

The characteristics of steam gasification of biomass and waste filter carbon

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Abstract—The carbon in a waste filter for water purification may be a new source of energy. The char of waste filter carbon and the char of wood chip have been gasified with steam in a thermobalance reactor under atmospheric pressure. The effect of gasification temperature (700-850 °C) and partial pressure of steam (0.3-0.9 atm) on the gasification rate has been investigated. Several gas-solid reaction models have been compared for their prediction ability of the gasification reaction behavior. The modified volumetric reaction model was used to evaluate kinetic data. The gasification rate of waste filter carbon has been compared with the rates of coal and wood chip biomass. The activation energies of filter carbon and wood chip were determined to be 89.1 and 171.4 kJ/mol, respectively. The apparent reaction rate equation for waste filter carbon has been presented.

Key words: Steam Gasification, Thermobalance, Kinetics, Filter Carbon, Wood Chip

INTRODUCTION

The energy crisis and environmental pollution caused by the excessive combustion of fossil fuels have forced a move to alternate renewable energy. Biomass, which is very important because of the large amount produced every year, is usually composed of cellulose, hemicellulose and lignin, same as other biomass. Most of them have been used to get heat in a low-efficiency way of combustion. The worldwide consumption of wood reaches 3.28 billion m³ in 1999 while the consumption for each person is 0.55 m³ per year (U.S. Census Bureau 2000b, "1999 world population estimates"; FAO 2001 "1999 world round wood consumption estimates"). However combustion provides much carbon dioxide.

Gasification technology can be used to get more fuel gas or for synthetic gas with low pollution problem. Gasification can be classified depending on the gasifying agent: air, steam, steam-oxygen, air-steam, O₂-enriched air, etc. Biomass air gasification seems to have feasible applications and has been developed actively for industrial applications. These applications even include food waste treatment [1]. However, this technology produces a gas with a low heating value (4-6 MJ/m³) and 8-14 vol% H₂ content only [2]. Biomass oxygen-rich air gasification is one effective way of producing medium heating value (MHV) gas but it is difficult to popularize. De Groot and Shafizadeh [3] gasified the chars from cotton wood and Douglas fir under carbon dioxide or steam atmospheres, and they found that in the case of steam, lower activation energy values were sufficient for the same conversions. Delgado et al. [4] reported that fluidized bed steam-gasification processes are also capable

of producing MHV (10-16 MJ/m³) gas with 30-60% H₂ content. Thus, steam was chosen as the reactant for gasification in our research.

A considerable amount of waste wood is abandoned from many industrial plants and city garbage, so waste wood should be a great resource for renewable energy production. On the other hand, many families in Korea use individual purification units for drinking water; thus quite a large amount of used filter carbon is released every year. These waste filters might be good fuel for a gasification process as carbon filters mainly consist of carbon, as will be seen in this study. For the design of a large scale gasification process for biomass of waste wood and waste filter carbon, the kinetic information of steam gasification should be obtained. The gasification reaction of biomass char with steam is:



Table 1. Ultimate analyses and proximate analyses of filter carbon and wood chip

| | Filter carbon | Wood chip |
|-------------------------|---------------|-----------|
| Ultimate analysis, wt% | | |
| Carbon | 81.27 | 46.53 |
| Hydrogen | 2.17 | 5.75 |
| Nitrogen | 0.3 | 0.25 |
| Sulfur | 0.66 | 0.11 |
| Oxygen | 4.42 | 43.51 |
| Proximate analysis, wt% | | |
| Moisture | 15.75 | 21.67 |
| Volatile | 4.99 | 60.14 |
| Fixed carbon | 70.56 | 3.85 |
| Ash | 8.70 | 14.34 |
| HHV**, kcal/kg | | 4130 |

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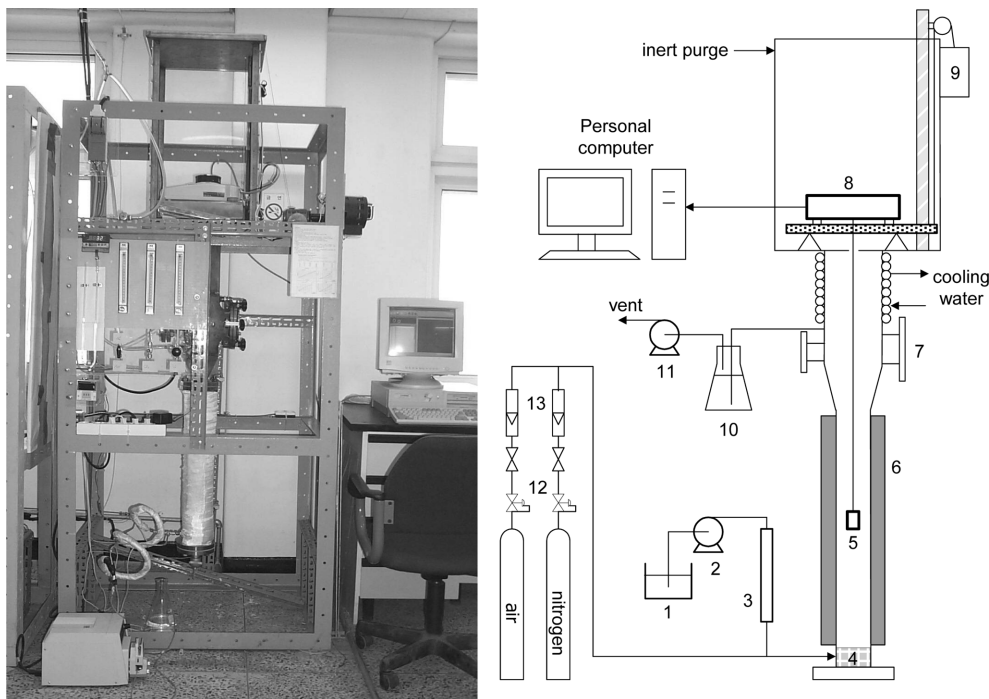


Fig. 1. Schematic diagram of thermobalance reactor.

- | | | | |
|--------------------|-----------------------|--------------------------------|----------------|
| 1. Distilled water | 5. Sample basket | 9. DC motor and winch assembly | 13. Flow meter |
| 2. Micro pump | 6. Electric heater | 10. Cold trap | |
| 3. Steam generator | 7. Hatch | 11. Vacuum pump | |
| 4. Gas preheater | 8. Electrical balance | 12. Gas regulator | |

EXPERIMENTAL

1. Materials

The ultimate analyses and proximate analyses of filter carbon and wood chip samples are presented in Table 1. It can be noticed that the carbon content is quite high, higher than 80%, whereas that of oxygen is less than 5% for filter carbon, which is a very small value compared to 43.5% for wood chips. The carbon content and oxygen content of wood chip represent the proper value from biomass. The proximate analysis shows that filter carbon has little volatile content, whereas the volatile matter of wood chips is over 60%.

2. Experimental Equipment

A photo and schematic diagram of the thermobalance reactor used in this study are shown together in Fig. 1. The main part of the thermobalance reactor is a 0.055-m i.d. \times 1.0-m-high stainless-steel tube equipped with 3 kW external electrical heater. The sample basket, which was made of stainless-steel mesh, was suspended from an electronic balance (Mettler Toledo) and the mass signal at the balance was transferred to a personal computer. Also, the change of mass is indicated as a dotted curve on the monitor. The temperature of the thermobalance was controlled by using a K-type thermocouple located 5 mm below the sample basket. Nitrogen was fed from the bottom of the thermobalance. The steam was produced from an electric steam generator that is a 1/8" copper tube of 1.0 m length on which a flexible electrical heating wire was coiled. The flow rate of steam was controlled by a micro-pump.

All the experiments were carried out with some amount of N_2 gas fed in the thermobalance in advance. When the reactor was heated

to the desired reaction temperature under nitrogen flow, the sample was placed in the sample basket through the hatch and the sample basket was moved down to the center of the reactor by using a motor-driven winch. There was an initial mass loss rapidly due to the evolution of moisture and volatile matter from the sample within several minutes. After this initial mass loss, the mass of sample became constant and then a mixture of steam and N_2 was introduced into the reactor for the gasification of the sample char. During the gasification, the variation of the sample mass was recorded continually every 3 seconds. When the sample mass became nearly constant again, which means the process of gasification was finished, the gaseous reactant was switched to air to burn the residual carbon out. The content of ash then could be determined. During the process of steam gasification, the carbon conversion is defined as:

$$X = \frac{W_0 - W}{W_0 - W_{ash}} \quad (1)$$

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 .

RESULTS AND DISCUSSIONS

1. Gas-solids Reaction Models

During the gasification process, structural changes should be taken into account. So different gas-solid reaction models should be applied to analyze the gasification rate of char and evaluate the reactivity quantitatively. Three different models, which are shrinking-core mod-

el, volumetric-reaction model and modified volumetric-reaction model, were applied to interpret the conversion data.

The time-conversion equation of shrinking-core model at the chemical reaction controlled regime which was given by Wen [5] is shown as below:

$$\psi/t = 1 - (1-X)^{1/3} \quad (2)$$

Ishida and Wen [6] proposed a volumetric-reaction model which assumes uniform gas diffusion in the entire particles and simplifies the heterogeneous gas-solid reaction. The model gives the time-conversion equation as:

$$\Omega t = -\ln(1-X) \quad (3)$$

The modified volumetric-reaction model which was proposed by Kasaoka et al. [7] is based in the volumetric-reaction model, but the apparent constant rate changes with solid conversion as the gasification reaction proceeds. The equation is given as below:

$$\alpha t^\beta = -\ln(1-X) \quad (4)$$

From Eq. (4) we can get that:

$$\beta \ln t = \ln[-\ln(1-X)] - \ln \alpha \quad (5)$$

Where α and β are 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:

$$k(X) = \frac{1}{1-X} \cdot \frac{dX}{dt} \quad (6)$$

By inserting Eq. (4) we can get:

$$k(X) = \alpha^{1/\beta} \cdot \beta [-\ln(1-X)]^{\beta-1/\beta} \quad (7)$$

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

$$k = \int_0^1 k(X) dX \quad (8)$$

2. Influence of Operating Variables

The gasification rate can be influenced by the reaction tempera-

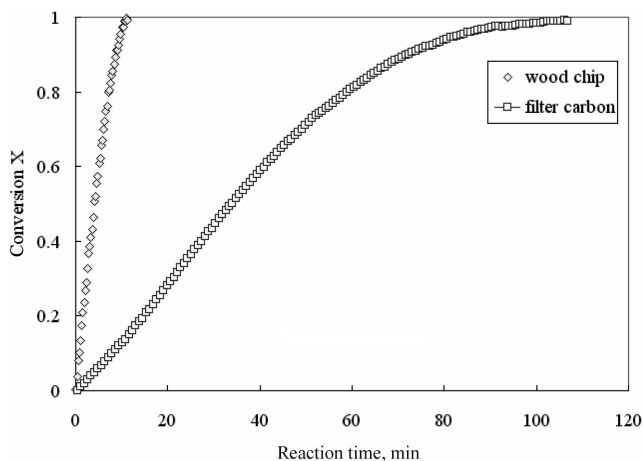


Fig. 2. Comparison of gasification rate of filter carbon and wood chip ($T=850^\circ\text{C}$, $P_{H_2O}=0.7\text{ atm}$).

ture and reactant concentration. A comparison of the gasification rate between filter carbon and wood chip has been made in Fig. 2. This plot shows the conversion behavior with reaction time. It can be seen that the time for carbon conversion to reach almost 1.0 (completion of gasification) showed a big difference between the two samples. The filter carbon needs a much longer time to reach $X=1$ than wood chip does. Thus the reaction rate of filter carbon is much slower compared to wood chip.

In this study, four different temperatures, 700, 750, 800 and 850°C , were chosen to study the effect of reaction temperature on the gasification rate. Fig. 3 shows the effect of temperature on filter carbon when partial pressure of steam is 0.5 atm. It can be seen clearly that higher temperature brings higher conversion and higher reaction rate.

The effect of steam partial pressure on carbon conversion of steam gasification is shown in Fig. 4. Steam pressures of 0.3 to 0.9 atm were applied for the steam gasification of filter carbon at 850°C . This plot shows high conversion rate in the beginning of reaction for all operating conditions, and the conversion slows down as time goes further. The values of X did not change much with the increase of partial pressure of steam increase from 0.3 to 0.9 atm. But the reaction time to reach $X=1$ changed considerably with increasing

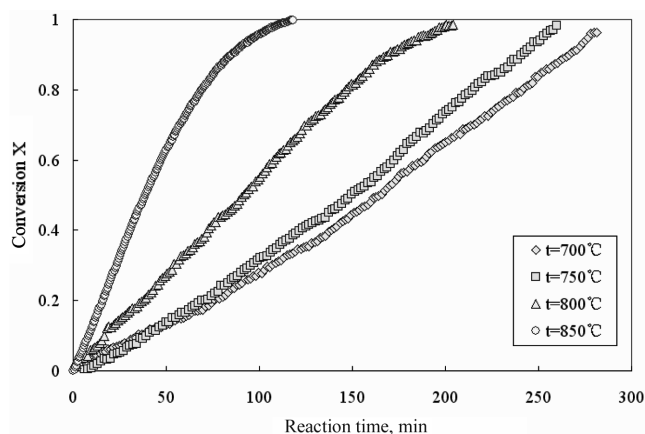


Fig. 3. Effect of temperature on the gasification rate of filter carbon ($P_{H_2O}=0.5\text{ atm}$).

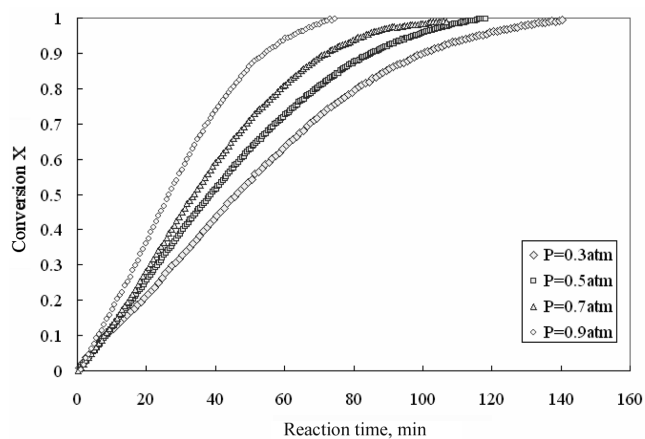


Fig. 4. Effect of steam pressure on the gasification of filter carbon at 850°C .

partial pressure of steam. When the steam partial pressure goes up, the reaction rate becomes high and reaction time for $X=1$ becomes shorter. Above results tell that the gasification reaction of filter carbon and wood chip with steam favors high temperature and high partial pressure of steam. It shows that the operating temperature and steam partial pressure do not affect the final conversion much because most conversion finally reached near one.

3. Comparison of the Gas-solids Reaction Models

To choose the best model to analyze the kinetic parameters, three different models proposed in the literature were applied to the experimental data from this study. To determine how well 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 filter carbon at steam pressure of 0.5 atm were selected. The relationship between $[-\ln(1-X)]$ and reaction time t for volumetric-reaction model at temperature of 700–850 °C is shown in Fig. 5. And the relationship between $\ln[-\ln(1-X)]$ and $\ln t$ for modified volumetric-reaction model is shown in Fig. 6. Also, the relationship between $[1-(1-X)^{1/3}]$ and t for the shrinking-core model is shown in Fig. 7. Because the model equation can be expressed in a linear form, the linearity of the conversion data in each plot gives information about the fitness of the model

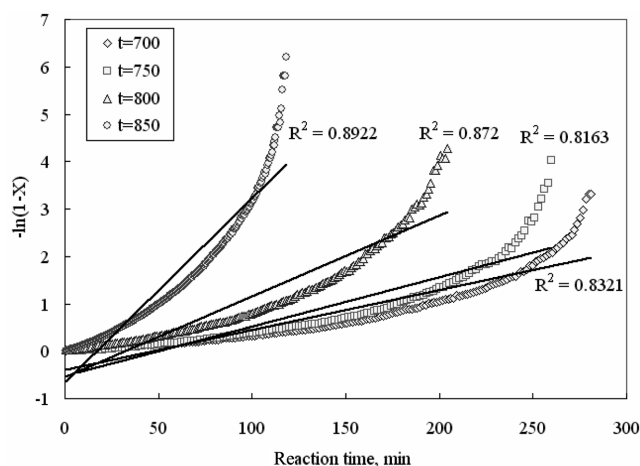


Fig. 5. Conversion vs. time based on the volume-reaction model.

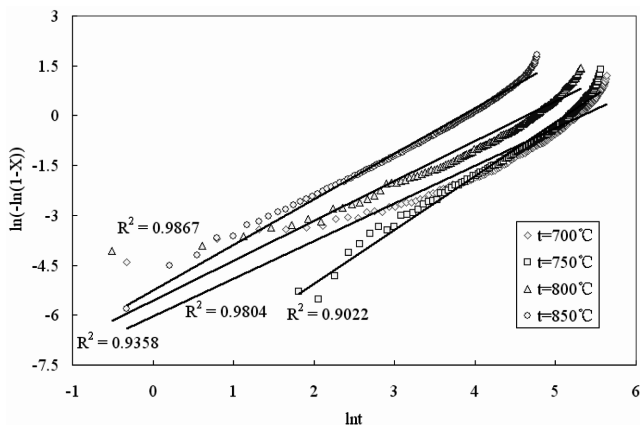


Fig. 6. Conversion vs. time based on the modified volume-reaction model.

el to the reaction behavior through the value of R^2 . That value of R^2 comes from the trend line and it is presented within the plots. If the value of R^2 is close to 1 for a model, that means the model fits the experiment perfectly. On the contrary, if the value of R^2 is far from, that means the model does not fit the experiment data. The plots for these models should cross the origin. But it should be noted that the linearity in Fig. 6 which is based on Eq. (5) does not cross the origin, for the expression of the equation has been changed to logarithmic form.

The plots of Fig. 5 to Fig. 7 tell that all the models fit the experimental data well. However, the value of R^2 for the volumetric-reaction model is around 0.8, which is not good enough. Both of the R^2 for shrinking-core model and modified volumetric-reaction model are good as 0.9. The value for modified volumetric-reaction model even reaches 0.99 at high temperatures. The appearance of the above plots tells that the modified volumetric-reaction model shows better appearance compared to the shrinking-core model. Therefore, it can be said that the modified volumetric-reaction model best fits the gasification data in the present study.

4. Activation Energy

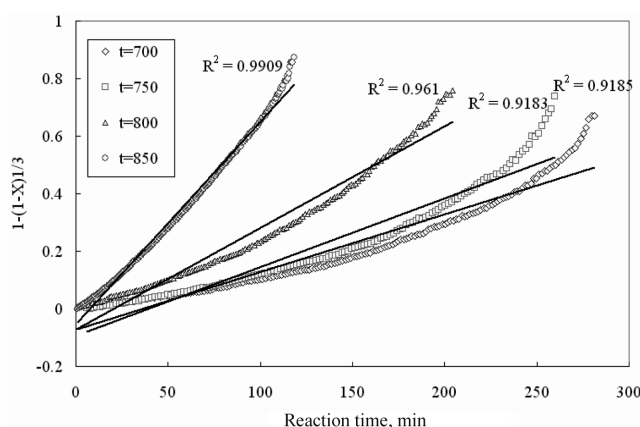


Fig. 7. Conversion vs. time based on the shrinking-core model.

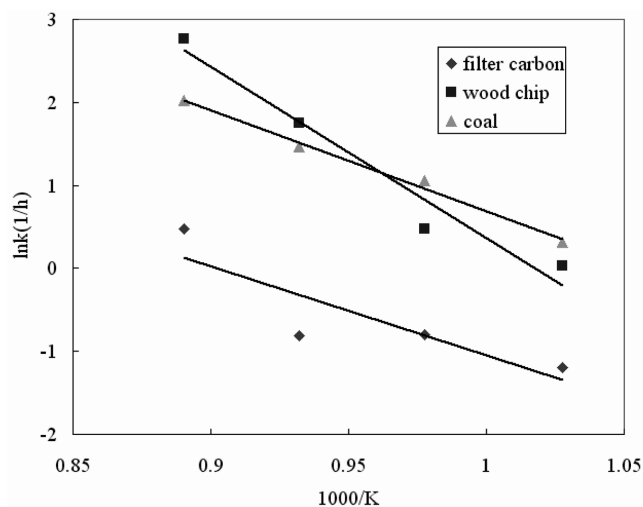


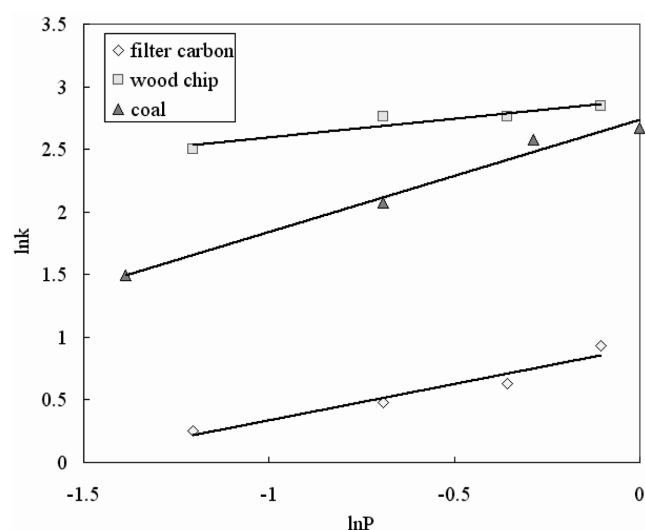
Fig. 8. Arrhenius plot of the average reaction rate for steam gasification of filter carbon, wood chip, and bituminous coal with $P_{H_2O}=0.5$ atm.

Table 2. Kinetic parameters for gasification of filter carbon and wood chip ($P_{H_2O}=0.5$ atm)

| Partial pressure of steam: 0.5 atm | | | | | | |
|------------------------------------|----------------|------|------|------|------------|---------------------|
| Sample | k (h^{-1}) | | | | E (kJ/mol) | k_0 (h^{-1}) |
| Temperature ($^{\circ}C$) | 700 | 750 | 800 | 850 | | |
| Filter carbon | 0.3 | 0.45 | 1.44 | 1.61 | 89.1 | 12.94×10^8 |
| Wood chip | 1.02 | 1.61 | 5.77 | 15.9 | 171.4 | 15.93×10^3 |

Among the three tested models, the modified volumetric reaction model has been proved to be the best one to predict the conversion behavior. So the reactivity (average reaction rate) of the sample was calculated based on Eqs. (7) and (8). Arrhenius plots for the steam gasification of filter carbon, wood chip and bituminous coal at steam pressure of 0.5 atm are presented in Fig. 8. The data of coal in the previous study [9] is shown together in this plot as a reference to confirm that the data in this study are reasonable. The activation energy can be determined from the slope of the straight line from linear regression of the average reaction rates. The data in the plot show good fitness to the linear trend line, although filter carbon somewhat shows scattering. The reactivity of filter carbon was found to be much lower than that of wood chip.

The reactivity of the samples at various conditions is calculated based on the conversion plot and summarized in Table 2. Activation energy for the steam gasification of filter carbon is found to be 89.1 kJ/mol and the pre-exponential factor is $12.94 \times 10^8 h^{-1}$. Whereas, the activation energy and pre-exponential factor of wood chip were found as 171.4 kJ/mol and $15.93 \times 10^3 h^{-1}$. It can be said that the gasification of filter carbon is relatively easy as its activation energy is lower than wood chip. The activation energy for bituminous coal shown in the plot was 101 kJ/mol. Lee [9] reported the activation energy of 51.1 kJ/mol from the gasification of waste tires at 750-900 $^{\circ}C$ and steam pressure of 25-61 kPa. Kayembe and Pulsifer [10] showed activation energy of 60-310 kJ/mol for steam gasification of coal. The above E values from literature tell that the ac-

**Fig. 9. The effect of partial pressure of steam on the average reaction rate for steam gasification of filter carbon, wood chip, and bituminous coal at 850 $^{\circ}C$.**

tivation energies of filter carbon and wood chip are reasonable values and they are available feed material for gasification.

5. Reaction Order

The effect of partial pressure of steam on the average reaction rate of steam gasification of filter carbon, wood chip, and bituminous coal is shown together in Fig. 9. 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 filter carbon was found to be 0.58 at 850 $^{\circ}C$. The reaction order for wood chip was found to be 0.3.

An order of 0.96 was reported from the gasification of Australian sub-bituminous coal-char at 850 $^{\circ}C$ [11] and of 0.87 from coal gasification at 1,000 $^{\circ}C$ [12]. The gasification of waste tire scrap presented an order of 0.78 [9]. And the CO_2 gasification of tire gave 0.68 [13]. Therefore, the reaction order for the filter carbon and wood chip determined in this experiment are not so high and are reasonable compared to other fuel materials. The reaction rates of steam gasification of the samples can be expressed by the following kinetic equations, respectively:

$$\frac{dX}{dt} = (12.94 \times 10^8) \exp\left(-\frac{89110}{RT}\right) (P_{H_2O})^{0.58} (1-X) \quad \text{For filter carbon (9)}$$

$$\frac{dX}{dt} = (15.93 \times 10^3) \exp\left(-\frac{171400}{RT}\right) (P_{H_2O})^{0.3} (1-X) \quad \text{For wood chip (10)}$$

CONCLUSIONS

The effects of operating condition on the steam gasification of filter carbon and wood chip have been investigated in a thermobalance. The result tells that both a higher temperature and higher partial pressure of steam enhance the gasification rate of the solid fuels. The modified volumetric reaction model predicts the conversion behavior best among the three reaction models tested in this study. The gasification rate of filter carbon was much lower than that of wood chip. The activation energies of filter carbon and wood chip were determined to be 89.1 and 171.4 kJ/mol, respectively, with data at a steam pressure of 0.5 atm based on the modified volumetric reaction model. The reaction orders were found to be 0.58 and 0.3 for filter carbon and wood chip. The expressions of apparent gasification rate of filter carbon and wood chip are presented for the design of biomass gasification process.

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NOMENCLATURE

E : activation energy [kJ/mol]
 k_0 : pre-exponential factor [$1/min$]
 $k(X)$: specific reaction rate based on the remaining carbon in the

- solid [1/h]
 k : average reaction rate defined by Eq. (8) [1/h]
 P_{H_2O} : partial pressure of water [atm]
 R : gas constant [8.314 J/mol K]
 T : reaction temperature [K]
 t : reaction time [min]
 W : sample mass at certain time [g]
 W_{ash} : mass of ash [g]
 W_o : initial mass of char on dry base [g]
 X : carbon conversion [-]

Greek Letters

- α, β : constants in Eq. (4) [-]
 Ψ : constant in shrinking core model in Eq. (2) [1/min]

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