Introduction

As a renewable energy, biomass has gained importance with the development of a serious energy crisis and increased environmental challenges. Co-gasification of coal and biomass is one of the most practical means of converting these fuels into clean gas for use as a fuel or a chemical precursor. This is because co-gasification has several advantages [1–4]: for example, the addition of biomass to coal can reduce CO\textsubscript{2} emissions and the problems caused by the harmful ash contained in coal. However, high cost for biomass processing, transportation, and drying, and large amount of tar generation are big problems for biomass utilization. Coal mixing is regarded as a good solution to solve the problems. On the other hand, biomass has a different H/C and O/C molar ratio than coal leading to different reactivity and thermal characteristics during co-gasification. For example, biomass with a high molar ratio of H/C may act as H\textsubscript{2} donors during pyrolysis of biomass and coal blends. Therefore, some synergistic effect producing more volatile products may occur [5–7].

Many researchers have also studied the effect of alkali metal and alkaline earth metal (AAEM) in biomass ash on co-gasification [8–10]. Wei et al. [8] concluded that AAEM in biomass ash, particularly K, can promote gasification and transform from biomass to another feedstock. Zhang et al. [9] performed experimentation on petroleum coke and corn cob co-gasification using thermogravimetric analysis (TGA). This study concluded that AAEM in biomass ash led to the promoted effect in co-gasification process. However, a high AAEM content in biomass feedstock resulted in serious challenges, such as ash slagging, fouling, agglomeration, deposition, and heated side corrosion.
in a high-temperature environment [11–14]. Based on the work mentioned above, woody biomass with less ash was added to coal for co-gasification in recent years. For example, Adeyemi et al. [15] compared gasification behavior of coal and woody biomass and concluded that Kentucky coal produced higher gasification efficiency than wood. Zhang and Zheng [16] conducted co-gasification experimentation of two types of biomass (one was woody biomass) and coal determining that the ash in woody biomass could bring a promoted effect on promoting gasification reactivity of coal char. They also discussed the difference between fuel mixture (coal and woody biomass mixture) and fuel separation for gasification in another paper [16], which expressed that fuel mixture showed a much bigger synergy degree than that of fuel separation.

In previous study, iron-loaded biochar was used and shown to increase gasification of AD by 20% when compared to a coal sample with the same amount of iron catalyst. As such, iron-loaded biochar can be used as raw sample and as catalyst for gasification [17]. In this method, the iron-loaded biochar must be initially prepared with the iron catalyst loaded with impregnation. From a practical perspective, an easy and low-cost operation was selected. Thus, development of a co-gasification process for direct application in a coal/woody biomass is necessary.

This study investigates the co-gasification of biomass and AD coal without catalyst and with an iron catalyst. With a limited number of studies on catalytic co-gasification, the effect of an iron catalyst addition on the change in synergy (interaction between biomass and AD coal) was unknown. Hence, this study focused on the effect of iron catalyst on the interaction between biomass and AD coal.

### Experimental

#### Samples

Indonesian Adaro subbituminous coal (AD) and Japanese cedar (SG) were used as coal and biomass samples, respectively. The particle size, the proximate, and the ultimate analyses were identical to our previous studies [17] as shown in Tables 1 and 2. The iron species was a commercial Fe$_2$O$_3$ (α-Fe$_2$O$_3$).

#### Preparation of mixed samples and iron catalyst loading

AD and SG were mixed in a mortar with a weight ratio of 1:1. After mixing the samples were stored in hermetic bags and labeled (SG+AD).

A physical mixing method was used for iron catalyst loading. To maintain a weight fraction of 10% loading, an applicable amount of iron species was added into AD, SG, and the mixed samples. The samples were mixed thoroughly, then labeled Fe$_2$O$_3$-SG, Fe$_2$O$_3$-AD, and Fe$_2$O$_3$-(SG+AD).

#### Pyrolysis and steam gasification

The fixed-bed reactor used in this study, as shown in Figure 1, is identical to the reactor in previous work published by Shen and Murakami [17]. Initially, approximately 0.5 g of one sample was placed on quartz wool in the center of the vertical fixed-bed-type reactor. The sample was heated from room temperature to 800°C at a heating rate of 300°C/min under a flowing He gas rate of 140 mL/min, at which it was then maintained for 10 min. The char was weighed and its yield was calculated using the following equation:

\[
Y_{\text{char}} = \frac{M_{\text{char}}}{M_{\text{sample}}} \tag{1}
\]

where $Y_{\text{char}}$ is the weight ratio of char yield and $M_{\text{char}}$ is the weight of char [g(dried, ash and catalyst free)]. $M_{\text{sample}}$ is the weight of the sample [g(dried, ash and catalyst free)].

After a 10 min pyrolysis, the char was maintained in a volume ratio of 50% H$_2$O/He for 60 min. With a MicroGC and flowmeter the gas evolution rate was calculated using the following equation:

\[
R = \frac{V_{\text{vol}} \times L}{22.4 \times M_{\text{char}}} \tag{2}
\]

where $R$ is the gas evolution rate [mmol/g-char-min], $V_{\text{vol}}$ is the volume fraction of each produced gas measured by the MicroGC, and $L$ is the total gas flow rate [mL/min]. $M_{\text{char}}$ is the weight of char [g].

Carbon conversion could be explained as the ratio of the amount of carbon evolved as gases to the amount of coal used.

### Tables

#### Table 1. Proximate and ultimate analyses of AD.

| Prox. analysis wt% (dry) | Ultimate analysis wt% (daf) |
|-------------------------|-----------------------------|
| Ash VM FC               | C H N S O(diff.)            |
| 2.5 46.7 50.8           | 67.8 5.1 0.44 0.14 26.5     |

Particle size: 150–250 µm.

#### Table 2. Proximate and ultimate analyses of SG.

| Prox. analysis wt% (dry) | Ultimate analysis wt% (daf) |
|-------------------------|-----------------------------|
| Ash VM FC               | C H N O(diff)               |
| 0.9 78.4 20.7           | 46.9 5.8 0.1 46.2          |

Particle size: <250 µm.
of carbon present in the char before gasification. It could be calculated using the following equation:

\[ X_{\text{Carbon}} = \frac{C_{\text{gas}}}{C_{\text{char}}} \]  

where \( X_{\text{Carbon}} \) is the carbon conversion, \( C_{\text{gas}} \) is the total mol content of carbon-containing gases (the sum of CO, CO\(_2\), CH\(_4\), C\(_2\)H\(_4\), and C\(_2\)H\(_6\) mol content), and \( C_{\text{char}} \) is the mol content of carbon in the char, in which the char was assumed to be 100% carbon.

**Characterization of the pyrolyzed char and gasified residue**

The form of iron catalyst after pyrolysis and steam gasification was measured by XRD under conditions that were identical to what was previously reported [17].

**Result and Discussion**

**The hydrogen evolution profiles for co-gasification of AD and SG**

Figure 2 shows the hydrogen evolution profiles for Adaro coal and cedar mixture (SG+AD) with and without Fe\(_2\)O\(_3\). As noted in this figure, the addition of Fe\(_2\)O\(_3\) had a higher hydrogen rate than (SG+AD). (Fe\(_2\)O\(_3\)-SG+Fe\(_2\)O\(_3\)-AD) showed the sum of the hydrogen rate for independent gasification of Fe\(_2\)O\(_3\)-SG and Fe\(_2\)O\(_3\)-AD, which did not contain the interaction of Fe\(_2\)O\(_3\)-SG and Fe\(_2\)O\(_3\)-AD. Comparing Fe\(_2\)O\(_3\)-(SG+AD) with (Fe\(_2\)O\(_3\)-SG+Fe\(_2\)O\(_3\)-AD) in Figure 2, allowed observing a significant increase in the center of the time range.

As reported in the previous study [17], the main reactions under the conditions should be as follows:

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} \]

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \] (WGS reaction)

Table 3 shows the amount of H\(_2\), CO\(_2\), CO, and ratio of H\(_2\)/CO for (SG+AD) and Fe\(_2\)O\(_3\)-(SG+AD). From Table 3, amount of H\(_2\) and CO\(_2\) largely increased after Fe\(_2\)O\(_3\) added, moreover, ratio of H\(_2\)/CO also increased from 7.1 to 13.8. Thus, Fe\(_2\)O\(_3\) addition promoted WGS reaction in the steam gasification.

**Synergy in noncatalyst co-gasification and catalytic co-gasification**

Synergy is the interaction between biomass and coal. Moreover, the synergy may be facilitation, but also may be an inhibition for gasification reaction. Therefore, for co-gasification it is important to know if a promoted synergistic effect existed.

In this study, the experimental amount of hydrogen evolution was compared with a calculated value to determine synergy. Equation 4 was used to calculate the value for co-gasification without a catalyst.

\[ \text{Amount(cal)} = \frac{\text{Amount(AD)} \times M(AD_{\text{char}}) + \text{Amount(SG)} \times M(SG_{\text{char}})}{M(AD_{\text{char}}) + M(SG_{\text{char}})} \]

where Amount(AD) is the amount of hydrogen evolution for 1 g of AD\(_{\text{char}}\); Amount(SG) is the amount of
hydrogen evolution for 1 g of SGchar; and M(ADchar) and M(SGchar) are weights of ADchar and SGchar, respectively.

For co-gasification with Fe$_2$O$_3$ Equation (5) was used.

\[
\text{Amount (cal)} = \frac{\text{Amount (FeAD)} \times M(\text{FeADchar}) + \text{Amount (FeSG)} \times M(\text{FeSGchar})}{M(\text{FeADchar}) + M(\text{FeSGchar})}
\]  

(5)

where Amount(FeAD) is the amount of hydrogen evolution for 1 g of Fe$_2$O$_3$-AD char; Amount(FeSG) is the amount of hydrogen evolution for 1 g of Fe$_2$O$_3$-SG char; and M(FeADchar) and M(FeSGchar) are weights of Fe$_2$O$_3$-ADchar and Fe$_2$O$_3$-SGchar, respectively.

Figure 3 shows the comparison of the experimental and calculated amount of hydrogen evolution for co-gasification. For co-gasification without catalyst, the experimental amount of (SG+AD) is 100 mmol/g-char while the calculated amount is 85 mmol/g-char. Therefore, the synergy for (SG+AD) results in a 15 mmol/g-char increase in H$_2$.

For co-gasification after added Fe$_2$O$_3$, the experimental H$_2$ amount of Fe$_2$O$_3$-(SG+AD) is 152 mmol/g-char and the calculated H$_2$ amount is 121 mmol/g-char. Therefore, the synergy for Fe$_2$O$_3$-(SG+AD) results in a 31 mmol/g-char increase in H$_2$, which is significantly higher than the synergy of (SG+AD) without catalyst.

**Effect of Iron on reactivity of char for co-gasification**

Specific rate, as calculated by equation (6), is used to compare the change in reaction activity as well as degree of reactivity.

\[
R_s = \frac{R_c}{W_{sc}}
\]  

(6)

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

As illustrated in Figure 4, the specific rate of (SG+AD) without iron catalyst is nearly constant during the complete gasification process. With the addition of Fe$_2$O$_3$, the specific rate of Fe$_2$O$_3$-(SG+AD) increased with increased carbon conversion. A continuing promoting effect was noted after the addition of Fe$_2$O$_3$. However, the specific rate of (Fe$_2$O$_3$-SG+Fe$_2$O$_3$-AD) increased initially then decreased similar to the change in Fe$_2$O$_3$-AD. This indicated that SG addition increased the Fe catalyst effect on char reactivity, which resulted in the difference of specific rate.

**Change with Fe$_2$O$_3$ addition during pyrolysis**

Figure 5 shows the difference between samples with and without Fe$_2$O$_3$ during pyrolysis. In all samples, the weight of char for the samples with the catalyst at 800°C was higher than for the samples without Fe$_2$O$_3$. However, a difference in reaction temperature was noted between the samples such that for Fe$_2$O$_3$-AD and AD, the change began at 480°C. The change began at approximately 250°C for Fe$_2$O$_3$-(SG+AD) and (SG+AD). Therefore, in Fe$_2$O$_3$-(SG+AD), the Fe catalyst reacted at a relatively low temperature. A similar result was reported in Zhang et al.’s study [18], in this case, iron catalyst was considered to be coordinated to a range of oxygen-containing ligands in coal or biomass, including O$_2^-$, OH$,^-$, and COO$,^-$, which

|                | H$_2$ (mmol/g-char) | CO$_2$ (mmol/g-char) | CO (mmol/g-char) | H$_2$/CO |
|----------------|---------------------|----------------------|----------------|-----------|
| SG+AD          | 100                 | 44                   | 14             | 7.1       |
| Fe$_2$O$_3$-(SG+AD) | 152                 | 71                   | 11             | 13.8      |

Table 3. Amount of H$_2$, CO$_2$, CO, and ratio of H$_2$/CO for (SG+AD) and Fe$_2$O$_3$-(SG+AD) during 60 min gasification.
were generally associated with tar precursors. In our study, SG produced a large amount of tar during pyrolysis, this may be an important reason why the difference appeared after SG added.

Figure 6 shows TG and DTG as a comparison of experimental and calculated values for iron-loaded samples. Fe₂O₃-(SG+AD)cal, which is the calculated value, was utilized for comparison to Fe₂O₃-(SG+AD). The weight loss for Fe₂O₃-(SG+AD) and Fe₂O₃-(SG+AD)cal occurred between 300°C and 430°C. At this temperature range, the coal and biomass cracked into small fragments. Comparing Fe₂O₃-(SG+AD) with Fe₂O₃-(SG+AD)cal, the primary mass loss for Fe₂O₃-(SG+AD)cal was larger than for Fe₂O₃-(SG+AD)cal during the pyrolysis shown in Figure 6(B) indicating that cracking of Fe₂O₃-AD was promoted. Above 430°C, a condensation reaction was the primary reaction. W Fe₂O₃-(SG+AD) was gradually lower than W Fe₂O₃-(SG+AD)cal as shown in Figure 6(A), indicating that the condensation reaction for Fe₂O₃-AD was suppressed.

Figure 7 shows the XRD patterns of a Fe₂O₃-loaded sample during pyrolysis. From the TG in Figure 6(B) it can be concluded that the cracking reaction was essentially complete at approximately 500°C. Fe catalyst remained as Fe₃O₄ and Fe₂O₃ in Fe₂O₃-(SG+AD); and
Fe$_2$O$_3$ in Fe$_2$O$_3$-AD. Above 800°C the Fe catalyst was reduced to FeO and α-Fe in Fe$_2$O$_3$-(SG+AD); and FeO in Fe$_2$O$_3$-AD. At 800°C for 10 min, the Fe catalyst remained as α-Fe and Fe-C(Austenite) in Fe$_2$O$_3$-AD and Fe$_2$O$_3$-(SG+AD).

In the cracking stage (<500°C), the release of tar significantly contributed to the sample weight loss. Tar may have been produced by the release of the small fragments in the coal or biomass with hydrogen radicals. Fe$_2$O$_3$ could react with hydrogen radicals as below.

$$3\text{Fe}_2\text{O}_3 + 2\text{H} \cdot \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$$

This is probably the reason why Fe$_2$O$_3$ in Fe$_2$O$_3$-(SG+AD) could be reduced at this temperature range. SG released active H not only reducing Fe$_2$O$_3$ to FeO, but also reacting with AD coal and promoting AD coal cracking (Fig. 6A). For the Fe$_2$O$_3$-AD sample, the weight of char only changed slightly as shown in Figure 6(A) and Fe$_2$O$_3$ was not reduced (Fig. 7A) indicating that the effect of Fe catalyst was minor at this stage. This may be because AD coal lacks volatile matters (most of H, O, and volatile carbon) while SG maintains a large amount of volatile matters. As the temperature increased above 500°C, the intermediate products (−COOFe and −COFe) continued to participate in the condensation and deoxidize reactions, forming new fixed carbon and increasing char weight. Then, Fe-O bonds disintegrated and resulted in the reduction of Fe catalyst. Thus, the iron catalyst remained as a reduced state of iron at last.

**Change during gasification**

Figure 8 shows that the Fe catalyst changed from a reduced state (α-Fe) to Fe$_3$O$_4$ (oxidation state) for Fe-loaded samples. This directly corresponded to the change Yu et al. [19] reported.

In the case of gasification without catalyst,

$$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$$

In the case of steam gasification by steam with Fe catalyst,

$$\text{Fe} + \text{H}_2\text{O} \rightarrow \text{Fe(O)} + \text{H}_2$$

$$\text{Fe(O)} + \text{C} \rightarrow \text{C(O)} + \text{Fe}$$

In the case of steam gasification with Fe$_n$O$_m$,

$$\text{Fe}_n\text{O}_m + \text{H}_2\text{O} \rightarrow \text{Fe}_n\text{O}_m(\text{O}) + \text{H}_2$$

$$\text{Fe}_n\text{O}_m(\text{O}) + \text{C} \rightarrow \text{C(O)} + \text{Fe}_n\text{O}_m$$

$$\text{C(O)} \rightarrow \text{CO}$$

Therefore, the Fe catalyst may have acted as an oxygen transfer agent in steam gasification as described by Yu et al. [19]. However, there was a difference between iron formed during gasification for different iron-loaded samples with a significant difference for the iron catalyst effect (Carbon conversion for Fe$_2$O$_3$-AD was 5% at 5 min and 38% at 30 min; Carbon conversion for Fe$_2$O$_3$-(SG+AD) was 6% at 5 min and 70% at 30 min). SG addition changed the effect of Fe catalyst. This indicated that when the Fe catalyst reacted with H$_2$O into Fe(O), the Fe(O) successfully transferred oxygen to carbon. This may have resulted from the change between the Fe catalyst and char during pyrolysis.

![Figure 7. XRD patterns of Fe$_2$O$_3$-loaded sample during pyrolysis. (A) Fe$_2$O$_3$-AD, (B) Fe$_2$O$_3$-(SG+AD).](image-url)
Figure 9 displays reactions in pyrolysis and gasification. As described above, in the noncatalyst case, SG initially cracked into small fragments and H⁺ and then formed tar and uncracked SG fragments. AD cracked into uncracked AD fragments; then the uncracked SG fragments and uncracked AD fragments formed a condensate of char. For gasification, char reacted with H₂O producing CO and H₂. With the addition of Fe₂O₃, the Fe catalyst attached to a range of oxygen-containing ligands, including O²⁻, OH⁻, COO⁻, and formed new fixed carbon at a low temperature. Additionally, H⁺ from SG cracking reacted with uncracked AD fragments, promoting AD cracking. Subsequently, uncracked AD fragments, uncracked SG fragments, and newly formed fixed carbon formed a condensate of Fe-char, which supported contacting the Fe catalyst with carbon. For gasification, the Fe catalyst reacted with H₂O initially, keeping the oxygen from the H₂O and forming Fe(O). The Fe(O) transferred the oxygen into carbon in the char, making gasification process easier for the catalyst samples.

With the SG and Fe catalyst, AD pyrolysis was changed, formed active carbon, and increased the reactivity of char. This is considered as an important reason for the increased synergy.

**Conclusion**

This study conducted steam gasification of Indonesian Adaro coal (AD) and Japanese cedar (SG) at a ratio of 1:1 with the physical addition of a weight ratio of 10%
Fe$_2$O$_3$ in a volume ratio of 50% H$_2$O at 800°C for 1 h. The conclusions are as follows:
1. The H$_2$ evolution for co-gasification without a Fe catalyst was 100 mmol/g-char, whereas H$_2$ evolution for co-gasification increased to 152 mmol/g-char with a catalyst.
2. Without an iron catalyst the specific rate of (SG+AD) remained nearly constant during the gasification process. Subsequent to the addition of Fe$_2$O$_3$ the specific rate of Fe$_2$O$_3$-(SG+AD) increased with increased carbon conversion.
3. With a SG and Fe catalyst, the promotion of AD cracking and the formation of active carbon increased the reactivity of char.

**Conflict of Interest**
None declared.

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