the wavelength [Å], β is the width of diffraction peak [rad], K is equal to 0.9, and θ is the diffraction angle [°].

3. Results and discussion

3.1 Hydrogen production behavior during steam gasification

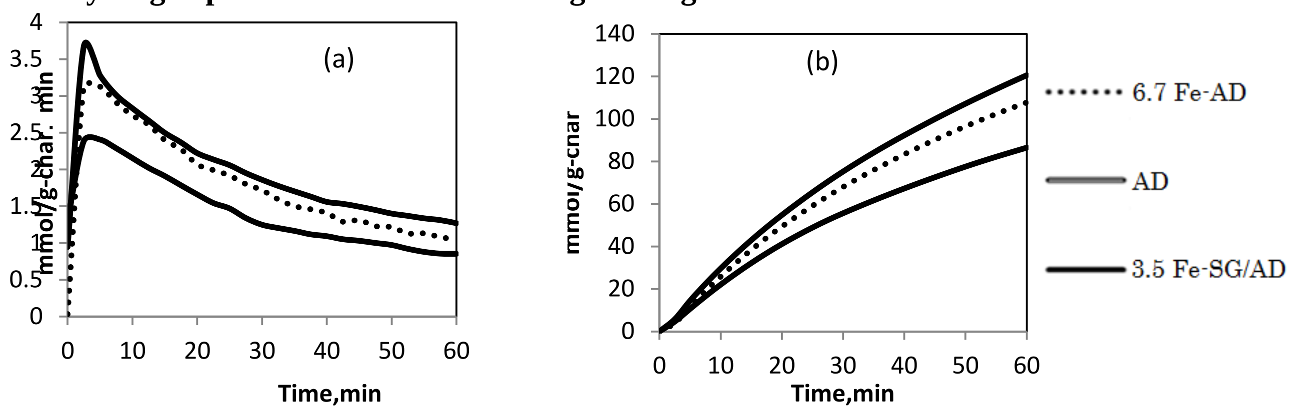

Fig. 2 (a) The H_2 evolution rate, (b) Amount of H_2 evolution.

Fig. 2(a) and Fig. 2(b) show the H_2 evolution rate and the amount of H_2 evolution during steam gasification at 800°C, respectively. Although the iron content in the 3.5Fe-SG/AD was about half of that in the 6.7Fe-AD, it was found from Fig. 2(a) that the H_2 evolution rate for the 3.5Fe-SG/AD was higher than that for the 6.7Fe-AD. Also, Fig. 2(b) revealed the amount of H_2 evolution for the 3.5Fe-SG/AD was about 1.5 times larger than that for the AD. Above results suggest that the iron catalyst on the biochar promotes to evolve the hydrogen from the AD.

3.2 Carbon conversion

The carbon conversion is calculated by the equation (2). And the results are shown in the Table 2.

$$\text{Carbon conversion [mol\%]} = \frac{\text{Carbon in the evolved gas } (CO+CO_2+CH_4+C2 \text{ hydrocarbon})\text{[mol]}}{\text{Amount of carbon in the char [mol]}} \times 100 \qquad (2)$$

From this table, it is found that the carbon conversion for the 6.8Fe-SG was higher than that for the 6.7Fe-AD. On the other hand, the carbon conversion for the 3.5Fe-SG/AD is 13% higher than that for the 3.2Fe-AD.

Table 2 Carbon conversion in the steam gasification at 800°C for 60 min

Samples	Carbon conversion, mol%
AD	48
3.2Fe-AD	54
3.5Fe-SG/AD	67
6.7Fe-AD	59
6.8Fe-SG	69

3.3 Specific rate

The specific rate is calculated by the following equation.

$$R_s = \frac{R_c}{W_{sc}} \qquad (3),$$

where R_s represents the specific rate [1/h], R_c represents the rate of carbon conversion [mol%/h], and W_{sc} represents the amount of residual carbon in the char [mol%].

Fig. 3 shows the relationship between specific rate and carbon conversion. From this figure, it is found that the specific rate increased with increasing the amount of the iron catalyst. In the case of AD and 3.2Fe-AD, it is observed that the specific rates decreased gradually with increasing the carbon conversion, indicating that the activity of iron catalyst decreased during the steam gasification. On the contrary, there is no obvious decrease in the activity of iron catalyst in the 1.8Fe-SG/AD and 3.5Fe-SG/AD.

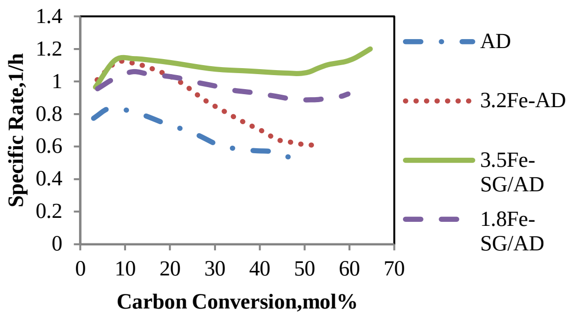

Fig. 3 Relationship between specific rate and carbon conversion.

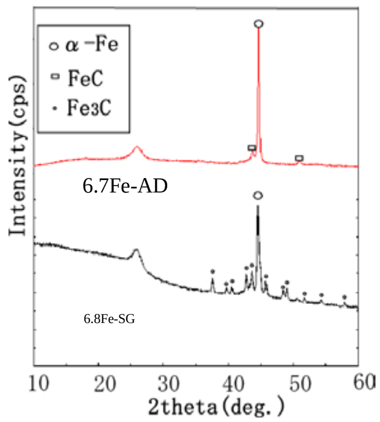

Fig. 4 XRD patterns after pyrolysis of coal and biomass.

3.4 Chemical form of Fe catalyst after pyrolysis and gasification of AD and SG and crystallite size

Fig. 4 shows the XRD patterns after the pyrolysis of 6.7Fe-AD and 6.8Fe-SG. After pyrolysis, the Fe catalyst exists as FeC and α-Fe on the coal sample, while Fe catalyst exists as α-Fe and Fe_3C on the SG. For the AD, the char yield increases slightly from 48% to 51% by adding Fe catalyst. On the other hand, the biochar yield increases significantly from 16% for SG to 35% for 6.8Fe-SG. This indicates that the iron catalyst reacts with the tar and changes to Fe_3C in the biochar.

Table 3 shows the chemical form of iron catalyst after 10 min and 60 min of steam gasification. It is found that iron catalyst exists as Fe_3O_4 and FeO on the AD after 10 min of gasification. In the 3.5Fe-SG/AD, the XRD pattern shows the presence of Fe_2C as well as Fe_3O_4 and FeO. After 60 min of gasification, the iron catalyst exists as Fe_3O_4 and FeO in the both samples.

Table 3 Chemical forms of Fe catalyst after steam gasification

Samples	After 10 min	After 60 min
3.2Fe-AD	Fe_3O_4, FeO	Fe_3O_4, FeO
3.5Fe-SG/AD	Fe_2C, Fe_3O_4, FeO	Fe_3O_4, FeO

Table 4 shows the change in the crystallite size after pyrolysis and after gasification. The α-Fe is the main chemical form of the iron catalyst after pyrolysis. It is found that there is no difference in the crystallite size between 3.2Fe-AD and 3.5Fe-SG/AD. On the contrary, after gasification, the crystallite size of 3.5Fe-SG/AD is much smaller than that of 3.2Fe-AD. This suggests that the iron species on the biochar maintains a highly dispersed state compared to the iron species on the AD coal.

Table 4 Change of the crystallite size

Samples	After pyrolysis α-Fe, nm	After gasification Fe_3O_4, nm
3.2Fe-AD	44	62
3.5Fe-SG/AD	43	47

4. Conclusion

The effect of the addition of the iron-loaded biochar on the steam gasification of the subbituminous coal was investigated in this study. The hydrogen evolution rate and carbon conversion for the mixed sample were much higher than that for the AD and 6.7Fe-AD. The chemical form of iron catalyst on the biochar was different from that on the AD coal char. From the data of specific rate, it is found that the iron catalyst in the mixed sample can keep a high activity, while the activity of iron catalyst in the iron-loaded coal lowered with reaction time. After gasification, the crystallite size of the iron catalyst on the mixed sample is much smaller than that on the iron-loaded AD coal.

5. References

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