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ABSTRACT
The six chars of low rank coals have been gasified with steam in a thermobalance reactor and one lignite in a fluidized bed to obtain the kinetic information needed for a design of coal gasifier. The gas-solid reaction models have been compared for their prediction ability of the gasification reaction behavior. The apparent reaction rate equations have been presented.

INTRODUCTION
With coal being a major source of fuel in most parts of the world, there is a continued interest in the efficient use of coal and the development of clean coal technologies. This requires a detailed understanding of the fundamental properties of coal, thus making the area of coal characterization of paramount importance. The kinetic information makes it possible to predict its behavior during conversion processes such as combustion, gasification, or liquefaction. Coal of different types exhibit wide variation in their devolatilization behavior because of different extends of coalification. The degree of aromatization in the coal structure increases with the increase in the rank of the coal. Coal gasification mainly involves two steps: the initial rapid devolatilization produces gases, tar, and char and the subsequent gasification of the generated char occurs. Char gasification, being the slower step, usually controls the overall conversion process, and a better understanding of the kinetics of this step is essential to the design and operation of a coal gasifier. The gasification reaction of coal char with steam is:

$$C + H_2O = CO + H_2 \quad \Delta H = 118.9\ \text{kJ/mol}$$

The aim of this study is to obtain the kinetic parameters and gasification performance of six low rank coals.

EXPERIMENTAL

Materials
The ultimate and proximate analysis of the coals is presented in Table 1. It can be noticed that the content of carbon increases with coal rank. The lignite coals have quite small carbon content and relatively high oxygen content around 35-50%. The highest content of sulfur of 0.78% is for Flame S.A. bituminous coal, and the other coals have very low sulfur. Thus these coals can be expected to decrease the load of downstream gas cleaning processes in coal gasification process. The chars from each coals are designated with number as seen in Table 1. The chars were prepared by heating the coal in a quartz tube from room temperature to 1173 K with

heating rate of 10 K min^{-1} under nitrogen atmosphere, and holding at 1173 K for 0.5 h.

Table 1. Ultimate and proximate analyses of the coals.

	Roto-South #5	Jembayan #4	Lignite++	STX #6	Felix #2	Flame S.A, #3	Taldivisky #1
Ultimate analysis (daf+)							
C	44.61	54.89	58.74	57.08	61.98	65.69	72.30
H	4.48	3.23	4.19	5.69	4.28	4.71	4.12
N	0.88	1.63	0.50	1.39	3.88	3.34	1.89
S	0.00	0.00	0.03	0.00	0.00	0.78	0.00
O*	50.03	40.25	36.54	35.84	29.86	25.48	21.69
Proximate analysis							
moisture	18.74	17.53	11.56	17.90	4.00	2.86	2.50
volatile	42.07	36.91	44.16	34.22	25.42	28.76	22.96
fixed carbon	36.79	45.51	36.22	41.75	52.42	41.59	52.54
ash	2.54	0.10	8.06	6.13	18.16	26.79	22.00
HHV**, kcal/kg	2,993	3,814	4,617	5,029	5,197	5,851	6,327

+: dry and ash free base, ++: fuel only for fluidized bed experiment
*: by difference, **: calculated by Dulong's formula

Experimental equipment

The thermobalance consists of a reactor, 0.055-m i.d.×1.0-m-high, made of stainless-steel tube and equipped with a 3 kW external electrical heater. Steam was generated from an electric steam generator which consists of a 1/8" copper tube, 1.0 m in length, on which was coiled a flexible electrical heater. The flow rate of steam was controlled by a micro-pump. The temperature of the thermobalance was controlled by a K-type thermocouple located 5 mm below a stainless-steel wire-mesh sample basket suspended from an electronic balance (Mettler Toledo), and the mass signal of the balance was recorded by a personal computer to monitor the change of mass during experiment. More details of thermobalance and operation can be found in our previous study (1).

The schematic diagram of the lab-scale fluidized bed reactor is illustrated in Fig. 1. This facility consists of the following components: the fluidized bed, temperature control section, fluidizing gas section, fuel delivery section, data acquisition section, and gas sampling section. The inside diameter of quartz reactor is 20 mm and the height is 600 mm. The gasifier is a bubbling fluidized bed, using sand as a fluidizing medium(d_p=0.3mm, density=2,600kg/m^3, U_{mf}=0.034m/s), nitrogen and steam mixture as gasifying agent. The feed rate of lignite was 0.15kg/h and its particle size is 0.5~3.0mm. The minimum fluidization velocity for sand material was measured to be 0.034m/s, practically it was observed that at least twice the minimum fluidization velocity is needed to maintain good fluidization for sand, and small amount (30ml/min) of purge gas was put into the feeder unit to ensure continuous and smooth feeding of coal. Nitrogen and steam are fed to the reactor through the distributor plate. Steam was fed to the reactor by micro pump and steam generator.

Initially the inert sand was loaded in the fluidized bed reactor at a ratio of depth to radius of around 1:1. For a given condition, the gasifier was operated in steady state for 20 - 30 minutes for gas sampling and analysis. After the char and dust carried in the gaseous product was separated in the cyclone, the part of product gas flow was passed through a cooling trap and a cotton filter and cellulose filter for drying and cleaning. Then the dry and clean gas was sent to on-line gas analyzer (ABB Inc.) to detect various gas compositions. Temperatures of 750-900°C and steam partial pressure of 0.15-0.95 atm were adapted for the gasification experiment.

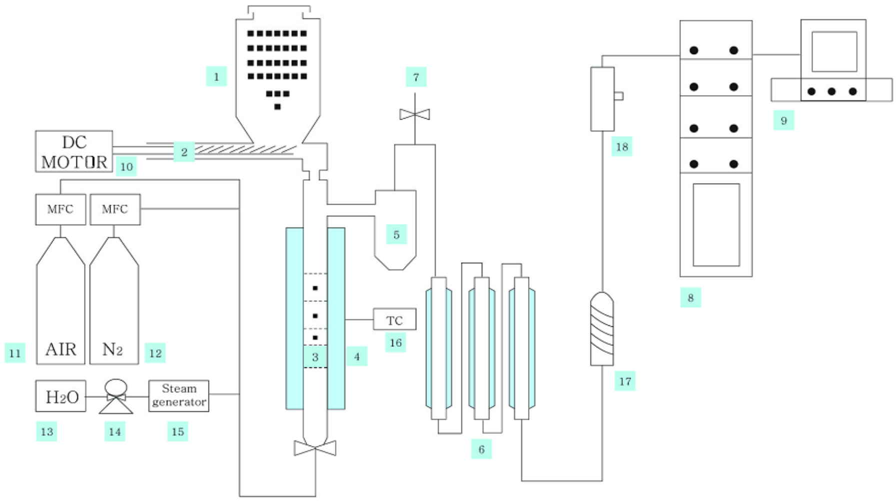

Figure 1. Schematic diagram of a miniature fluidized bed reactor.
1. fuel hopper, 2. screw feeder, 3. quartz main reactor, 4. furnace, 5. cyclone, 6. condenser, 7. gas samples, 8. gas analyzer, 9. computer, 10. DC motor, 11. air source, 12. nitrogen source, 13. water, 14. water pump, 15. steam generator, 16. thermocouple, 17. thimble filter session, 18. sample collector.

RESULT AND DISCUSSION

Gas-solids reaction models

Gas-solid reaction model can be applied to analyze the gasification rate of char and evaluate the reactivity quantitatively. The carbon conversion was defined as:

$$X = \frac{W_0 - W}{W_0 - W_{ash}} \tag{1}$$

Where W_0 is the initial mass of the sample in the gasification stage, W_{ash} is the mass of ash in the sample, W is the sample mass at time *t.* The time-conversion equations from shrinking-core model at chemical reaction controlled regime (2), the volumetric-reaction model (3), and the modified volumetric-reaction model (4) are:

$$\Psi t = 1 - (1 - X)^{1/3} \tag{2}$$

$$\Omega t = -\ln(1 - X) \tag{3}$$

$$\alpha t^{\beta} = -\ln(1-X) \qquad (4)$$

Where ψ, Ω, α, and β are constants determined from the conversion data by the least-squares method. We can consider the specific reaction rate *k(X)* as the gasification rate per unit mass of fixed carbon remained:

$$k(X) = \frac{1}{1-X} \cdot \frac{dX}{dt} \qquad (5)$$

By inserting Equation (4) we can get the specific rate from the modified volumetric model:

$$k(X) = \alpha^{1/\beta} \cdot \beta\left[-\ln(1-X)\right]^{\frac{\beta-1}{\beta}} \qquad (6)$$

As a measure of char reactivity, the average reaction rate (reactivity) is defined as,

$$k = \int_0^1 k(X)dX \qquad (7)$$

Comparison of the reaction models

To determine how the model explains the gasification behavior, the linearity of data was checked according to the relationship of each model. For a comparison of the three models, the gasification data of Taldivisky char at steam pressure of 0.5atm were used. The conversion vs. time by each relationship from three models are shown in Fig. 2. The linearity of the conversion data in each plot gives information about the fitness of the model to the reaction behavior through the value of R^2. The value of R^2 comes from the trend line and it is presented with in the plots. The extent of the value of R^2 close to 1 for each model mean show the model fits the experiment. The plots tell that all the models generally fit the experimental data well. Both of the R^2 for shrinking-core model and modified volumetric-reaction model are above 0.95, however the linearity of modified volumetric-reaction model is a little bit better. Therefore it can be said that the modified volumetric–reaction model beast fits the gasification in the present study.

Influence of operating variables

The effect of steam partial pressure on char conversion of steam gasification has been studied and the result is shown in Fig. 3. Steam pressures from 0.3 to 0.9 atm were applied for the steam gasification of all the coal char at 900℃. These plots show that the chars reacted rapidly in the early stage of reaction for all operating conditions and the char conversion slowed down as time went further. The carbon conversion obtained in a same reaction time interval increases when the partial pressure of steam increases from 0.3 to 0.9 atm. That is, the reaction time needed to achieve a given conversion becomes shorter with increasing steam partial pressure. This result indicates that higher partial pressure of steam favors the gasification reaction.

The diffusion resistance of reactant gas through the char sample might become important when reaction takes place at high temperatures, then this can cause a decrease in the reaction rate. On the other hand, higher temperature may cause an enlargement of pore in solid particles which could accelerate the reaction rate. The previous study with the same thermobalance reactor (1) showed that the measured char reactivity is not much affected by sample mass in the range of 0.3 ~ 0.9g.

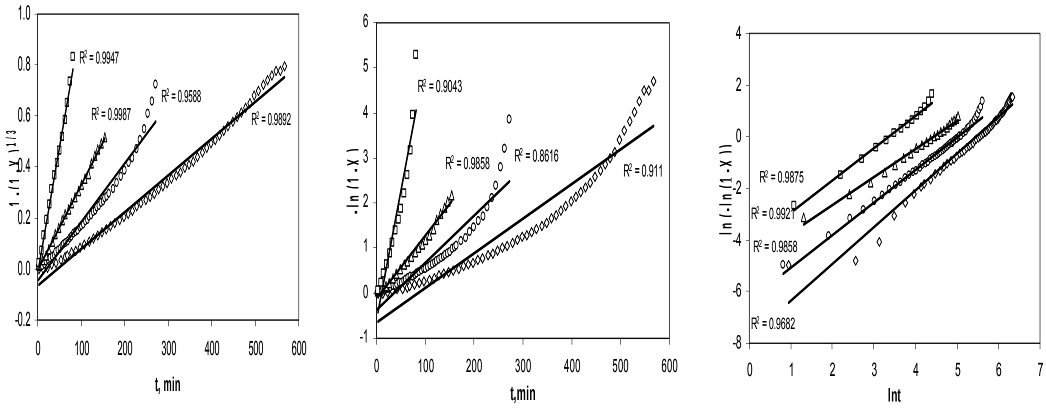

Figure 2. Conversion vs. time based on the modified volumetric-reaction model.

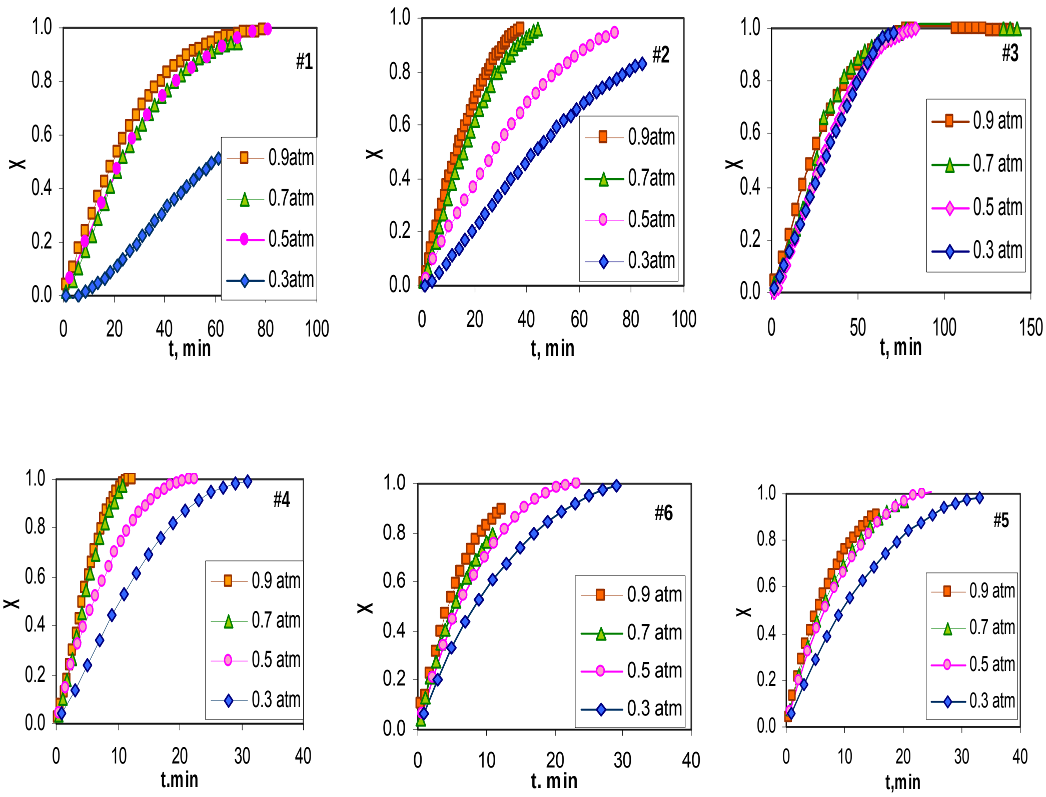

Figure 3. Effect of steam pressure on the gasification of chars at 900℃

Influence of coal type

The effect of coal type on the carbon conversion of steam gasification has been studied. It can be seen that the three lignite coal chars have much higher gasification reactivity than the three bituminous coal chars. This fact is because of their different coal ranks. The degree of aromatization in the coal structure increases with the increase in the rank of coal and the complexity of the aromatization decide the gasification rate.

The reactivity order among the three lignite chars depends on the gasification temperature. However, not a strong order of reactivity was found. In case of bituminous chars, the specific reaction rate of bituminous char#1 is low comparing to char#2 and char#3. Although the difference of reaction rate between char#2 and char#3 are not large, the specific reaction rate of #2 is relatively higher than that of #3 at the beginning of reaction especially at high partial pressure of steam, 0.7 and 0.7 atm.

Activation energy

Activation energy calculated in the Arrhenius plot, Fig. 4, for the steam gasification of Taldivisky char is found to be 53.57kJ/mol and the pre-exponential factor is $2.13\times10^{2}h^{-1}$. While the activation energy and pre-exponential factor of chars from Felix char, Flame S.A char were found to be 111.82kJ/mol, 91.05kJ/mol and $1.87\times10^{5}h^{-1}$, $2.28\times10^{4}h^{-1}$, respectively. No obvious difference of the six coal chars in their activation energy was found. On the other hand, the activation energy for the coal-char was reported to be 99.3kJ/mol in Jang's work (5). Lee (6) reported the activation energy of 51.1kJ/mol from the gasification of waste tire at 750 - 900℃ and steam pressure of 25 - 61 kPa. Kayembe and Pulsifer (7) showed activation energy of 60 - 310 kJ/mol for steam gasification of coal. The above E values from the literature tell that the activation energies of chars from the six coals are reasonable values and they can be available feed material for gasification.

Reaction order

The effect of partial pressure of steam on the average reaction rate of steam gasification of Taldivisky coal, Felix coal, Jembayan coal, Roto-South coal and STX has been made in this study. The average reaction rate was found to be proportional to the partial pressure of steam. From the slope of the log-log plot of k vs. steam partial pressure, the reaction order for Taldivisky char, Felix char, Jembayan coal, Roto-South coal and STX coal were evaluated to be 1.16, 0.93, 0.16, 1.00, 0.39 and 0.52 respectively. The order of 0.96 was reported from the gasification of Australian sub-bituminous coal char at 850℃ (6) and the order of 0.87 from coal gasification at 1000℃ (8). Therefore the reaction orders for the Taldivisky coal and Felix coal, Jembayan coal, Roto-South coal and STX coal determined in this experiment seem to be reasonable. The reaction rates of steam gasification of the char samples can be expressed by the following equations:

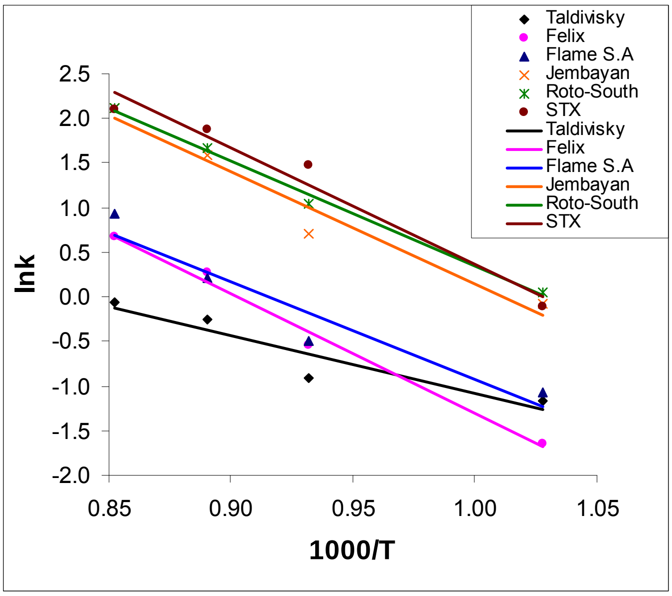

Figure 4: Arrhenius plot for the steam gasification of various low rank coal chars at P_{H2O}=0.5atm.

$$\frac{dX}{dt} = (2.13\times10^{2})\exp(-\frac{53570}{RT})(P_{H_2O})^{1.16}(1-X) \quad \text{for Taldivisky coal}$$

$$\frac{dX}{dt} = (1.87\times10^{5})\exp(-\frac{111820}{RT})(P_{H_2O})^{0.93}(1-X) \quad \text{for Felix coal}$$

$$\frac{dX}{dt} = (2.28\times10^{4})\exp(-\frac{91050}{RT})(P_{H_2O})^{0.16}(1-X) \quad \text{for Flame S.A coal}$$

$$\frac{dX}{dt} = (3.46\times10^{5})\exp(-\frac{104880}{RT})(P_{H_2O})^{1.00}(1-X) \quad \text{for Jembayan coal}$$

$$\frac{dX}{dt} = (1.88\times10^{5})\exp(-\frac{98160}{RT})(P_{H_2O})^{0.39}(1-X) \quad \text{for Roto-South coal}$$

$$\frac{dX}{dt} = (6.50\times10^{5})\exp(-\frac{108240}{RT})(P_{H_2O})^{0.52}(1-X) \quad \text{for STX coal}$$

The composition of product gas in fluidized bed

A low rank coal have been gasified with steam in a fluidized bed reactor, and the effect of partial pressure of steam on the composition of product gas was shown in Fig. 5. It can be noticed that hydrogen produced is higher than carbon monoxide for all fuel. This may due to the occurrence of some extent of water gas shift reaction at the exit section of apparatus like cyclone or exit wall. Anthracite provided relatively high concentration of calorific gases and it showed LHV of 10.0 MJ/m^3 at T=900 C and at partial pressure of steam of 95%. Also it can be known in Fig. 5 that the concentrations of each gas steadily increase with an increase in partial pressure of steam. The maximum concentration of H_2 and CO are 25.8 and 13.6% for pet-coke, and those values are 44.5 and 27.2% for anthracite, and 34.0, 20.5% for lignite.

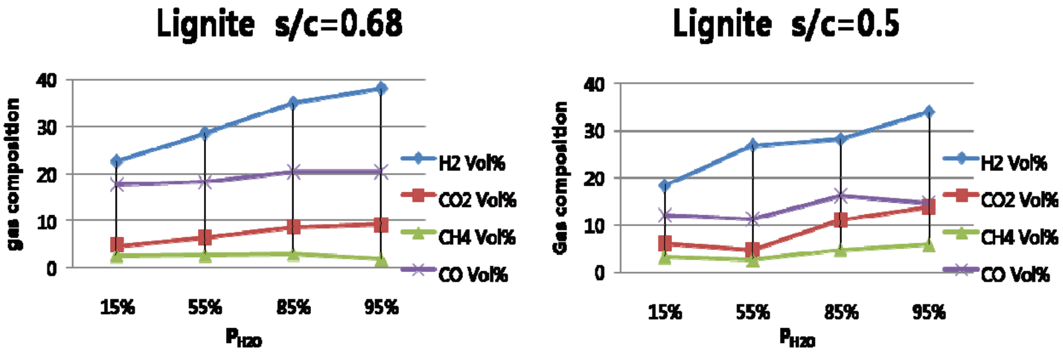

Figure 5. Effect of partial pressure on the composition of product gas for the steam gasification of Lignite coal (Temp.=900°C, S/C : steam to carbon mass ratio)

CONCLUSIONS

The kinetics information of the steam gasification of chars from six low rank coals has been obtained. The experimental results tell that high temperature and high partial pressure of steam increase the gasification rate of the chars. The modified volumetric reaction model showed the best prediction performance thus that model was applied to evaluate the kinetic parameters. The activation energy for the steam gasification of chars from Taldivisky coal, Felix coal, Flame S.A coal Jembayan coal, Roto-South coal and STX coal were determined to be 53.6, 111.8, 91.0, 104.9, 98.2 and 108.2kJ/mol respectively with data at steam pressure of 0.5 atm. The proposed reaction rate expression can be used for designing large scale gasification processes. The gasification of a bituminous coal in a fluidized bed showed that the concentration of most gaseous species increased with an increase in reaction temperature. The product syngas from the gasification of low rank fuel were composed of H_2(20-35%), CO(10-20%), CO_2(4-14%), CH_4(1-6%), and the heating value of the product gas was about 7,000kJ/m^3 at the employed experimental conditions.

ACKNOWLEDGMENT

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