Korean J. Chem. Eng., **26**(4), 1009-1015 (2009)
DOI: 10.1007/s11814-009-0168-9

CO_2 gasification of Thai coal chars: Kinetics and reactivity studies

Supaporn Sawettaporn*, Kunchana Bunyakiat*,,†, and Boonyarach Kitiyanan**,*****

*Fuels Research Center, Department of Chemical Technology, Faculty of Science, Chulalongkorn University
**Centers of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University
***The Petroleum and Petrochemical College, Chulalongkorn University
(*Received 26 November 2007 • accepted 14 January 2009*)

Abstract−Two sized fractions (<75 μm and 150-250 μm) of Ban Pu lignite A and Lampang subbituminous B coals were pyrolyzed in a drop tube fixed bed reactor under nitrogen atmosphere at 500-900 °C. Gasification of coal chars with excess carbon dioxide was then performed at 900-1,100 °C. The result was analyzed in terms of reactivity index, reaction rate and activation energy. It was found that chars at lower pyrolysis temperature had highest carbon conversion, and for chars of the same sized fraction and at the same pyrolysis temperature, reactivity indices increased with gasification temperature. The lower rank Ban Pu lignite A had higher R_s values than higher rank Lampang subbituminous B coals. Smaller chars from both coals had higher R_s values, due to the higher ash content. At present, it can be concluded that, within the gasification temperature range studied, gasification rates of chars obtained at various pyrolysis temperatures showed a linear correlation with temperature. However, additional experiment is needed to verify the correlation.

Key words: Coal Chars, Reactivity, Kinetics, Gasification

INTRODUCTION

In coal thermal conversion processes, a pyrolysis reaction takes place prior to other reactions. Therefore, understanding pyrolysis behavior is important in developing new coal utilization technologies. Pyrolysis can be defined as decomposition of coal when coal is heated to elevated temperature in an oxygen-free or inert atmosphere, resulting in a hydrogen-rich volatile fraction which consists of gases, vapor and tar components and a carbon-rich solid residue, called char. The characteristics of the resultant char control subsequent processes, including combustion, and in particular gasification, reactivity and kinetics of coal char with steam and carbon dioxide provide valuable information and have been widely studied.

Gasification reactivity is usually quantified by a reactivity index, R_S, defined as the following equation [1]:

$$R_S=0.5/\tau_{0.5} \quad (1)$$

where $\tau_{0.5}$ denotes the time (h) required to reach 0.5 of the fractional fixed carbon conversion. This definition is commonly used in the literature for comparison of gasification reactivity of different coals. There are are several factors affecting coal char reactivity: coal properties, catalytic effect of inorganic matter in coal, pyrolysis reaction conditions and other factors. Coal properties include coal rank, which is one important coal property characterization, but it does not provide adequate information about its reactivity. There is no general trend for the effect of coal rank on reactivity [2]. Low-rank coals generally have higher but widely spread reactivities than high-rank coals, due to the high concentration of active oxygen-containing functional groups, high proportion of transitional and macropores, and high dispersion of catalytic inorganic constituents [1]. In addition to coal properties, pyrolysis temperature [3-6] and structural properties of char and their variation during pyrolysis also have significant effects on coal gasification reactivity [4,7-9].

Following pyrolysis, coal char undergoes either combustion or gasification. Coal char gasification is in both cases the rate-limiting step. To better understand the overall coal gasification phenomenon, kinetics studies of char gasification are important and necessary. Gasifying media may be either O_2, H_2O or CO_2 and/or mixtures of these gases. Among char-O_2/H_2O/CO_2 reactions, the char-CO_2 gasification system is the simplest since the reaction is endothermic at relatively slow rate and the single product evolved (CO) makes analysis simple and highly reliable. Many different models have been proposed for the gasification kinetics [1,10-13]. These models include the homogeneous model, non-reacted core model, random pore model and other empirical models. Homogeneous and shrinking-core models are the simplest, which, in many cases, describe the conversion-time behavior well [14]. Experimental kinetic studies are performed in a thermogravimetric analyzer (TGA), a drop tube reactor, a fixed/fluidized bed reactor, or a single particle reactor, at or above atmospheric pressure [8,9]. For char-CO_2 gasification in a TGA, at 700-900 °C, it was found that gasification rates of chars with high ash content were higher than those of similarly prepared char with low ash content, due to the presence of catalytically active inorganic constituents, and the gasification rate increased with CO_2 concentration in the reaction gases. The effects of heating rate and CO_2 concentration on char gasification rate were more pronounced for samples from untreated lignite than for those from acid-washed lignite [3]. While in a single-particle reactor at 714-892 °C, it was found that gasification rate was independent of particle size, suggesting that the gasification rate follows the homogeneous model. The reactivity of coal with high inherent content of inorganic matter was far higher than other coals. Acid-washed coal has similar reactivity to other low-inorganic-content low-rank coals. Gasification reactivity follows

†To whom correspondence should be addressed.
E-mail: Kunchana.b@chula.ac.th

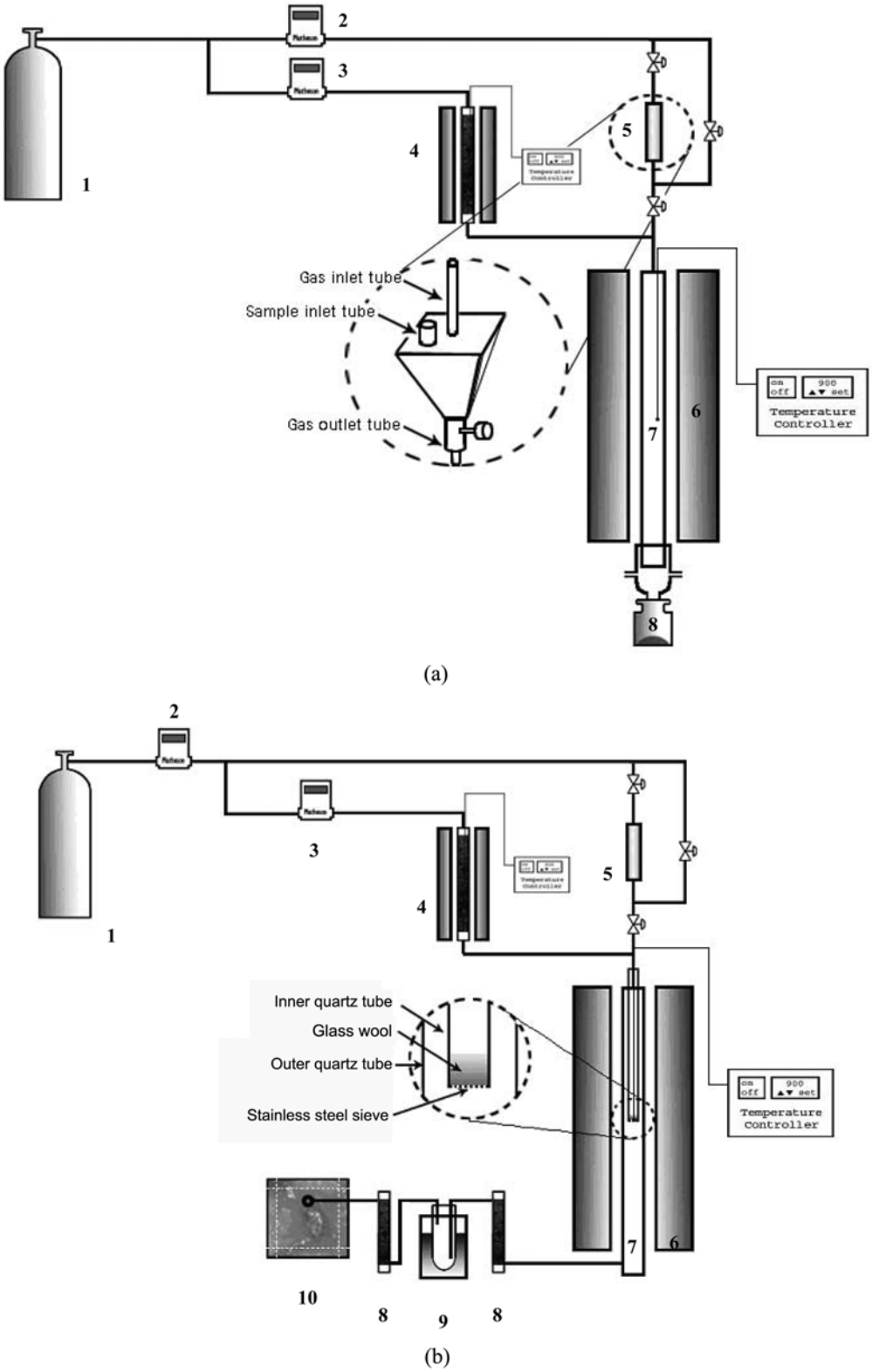

Fig. 1. (a) Schematic diagram of apparatus for pyrolysis.

1. Nitrogen cylinder
2. Main mass flow controllers
3. Auxiliary mass flow controllers
4. Gas preheater
5. Sample holder
6. Tubular furnace
7. Drop tube reactor
8. Sample collector with cooling jacket

(b) Schematic diagram of apparatus for CO_2 gasification.

1. Carbon dioxide cylinder
2. Main mass flow controllers
3. Auxiliary mass flow controllers
4. Gas preheater
5. Sample holder
6. Tubular furnace
7. Drop tube fixed bed reactor
8. Moisture trap
9. Tar trap
10. Gas bag

the order Na>K>Ca>Ni with the same anions [1]. Another work reported gasification kinetics of an Indonesian subbituminous coal-char with CO_2 at elevated pressure with a pressurized drop tube furnace reactor and found that the gasification rate was dependent on the total system pressure with the same partial pressure and temperature [11]. A more recent work by Park et al. [15] on reactivity of CO_2 gasification of five coal chars in a pressurized thermogravimetric analyzer (PTGA) in the temperature range 850-1,000 °C and the total pressure range 0.5-2.0 MPa found that the reactivity of low rank coal chars was better than that of high rank coal chars, and determined the kinetic parameters based on the shrinking particle model.

The aim of the present work was to study the reactivities and kinetics of chars gasification with CO_2. Chars were prepared from Thai low-rank coal, Ban Pu lignite, and Lampang subbituminous coals. Homogeneous and shrinking-core models were tested and presented.

EXPERIMENTAL

1. Coal Samples

Ban Pu (denoted BP) lignite and Lampang (denoted LP) subbituminous coal samples were crushed and sieved and divided into two narrow-sized fractions (<75 μm (denoted S) and 150-250 μm (denoted L)), employing the standard method [16].

2. Pyrolysis in a Drop-tube Reactor (DTR)

Pyrolysis experiments were conducted in a drop tube fixed bed reactor which was made of a quartz tube with an internal diameter of 16 mm. and length of 1,000 mm. The tube was placed inside a tubular furnace, Carbolite, Model 201, which was placed in a vertical position as illustrated in Fig. 1(a). N_2 was used as both the primary (to pass through the reactor) and secondary gas (to carry the coal particles into the reactor) and the pressure inside the tube was maintained at atmospheric. The temperature could be controlled to within ±5 °C. Pyrolysis was carried out at 500-900 °C. For each run, coal particles were injected to the top of the reactor, together with the carrier gas, through an injection tube attached to the upper part of the reactor, and the reacted coal particles were collected at the probe attached to the lower part of the reaction tube. Chars obtained from pyrolysis at 500, 700 and 900 °C were analyzed for their proximate and ultimate carbon analyses.

3. Gasification in a Drop-tube/Fixed-bed Reactor

Char was gasified isothermally with CO_2 gas in a drop tube fixed bed reactor. The general experimental setup was the same as for the pyrolysis experiment, except for the sample holder part, which was a straight tube connected to the entrance of the inner tube of the reactor, and the moisture and tar traps which were connected at the exit, as illustrated in Fig. 1(b). The reactor consisted of an inner quartz tube with 10 mm i.d. and an outer quartz tube with 16 mm i.d. and length of 1,000 mm. The inner tube was fitted with a stainless steel sieve at its lower end, together with a small amount of loosely packed glass wool for effective gas/solid separation. Gasification was carried out at 900, 1,000 and 1,100 °C. Temperature inside the reactor was calibrated prior to the experiment and the temperature profile was determined under N_2 flow at atmospheric pressure. In each gasification run, about 100 mg char particles were charged into the sample holder. CO_2 was continuously supplied from the start before the test into the inner tube at a rate of 660 ml (S.C.)/min, first to eliminate the air and then to gasify the char sample. After steady temperature of the reactor was attained, the valve at the lower end of the sample holder was instantaneously open and char particles were injected into the inner tube by expansion of the pressurized CO_2 gas. The particles were dropped onto the glass wool bed and underwent gasification, during which CO formed by the reactions between CO_2 and char particles was immediately swept away from the vicinity of solid residue by the gas flow forced through the glass wool bed and the sieve. A gas chromatograph (Thermo-Finnegan Model 2000), equipped with a packed column with Carbosphere-Carbon Molecular Sieve (1/8"×10') and a Methanizer-FID detector with nitrogen as the carrier gas was used to analyze the gaseous product. The gas chromatograph was standardized by external standard prior to use. For each run, gaseous products were collected in gas bags at 1-minute intervals until no CO was observed.

The CO concentration in each run was used to calculate the mole fraction of carbon conversion (X) by the following equation [17];

$$X = \int_0^t [f_{CO} M_C / (2 W_0)] dt \quad (2)$$

where; X=mole fraction of carbon conversion, f_{CO}=CO formation rate, mol/min, M_C=Molecular Mass of carbon, and W_o=mol of carbon in the original char.

To define a reaction temperature of a char particle, it was assumed that the temperature of the reacting char particles were the same as that of the reactor as the particles were small, the reaction was slow and the char-CO_2 reaction was endothermic. The concentration of the reactant gas surrounding the char particles should not change considerably during the gasification of char particle due to the excessive supply of CO_2.

RESULTS AND DISCUSSION

1. Coal and Coal Char Sample Analysis

Table 1. Proximate analyses of coal samples

Sample	Particle size μm	Air-dried basis				Dry basis		
		Moisture %	Ash % w/w	Volatile matter % w/w	Fixed carbon % w/w	Ash % w/w	Volatile matter % w/w	Fixed carbon % w/w
BP	<75	7.05	15.21	38.65	39.09	16.36	41.58	42.06
	150-250	6.91	9.55	38.85	44.69	10.26	41.73	48.01
LP	<75	5.93	9.69	42.32	42.06	10.30	44.99	44.71
	150-250	5.62	6.98	40.98	46.42	7.39	43.42	49.19

Table 2. Proximate analyses (dry) and % ultimate carbon (dry, ash-free) of coal chars at various pyrolysis temperatures

Sample	Particle size μm	Pyrolysis temperature °C	Ash % w/w	Volatile matter % w/w	Fixed carbon % w/w	Carbon %, dry, ash-free
CBP	<75	500	16.33	35.62	48.05	58.26
		700	20.75	24.96	54.29	62.28
		900	22.82	18.66	58.52	64.71
	150-250	500	8.7	41.93	49.37	58.63
		700	13.43	28.85	57.72	66.27
		900	15.14	20.6	64.26	64.31
CLP	<75	500	12.27	36.36	51.37	63.21
		700	13.17	28.55	58.28	67.56
		900	14.97	19.89	65.14	69.99
	150-250	500	6.34	43.58	50.08	61.80
		700	6.38	35.32	58.29	68.82
		900	10.39	20.51	69.10	68.85

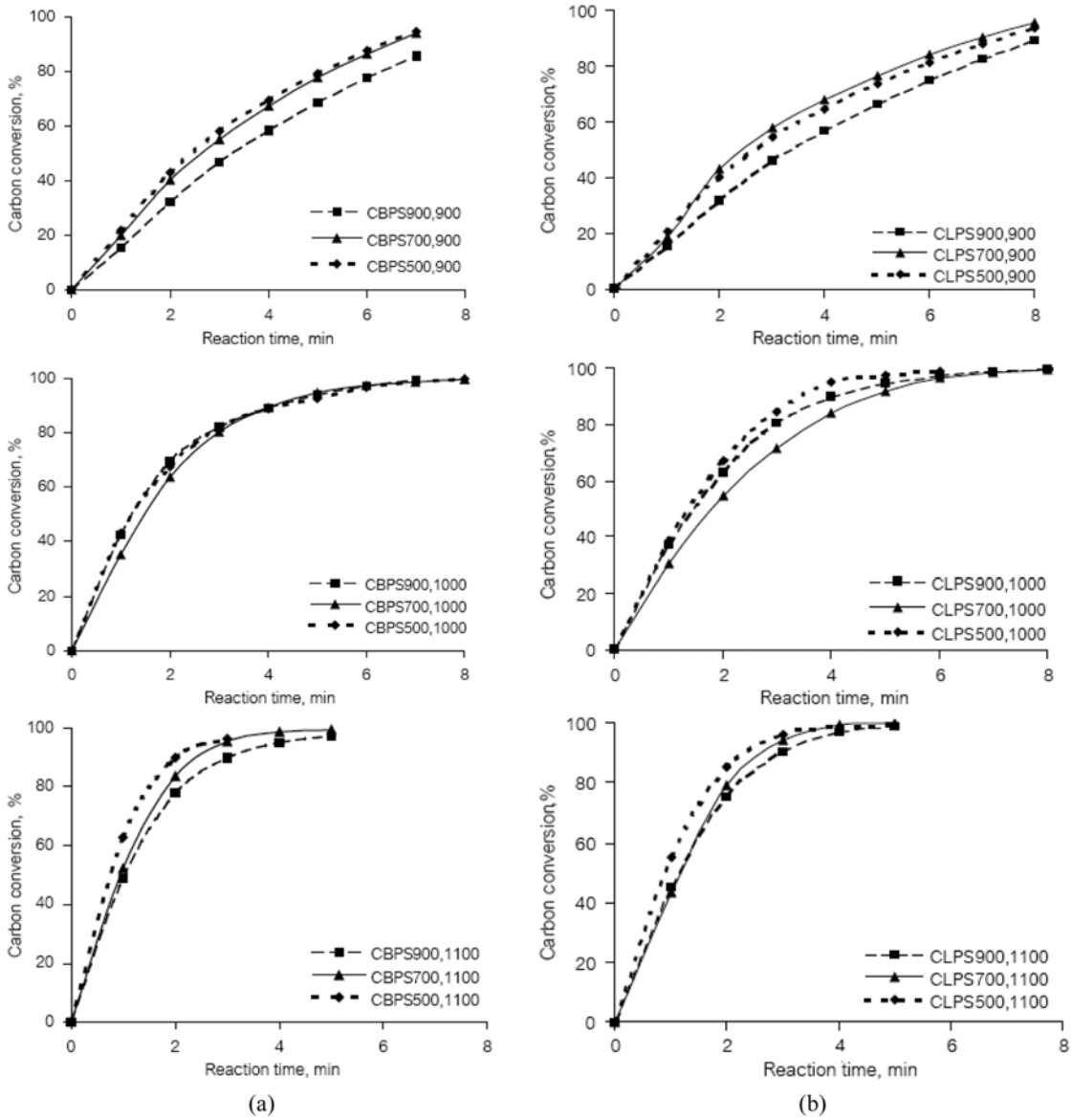

Fig. 2. Carbon conversion of BP (a) and LP (b) chars during CO_2 gasification at different gasification temperatures (particle size fraction: <75 μm).

Coal samples employed in this study were analyzed for their proximate analyses as shown in Table 1. BP lignite contained lower percent ash and higher percent fixed carbon than LP subbituminous. Comparing the smaller sized coal samples and the larger ones, the former contained higher percent ash. After pyrolysis at 500, 700 and 900 °C, the chars obtained were then analyzed for their proximate analyses, as shown in Table 2. It can be seen that, for all samples, percent volatile matter decreased with increasing pyrolysis temperature, whereas percent fixed carbon increased. The lowest percent volatile matter obtained was around 20.5% at 900 °C pyrolysis temperature in larger sized chars from both coal samples. The char samples were also analyzed for their percent ultimate carbon, and shown in Table 2.

2. Carbon Conversion

Figs. 2 and 3 show carbon conversion during CO_2 gasification against reaction time of BP and LP chars of different size fractions (<75 μm and 150-250 μm) and at different pyrolysis temperatures (500, 700 and 900 °C), respectively. At the same gasification temperature, both BP and LP chars at 500 °C pyrolysis temperature had the highest carbon conversion, especially at initial time, as noticed from the slope of the plot. This conforms with previous findings [7], since at 500 °C pyrolysis temperature, decomposition of the coal was incomplete, as noticed from the high percentage of the volatile matter (Table 2) and provided active sites for gasification. At higher pyrolysis temperature, char structure rearrange to a more stable form and lose some active sites, thus lowering its reactivity [5].

3. Reactivity Index

To better compare the reactivity of coal chars of different reserves and size fractions prepared under different pyrolysis temperatures, percent carbon conversion was recalculated into reactivity index as defined in (1), and the result is shown in Table 3. It can be seen that

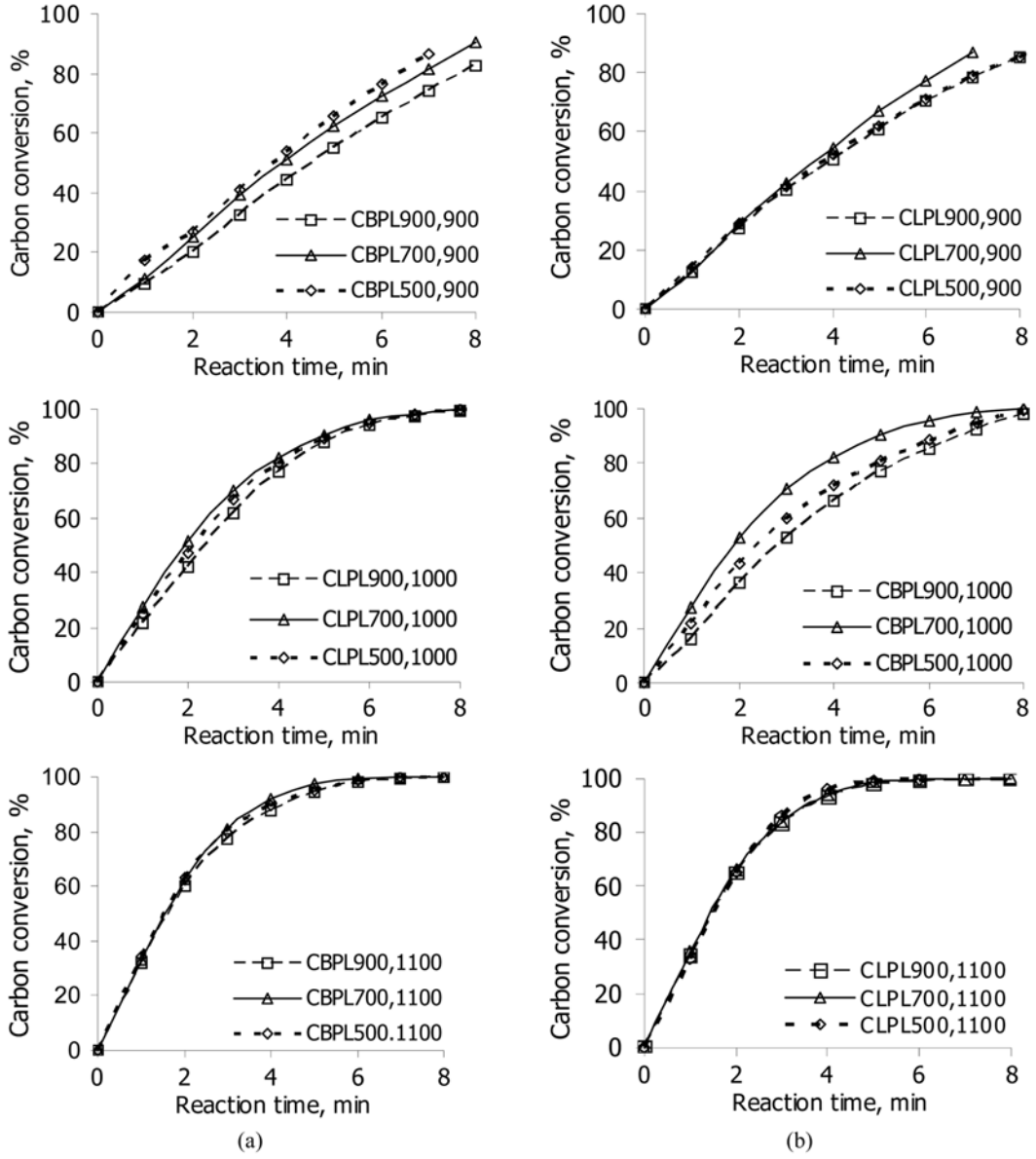

Fig. 3. Carbon conversion of BP (a) and LP (b) chars during CO_2 gasification at different gasification temperatures (particle size fraction: 150-250 μm).

Table 3. Reactivity indices of coal chars under different pyrolysis and gasification temperatures

Sample	Particle size μm	Pyrolysis temperature °C	$R_s=0.5/t_{0.5}$ (h^{-1})		
			Gasification temperature (°C)		
			900	1,000	1,100
CBP	<75	500	12.14	23.33	37.66
		700	11.25	19.66	31.30
		900	9.15	23.42	28.76
	150-250	500	8.13	12.45	19.36
		700	7.69	15.99	19.02
		900	6.62	10.61	18.28
CLP	<75	500	11.13	21.42	33.12
		700	12.16	16.54	25.36
		900	8.86	20.01	26.08
	150-250	500	7.92	14.04	19.60
		700	8.28	15.56	20.35
		900	7.65	12.49	19.89

for chars of the same sized fraction and at the same pyrolysis temperature, reactivity indices increased with gasification temperature. At 1,100 °C, smaller BP chars had higher Rs values between 37.66 and 28.76 h^{-1}, while larger ones had lower Rs values between 19.36 and 18.28 h^{-1} respectively. The same holds true for LP chars, and Rs values ranged from 33.12 and 25.36 and 20.35 and 19.60 h^{-1} for smaller and larger chars, respectively. For smaller chars, there was a good trend in decreasing Rs values with increasing pyrolysis temperature, but for larger chars, Rs values seem to vary within the same low range. Comparing coal chars of the same size fraction, at the same pyrolyzed and gasified temperatures, it can be concluded that the lower rank BP lignite coal had higher Rs values than the higher rank LP subbituminous coal.

3. CO_2 Gasification Kinetic of Chars

Several kinetic models have been proposed for describing gasification of coal particles, such as the homogeneous model, the chemical reaction model, the pore-diffusion model, and the heterogeneous model [1,2,6,11,13,17-20]. Among these, the simplest are the homogeneous and shrinking-core models. The homogeneous model assumes that the carbon-gas reactions occur at active sites which are uniformly distributed throughout the whole particle. As the reaction proceeds, the particle size remains constant while the density decreases. The overall rate of gasification is independent of particle size. The carbon mass balance can be expressed as follows:

The homogeneous model:

$$\frac{dx}{dt} = k(1-X) \quad (3)$$

where X=fractional carbon conversion, k=first-order reaction rate constant

The shrinking-core model assumes that gaseous reactants diffuse through a gas film surrounding the particle, then diffuse through the ash layer and react on the unreacted core surface. As the reaction progresses, the unreacted core keeps shrinking; at any time during the reaction there exists an unreacted core. The reaction rate is a function of coal particle size and varies depending on different assumptions. The carbon mass balance for chemical reaction control can be expressed as follows:

The shrinking-core model:

$$\frac{dx}{dt} = k(1-X)^{2/3} \quad (4)$$

where X=mole fraction of carbon conversion, k=apparent reaction rate constant

In the present study, a preliminary test was carried out by fitting the experimental data obtained from each coal char with these two kinetic models and it was found that the shrinking-core model was better fitted and could describe the relationship between carbon conversion and reaction time well. At present, it can be concluded that, within the gasification temperature range studied from 900 to 1,100 °C, for gasification rates of chars obtained at the pyrolysis temperatures between 500 and 900 °C a linear correlation with temperature was evident. However, additional experiment is needed to verify the correlation and then the Arrhenius plot can be applied.

CONCLUSION

Gasification kinetics of BP lignite and LP subbituminous coal chars with CO_2 were investigated by performing in a drop tube fixed bed reactor at atmospheric pressure. The following results were obtained.

1. BP lignite chars had higher gasification reactivity than LP subbituminous chars.
2. At the same pyrolysis and gasification temperatures, gasification reactivities of BP and LP chars of smaller size (<75 μm) were higher than those of larger size (150-250 μm).
3. Preliminary test showed that the shrinking-core model was better fitted and could describe the relationship between carbon conversion and reaction time well.
4. At present, it can be concluded that, within the gasification temperature range studied from 900 to 1,100 °C, for gasification rates of chars obtained at the pyrolysis temperatures between 500 and 900 °C a linear correlation with temperature was evident. However, additional experiment is needed to verify the correlation and then the Arrhenius plot can be applied.

ACKNOWLEDGMENT

The authors would like to acknowledge Centers of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University and the Graduate School, Chulalongkorn University for their scholarship and financial support.

REFERENCES

1. D. P. Ye, J. B. Agnew and D. K. Zhang, *Fuel*, **77**, 1209 (1998).
2. K. van Heek and H. J. Mulen, *Fuel*, **64**, 1405 (1985).
3. P. Samaras, E. Diamadopoulos and G. P. Sakellaropoulos, *Fuel*, **75**, 1108 (1996).
4. H. Liu, M. Kaneko, C. Luo, S. Kato and T. Kojima, *Fuel*, **82**, 523 (2003).
5. H.-Y. Cai, A. J. Guell, I. N. Chatzakis, J.-Y. Lim, D. R. Dugwell and R. Kandiyoti, In: J. A. Pajares and J. M. D. Tascon, editors, Coal

Science: Elsevier, 515 (1995).
6. A. Sinag, K. Sinek, A. T. Tekes, Z. Misirlioglu, M. Canel and L. Wang, *Chemical Engineering and Processing*, **42**, 1027 (2003).
7. K. Matsuoka, H. Akiho, W. Xu, R. Gupta, T. F. Wall and A. Tomita, *Fuel*, **84,** 63 (2005).
8. S. H. Ng, D. P. Fung and S. Kim, *Fuel*, **67**, 700 (1988).
9. Y. Sekine, K. Ishikawa, E. Kikuchi, M. Matsukata and A. Akimoto, *Fuel*, **85**, 122 (2006).
10. J. L. Johnson, *Kinetics of coal gasification*, John Wiley & Sons, New York (1979).
11. D. H. Ahn, B. M. Gibbs, K. H. Ko and J. J. Kim, *Fuel*, **80**, 1651 (2001).
12. S. Kajitani, S. Hara and H. Matsuda, *Fuel*, **81**, 539 (2002).
13. S. Kajitani, N. Suzuki, M. Ashizawa and S. Hara, *Fuel*, **85**, 163 (2006).
14. O. Levenspiel, *Chemical reactions engineering*, John Wiley & Sons, New York (1999).
15. H. Y. Park and D. H. Ahn, *Korean J. Chem. Eng.*, **24**, 24 (2007).
16. ASTM Standard, D2013 - 86, *Preparing coal samples for analysis*, American Society for Testing and Materials, U.S.A. (2000).
17. C. Luo, T. Watanabe, M. Nakamura, S. Uemiya and T. Kojima, *Fuel*, **80**, 233 (2001).
18. Q. Sun, W. Li, H. Chen and B. Li, *Fuel*, **83**, 1787 (2004).
19. J. Ochoa, M. C. Cassanello, P. R. Bonelli and A. L. Cukierman, *Fuel Processing Technology*, **74**, 161 (2001).
20. A. Arenillas, C. F. Pevida, Rubiera and J. J. Pis, *Fuel*, **82**, 2001 (2003).