

Catalytic effects of potassium on lignin steam gasification with $\gamma\text{-Al}_2\text{O}_3$ as a bed material

Prapan Kuchonthara^{*,†}, Tharapong Vitidsant^{*}, and Atsushi Tsutsumi^{**}

^{*}Fuels Research Center, Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Phyathai Road, Patumwan, Bangkok 10330, Thailand

^{**}Collaborative Research Center for Energy Engineering, Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

(Received 4 June 2007 • accepted 2 October 2007)

Abstract—The effects of potassium on the reactivity of biomass-char steam gasification with the presence of a porous material were investigated by using a thermogravimetric reactor with high-heating rates. Lignin was employed as a char-rich biomass model compound. The potassium carbonate (K_2CO_3) was added to lignin and a mixture of lignin and $\gamma\text{-Al}_2\text{O}_3$ porous particles by means of aqueous impregnation. The effects of K_2CO_3 and $\gamma\text{-Al}_2\text{O}_3$ addition on pyrolysis of lignin and steam gasification of lignin-derived char were evaluated in terms of lignin conversion and the gaseous products. Results showed that K_2CO_3 slightly increased the steam gasification rate of lignin-derived char, but it did not influence the conversion in both the pyrolysis and steam gasification steps. In addition, tar was reduced by adding K_2CO_3 because of the increment of carbon conversion to gas product. The presence of $\gamma\text{-Al}_2\text{O}_3$ was found to induce the lower reactivity of resulting char after pyrolysis, reducing the gasification rate and conversion. A significant improvement in gasification conversion was observed with the presence of both K_2CO_3 and $\gamma\text{-Al}_2\text{O}_3$. Especially, almost complete gasification was achieved at a reaction temperature of 1,073 K.

Key words: Biomass, Lignin, Steam Gasification, Catalyst, Potassium

INTRODUCTION

Biomass is known as a CO_2 -neutral energy source and is expected to reduce CO_2 emission if it is utilized instead of fossil fuels. The amount of carbon dioxide emissions in biomass combustion is equivalent to the amount of carbon dioxide absorbed by photosynthesis. Therefore, the use of biomass does not increase the net amount of atmospheric carbon dioxide [1,2]. In the biological and thermochemical conversion technology of biomass, the steam gasification of biomass is promoted as a promising technology for biomass utilization and also for hydrogen production [3-5]. An impediment to using biomass is the large amount of tar produced from biomass in conventional processes, which causes deposition problems in the back-pass. Tar can deposit on surfaces in filters, heat exchangers and engines. As a result, this reduces the component performance and increases maintenance requirements. Since biomass has a low energy density compared to fossil fuels, such as coal and petroleum, a commercial biomass gasification process is required to achieve higher thermal efficiency. Low temperature gasification can reduce thermal loss, leading to higher thermal efficiency. However, this induces a higher yield of tar production. A number of researches have been devoted to developing effective catalysts to enhance the thermal decomposition of tar [6-11]. However, deactivating caused by carbon deposit seems to be the main problem of using catalysts. Recently, a new approach has been proposed to solve the problem of tar by employing porous solids as bed materials. The porous materials are expected to promote the capture of volatile matter as carbon deposits in their pores [12-14].

Alkali and alkaline earth oxides and salts have been revealed as

effective catalysts for the gasification of carbon by CO_2 and H_2O . So far, a number of intensive works have been carried out to investigate the catalytic mechanism of coal/char gasification [15-23]. However, few studies have mentioned the catalytic effects on reactivity of biomass-derived char and on gaseous products. Particularly, the synergetic effect of porous materials and alkali-catalysts has been not explored. Therefore, the purpose of the present work is to investigate the catalytic effects of alkali on the steam gasification of biomass with porous materials. Potassium carbonate (K_2CO_3) was employed as the alkali-catalyst because of its good catalytic effects on both carbon dioxide and steam gasification [24-26]. So far, K_2CO_3 is well known as a good alkali catalyst for the gasification of carbon. It has been suggested that the formation of intercalation compounds between potassium (K) and carbon (graphite) takes place during gasification [15,27]. The formation of a K-C bond may cause a weakening of adjacent C-C bonds in the carbon network with the rupture of aromatic rings leading to the formation of highly reactive aliphatic fragments. Mims and Pabst mentioned that K_2CO_3 reacts with char or carbon to form surface salt complexes such as surface phenoxide groups [17]. They suggested that nucleophilic sites $\text{K}^+-\text{O}-\text{C}$ are formed on the carbon surface by reaction with K_2CO_3 and act as active sites during the gasification reaction. Saber et al. reported that the oxide on the carbon surface is cable of stabilizing potassium on carbon [18]. The $\gamma\text{-Al}_2\text{O}_3$ was used as the porous material. All experiments were carried out in a thermogravimetric reactor with high heating rates.

METHOD AND MATERIALS

The experimental apparatus [28,29] mainly consists of a 25-mm in inner diameter quartz thermobalance reactor, an inner quartz tube of 13-mm in inner diameter, an infrared gold image furnace and a

[†]To whom correspondence should be addressed.

E-mail: prapan.k@chula.ac.th

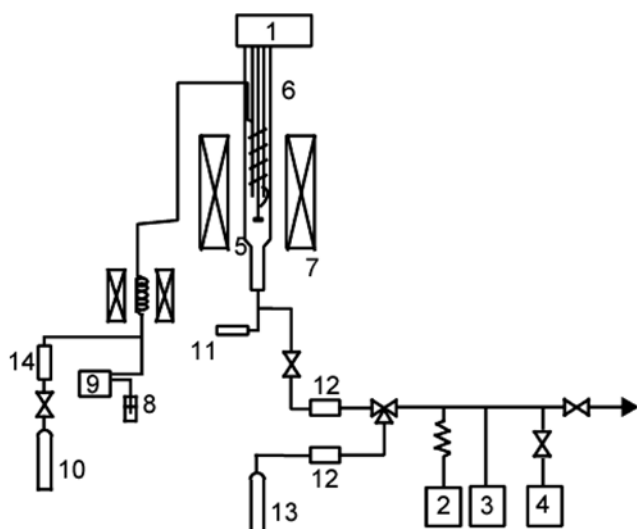


Fig. 1. Experimental apparatus.

- | | |
|--------------------------------|----------------------------|
| 1. Thermobalance | 8. Water |
| 2. Mass spectrometer | 9. Water pump |
| 3. Micro GC | 10. Ar carrier gas |
| 4. Gas bag | 11. Steam trap |
| 5. Sample (Biomass) | 12. CaCl_2 column |
| 6. Quartz glass tube | 13. Sample gas |
| 7. Infrared gold image furnace | 14. Mass flow controller |

balance sensor (Fig. 1). The inner quartz tube was installed to avoid the influence of buoyancy change due to gas convection during heating. An 8-mm-diameter, 10-mm-long ceramic basket was suspended in the thermobalance. Two platinum mesh sheets (150 mesh) were placed at the bottom of the ceramic basket. The temperature was measured by an R-type thermocouple placed near the sample. Steam was fed through a coil above the sample basket.

The γ - Al_2O_3 was supported by Mizusawa Industrial Chemical. Its particle size is in the range from 70 to 200 μm , with a BET surface area of about 205 $\text{m}^2 \text{g}^{-1}$. The K_2CO_3 catalyst was added to the mixture between lignin and γ - Al_2O_3 by aqueous impregnation (wet mixing). The thick slurry obtained upon addition of the lignin and alumina to the catalyst solution was dried at about 350 K for 12 h. The sample without the catalyst was also wetted and dried in the same manner. The ratio of lignin to γ - Al_2O_3 was 1 : 1 by weight. The amount of K_2CO_3 added was 10% by weight of the mixture between lignin and K_2CO_3 .

A sample of 20–40 mg was put into the ceramic basket of the thermogravimetric reactor. Initially, Ar gas of 2.72 $\text{cm}^3 \text{s}^{-1}$, which is equivalent to gas velocity of 0.55 cm s^{-1} at the standard state, was fed into the thermobalance reactor to purge oxygen from the reactor tube. After the oxygen concentration fell below 100 ppm, the reactor was heated at 383 K to dry the sample. After 10 min drying, the temperature was increased and was kept at 473 K for 5 min. Subsequently, the temperature was stepped up to reaction temperatures, i.e., 973 K and 1,073 K, with a heating rate of about 100 K s^{-1} . The temperature and weight loss of the sample during the reaction were recorded on a personal computer at sampling rates of 5 Hz. Pyrolysis was carried out at an early stage. After insignificant change in weight and gas evolution was observed, the steam was introduced into the reactor with carrier gas Ar (50 : 50 vol%) to start

Table 1. Properties of lignin

Elemental composition (wt%, daf basis)	
Carbon	64.5
Hydrogen	5.6
Oxygen	27.0
Sulfur	2.9

the steam gasification. Hence, steam gasification of char produced by the pyrolysis of the sample took place. The gaseous products were analyzed by a quadrupole mass spectrometer (Standom; ULVAC, Inc.) at time intervals of 2 s. Ions of $m/z=2$, 15, 28, and 44 were selected to measure the concentrations of H_2 , CH_4 , CO, and CO_2 , respectively. In conjunction with mass spectrometry, gas compositions were also measured by a TCD micro-gas chromatograph (model M-200H; Hewlett-Packard Co.) to verify the accuracy of the mass spectrometer data. An MS-5A column was used to measure concentrations of H_2 , O_2 , N_2 , CH_4 , and CO with Ar carrier gas. The concentration of CO_2 was measured with a Pora Plot Q column and Ar carrier gas. The sampling time interval of the micro-GC was approximately 90 s. Effluent gas from the reactor was collected in a gas bag to measure the total amount of gaseous product. This gas was analyzed with the micro-gas chromatograph. After the steam gasification, the residue was burnt off by switching Ar carrier gas to air. The refractory char was determined from the weight change through the combustion step. The TGA result was presented in terms of relative mass profiles. The relative mass was calculated based on the total combustible portion in the sample. This portion was defined as the weight change from 473 K to the final step of combustion. Lignin was employed as a char-rich biomass model compound. The elemental composition of lignin is listed in Table 1. The ash of employed lignin consisted mainly of oxides of sodium (37.2%), potassium (7.5%), silicon (3.3%) and aluminum (1.9%), along with small concentrations of magnesium, calcium, iron, phosphorus and titanium (<0.4%).

In the case of lignin/ γ - Al_2O_3 /10 wt% K_2CO_3 , the sample basket was taken out from the thermobalance reactor after the pyrolysis step as well as the steam gasification step. The samples were analyzed to ensure the existence of potassium by using a scanning electron microscope with energy dispersive spectrometer, SEM-EDS, (Hitachi High-Technology Co., S-4200) with a Kevex superdry detector.

RESULTS AND DISCUSSION

1. Effects of K_2CO_3 on the Pyrolysis and Gasification of Lignin

In the present study, the catalytic effect on steam gasification of biomass-derived char was investigated by using lignin as a char-rich biomass model compound. Fig. 2 illustrates the relative mass profiles of lignin in the case of lignin alone and the case of lignin with 10 wt% K_2CO_3 at temperature of 1,073 K. Although K_2CO_3 slightly increased the rate of weight change in the steam gasification step, it was not observed to have a significant influence on the conversion in both the pyrolysis and steam gasification steps. The unreacted carbon after the steam gasification is expected to become coke or refractory carbon, which seems to be less reactive in an oxygen-free atmosphere. As mentioned above, the K_2CO_3 has been re-

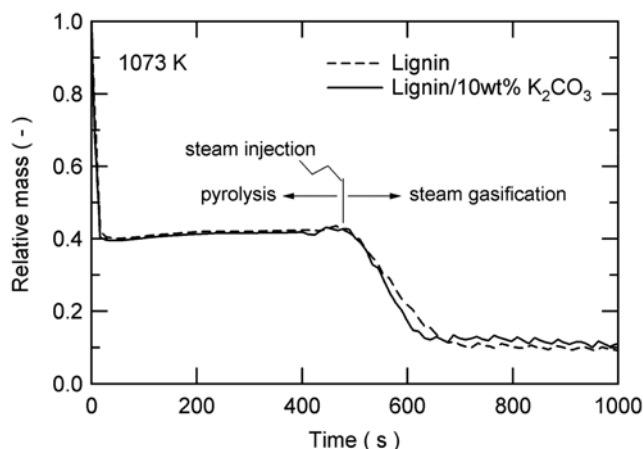


Fig. 2. Effects of K_2CO_3 addition on relative mass profiles of lignin.

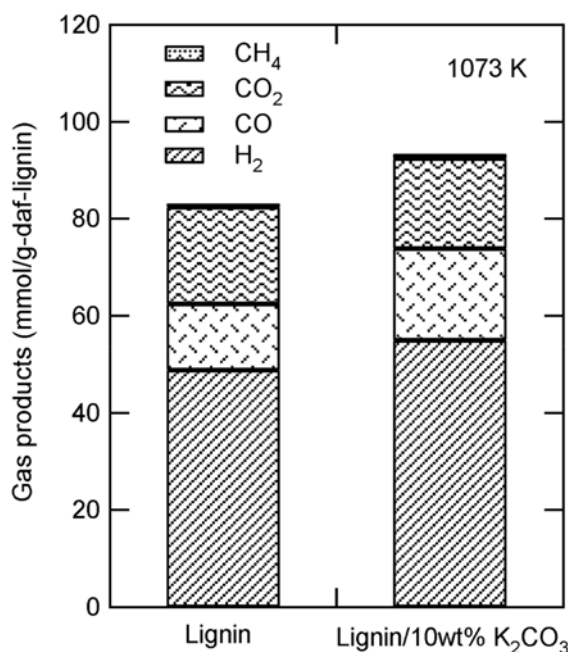


Fig. 3. Effects of K_2CO_3 addition on gaseous products of lignin.

ported about its catalytic effects on carbon gasification. However, it is likely not able to enhance the reactivity of lignin-coke in the steam gasification.

Fig. 3 shows the composition of the produced gas in the cases of lignin and lignin/10 wt% K_2CO_3 . In the case of lignin/10 wt% K_2CO_3 , the amount of H_2 and CO was observed to increase. The hydrocarbon gas, i.e., CH_4 , was observed in small amount, indicating effective reforming reactions. The gas evolution rate profiles of H_2 and CO_2 for both cases are depicted in Fig. 4. The first and second peaks denote the gas evolved in the pyrolysis step and in the steam gasification step, respectively. Note that area of each peak represents the amount of gas released in each step. As can be seen, the lignin/10 wt% K_2CO_3 gave a larger amount of gas product, especially H_2 and CO. The product gas after pyrolysis was estimated by integrating the profile of gas evolution rate. Table 2 summarizes results of gas product after each step and carbon conversion. Com-

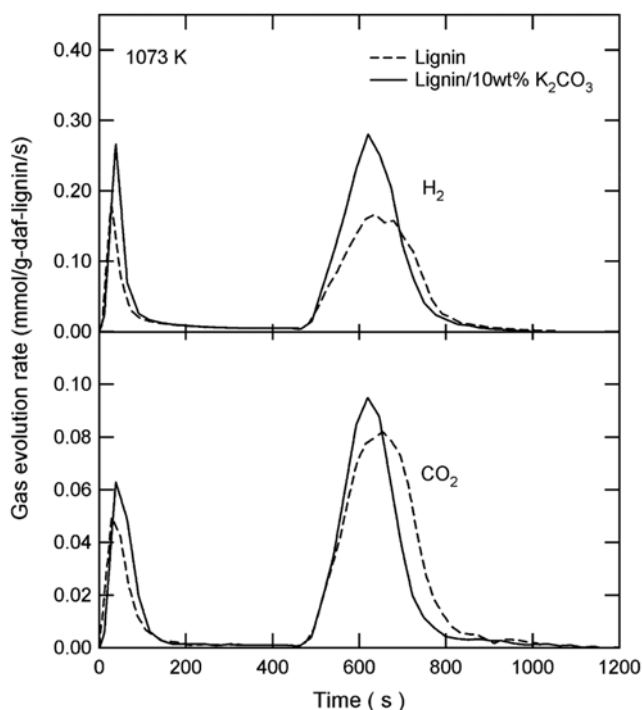


Fig. 4. Effects of K_2CO_3 addition on H_2 and CO_2 evolution rate profiles of lignin.

paring lignin and lignin/10 wt% K_2CO_3 at 1,073 K, the carbon conversion was increased with the presence of K_2CO_3 . Owing to the absence of change in solid conversion as shown in Fig. 2, the increase in carbon conversion to gas is considered to stem from the reduction of tar. The higher amount of gas product at 973 K likely resulted from the water-gas shift reaction, which is slightly exothermic and favors low temperatures.

Elliott and Baker reported that alkali catalysts can reduce tar product by means of either stopping tar formation initially or by catalyzing tar decomposition [30]. Hence, the increase in gas product in the pyrolysis step is due to the catalytic effect of K_2CO_3 on tar decomposition. In addition, K_2CO_3 was found to promote H_2 production during the steam gasification. Therefore, it can be concluded that K_2CO_3 performs as a catalyst for steam gasification of the biomass-derived char and tar decomposition.

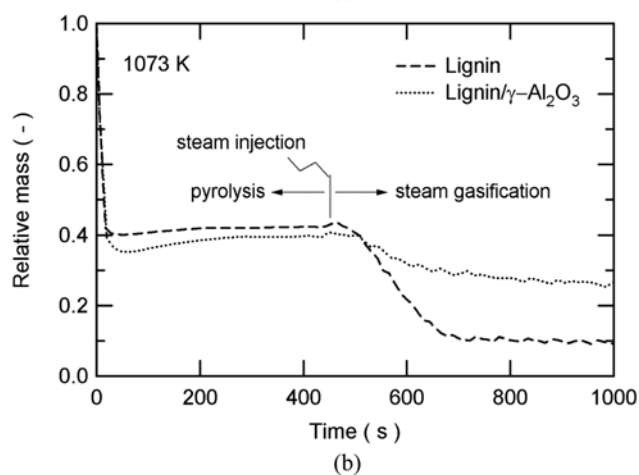
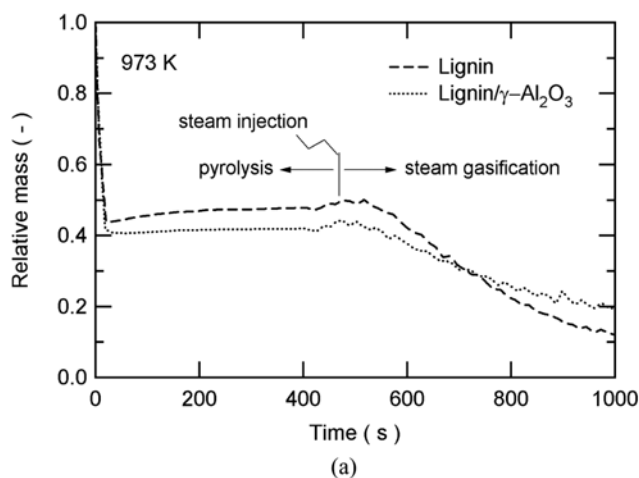
2. Effects of $\gamma-Al_2O_3$ on the Pyrolysis and Gasification of Lignin

Fig. 5 shows a comparison of the relative mass profile between lignin and lignin/ $\gamma-Al_2O_3$ for temperatures of 973 K and 1,073 K. Fig. 6 presents the effect of $\gamma-Al_2O_3$ on the total amount of gas product. The evolution rate profiles of H_2 and CO_2 are depicted in Fig. 7. In the pyrolysis step, lignin/ $\gamma-Al_2O_3$ gave a lower relative mass while the carbon conversion to gas product was decreased, as can be seen in Table 2. This means the higher amount of volatile (tar) was liberated. The porous material, $\gamma-Al_2O_3$ was found to have a tendency to stimulate the coking reaction of tar released during pyrolysis and gasification [12,13]. It was proposed that the tar released during the pyrolysis step is captured on $\gamma-Al_2O_3$ particles as coke by means of dehydrogenation. However, the reaction unlikely took place in this study. This is attributable to the diminution of alumina porosity resulting from the mixing procedure. A reason for the drop

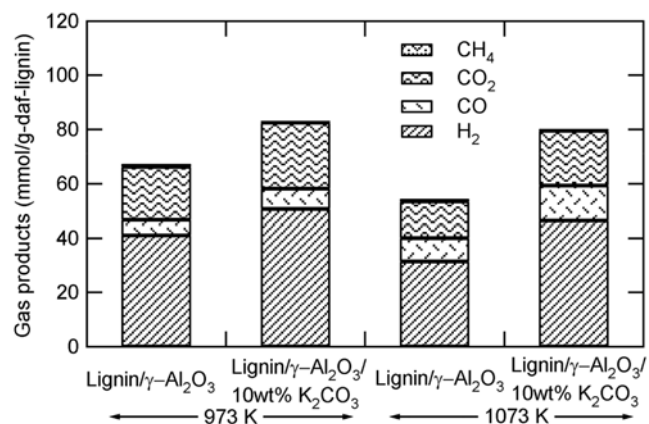
Table 2. Summary of gas product and conversion

	Temperature (K)	*	Gas evolution (mmol/g-daf-lignin)				Carbon conversion (-)
			H ₂	CH ₄	CO	CO ₂	
Lignin	973	PY	9.86	1.18	6.10	3.11	0.193
		GS	73.21	1.18	7.56	32.25	0.763
	1,073	PY	9.60	0.83	7.79	3.25	0.221
		GS	48.75	0.83	13.64	19.91	0.640
Lignin/ γ -Al ₂ O ₃	973	PY	7.68	1.05	4.63	3.46	0.170
		GS	41.00	1.05	5.59	19.56	0.487
	1,073	PY	9.67	1.11	5.86	3.74	0.199
		GS	31.46	1.11	8.54	13.28	0.427
Lignin/ γ -Al ₂ O ₃ /10 wt%K ₂ CO ₃	973	PY	7.03	0.81	5.70	3.42	0.185
		GS	50.56	0.81	7.58	24.24	0.607
	1,073	PY	8.61	0.78	7.37	3.56	0.218
		GS	46.36	0.78	12.88	20.14	0.629
Lignin/10 wt%K ₂ CO ₃	1,073	PY	11.72	0.97	9.31	4.06	0.267
		GS	54.85	0.97	19.02	18.50	0.716

*PY: After the pyrolysis step. GS: After the gasification step

**Fig. 5. Effects of γ -Al₂O₃ addition on relative mass profiles of lignin at temperatures of (a) 973 K and (b) 1,073 K.**

in relative mass in the case of lignin/ γ -Al₂O₃ would be the suppression of the secondary reaction of tar with carbon in char. In a ther-

**Fig. 6. Effects of γ -Al₂O₃ addition on gaseous products of lignin.**

mal decomposition process, the released tar or volatile can react with the carbon in the char to form a solid product, i.e., coke or refractory carbon [31]. This reaction was expected in the case of lignin alone. On the other hand, in the case of lignin/ γ -Al₂O₃ the lignin was expected to disperse on the alumina particle, reducing the possibility of the reaction between volatiles and lignin-carbon. In addition, the dispersion of lignin would promote the volatilization, leading to the increase in tar. In the gasification step, the gasification rate declined especially at a high temperature and the final conversion became lower with the presence of γ -Al₂O₃, as shown in Fig. 5. An increase in temperature obviously increased the carbon conversion to gas products in the pyrolysis step, but gave a lower conversion through the gasification step (see Table 2). Therefore, the γ -Al₂O₃ would contribute to less-reactive char and coke which is hardly converted in oxygen-free atmosphere.

3. Effects of K₂CO₃ on the Pyrolysis and Gasification of Lignin with the Presence of γ -Al₂O₃

Fig. 8 illustrates the relative mass profiles of lignin between the cases of lignin/ γ -Al₂O₃ and lignin/ γ -Al₂O₃/10wt% K₂CO₃ for tem-

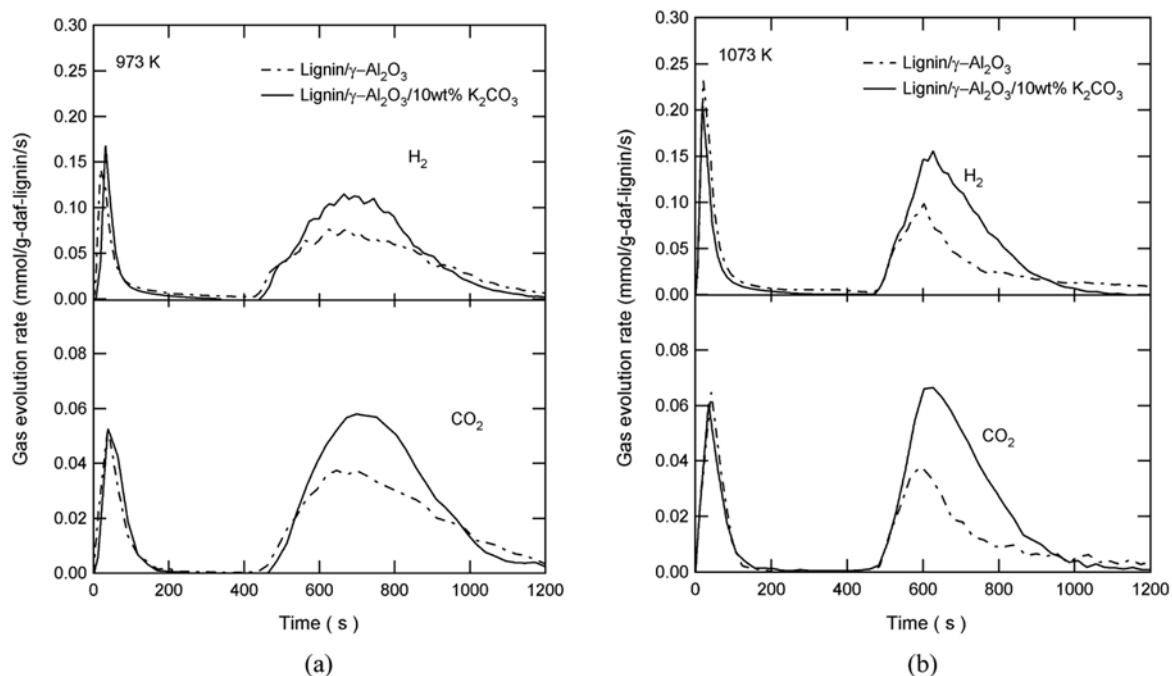


Fig. 7. Effects of $\gamma\text{-Al}_2\text{O}_3$ addition on H_2 and CO_2 evolution rate profiles of lignin at temperatures of (a) 973 K and (b) 1,073 K.

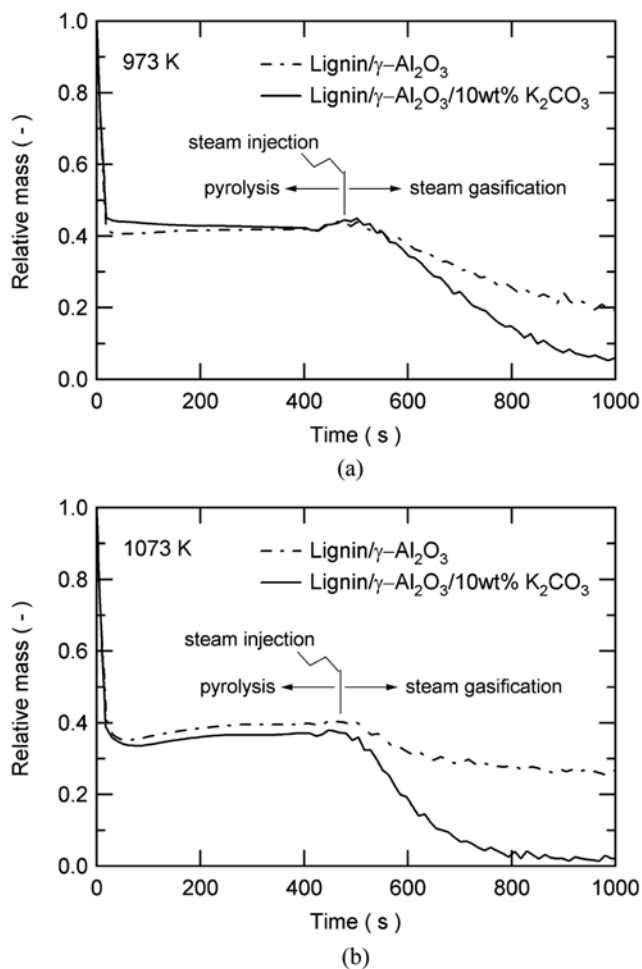


Fig. 8. Effects of $\gamma\text{-Al}_2\text{O}_3$ and K_2CO_3 additions on relative mass profiles of lignin at temperature of (a) 973 K and (b) 1,073 K.

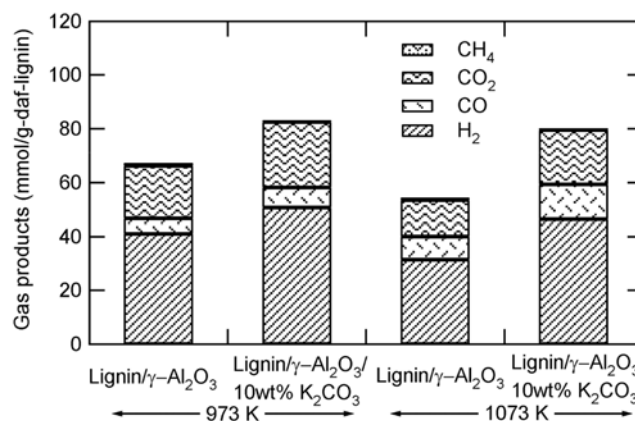


Fig. 9. Effects of $\gamma\text{-Al}_2\text{O}_3$ and K_2CO_3 addition on gaseous products of lignin.

peratures of 973 K and 1,073 K. Figs. 9 and 10 show the amount of gaseous products and the gas evolution rate profiles of lignin/ $\gamma\text{-Al}_2\text{O}_3$ and lignin/ $\gamma\text{-Al}_2\text{O}_3$ /10 wt% K_2CO_3 , for temperatures of 973 K and 1,073 K. The addition of K_2CO_3 was observed to increase the total conversion of lignin and the overall amount of gas product. As can be seen in Figs. 8 and 10, in the pyrolysis step K_2CO_3 did not have a significant influence on the conversion of lignin and gas production of H_2 and CO_2 , compared to the case of lignin/ $\gamma\text{-Al}_2\text{O}_3$. Nonetheless, a slightly increase in carbon conversion as shown in Table 2 would be an indication of tar reduction by K_2CO_3 .

After steam injection, the gasification rate of carbon was considerably accelerated and the gasification conversion was increased. The gas production in the steam gasification step was also increased, as can be seen in Fig. 10. This indicates that K_2CO_3 can catalyze the gasification of carbonaceous compounds in char and coke depos-

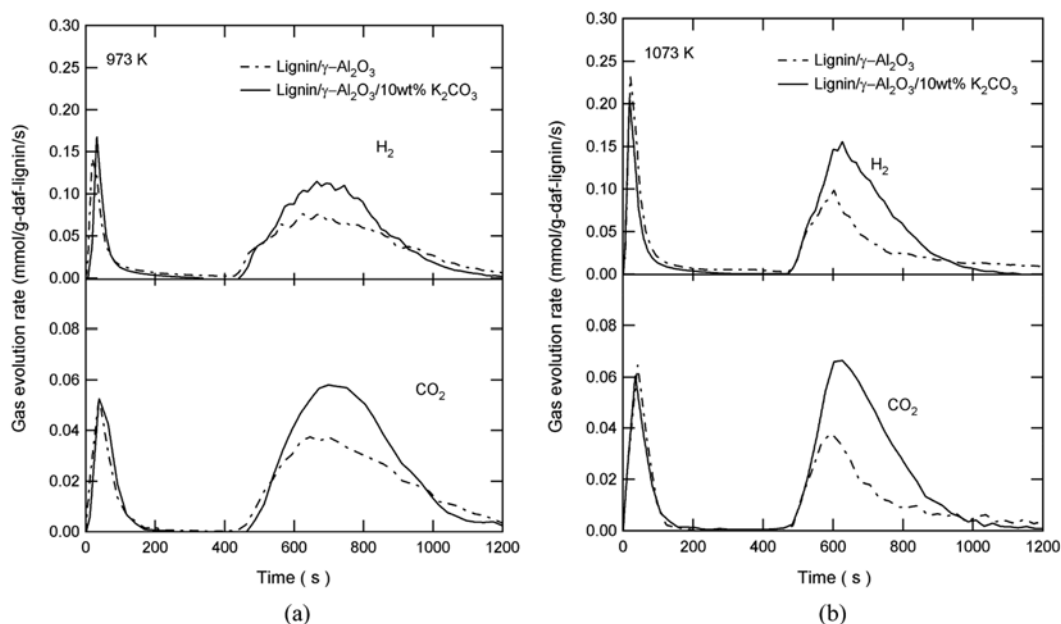


Fig. 10. Effects of γ - Al_2O_3 and K_2CO_3 additions on H_2 and CO_2 evolution rate profiles of lignin at temperature of (a) 973 K and (b) 1,073 K.

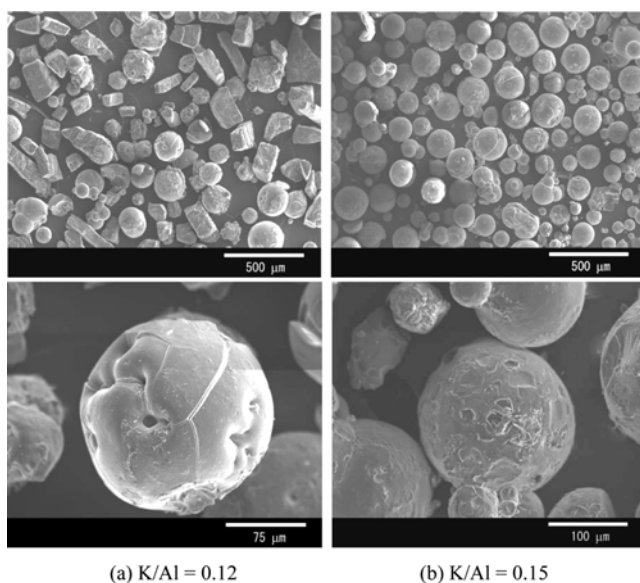


Fig. 11. SEM photographs of alumina particle at 1,073 K for lignin/ γ - Al_2O_3 /10 wt% K_2CO_3 : (a) after pyrolysis and (b) after steam gasification.

ited on γ - Al_2O_3 particles. Almost complete conversion was achieved at 1,073 K in the case of lignin/ γ - Al_2O_3 /10 wt% K_2CO_3 . For lignin/ γ - Al_2O_3 , the superior conversion compared to that in the case of lignin alone is attributable to the dispersion of char in the mixture with the bed material, reducing the formation of refractory carbon. Figs. 11(a) and 11(b) depict SEM photographs of a γ - Al_2O_3 particle after pyrolysis and after steam gasification, respectively. The amount of potassium on the alumina particle detected by EDS system is shown in terms of a ratio of potassium (K) to alumina (Al). The potassium seems to persist on the surface of γ - Al_2O_3 particles even after the steam gasification. This suggests that a large amount of potas-

sium can exist on γ - Al_2O_3 particles throughout the reaction, leading to high gasification rate.

CONCLUSIONS

The catalytic effect of an alkali-catalyst, K_2CO_3 , on the steam gasification of lignin with the presence of a bed material, γ - Al_2O_3 , was investigated by using a thermogravimetric reactor with high heating rates. K_2CO_3 slightly improves the steam gasification rate of lignin-derived char. In addition, K_2CO_3 is found to perform as a catalyst promoting tar decomposition during pyrolysis and steam gasification, increasing the carbon conversion to gas product. The addition of γ - Al_2O_3 alone induces the formation of less-reactive char and refractory carbon, decreasing the steam gasification rate and also the overall conversion. The steam gasification rate of this carbonaceous compound is improved with the presence of K_2CO_3 , leading to a higher conversion. Particularly, an almost complete gasification conversion was achieved at 1,073 K. Therefore, it can be concluded that K_2CO_3 is a good catalyst to promote the steam gasification of char with the presence of bed materials.

ACKNOWLEDGMENTS

The authors acknowledge financial support for this study by the Thailand Research Fund (TRF) MRG4980098 and are grateful for the opportunity to do collaborative research in Japan within the Thailand-Japan Technology Transfer Project (TJTTP). The authors also thank Dr. K. Kuramoto at the National Institute of Advanced Industrial Science and Technology in Japan and Dr. C. Fushimi at the University of Tokyo for invaluable advice and comments.

REFERENCES

1. P. McKendry, *Bioresource Technol.*, **83**, 37 (2002).

2. D. L. Klass, *Biomass for renewable energy, fuels, and chemicals*, Academic Press (1998).
3. E. Natarajan, A. Nordin and A. N. Rao, *Biomass Bioenergy*, **14**, 533 (1998).
4. E. Henrich, S. Bürkle, Z. I. Meza-Renken and S. Rumpel, *J. Anal. Appl. Pyrol.*, **49**, 221 (1999).
5. H. Sun, B. H. Song, Y. W. Jang, S. D. Kim, H. Li and J. Chang, *Korean J. Chem. Eng.*, **24**, 341 (2007).
6. M. Asadullah, T. Miyazawa, S.-i. Ito, K. Kunimori and K. Tomishige, *Energy Fuel*, **17**, 842 (2003).
7. S. Rapagnà, N. Jand, A. Kiennemann and P. U. Foscolo, *Biomass Bioenergy*, **19**, 187 (2000).
8. J. Corella, A. Orío and J.-M. Toledo, *Energy Fuel*, **13**, 702 (1999).
9. D. Sutton, B. Kelleher and J. R. H. Ross, *Fuel Process Technol.*, **73**, 155 (2001).
10. T. Furusawa and A. Tsutsumi, *Appl. Catal A*, **278**, 195 (2005).
11. X. Chen, K. Honda and Z. Zhang, *Appl. Catal A*, **279**, 263 (2005).
12. S. Hosokai, Y. Kobayashi, N. Sonoyama, T. Shimada, K. Kuramoto, J.-i. Hayashi and T. Chiba, *Proceedings of the 10th APCCChE Congress*, Kitakyushu, Japan (2004).
13. T. Shimizu, Y. Konaka, K. Koseki and T. Teramae, *Proceedings of the 10th APCCChE Congress*, Kitakyushu, Japan (2004).
14. Y. Suzuki, H. Hatano, T. Minowa, T. Teramae and T. Namioka, *Proceedings of the 10th APCCChE Congress*, Kitakyushu, Japan (2004).
15. D. W. McKee, *Fuel*, **62**, 170 (1983).
16. F. Huhn, J. Klein and H. Jüntgen, *Fuel*, **62**, 196 (1983).
17. C. A. Mims and J. K. Pabst, *Fuel*, **62**, 176 (1983).
18. J. M. Saber, J. L. Falconer and L. F. Brown, *Fuel*, **65**, 1356 (1986).
19. W. Schumacher, H.-j. Mühlen, K. H. Van Hek and H. Jüntgen, *Fuel*, **65**, 1360 (1986).
20. G. Bruno, L. Carvani and G. Passoni, *Fuel*, **65**, 1473 (1986).
21. M. J. Veraa and A. T. Bell, *Fuel*, **57**, 194 (1978).
22. D. Douchanov and G. Angelova, *Fuel*, **62**, 231 (1983).
23. W. J. Lee, S. D. Kim and B. H. Song, *Korean J. Chem. Eng.*, **18**, 640 (2001).
24. P. L. Jr. Walker, S. Matsumoto, T. Hanzawa, T. Muira and I. M. K. Ismail, *Fuel*, **62**, 140 (1983).
25. R. J. Lang and R. C. Neavel, *Fuel*, **61**, 620 (1982).
26. C. Guo and L. Zhang, *Fuel*, **65**, 1364 (1986).
27. S. G. Chen and R. T. Yang, *Energy Fuel*, **11**, 421 (1997).
28. C. Fushimi, K. Araki, Y. Yamaguchi and A. Tsutsumi, *Ind. Eng. Chem. Res.*, **42**, 3922 (2003).
29. C. Fushimi, K. Araki, Y. Yamaguchi and A. Tsutsumi, *Ind. Eng. Chem. Res.*, **42**, 3929 (2003).
30. D. C. Elliott and E. Baker, *Biomass*, **9**, 195 (1986).
31. K. Miura, H. Nakagawa, S. Nakai and S. Kajitani, *Chem. Eng. Sci.*, **59**, 5261 (2004).