

Catalytic Effects of Biomass-Derived Ash on Loy Yang Brown Coal Gasification

Boodsakorn Kongsomart *, Naokatsu Kannari and Takayuki Takarada

Department of Environmental Engineering Science, Graduate School of Science and Technology,
Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma, 376-8515, Japan

Abstract

In this paper, the catalytic effects of two different biomass-derived ash catalysts, chicken dropping compost ash (CCA) and empty fruit bunch ash (EFBA) on the performance of CO₂ gasification of Loy Yang brown coal (LY) char were studied. The CO₂ gasification was done at temperatures between 650 to 800 °C. It was found that the reaction rate is strongly dependent on the CO₂ gasification temperature and the carbon conversion increases by increasing the CO₂ gasification temperature. By using LY mixed with 10 wt% of EFB ash (EFBA), the maximum char conversion of 1.0 with a high gasification rate was obtained when CO₂ gasification was carried out at 800°C for 30 min. Finally, the EFBA is more efficient in catalytic activity compared to the CC ash (CCA) under the same conditions.

Keywords : Biomass, Brown coal char, CO₂ gasification, Chicken dropping compost, Empty fruit bunch

1 Introduction

In recent years, carbon dioxide (CO₂) is the primary greenhouse gas that is emitted through human activities such as the combustion of fossil fuels from transportation and industrial process. The CO₂ gas in the atmosphere acts like a radiatively active gas, which radiates energy in all directions. Part of this radiation is directed towards the earth surfaces, thus warming it. This process is the fundamental cause of the greenhouse effect, which has an impact on the global climate change [1]. To meet emission limitations of CO₂, the novel technologies that limit the fossil fuel processing is necessary to be developed. Among important technologies, gasification process is found to be promising for dealing with the commercial-scale release of CO₂.

It is well known that the gasification is a series of processes producing synthesis gas such as H₂ and CO from carbonaceous materials. Over the past several years, the concept of polygeneration gasification technology that combines power generation with chemical production from synthesis gases were considered. Therefore, most of the current research works focus on the increasing of gasification process performance. As presented elsewhere, the pressurized CO₂ enriched gasification of coal is considered as competitive to conventional gasification technology [2].

In coal gasification, the first stage starts with a rapid devolatilization, leaving a char mainly composed of carbon. The second stage is the gasification of a nascent char that can be converted to fuel gas [3-5]. The fuel gas can be used instead of synthetic biofuel for feeding gas engines and gas turbines. The most important heterogeneous reaction, which takes

place during the gasification process, is the carbon conversion by reaction mechanism shown in Equation 1.



It was reported that the catalytic gasification technique has more efficiency to improve the reaction rate and the conversion efficiency by using lower reaction temperature compared to conventional gasification techniques [6-9]. Generally, the coal gasification with CO₂ is a high temperature process but low temperature gasification is desired to reduce the total process cost. Therefore, the use of catalysts has been proposed for low temperature gasification to overcome the slow reaction rate of carbon with CO₂. The previous works reported that hydroxide, an oxide of alkaline and alkaline earth metal (AAEM), transition metal salts, and partial transition metals are effective catalysts on coal char gasification. AAEM catalysts are mostly used as effective catalysts [10-14].

For catalytic gasification of low-rank coals, the mineral matters from catalyst such as sodium and calcium occur as cations during the gasification process that associated with the carbonaceous matrix. By heating coals into the temperature range of 400°C or above, the carboxyl groups are destroyed and left the associated cations behind the resulting char that leads to the formation of highly dispersed metals. Those highly dispersed metals composing mineral matter in the carbonaceous matrix can be used as a catalyst to increase the gasification rate.

For the sub-bituminous char, the catalytic effects due to mineral matter content were detected up to 1060 °C. However, the current gasification temperature is too high to meet the

economic point-of-view [15]. Fortunately, the iron-loaded on activated carbon or carbon black has high activity in the CO₂ gasification that yields the rapid gasification. Both steps in the oxidation and reduction of iron species proceeded very fast. However, the key step for the CO₂ gasification is the oxidation step of iron metal in the redox cycle [16].

This paper focuses on the utilizing of Loy Yang brown coal (LY) as natural starting material for CO₂ gasification. The char conversion of LY mixed with two different types of ash was measured to investigate the catalytic effect of the ash. The two ash samples were prepared from chicken dropping compost (CC) and empty fruit bunch (EFB). The effects of various parameters including the type of catalyst and gasification temperature on the char conversion profile of the CO₂ gasification process were investigated.

Table 1 Proximate and ultimate analysis of the Loy Yang brown coal.

Volatile matter	Proximate analysis (wt%, dry basis)			Ultimate analysis (wt%, dry basis)		
	Ash	Fixed carbon	C	H	N	O (diff)
52.36	0.93	46.71	63.79	7.01	0.62	28.58

In this experiment, two types of ash prepared from empty fruit bunch (EFB) from Malaysia and chicken dropping compost (CC) from Japan with the size between 0.5 to 1.0 mm were used as catalysts. The chicken dropping compost ash (CCA) and empty fruit bunch ash (EFBA) were prepared by TGA in O₂ gas with temperature ramping from 500 to 815 °C. After heating up to 815 °C, the temperature was maintained for 30 min, then cooled down to room temperature.

2.2 Catalytic gasification

LY sample was mixed with two different biomass ashes, CCA and EFBA, and two different chemical reagents, K₂CO₃ and CaCO₃. In this experiment, the designations of LY mixed with EFBA, LY mixed with CCA, LY mixed with K₂CO₃ and LY mixed with CaCO₃ are LY1, LY2, LY3, and LY4, respectively.

The coal char was produced by TGA at maximum heat treatment of 650 to 800°C for 30 min. The heating rate was at 100°C/min under pure Ar gas atmosphere. The samples were continuously gasified under a CO₂ gas ambient for 2 hours. The initial char mass of dry ash free (m₀) and the instantaneous of char mass of dry ash free (m_t) were calculated by subtraction the weight of initial char mass (w₀) and the weight of instantaneous char

2 Experimental

2.1 Materials

Loy Yang brown coal (LY) from Australia, which contains low ash content with the size between 0.5 to 1.0 mm, was used as a raw material. The proximate and ultimate analyses of the LY are shown in Table 1. The moisture, volatile matter and ash contents were measured by a thermogravimetric analyzer (TGA 701, Leco Co., Ltd.). The content of C, H, N and O elements were determined using an elemental analyzer (TruSpec CHN, version 100, Leco Co., Ltd). The LY was dried in an oven at 107 °C for 1 hour before mixed with biomass ashes. The moisture content of LY was 18 wt%.

mass (w_t) that obtained from TGA with the weight of ash (w_a). Hence, the char conversion (X_{ch}) can be calculated by using the fraction of weight loss as shown in the Equation 2 given below;

$$X_{ch} = \frac{m_0 - m_t}{m_0} = \frac{(w_0 - w_a) - (w_t - w_a)}{w_0 - w_a} \quad (2)$$

3 Results and Discussion

3.1 Characteristic of biomass ash

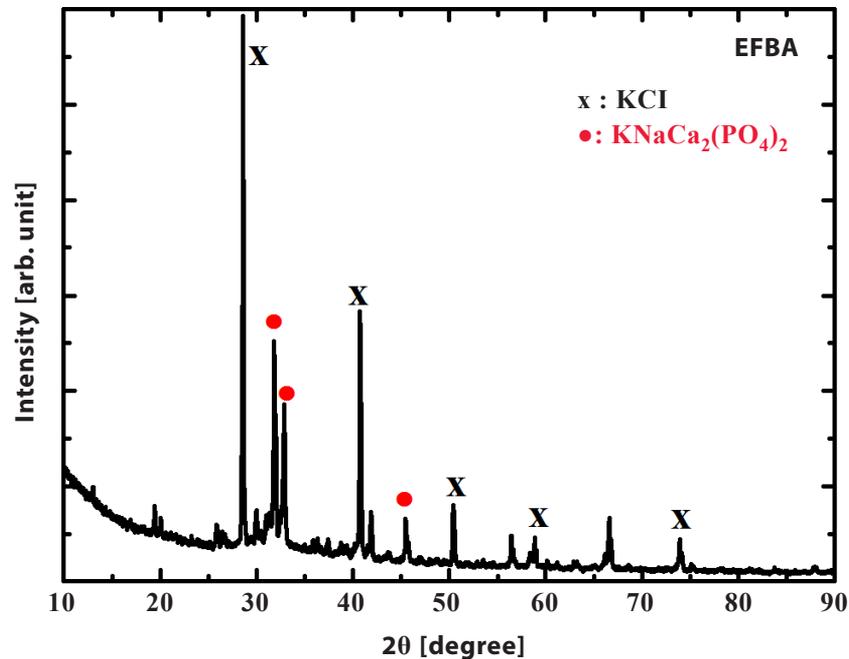
Forest residues and wood wastes represent a large potential resource for long-term renewable energy. In general, EFB and CC are abundant in Malaysia and Japan, respectively. Generation of EFB and CC amounts to 19 and 13 million tons per year, respectively. Fortunately, EFBA and CCA contain low amount of Si component (< 20 wt%) as the information shown in Table 2. EFBA contains high amount of potassium, K (~ 62 wt%) and CCA contains high amount of calcium, Ca (~ 83 wt%). Therefore, EFBA and CCA are very interesting catalysts for catalytic gasification.

Table 2 Elements of biomass ash

Biomass ash	Elemental composition (wt%, dry basis)						
	K	Si	Ca	P	Fe	S	Cl
EFBA	62.1	15.7	7.5	–	1.4	1.3	10.9
CCA	10.0	0.7	83.3	2.4	1.5	0.6	-

After ash preparation, the biomass ash was characterized by X-ray diffraction (XRD) method. For EFBA, the potassium was observed in the form of potassium chloride (KCl) and potassium sodium calcium phosphate ($\text{KNaCa}_2(\text{PO}_4)_2$) as shown in Figure 1. On the other hand, the calcium in CCA was observed in the form of calcium hydroxide ($\text{Ca}(\text{OH})_2$), calcium silicate hydrate ($\text{CaSiO}_3\text{H}_2\text{O}$) and Calcic ferrite (CaFe_4O_7) as shown in Figure 2. The presence of metal complex compounds after ash preparation in Figures 1 and 2 might be explained by the following mechanism. During the preparation of CCA by combustion under O_2 atmosphere at 815°C for 30 min, many complex chemical reactions occurred. Therefore, the

exact mechanism of the compounds formation cannot be explained. However, the results in Table 2 show that the main components of CCA include various metal elements such as K, Si, Ca, P, Fe and S. These elements in CCA, especially Ca (83.3 wt%), K (10 wt%) and Fe (1.5 wt%), reacted with oxygen during the combustion process and formed complex compounds such as calcium hydroxide ($\text{Ca}(\text{OH})_2$), calcium silicate hydrate ($\text{CaSiO}_3\text{H}_2\text{O}$) and Calcic ferrite (CaFe_4O_7) as the XRD patterns shown in Figure 2. The presence of potassium sodium calcium phosphate ($\text{KNaCa}_2(\text{PO}_4)_2$) from EFBA also might be explained by the similar mechanism.

**Figure 1** XRD patterns of EFBA

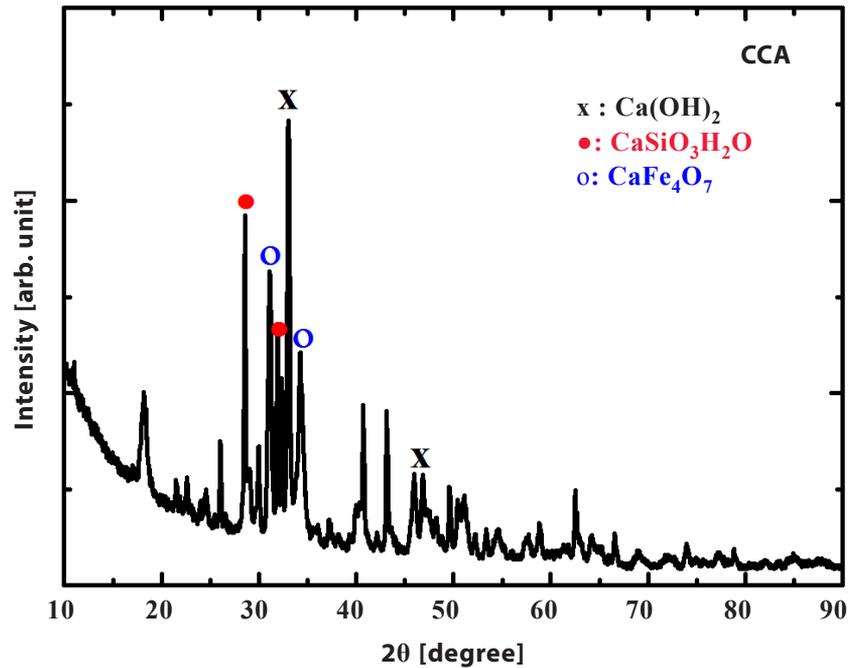


Figure 2 XRD patterns of CCA

3.2 Effect of gasification temperature on LY char conversion

The gasification temperature is one of the most important parameters to control the gasification rate and conversion

[17-20]. In this experiment, the gasification temperature was varied at 650, 700, 750 and 800°C. The CO₂ gasification profiles of LY char are shown in Figure 3. It was found that when the gasification temperature increased from 650 to 800°C, the char conversion at 120 min gradually increased from 0.1 to 0.4.

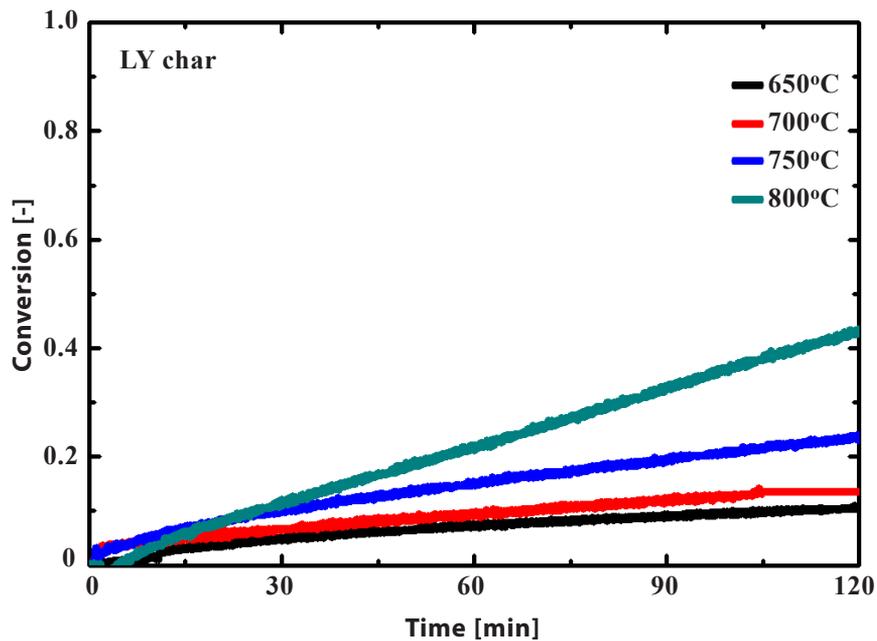


Figure 3 CO₂ gasification profiles of LY char

3.3 Effect of biomass ash content

The results in Figure 4 show that when the EFBA content of LY1 char in catalytic gasification increased from 2 to 10 wt%, the char conversion increased due to the catalytic effect of potassium. This trend may be attributed to increase the interaction between the active metal and char surface with an increasing EFBA content. The catalytic effect of potassium for EFBA-catalyzed CO₂ gasification of LY char can be explained by the redox mechanism. Under gasification conditions, the

oxidation and the reduction occur concurrently. The catalytic reduction involves a series of reaction in the catalyst. During gasification process, the completely reduced group is readily decomposed to free potassium, sodium and calcium metals, which are easily vaporized at the gasification temperatures. After the reduction process was completed, the catalyst was oxidized by CO₂ and the gasification process was initialized. The active metal ions are connected to the carboxylic and phenolic groups to form active sites on coal surface to perform the catalytic activity [21-23].

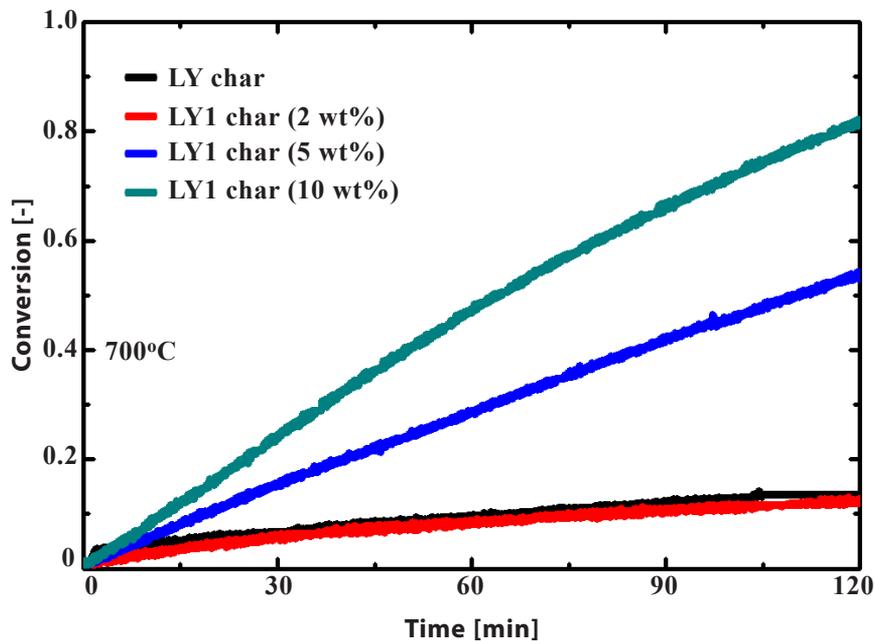


Figure 4 CO₂ gasification profiles of LY1 char at different EFBA contents of 2 to 10 wt%

3.4 Effect of biomass-derived ash type

The catalytic CO₂ gasification profiles of LY1 char (10 wt% of EFBA) and LY2 (10 wt% of CCA) char at various gasification temperatures are shown in Figures 5 and 6, respectively. It was found that the catalytic gasification rate and conversion are dependent on the type of biomass-derived ash added to char as a catalyst. The conversion of both LY1 char and LY2 char reached 100% when the gasification temperature was 800 °C. This means that the catalytic activity is strongly dependent on the reaction temperature and a high gasification temperature is required to obtain a high conversion rate.

The results in Figure 3 show that the char conversion of pure LY was very low. However, the char conversion of LY1 (10 wt% of EFBA) linearly increased at the beginning stage and then asymptotically decreased towards the end of the reaction as shown in Figure 5. When the gasification temperature is higher than 700°C, the char conversion reached the maximum value (1.0). Increasing the gasification temperature from 750 to 800 °C can decrease the duration time to reach the maximum conversion from 60 to 30 min. It was confirmed that the reaction rate is strongly dependent on the gasification temperature.

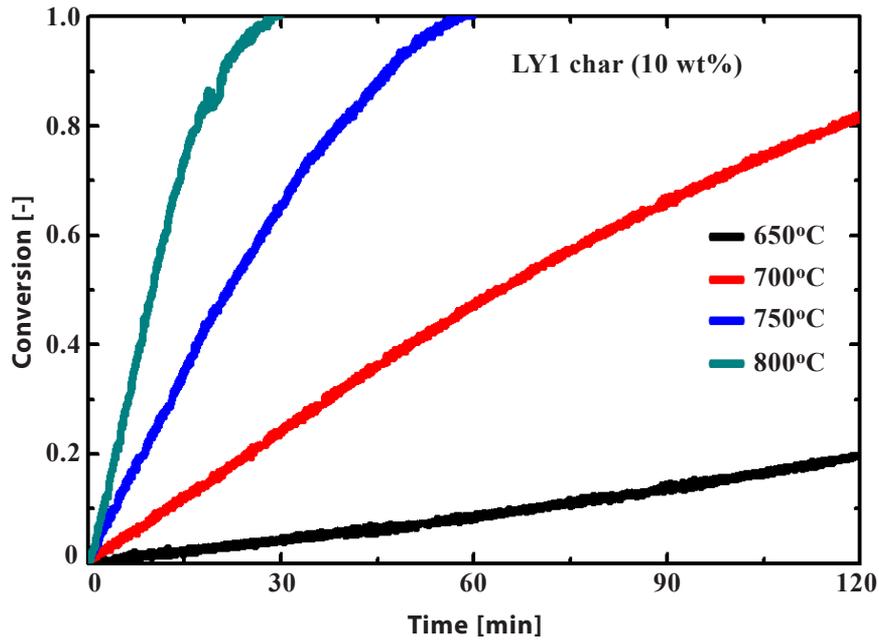


Figure 5 CO₂ gasification profiles of LY1 char (10 wt% of EFBA)

The results in Fig. 6 show the conversion of LY2 char (10 wt% of CCA). The char conversion of LY2 increased twice compared to that of pure LY at gasification temperatures between 650 to 700°C. When the reaction temperature is higher than 750°C, the char conversion reached the maximum value (1.0). The

increasing of char conversion of LY2 (10 wt% of CCA) with temperature might be related to the formation of a crystalline layer of Ca on char surface and the adsorption of CO₂ by Ca(OH)₂ before the CO₂ gasification occurs.

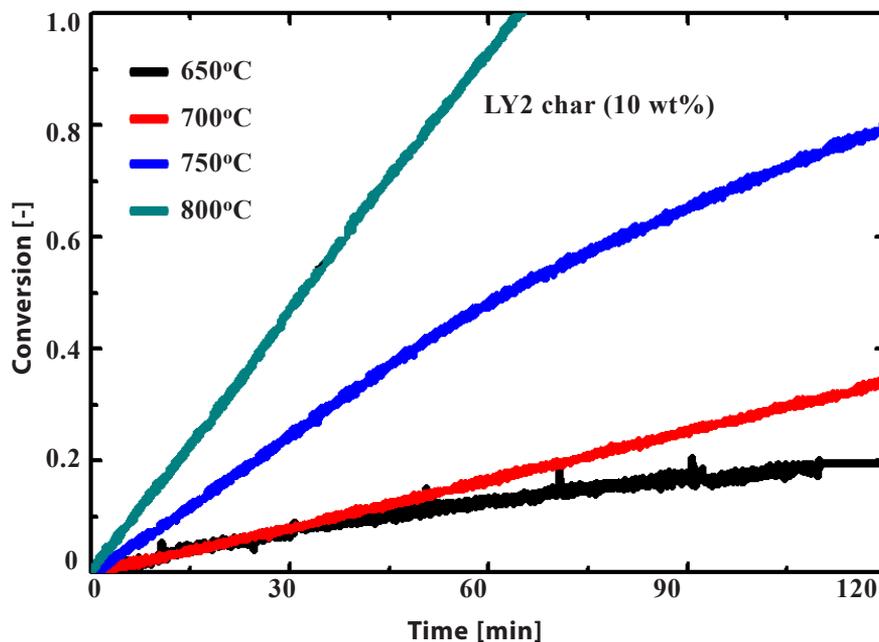


Figure 6 CO₂ gasification profiles of LY2 char (10 wt% of CCA)

The results in Figs. 7 and 8 show then XRD patterns of LY1 char (10 wt% of EFBA) and LY2 char (10 wt% of CCA), respectively. It was found that after the gasification process, the components

of raw materials remained by comparing these results with the results shown in Figures 1 and 2, respectively.

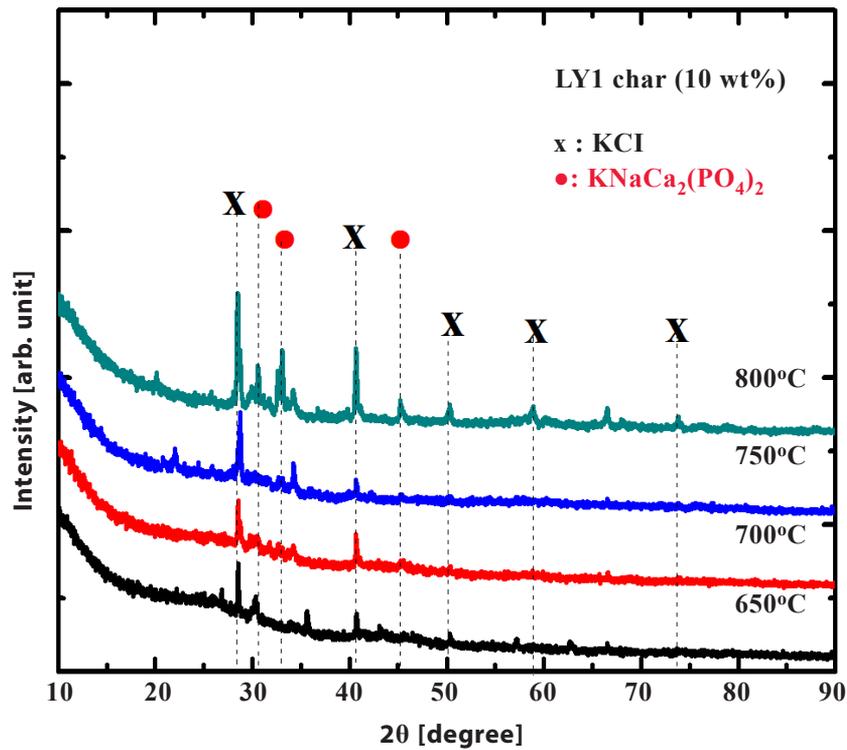


Figure 7 XRD patterns of LY1 char (10 wt% of EFBA) after CO_2 gasification

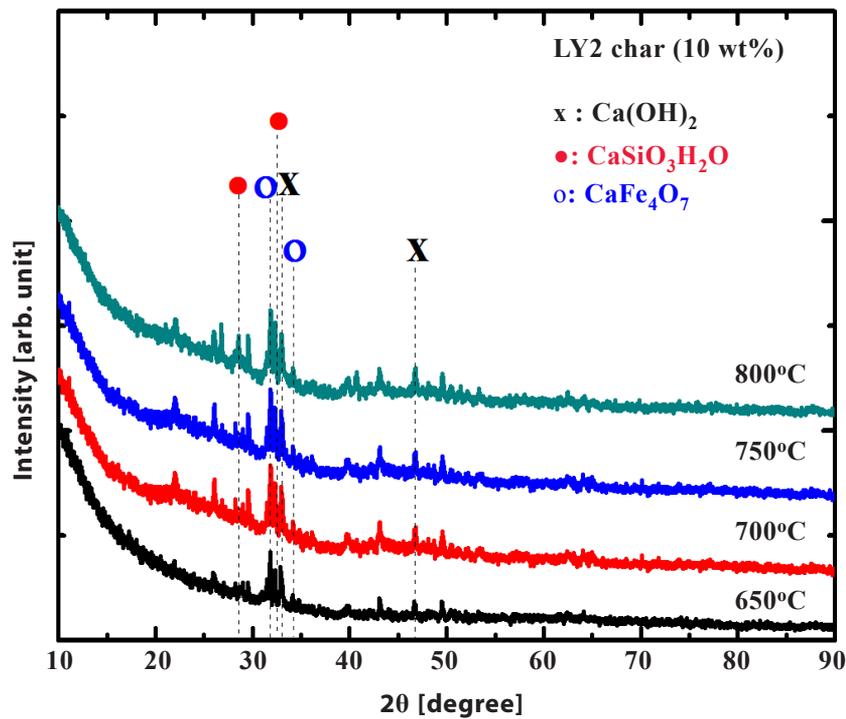


Figure 8 XRD patterns of LY2 char (10 wt% of CCA) after CO_2 gasification

The result in Figure 9 shows the effect of gasification temperature on the char conversion of LY without ash, LY1 (10 wt% of EFBA) and LY2 (10 wt% of CCA). It was found that the char conversion rate of LY without mixing ash (LY char) is lower than that of the LY mixed with ashes. This means that

when LY is mixed with the ashes, the efficiency of conversion increased. The conversion rate increased when the gasification temperature increased. Moreover, LY1 char (10 wt% of EFBA) has higher reactivity than LY2 char (10 wt% of CCA).

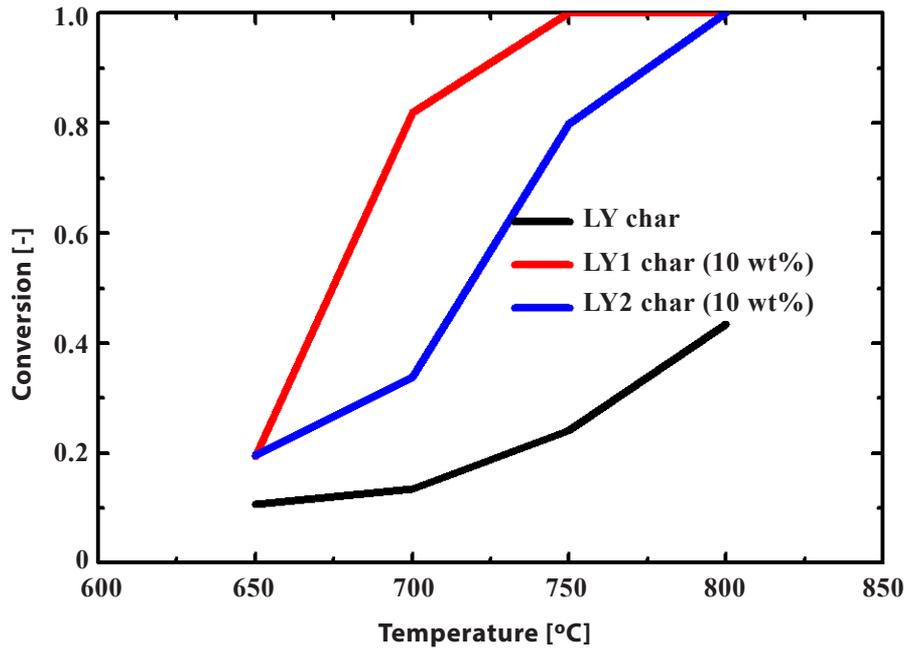


Figure 9 Effect of gasification temperature on the conversion of LY char with and without mixing with 10 wt% of EFBA and 10 wt% of CCA

3.5 Comparison of chemical reagent with ash

The results in Figures 10 and 11 show the comparison of char conversion with biomass ashes and chemical reagents at 700 °C. Figure 10 shows the LY1 char (10 wt% of EFBA) is more effective in char conversion compared to the LY3 char (10 wt% of K_2CO_3)

when the gasification time is longer than 30 min. However, the char conversion of LY3 char (10 wt% of K_2CO_3) is slightly higher than LY1 char (10 wt% of EFBA) when the gasification time is shorter than 30 min. On the contrary, the conversion of LY4 char (10 wt% of $CaCO_3$) is similar to LY2 char (10 wt% of CCA) as shown in Figure 11.

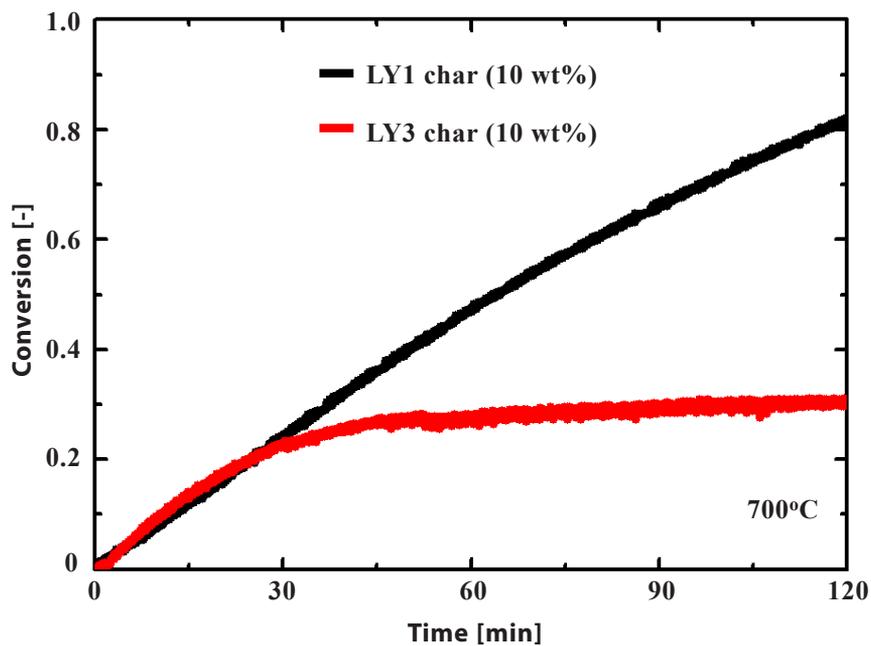


Figure 10 Comparison of conversion of LY1 char (10 wt% of EFBA) and LY3 char (10 wt% of K_2CO_3) at 700 °C.

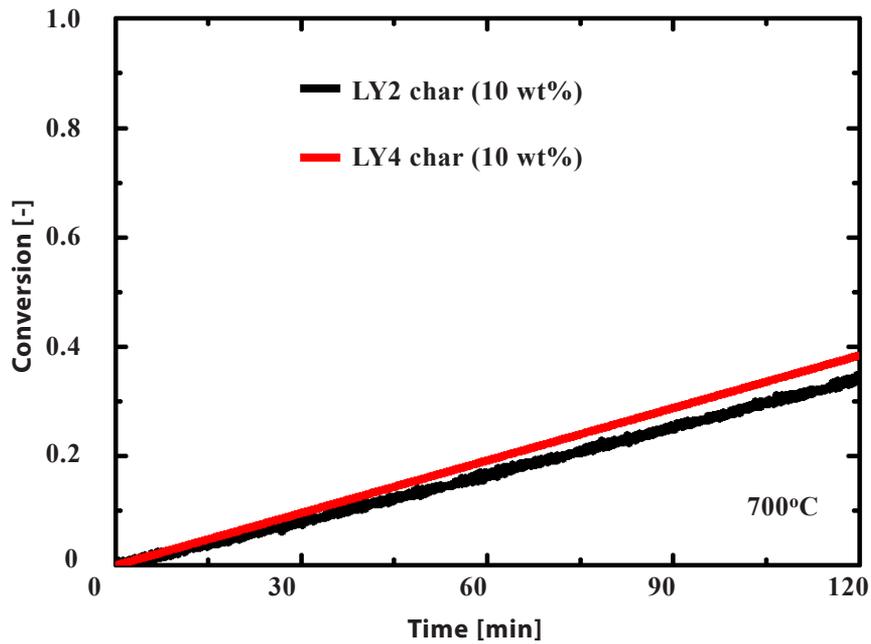


Figure 11 Comparison of conversion of LY2 char (10 wt% of CCA) and LY4 char (10 wt% of CaCO_3) at 700 °C

The high efficiency of EFBA can be explained by using XRD patterns shown in Fig. 12. The reason may be attributed that EFBA might be able to generate more effective atom (K, Na, Ca) than K_2CO_3 chemical reagent. Therefore, the char conversion is

higher than K_2CO_3 chemical reagent. In the case of CCA, the Ca atom in CaCO_3 chemical reagent can absorb CO_2 similar with $\text{Ca}(\text{OH})_2$. Therefore, carbon conversion of chemical reagent is similar to ash as the XRD patterns shown in Figure 13.

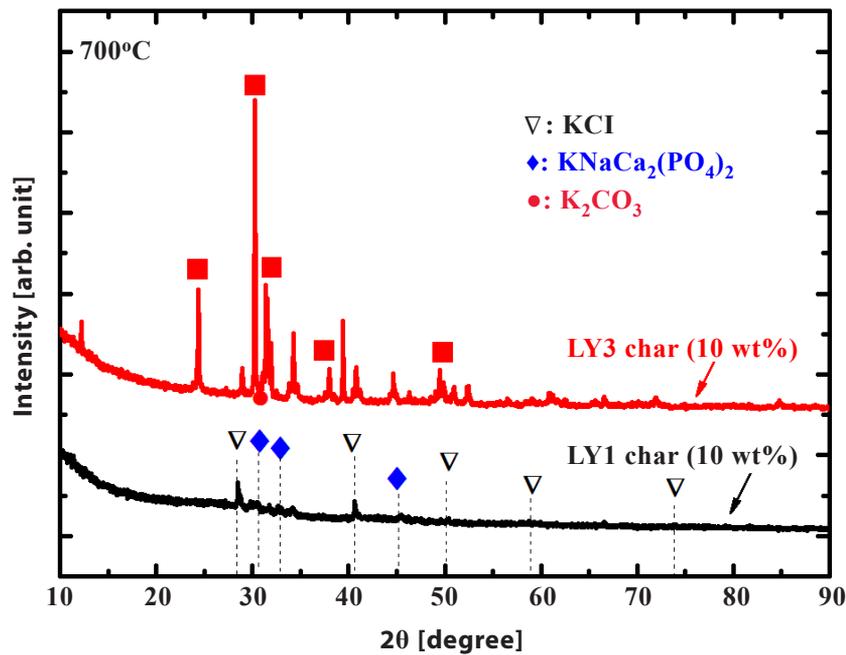


Figure 12 XRD patterns of LY1 char (10 wt% of EFBA) and LY3 char (10 wt% of K_2CO_3) after gasification at 700 °C

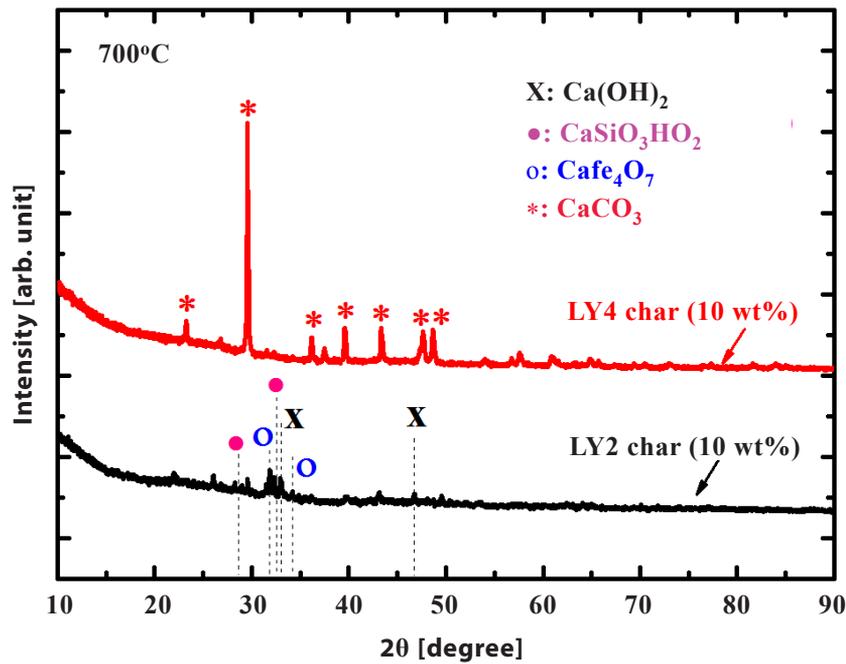


Figure 13 XRD patterns of LY2 char (10 wt% of CCA) and LY4 char (10 wt% of CaCO_3) after gasification at 700 °C

4 Conclusion

The effects of two different biomass-derived ash catalysts, chicken dropping compost ash (CCA) and empty fruit bunch ash (EFBA), on the performance of the CO_2 gasification of Loy Yang brown coal (LY) were investigated. By mixing LY with CCA and EFBA, the CO_2 gasification rate and conversion of the LY increased. It was shown that the catalytic activity starts to become prominent at the temperature of 650°C. Furthermore, the EFBA is more efficient in increasing the catalytic activity compared to the CCA under the same conditions.

5 Acknowledgements

This work was supported by JST-MOST project, Japan.

References

- [1] C. Higman, M. J. Van der Burgt, *Gasification*, 2nd Edition, New York: Elsevier, 2008.
- [2] C. Y. Wen, E. S. Lee, *Coal conversion technology. Advance book program reading*, Massachusetts: Addison-Wesley Publishing Company, 1979.
- [3] M. Tomaszewicz, G. Labojko, G. Tomaszewicz, K.M. Michalina, "The kinetics of CO_2 gasification of coal chars" in *J. Thermo. Anal. Calorim*, 113,1327-1335, 2013.
- [4] Y. Zhang, M. Ashizawa, S. Kajitani, S. Hara, "A New approach to catalytic coal gasification: The recovery and reuse of calcium using biomass derived crude vinegars" in *Fuel*, 89, pp. 417-422, 2010.
- [5] A. Gomez, N. Mahinpey, "Kinetic study of coal steam and CO_2 gasification: A new method to reduce interparticle diffusion", in *Fuel*, 2015, 148,160-167.
- [6] L. Ding, Z. Zhou, Q. Guo, W. Huo, G. Yu, "Catalytic effects of Na_2CO_3 additive on coal pyrolysis and gasification", *Fuel*, 142, 134-144, 2015.
- [7] L. Meng, M. Wang, H. Yang, H. Ying, L. Chang, "Catalytic effect of alkali carbonates on CO_2 gasification of Pingshuo coal", in *Mining Sci. and Tech. (China)*, 21, 587-590, 2011.
- [8] M. Q. Jiang, R. Zhou, J. Hu, F. C. Wang, J. Wang, "Calcium-promoted catalytic activity of potassium carbonate for steam gasification of coal char: Influences of calcium species", in *Fuel*, 99, pp 64-71, 2012.
- [9] P. Lahigani, Z. A. Zainal, A. R. Mohamed, "Catalytic effect of iron species on CO_2 gasification reactivity of oil palm shell char", in *Thermochim. Acta*, 546, pp. 24-31, 2012.
- [10] J. Hu, L. Liu, M. Cui, J. Wang, "Calcium-promoted catalytic activity of potassium carbonate for gasification of coal char: The synergistic effect unrelated to mineral matter in coal", in *Fuel*, 111, pp.628-635, 2013.
- [11] X. Xiao, J. Cao, X. Meng, D. D. Le, L. Li, Y. Ogawa, K. Sato, T. Takarada, "Synthesis gas production from catalytic gasification of waste biomass using nickel-loaded brown coal char", in *Fuel*, 103, 135-140, 2013.

- [12] Y. K. Kim, L. F. Hao, J. I. Park, J. Miyawaki, I. Mochida, S. H. Yoon, "Catalytic activity and activation mechanism of potassium carbonate supported on perovskite oxide for coal char combustion", in *Fuel*, , 94, pp.516-522, 2012.
- [13] K. Mitsuoka, S. Hayashi, H. Amano, K. Kayahara, E. Sasaoaka, M. A. Uddin, "Gasification of woody biomass char with CO₂: The catalytic effects of K and Ca species on char gasification reactivity", in *Fuel Process. Technol.*, 92, pp. 26-31, 2011.
- [14] P. Lahijani, Z. A. Zainal, A. R. Mohamed, M. Mohammadi, "CO₂ gasification reactivity of biomass char: Catalytic influence of alkali, alkaline earth and transition metal salts", in *Bioresour. Technol*, 144, pp. 288-295, 2013.
- [15] J. Ochoa1, M. C. Cassanello, Bonelli P. R., Cukierman A. L., "CO₂ gasification of Argentinean coal chars: a kinetic characterization". *Fuel Process Technol*, 74, pp. 161-176, 2001.
- [16] H. Ohme, T. Suzuki, "Mechanisms of CO₂ gasification of carbon catalyzed with group VIII metals. 1. Iron-catalyzed CO₂ gasification" in *Energy Fuels*, 10, pp. 980-987, 1996.
- [17] G. R. Jaffri, J. Y. Zhang, "Catalytic gasification of Fujian anthracite in CO₂ with black liquor by thermogravimetry", in *J. Fuel Chem. and Technol*, 35(2), pp. 129-135, 2007.
- [18] G. Aranda, A. J. Grootjes, C. M. Van der Meijden, A. Van der Drift, D. F. Gupta, R. R. Sonde, S. Poojari, C. B. Mitra, "Conversion of high-ash coal under steam and CO₂ gasification conditions" in *Fuel Proc. Technol*, 141, pp. 16-30, 2016.
- [19] Y. K. Kim, J. I. Park, D. W. Jung, J. Miyawaki, S. H. Yoon, I. Mochida, "Low-temperature catalytic conversion of linite: 1. Steam gasification using potassium carbonate supported on perovskite oxide", in *J. Ind. and Eng. Chem*, 20, pp. 216-221, 2014
- [20] G. R. Jaffri and J. Y. Zhang, "Catalytic activity of the black liquor and calcium mixture in CO₂ gasification of Fujian anthracite", in *Chin. J. Chem. Eng.*, 15(5), pp. 670-679, 2007.
- [21] D. A. Sams and F. Shadman. "Mechanism of potassium-catalyzed carbon/CO₂ reaction" in *AIChE J.*, 32(7), 1132-1137, 1986.
- [22] M. Perander, N. Demartini, A. Brink, J. Kramb, O. Karlstrom, J. Hemming, A. Moilanen, J. Konttinen, M. Hupa, "Catalytic effect of Ca and K on CO₂ gasification of spruce wood char", in *Fuel*, 150, pp. 464-472, 2015.
- [23] D. Sams, F. Shadman, "Catalytic effect of potassium on the rate of char-CO₂ gasification" in *Fuel*, 62, pp. 880-882, 1993.