

## A reaction kinetic study of CO<sub>2</sub> gasification of petroleum coke, coals and mixture

Jin Woo Kook\*, In Seop Gwak\*, You Ra Gwak\*, Myung Won Seo\*\*, and See Hoon Lee\*,†

\*Department of Resources and Energy Engineering, Chonbuk National University, Jeonju 54896, Korea

\*\*Clean Fuel Department, KIER, Daejeon 34129, Korea

(Received 25 January 2017 • accepted 4 August 2017)

**Abstract**—Characteristics of Char-CO<sub>2</sub> gasification were compared in the temperature range of 1,100-1,400 °C using a thermogravimetric analyzer (TGA) for petroleum coke, coal chars and mixed fuels (Petroleum coke/coal ratios: 0, 0.25, 0.5, 0.75, 1). The results showed that reaction time decreased with increasing gasification temperature, BET surface area and alkali index of coal. Mixed fuels composed of petroleum coke/coal exhibited reduced activation energies. Modified volumetric reaction model and shrinking core model might be suitably matched with experimental data depending on coal type and petroleum coke/coal ratio. Rate equations were suggested by selecting gas-solid reaction rate models for each sample that could simulate CO<sub>2</sub> gasification behavior.

Keywords: Gasification, Coal, Petroleum Coke, Mixed Fuel, Kinetic

### INTRODUCTION

The need for clean energy is increasing worldwide, so gasification processes with pre-combustion CO<sub>2</sub> capture and sequestration and oxy-combustion processes with CO<sub>2</sub> recycling have been developed to minimize the cost of CO<sub>2</sub> capture and storage [1]. In gasification processes with oxidative gases such as oxygen, steam and carbon dioxide, various carbonaceous solid materials such as coal, biomass, petroleum coke and so on could be converted into numerous products which might be chemical substances such as ammonia, methanol, and synthetic natural gas, synthetic oil, and power.

In general, the gasification process in the gasifier is very complex and includes water evaporation, volatiles pyrolysis, combustion, volatiles gasification char gasification. Among these processes, char gasification is the controlling step because of its slower reaction rate [2]. Also, air (O<sub>2</sub>/N<sub>2</sub>) is substituted by pure oxygen mixed with recycled flue gas (mainly consisting of CO<sub>2</sub>) before injection into a combustor in oxy-combustion technologies. Therefore, CO<sub>2</sub> gasification reaction could vigorously happen in oxy-combustors, too. CO<sub>2</sub> gasification has been regarded as a potential technology to directly utilize greenhouse gas. The CO<sub>2</sub> gasification rate of chars is even lower than the steam gasification rate of chars, so char-CO<sub>2</sub> gasification rate is considered as the rate-determining step [4]. Therefore, a clear understanding of char-CO<sub>2</sub> kinetics is important for design and stable operation of gasifiers [5].

Co-gasification or Co-combustion of coal and other carbonaceous solid materials supplies a promising possibility for high thermal efficiency energy conversion, achievement of production economy, operational stability and friendly environmental technology [6]. Unlike coal and biomass, petroleum coke is a byproduct of the oil refining process, and the production of petroleum coke is expected to increase because the increasing demand of liquid fuels has

resulted in the increase of refineries in the world [7]. Petroleum coke contains 7-8 wt% of sulfur and is classified as toxic waste; however, the emphasis on eco-friendly energy conversion has increased attempts to establish petroleum coke as a valuable resource [8]. Representative plants using petroleum coke as gasification feedstock include Ube City CO Plant (Japan), Ube Ammonia Industry Co. Ltd. (Japan), Wabash River Energy Limited (USA), El Dorado IGCC Plant (USA) and Puertollano IGCC Plant (Spain). It is mainly used as fuel by mixing petroleum coke and coal [9].

Petroleum coke has a high heat quantity, is abundantly available, and is cheaper than coal. However, it includes low volatile matter and higher sulfur content as compared to coal. Heat quantity control and reduction of sulfur content can be supplemented by mixing petroleum coke with low grade coal, which has more volatile matter and a lower heat quantity [10-12].

By mixing with other carbonaceous solid materials, petroleum coke is increasingly applied in gasification processes, which produce hydrogen and carbon monoxide, the primary byproducts of the petrochemical industry [7,13,14]. To apply a mixed fuel composed of petroleum coke and coal to gasification, a stable supply of fuel is essential in addition to chemical kinetic interpretations, which are applied to reactor design, operating conditions, and gasification reaction interpretations [8,15,16].

Most preceding studies regarding the reaction of petroleum coke and mixed fuels have used entrained reactors and TGAs employing oxygen, steam, and other substances as gasifying agents. For example, Yoon et al. [8] studied the characteristics and the isothermal kinetics of combustion in the temperature range of 1,100-1,400 °C by using TGA for coal and petroleum coke mixtures. The activation energies of Yoon et al. [8] were calculated by using both a shrinking core model and a modified volumetric reaction model. Fierro et al. [10] investigated the effect of operation variables on gas production during co-gasification of coal with biomass and petroleum coke. They found that the temperature and oxygen concentration had the greatest influence on the final products and they observed a synergistic effect for blends of coal and petroleum coke. Huo et al. [13] studied CO<sub>2</sub> gasifi-

†To whom correspondence should be addressed.

E-mail: donald@jbnu.ac.kr

Copyright by The Korean Institute of Chemical Engineers.

**Table 1.** The ultimate, proximate, higher heating value, ash and bet surface area analysis of samples

| Sample                               | Ultimate analysis (wt%)<br>(as dried basis) |                                |                 |                                |        | Proximate analysis (wt%)<br>(as received basis) |                 |                   |              | HHV<br>(kcal/kg) |
|--------------------------------------|---|--------------------------------|-----------------|--------------------------------|--------|---|-----------------|-------------------|--------------|------------------|
|                                      | Nitrogen                                    | Carbon                         | Hydrogen        | Sulfur                         | Oxygen | Moisture  | Volatile matter | Ash               | Fixed carbon |                  |
| Pet coke                             | 1.1   | 87                             | 3.5             | 7.9                            | 0.6    | 1.4   | 10.3            | 0.3               | 88           | 8523             |
| White haven                          | 1.3   | 67.43                          | 4.46            | 0.78                           | 26.03  | 19.33   | 44.89           | 4.68              | 31.12        | 6627             |
| KPU                                  | 0.8   | 56.79                          | 5.34            | 0.06                           | 37.01  | 9.1   | 76.2            | 1.8               | 12.9         | 6570             |
| Ash analysis (wt%)                   | SiO <sub>2</sub>                            | Al <sub>2</sub> O <sub>3</sub> |                 | Fe <sub>2</sub> O <sub>3</sub> |        | CaO   | MgO             | Na <sub>2</sub> O |              | K <sub>2</sub> O |
| White haven                          | 56.44                                       | 31.96                          |                 | 4.52                           |        | 5.34  | 0.72            | 0.30              |              | 0.72             |
| KPU                                  | 36.99                                       | 20.99                          |                 | 8.06                           |        | 19.6  | 6.12            | 6.64              |              | 1.59             |
| BET surface area (m <sup>2</sup> /g) |   |                                | Original sample |                                |        |   |                 | Char              |              |                  |
| White haven                          |   |                                | 5.04            |                                |        |   |                 | 2.10              |              |                  |
| KPU                                  |   |                                | 0.82            |                                |        |   |                 | 24.91             |              |                  |

cation reaction of petroleum coke, coal, and biomass by using TGA and concluded that the crystalline structures were an important factor to evaluate gasification reactivities, and gasification rates were affected significantly by pore diffusion under conditions of high temperatures and large particle sizes. Jayaraman and Gokalp [14] concluded that temperature and particle size had the greatest influence on the gasification rate and final products and a synergistic effect was ascertained during the gasification of coal and petroleum coke mixture in steam ambience. Edreis et al. [16] studied the effect of mixed ratio of CO<sub>2</sub> gasification for mixture of sugar cane and petroleum coke by using TGA in temperature range of 970-1,190 °C. The kinetics of CO<sub>2</sub> gasification was calculated by using various gas-solid reaction models. Goyal et al. [17] modeled the co-gasification of coal and petroleum coke in a bubbling fluidized bed coal gasifier and reported that the increase in petroleum coke reduces the carbon conversion efficiency, but it increases the syngas production rate. Gong et al. [18] calculated activation energy of petroleum coke, wood chip, lignite, bituminous coal, and anthracite coal in steam gasification in temperature range of 600-800 °C by using MVRM.

In this study, petroleum coke, sub bituminous coal, and bituminous coal were selected and gasified with CO<sub>2</sub> under similar temperature conditions to entrained-flow gasifiers or oxy-pulverized combustion boilers using a TGA. Recently, interest in carbon dioxide gasification reaction has increased due to the development of gasifiers and oxy-combustion. Nonetheless, the number of studies regarding CO<sub>2</sub> gasification using mixed fuel is scant at higher temperature conditions, and substantially more studies are required for efficient energy utilization. Therefore, char-CO<sub>2</sub> gasification reaction characteristics for different mixed fuels (Petroleum coke/coal ratio: 0, 0.25, 0.5, 0.75, 1) between petroleum coke and coals were analyzed. Also, various kinetic models for mixed samples were used and the reaction rates of CO<sub>2</sub> gasification were determined using the most suitable kinetic model.

## EXPERIMENTAL

### 1. Samples Preparation

Samples used in experiments included petroleum coke from oil refinery company H, White Haven (WH) coal from Australia as

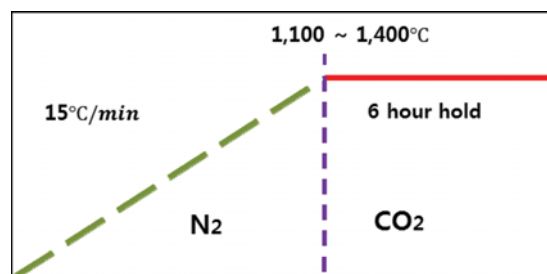
bituminous coal, and KPU from Indonesia as sub bituminous coal. Based on production method of char from Timpe et al. [19], char was produced by maintaining a constant temperature of 650 °C for 5 h after the nitrogen was injected at 50 mL/min for sufficient devolatilization. The char obtained through pyrolysis was separated using a sieve with a pore size less than 200 µm. According to Ballal et al. [20], there is rarely influence of diffusion in pore size less than 200 µm. The analysis result of the samples is shown in Table 1.

### 2. Experimental Apparatus

TGA was used to measure and compare the high temperature reactivity of char samples from petroleum coke, WH, and KPU. The TGA instrument used was the Labsys model from SETARAM of France and an electronic scale with an accuracy of 10<sup>-6</sup> g. The signals from the scale were sent to a computer through a program whereupon the weight changes were analyzed. The reactant gas was injected into the lower part and was emitted from the upper part. Samples were placed in the alumina crucible (30 mm I.D.×50 mm height) hanging within the reactor during the reaction. The thermocouple, which detects the reaction temperature inside the TGA, was placed next to the alumina crucible. The heating element, composed of graphite, was located at the center of the cylindrical TGA furnace, which was cooled by circulating water. All data were checked by the computer. The flow rate of the reactant gas flowing into the TGA was controlled with a flowmeter.

### 3. Experimental Method

Experiments regarding isothermal gasification were conducted at 1,100-1,400 °C to create an entrained gasifier environment, and

**Fig. 1.** Experiment of isothermal CO<sub>2</sub> gasification.

temperatures were raised at a heating rate of 15 °C/min after the nitrogen was injected at 30 mL/min, as shown in Fig. 1. Sample weight data were acquired for 6 h after the reactor reached the appropriate temperature and the nitrogen atmosphere was switched to carbon dioxide while the temperature was maintained. The weight of the alumina crucible was not considered during weight changes, so that only the change in sample weight was observed in all experiments. After the end of CO<sub>2</sub> gasification reaction, the system was cooled to room temperature by circulating water and nitrogen flow.

#### 4. Kinetic Analysis

The carbon conversion of char in gasification is defined in Eq. (1)

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

where  $W_0$  is the mass of the initial sample,  $W_{ash}$  is the mass of remaining ash, and  $W_t$  is the mass of sample at time  $t$ . The kinetic interpretation of gasification considered as a simple  $n^{\text{th}}$  reaction can be expressed as follows:

$$\frac{dX}{dt} = k(1-X)^n \quad (2)$$

where  $k$  is the reaction rate constant and  $n$  is the degree of reaction for solid reactants.  $k$  depends on temperature, and the temperature dependency of the reaction rate constant can be expressed as follows using the Arrhenius formula:

$$k = A \exp\left(\frac{E_a}{RT}\right) \quad (3)$$

where  $A$  is the frequency factor ( $\text{min}^{-1}$ ),  $E_a$  is the activation energy (kJ/mol),  $R$  is the gas constant ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ), and  $T$  is the absolute temperature (K). Eq. (3) is obtained by substituting Eq. (2) into Eq. (4), and the reaction characteristics of gasification can be analyzed by considering this equation as the basic reaction rate equation.

$$\frac{dX}{dt} = A(1-X)^n \exp\left(\frac{E_a}{RT}\right) \quad (4)$$

It is very difficult to accurately predict the degree of conversion in gas-solid reactions, and it is even more difficult to do so in reactions involving solids with gas pockets. Many researchers have suggested various gas-solid reaction rate models to simulate gasification or deduce reaction rate information [21-24].

The volumetric reaction model (VRM) simplifies the heterogeneous nature of the gas-char reaction by treating it as homogeneous and assumes that the inside and outside of char react uniformly in all possible places. As the reaction progresses, the size of the char is maintained while the density decreases. The reaction equation is as follows:

$$\frac{dX}{dt} = k(1-X), -\ln(1-X) = kt \quad (5)$$

The shrinking core model (SCM) assumes that the reactant gas begins on the char surface and progressively works its way inside to react at the surface of the non-reacted core. Hence, as the reaction progresses, the size of the char decreases. The reaction equation is as follows:

$$\frac{dX}{dt} = k(1-X)^{\frac{2}{3}}, 3\left[1 - (1-X)^{\frac{1}{3}}\right] = kt \quad (6)$$

The volumetric reaction model and shrinking core model assume that if the chemical reaction is the rate determining step, the transfer resistance inside the particle can be ignored. At high temperatures, however, the shrinking core model explains the experimental data more appropriately. This is because at high temperatures, due to the fast reaction rate, the gas diffusion into the particle is relatively slow, whereas at low temperatures, due to the slower reaction rate, the reactant diffuses into the pores of the sample particles faster.

The modified volumetric reaction model (MVRM) calculates the reaction rate on the basis of the time-dependent integral rate equation in a homogeneous reaction model based on the volumetric reaction model. It can be expressed as follows using the burn-off equation of the MVRM.

$$\alpha t^\beta = -\ln(1-X) \quad (7)$$

Here,  $\alpha$  and  $\beta$  can be obtained from the change in the conversion with time using the least square method, and are dimensionless constants related to the physiochemical properties, temperature, and gasifying agent of char. The natural log of Eq. (7) is given as Eq. (8).

$$\beta \ln t = \ln[-\ln(1-X)] - \ln \alpha \quad (8)$$

Gasification speed per fixed carbon mass remaining in the sample depends on the conversion and can be defined as the specific reaction rate, as expressed by Eq. (9);  $k$  is defined as shown below by integrating the gasification reaction rate  $k_s(X)$  the entire conversion rate range:

$$k(X) = \alpha^{\frac{1}{\beta}} \left[ -\ln(1-x) \right]^{\frac{\beta-1}{\beta}}, k = \int_0^1 k_s(X) dX \quad (9)$$

## RESULTS AND DISCUSSION

### 1. Comparison of Carbon Conversion

The carbon conversion results for the experiments conducted at 1,100-1,400 °C illustrate the CO<sub>2</sub> gasification reaction characteristics of petroleum coke, coal chars, and mixed fuel chars with petroleum coke/coal ratios of 0.25, 0.5, and 0.75, as shown in Fig. 2. Although the time required for the complete reaction was different, the carbon was completely converted in all cases. Furthermore, higher reaction temperatures led to faster char gasification reaction.

The carbon conversion of the original sample and mixed fuel composed of petroleum coke and coal is shown in Fig. 2. The petroleum coke required for CO<sub>2</sub> gasification was between 20-240 minutes as shown in section (a) of Fig. 2, which was significantly longer than that for WH and KPU. Section (b) and (c) of Figs. 2 show that WH finished reaction within 50 min, whereas, KPU completed reaction rapidly within 20 min.

Generally, the higher the water content, the lower the grade of coal is. Coal that has a high volatile content typically develops many pores in the char during devolatilization and has more active sites in the pores. It results in an increase of char reactivity [23]. This is consistent with the observation that when coal with a high volatile content, as shown in Table 1, undergoes pyrolysis, the BET surface area of its char is also great. KPU has high reactivity than WH due

to the high BET surface area.

In addition, Coal is affected by catalytic effects owing to the alkali elements in ash, although the catalytic effect is more minor than carbon structure such as coal rank. To quantify the catalytic effects of ash, Zhang et al. [23] proposed an alkali index, using Eq. (10) shown below:

$$\text{Alkali Index} = \text{ash}(\text{wt}\%) \times \frac{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} \quad (10)$$

The catalytic effects of the char-CO<sub>2</sub> gasification reaction were also identified in a preliminary study [10]. It is expected that KPU, which is most affected by catalytic effects owing to the alkali elements con-

tained in its ash, might lead to a quick gasification reaction, WH, which includes insufficient alkali elements, might show the slow reactivity as shown in Table 1. The alkali indexes of WH and KPU are calculated by 2.52, 4.2, respectively.

More than 210 min was required for the complete reaction of the 0.25 mixed fuel char composed of petroleum coke and WH at 1,100 °C, whereas the char-CO<sub>2</sub> gasification for the 0.25 mixed fuel char composed of petroleum coke and KPU was completed in less than 180 min. The reaction of the 0.5 mixed fuel char was completed in less than 220 min at 1,100 °C, confirming a faster reaction than that of the 0.75 mixed fuel char as shown in sections (c) and (d). Sections (f) and (g) show that gasification of the 0.5 mixed fuel

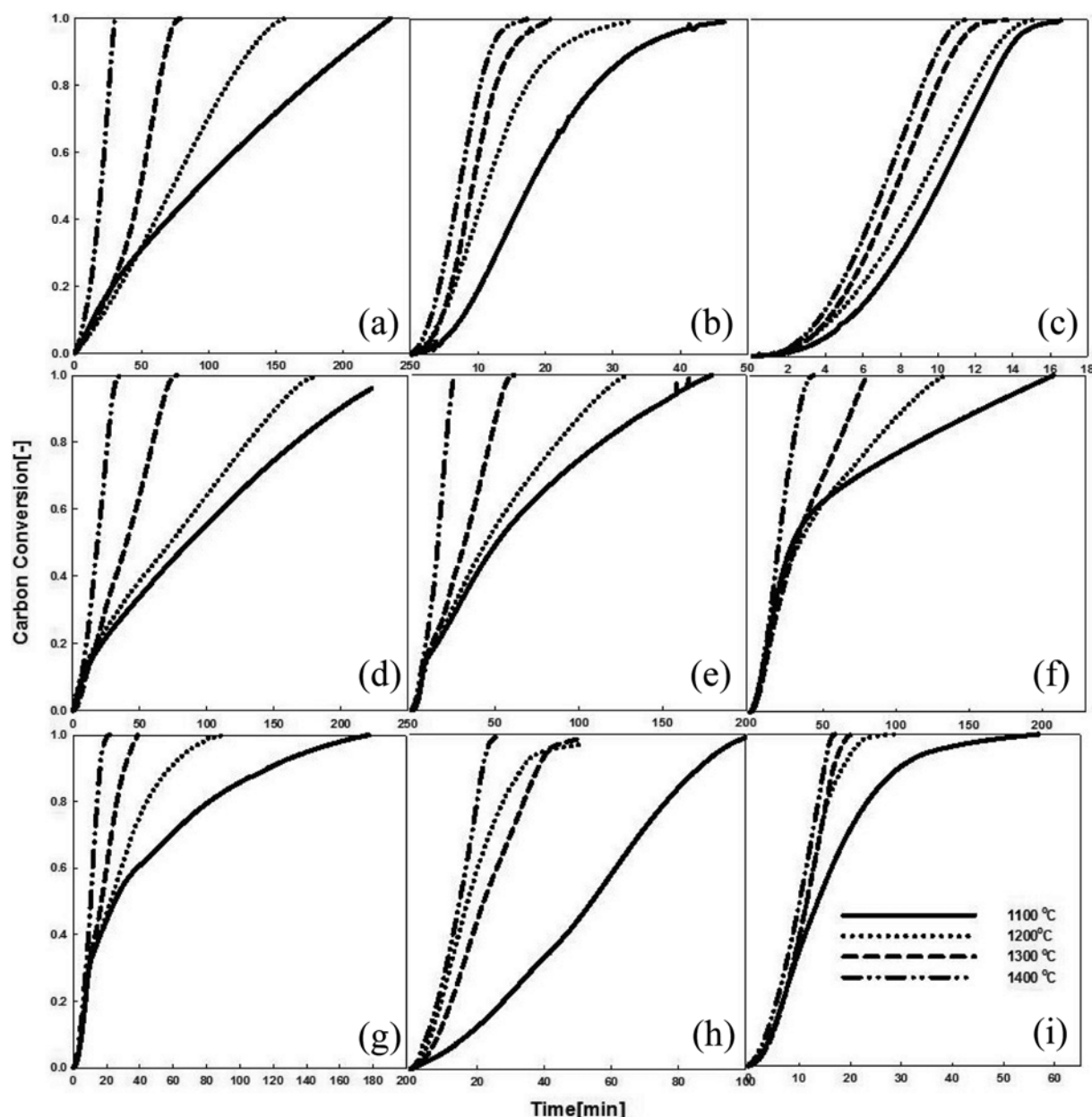


Fig. 2. Carbon conversion of CO<sub>2</sub> gasification of petroleum coke, coal, and mixed fuels with different compositions.

(a) Petroleum coke (b) WH (c) KPU (d) COKE-WH(0.25) (e) COKE-KPU(0.25) (f) COKE-WH(0.5) (g) COKE-KPU(0.5) (h) COKE-WH(0.75) (i) COKE-KPU(0.75)

chars was completed between 100–120 min above 1,200 °C, and in less than 1 h above 1,300 °C. At 1,100 °C, the 0.75 mixed fuel char took 100, 60 min for the mixed fuel chars composed of WH, in section (h) and (i) of Fig. 2 to reach a complete reaction. At 1,200 °C or above, the reaction times were required within 45 min and 30 min for WH, KPU respectively. Even in the case of mixed fuel, large reaction site and alkali content might contribute to reduction of reaction time.

## 2. Reactive Factor

In the gas-solid reaction model,  $R^2$  is the meaning of superior simulation in the gasification reaction. Figs. 3–5 show the results upon applying the three reaction models to  $\text{CO}_2$ -gasification reac-

tion at 1,100–1,400 °C.  $R^2$  was obtained from Figs. 3–5 by illustrating the trend line.

$R^2$  of petroleum coke, WH, KPU and mixed fuel is indicated on Table 2.  $R^2$  of petroleum coke, WH and KPU were calculated average 0.71, 0.9, and 0.65 in VRM, respectively. As in SCM,  $R^2$  was calculated on average 0.94, 0.98, and 0.85, respectively. In the case of MVRM,  $R^2$  indicated on average 0.95, 0.99, and 0.98 in MVRM, respectively. In the mixed fuel,  $R^2$  of pet-coke with WH(0.25), pet-coke with KPU(0.25), pet-coke with WH(0.5), pet-coke with KPU(0.5), pet-coke with WH(0.75) and pet-coke with KPU(0.75) were calculated on average 0.75, 0.73, 0.78, 0.83, 0.88, and 0.75 in VRM, respectively. In the SCM, mixed fuels were indicated on aver-

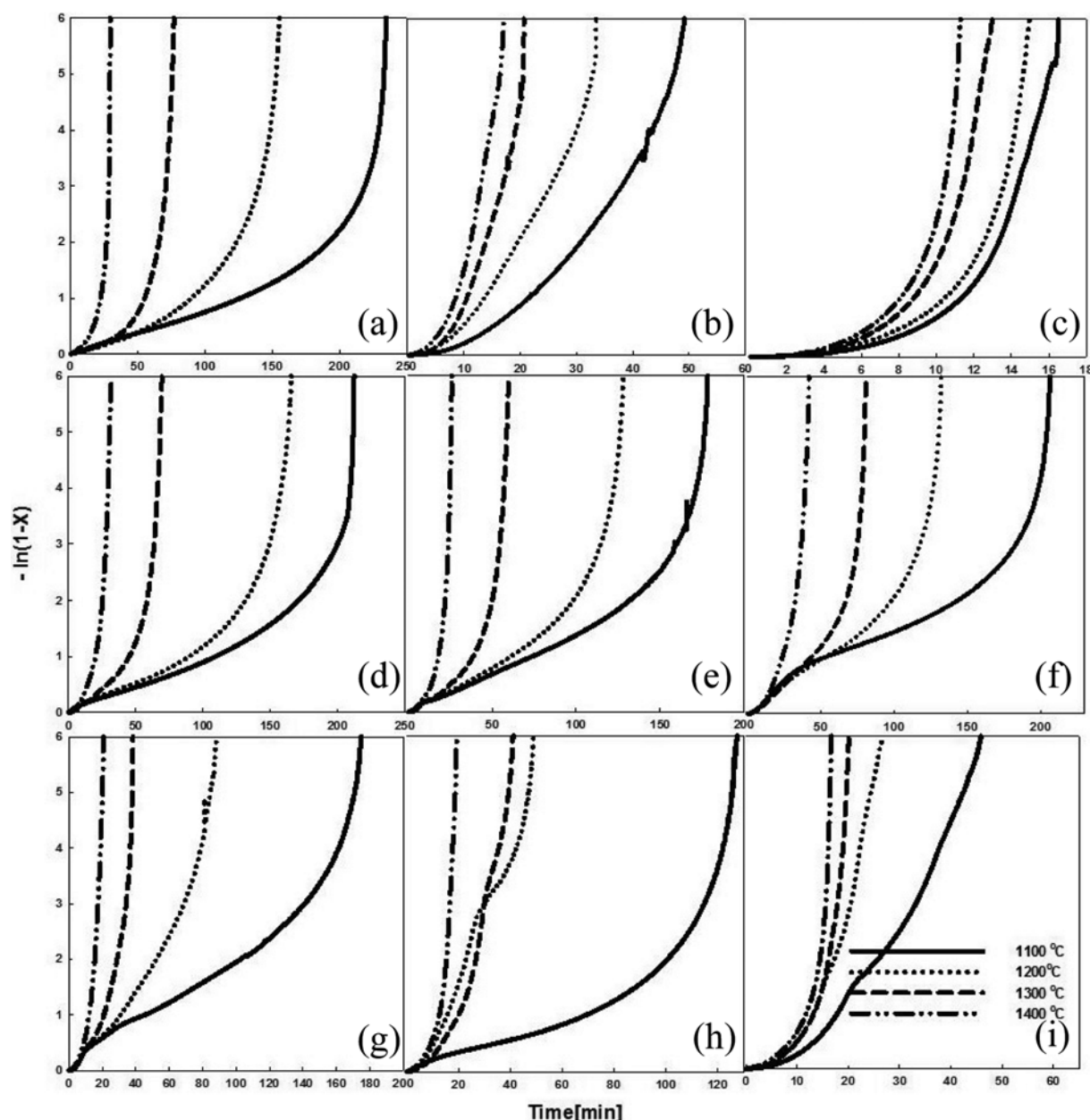


Fig. 3. Reactivity of  $\text{CO}_2$  gasification of petroleum coke, coal, and mixed fuels with different compositions-volumetric reaction model.

(a) Petroleum coke (b) WH (c) KPU (d) COKE-WH(0.25) (e) COKE-KPU(0.25) (f) COKE-WH(0.5) (g) COKE-KPU(0.5) (h) COKE-WH(0.75) (i) COKE-KPU(0.75)

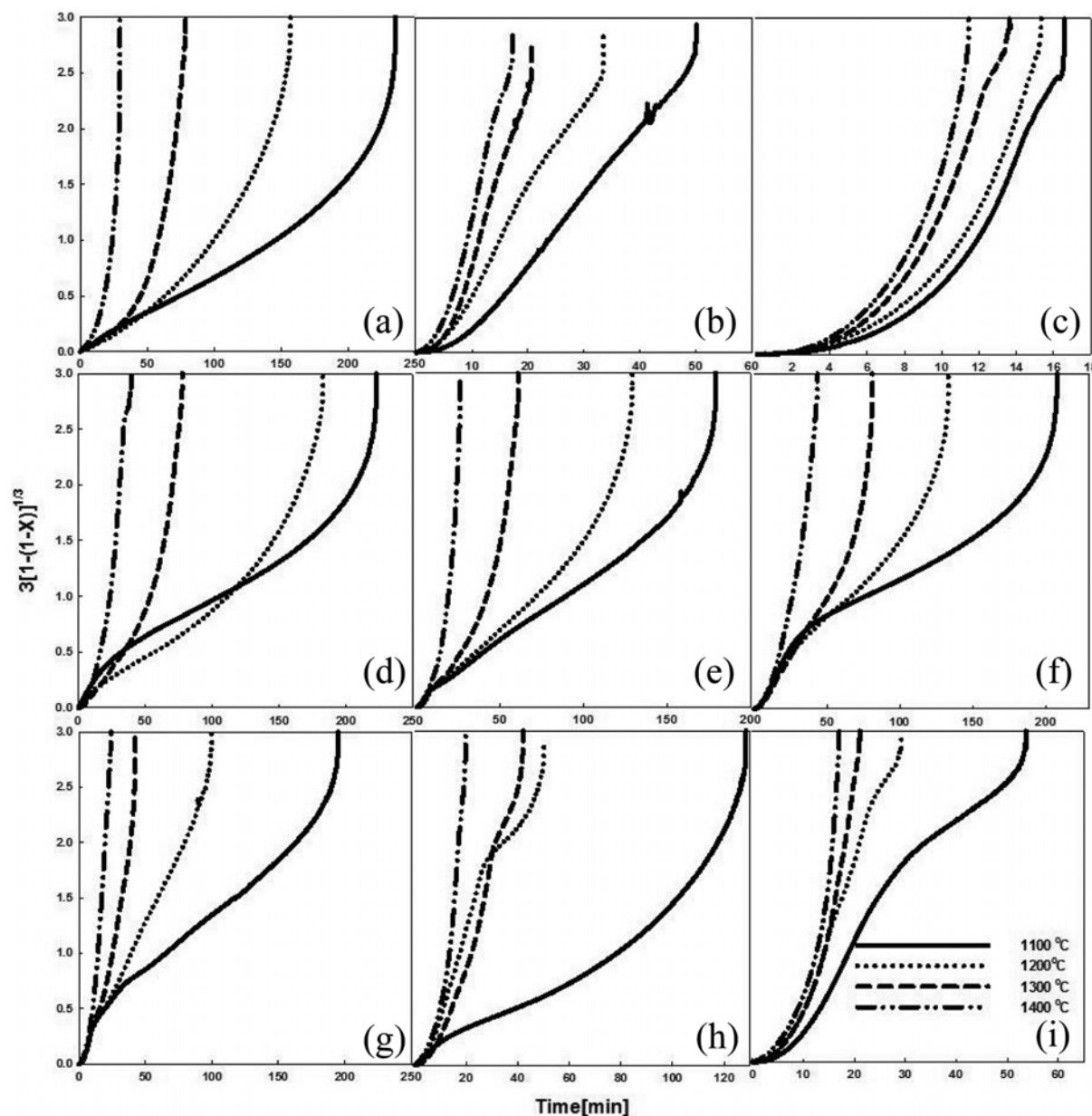


Fig. 4. Reactivity of CO<sub>2</sub> gasification of petroleum coke, coal, and mixed fuels with different compositions-shrinking core model.

(a) Petroleum coke (b) WH (c) KPU (d) COKE-WH(0.25) (e) COKE-KPU(0.25) (f) COKE-WH(0.5) (g) COKE-KPU(0.5) (h) COKE-WH(0.75) (i) COKE-KPU(0.75)

age 0.92, 0.92, 0.95, 0.97, 0.94, and 0.9, respectively. As in MVRM, mixture of pet-coke with coals were calculated on average 0.96, 0.96, 0.96, 0.97, 0.98, and 0.98, respectively, as shown in Table 2.

R<sup>2</sup> of MVRM and SCM showed high level on average compared with VRM. This indicated that MVRM and SCM can simulate reliable CO<sub>2</sub> gasification reaction. On the other hand, VRM could not adequately simulate CO<sub>2</sub> gasification reaction because of low R<sup>2</sup>.

### 3. Derived Rate Equation of CO<sub>2</sub> Gasification

The kinetic parameters of CO<sub>2</sub> gasification for each sample at 1,100-1,400 °C under SCM and MVRM were investigated. The reaction rate constant for the CO<sub>2</sub> gasification of char can be obtained from the slope of the trend line obtained by applying each model as a function of reaction temperature. The relationships between

the inverse reaction temperature (1/T) and char-CO<sub>2</sub> gasification reaction rate constant *k* of petroleum coke, coal, and petroleum coke/coal mixed fuels are plotted in Fig. 6. The frequency factor and activation energy calculated using the slope and intercept values for SCM and MVRM are organized in Table 3. The activation energy of petroleum coke, WH, and KPU was 123.4, 61.9, and 19.6 KJ/mol with SCM, respectively. In the MVRM, The activation energy of petroleum coke, WH, and KPU was 140.98, 55.2, and 15.6 KJ/mol, as shown in Table 3. This revealed that the heat required for the CO<sub>2</sub> gasification of petroleum coke was more than that of coal; therefore, petroleum coke has a lower reactivity. In the case of catalytic low-rank coal gasification under CO<sub>2</sub> atmosphere [25,26], the activation energy values from six different low-rank coals by using

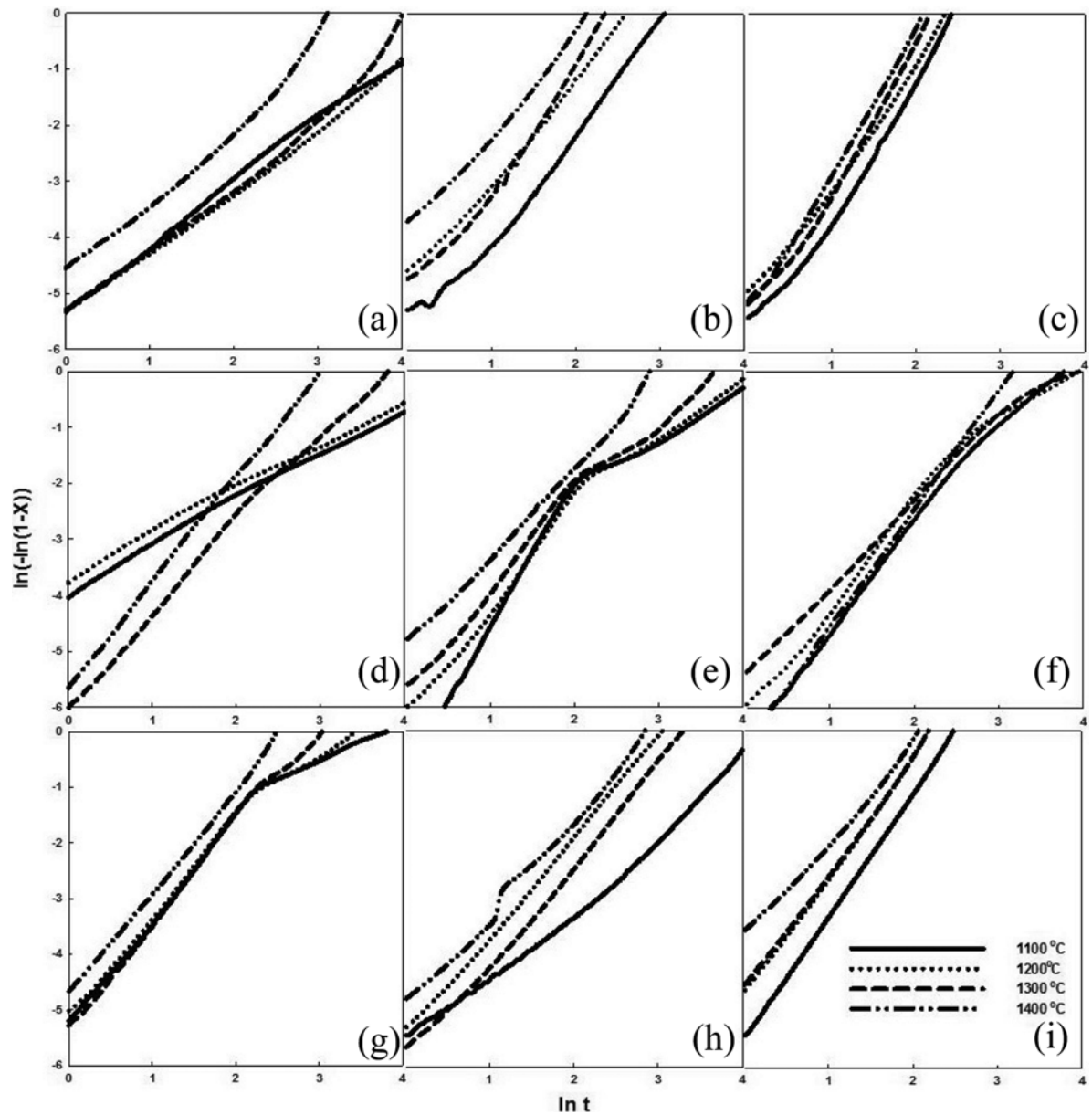


Fig. 5. Reactivity of CO<sub>2</sub> gasification of petroleum coke, coal, and mixed fuels with different compositions-modified volumetric reaction model. (a) Petroleum coke (b) WH (c) KPU (d) COKE-WH(0.25) (e) COKE-KPU(0.25) (f) COKE-WH(0.5) (g) COKE-KPU(0.5) (h) COKE-WH(0.75) (i) COKE-KPU(0.75)

Table 2. R<sup>2</sup> of gas-solid reaction

| Temperature (°C) | VRM  |      |      |      | SCM  |      |      |      | MVRM |      |      |      |
|------------------|------|------|------|------|------|------|------|------|------|------|------|------|
|                  | 1100 | 1200 | 1300 | 1400 | 1100 | 1200 | 1300 | 1400 | 1100 | 1200 | 1300 | 1400 |
| Petroleum coke   | 0.78 | 0.73 | 0.68 | 0.65 | 0.95 | 0.93 | 0.94 | 0.92 | 0.97 | 0.99 | 0.90 | 0.94 |
| WH               | 0.89 | 0.95 | 0.89 | 0.88 | 0.99 | 0.99 | 0.97 | 0.97 | 0.99 | 0.99 | 0.99 | 0.99 |
| KPU              | 0.70 | 0.63 | 0.65 | 0.63 | 0.84 | 0.84 | 0.86 | 0.86 | 0.98 | 0.98 | 0.98 | 0.99 |
| COKE-WH(0.25)    | 0.84 | 0.74 | 0.65 | 0.75 | 0.96 | 0.93 | 0.88 | 0.92 | 0.94 | 0.98 | 0.96 | 0.97 |
| COKE-KPU(0.25)   | 0.84 | 0.78 | 0.66 | 0.65 | 0.98 | 0.96 | 0.87 | 0.85 | 0.96 | 0.97 | 0.95 | 0.96 |
| COKE-WH(0.5)     | 0.84 | 0.81 | 0.74 | 0.73 | 0.95 | 0.96 | 0.94 | 0.94 | 0.96 | 0.97 | 0.95 | 0.96 |
| COKE-KPU(0.5)    | 0.87 | 0.88 | 0.82 | 0.74 | 0.98 | 0.99 | 0.96 | 0.93 | 0.95 | 0.94 | 0.98 | 0.99 |
| COKE-WH(0.75)    | 0.97 | 0.96 | 0.87 | 0.71 | 0.94 | 0.97 | 0.98 | 0.88 | 0.95 | 0.98 | 0.99 | 0.98 |
| COKE-KPU(0.75)   | 0.91 | 0.87 | 0.63 | 0.57 | 0.99 | 0.90 | 0.87 | 0.83 | 0.99 | 0.99 | 0.97 | 0.95 |

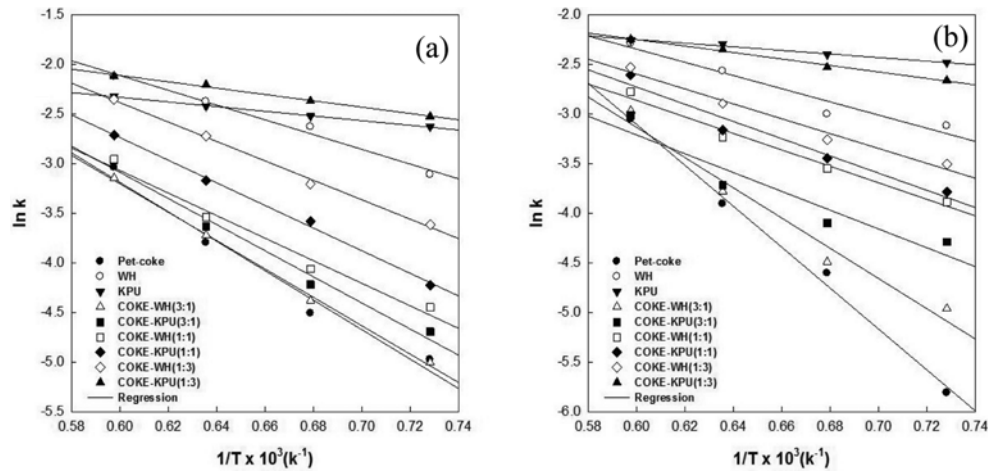


Fig. 6. Arrhenius plot.

(a) Shrinking core model (b) Modified volumetric reaction model

Table 3. Frequency factor and activation energy

|                | SCM   |                            | MVRM    |                            |
|----------------|-------|----------------------------|---------|----------------------------|
|                | A     | Activation energy [KJ/mol] | A       | Activation energy [KJ/mol] |
| Petroleum coke | 304.5 | 123.4                      | 1071.26 | 140.98                     |
| WH             | 10.5  | 61.9                       | 5.3     | 55.2                       |
| KPU            | 0.4   | 19.6                       | 0.3     | 15.0                       |
| COKE-WH(0.25)  | 217.3 | 119.0                      | 404.7   | 126.6                      |
| COKE-KPU(0.25) | 122.4 | 109.4                      | 11.8    | 78.7                       |
| COKE-WH(0.5)   | 42.6  | 94.5                       | 8.3     | 69.0                       |
| COKE-KPU(0.5)  | 60.4  | 94.8                       | 11.9    | 72.1                       |
| COKE-WH(0.75)  | 32.8  | 81.4                       | 6.7     | 62.3                       |
| COKE-KPU(0.75) | 0.8   | 26.5                       | 0.8     | 27.2                       |

Table 4. Rate equation of petroleum coke, coal, and mixed fuel

|                | SCM  | MVRM  |
|----------------|--|---|
|                | Rate equation  | Rate equation   |
| Pet coke       | $\frac{dX}{dt} = 304.5 \exp\left(-\frac{123.4}{RT}\right) (1-X)^{\frac{2}{3}}$ | $\frac{dX}{dt} = 1071.26 \exp\left(-\frac{140.98}{RT}\right) (1-X)$ |
| WH             | $\frac{dX}{dt} = 10.5 \exp\left(-\frac{61.9}{RT}\right) (1-X)^{\frac{2}{3}}$   | $\frac{dX}{dt} = 5.3 \exp\left(-\frac{55.2}{RT}\right) (1-X)$       |
| KPU            | $\frac{dX}{dt} = 0.4 \exp\left(-\frac{19.6}{RT}\right) (1-X)^{\frac{2}{3}}$    | $\frac{dX}{dt} = 0.3 \exp\left(-\frac{15}{RT}\right) (1-X)$         |
| COKE-WH(0.25)  | $\frac{dX}{dt} = 217.3 \exp\left(-\frac{119}{RT}\right) (1-X)^{\frac{2}{3}}$   | $\frac{dX}{dt} = 404.7 \exp\left(-\frac{126.6}{RT}\right) (1-X)$    |
| COKE-KPU(0.25) | $\frac{dX}{dt} = 112.4 \exp\left(-\frac{109.4}{RT}\right) (1-X)^{\frac{2}{3}}$ | $\frac{dX}{dt} = 11.8 \exp\left(-\frac{78.7}{RT}\right) (1-X)$      |
| COKE-WH(0.5)   | $\frac{dX}{dt} = 42.6 \exp\left(-\frac{94.5}{RT}\right) (1-X)^{\frac{2}{3}}$   | $\frac{dX}{dt} = 8.3 \exp\left(-\frac{69}{RT}\right) (1-X)$         |
| COKE-KPU(0.5)  | $\frac{dX}{dt} = 60.4 \exp\left(-\frac{94.8}{RT}\right) (1-X)^{\frac{2}{3}}$   | $\frac{dX}{dt} = 11.9 \exp\left(-\frac{72.1}{RT}\right) (1-X)$      |
| COKE-WH(0.75)  | $\frac{dX}{dt} = 32.8 \exp\left(-\frac{81.4}{RT}\right) (1-X)^{\frac{2}{3}}$   | $\frac{dX}{dt} = 6.7 \exp\left(-\frac{62.3}{RT}\right) (1-X)$       |
| COKE-KPU(0.75) | $\frac{dX}{dt} = 0.8 \exp\left(-\frac{26.5}{RT}\right) (1-X)^{\frac{2}{3}}$    | $\frac{dX}{dt} = 0.8 \exp\left(-\frac{27.2}{RT}\right) (1-X)$       |



MVRM varied from 138 KJ/mol to 255 KJ/mol at the temperature range of 750–900 °C.

Yoon et al. [8] obtained for activation energy of petroleum coke (SCM: 4.8 KJ/mol, MVRM: 2.64 KJ/mol) and anthracite coal (SCM: 2.62 KJ/mol, MVRM: 1.94 KJ/mol) for combustion reaction. This revealed that CO<sub>2</sub> gasification reaction was slower than combustion reaction. Gong et al. [18] calculated activation energy of petroleum coke, wood chip, lignite, bituminous coal, and anthracite coal in steam gasification in temperature range of 600–800 °C by using MVRM. Activation energy was 168.9, 260.3, 167.9, 134.6, 82.2 KJ/mol, respectively. As compared with single sample of petroleum coke, Activation energy of pet-coke with WH(0.25), pet-coke with

KPU(0.25), pet-coke with WH(0.5), pet-coke with KPU(0.5), pet-coke with WH(0.75) and pet-coke with KPU(0.75) was reduced for SCM by 4.4, 14, 28.29, 28.26, 42, and 96.9 KJ/mol, respectively. As in MVRM, the activation energy results of pet-coke with WH(0.25), pet-coke with KPU(0.25), pet-coke with WH(0.5), pet-coke with KPU(0.5), pet-coke with WH(0.75) and pet-coke with KPU(0.75) were reduced by 14.38, 62.28, 71.98, 68.88, 78.68, and 113.78 KJ/mol, respectively. In all models, the mixed fuels composed of petroleum coke/coal exhibited reduced activation energies. These results are similar that Yoon et al. [8] obtained for decrease of activation energy from petroleum coke by mixing petroleum coke with anthracite coal (0.5) in SCM (3.4 KJ/mol) and MVRM (0.71 KJ/mol) and Edreis

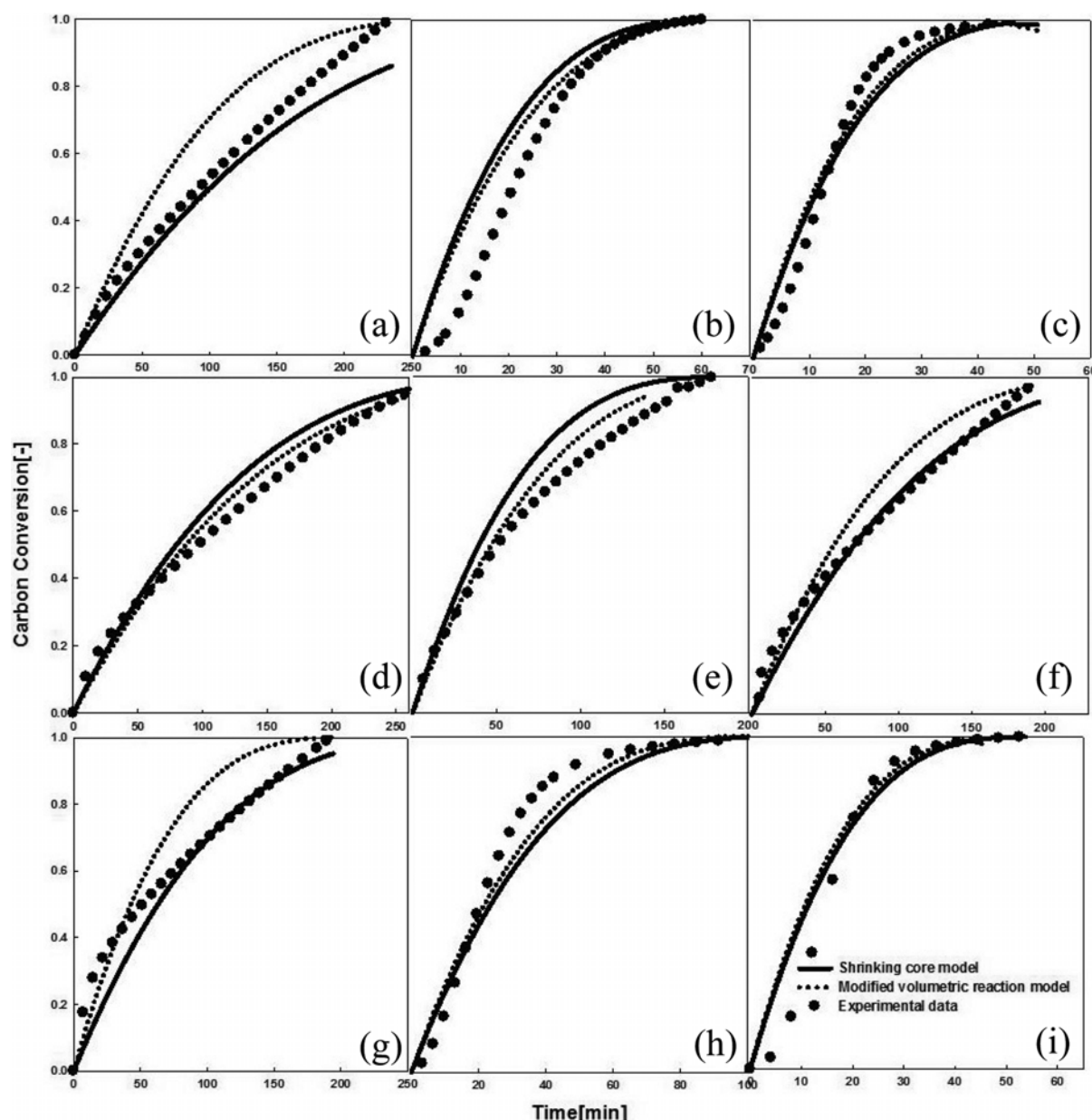


Fig. 7. Comparison between the conversion of experimental data and conversion of results from the Shrinking core model, and modified volumetric reaction model at 1,100 °C.

(a) Petroleum coke (b) WH (c) KPU (d) COKE-WH(0.25) (e) COKE-KPU(0.25) (f) COKE-WH(0.5) (g) COKE-KPU(0.5) (h) COKE-WH(0.75) (i) COKE-KPU(0.75)

et al. [16] studied for decrease of activation energy from petroleum coke (10 KJ/mol) by mixing petroleum coke with Sugar cane (0.75) in temperature range of 970-1,190 °C. Previous researchers found that a synergistic effect to improve reaction could be achieved by mixing the highly reactive fuel with the less reactive fuel [8,16,27].

Based on the above results, rate equations of petroleum coke, coal, and mixed fuel are presented in Table 4. Comparisons between the conversion of experimental data and conversion of results from the shrinking core model, and modified volumetric reaction model are provided in Fig. 7. For the reaction mechanism of the shrinking core model, the reaction is controlled by the diffusion because the reaction happens very fast, and the resistance of diffusion is much higher than the chemical reaction. However, in modified volumetric reaction model, the reaction controlled by the chemical, the effect of intra-particle diffusion can be ignored, and the reaction happens simultaneously in the whole particle. As can be seen, the shrinking core model for petroleum coke and CO<sub>2</sub> gasification was better than modified volumetric model. In case of WH and KPU, the shrinking core model and modified volumetric reaction model for CO<sub>2</sub> gasification might be applicable. In case of mixtures, the modified volumetric model was generally acceptable with increasing coal mixture ratio. As shown in Table 1, high moisture and volatile matter content in coals compared with petroleum coke might generate more pores when particles have been heated. These phenomena might make a difference in gas diffusion and char-CO<sub>2</sub> gasification reaction. Therefore, gas-solid reaction model for predicting CO<sub>2</sub> gasification should be applied, depending on coal type and petroleum coke/coal ratio due to gas diffusion.

## CONCLUSION

Char-CO<sub>2</sub> gasification characteristics of petroleum coke, coal, and petroleum coke/coal mixed fuels were compared in the temperature range of 1,100-1,400 °C using TGA. Generally, reaction time decreased as the reaction temperature increased in the CO<sub>2</sub> gasification reactions of petroleum coke, coal, and mixed fuels. With the mixed fuels, the required reaction time decreased as the coal content increased. Experimental results suggested that different gas-solid reaction models should be applied depending on coal type and petroleum coke/coal ratio due to gas diffusion. As a result, reaction rate equations for design and stable operation of gasifiers were suggested by selecting gas-solid reaction rate models for each sample that could simulate CO<sub>2</sub> gasification behavior.

## ACKNOWLEDGEMENTS

This research was supported by the Basic Science Research Program through the Energy Efficiency & Resources Core Technology Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (20123040050010) and by the National Research Council of Science & Technology (NST) grant by the Korea government (MSIP) (No. CRC-15-07-KIER).

## REFERENCES

1. S. H. Lee, S. T. Park, R. Lee, J. H. Hwang and J. M. Sohn, *Korean J. Chem. Eng.*, **33**, 3523 (2016).
2. C. Dupont, T. Nocquet, J. A. Da Costa and C. Verne-Tournon, *Bioresour. Technol.*, **102**, 9743 (2011).
3. C. Bu, A. Gómez-Barea, X. Chen, B. Leckner, D. Liu, D. Pallarès and P. Lu, *Appl. Energy*, **177**, 247 (2016).
4. D. G. Roberts and D. J. Harris, *Energy Fuels*, **14**, 483 (2000).
5. J. H. Zou, Z. J. Zhou, F. C. Wang, W. Zhang, Z. H. Dai, H. F. Liu and Z. H. Yu, *Chem. Eng. Process.*, **46**, 630 (2007).
6. E. M. A. Edreis, G. Luo, A. Li, C. Xu and H. Yao, *Energy Convers. Manage.*, **79**, 355 (2014).
7. J. H. Shin, R. S. Lee and S. H. Lee, *Korean Chem. Eng. Res.*, **54**, 1 (2016).
8. S. J. Yoon, Y. C. Choi, S. H. Lee and J. G. Lee, *Korean J. Chem. Eng.*, **24**(3), 512 (2007).
9. B. N. Murthy, A. N. Sawarkar, N. A. Deshmukh, T. Mathew and J. B. Joshi, *Canadian J. Chem. Eng.*, **92**(3), 441 (2014).
10. J. Feroso, B. Arias, M. Plaza, C. Pevida, F. Rubiera, J. Pis, F. Garcia-Pena and P. Casero, *Fuel Process. Technol.*, **90**, 926 (2009).
11. S. H. Lee, S. J. Yoon, H. W. Ra, Y. I. Son, J. C. Hong and J. G. Lee, *Energy*, **35**, 3239 (2010).
12. C. Zhao, L. Lin, K. Pang, W. Xiang and X. Chen, *Fuel Process. Technol.*, **91**, 805 (2010).
13. W. Huo, Z. Zhou, X. Chen, Z. Dai and G. Yu, *Bioresour. Technol.*, **159**, 143 (2014).
14. K. Jayaraman and I. Gokalp, *Appl. Therm. Eng.*, **80**, 10 (2015).
15. B. R. Clements, Q. Zhuang, R. Pomalis, J. Wong and D. Campbell, *Fuel*, **97**, 315 (2012).
16. E. M. A. Edreis, G. Luo, A. Li, C. Chao, H. Hu, S. Zhang, B. Gui, L. Xiao, K. Xu, P. Zhang and H. Yao, *Bioresour. Technol.*, **136**, 595 (2013).
17. A. Goyal, S. Pushpavanam and R. K. Voolapalli, *Fuel Process. Technol.*, **91**, 1296 (2010).
18. S. J. Gong, X. Zhu, Y. J. Kim, B. H. Song, W. Yang, W. S. Moon and Y. S. Byoun, *Korean Chem. Eng. Res.*, **48**, 80 (2010).
19. R. C. Timpe, R. E. Sears and G. G. Montgomery, *Prepr. Pap., Am. Chem. Soc., Div. Fuel Chem.*, **32** (1987).
20. G. Ballal, N. Girish and R. Amundson, *Chem. Eng. Sci.*, **44**, 1763 (1989).
21. S. Dutta and C. Y. Wen, *Ind. Eng. Chem. Proc. Dev.*, **16** (1977).
22. S. Nagpal, T. K. Sarkar and P. K. Sen, *Fuel Process. Technol.*, **86**, 617 (2005).
23. L. Zhang, J. Huang, Y. Fang and Y. Wang, *Energy Fuels*, **20**, 1201 (2006).
24. M. F. Irfan, M. R. Usman and K. Kusakabe, *Energy*, **36**, 12 (2011).
25. S. K. Kim, C. Y. Park, J. Y. Park, S. H. Lee, J. H. Rhu, M. H. Han, S. K. Yoon and Y. W. Rhee, *J. Ind. Eng. Chem.*, **20**, 356 (2014).
26. S. K. Kim, J. Y. Park, D. K. Lee, S. C. Hwang, S. H. Lee and Y. W. Rhee, *J. Energy Eng.*, **142** (2015), DOI:10.1061/(ASCE)EY.1943-7897.0000294.