Thermogravimetric study of coal and petroleum coke for co-gasification

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Abstract−As a preliminary study of gasification of coal and petroleum coke mixtures, thermogravimetric analyses were performed at various temperatures (1,100, 1,200, 1,300, and 1,400 °C) and the isothermal kinetics were analyzed and compared. The activation energies of coal, petroleum coke and coal/petroleum coke mixture were calculated by using both a shrinking core model and a modified volumetric model. The results showed that the activation energies for the anthracite and petroleum coke used in this study were 9.56 and 11.92 kcal/mol and reaction times were 15.8 and 27.0 min. In the case of mixed fuel, however, the activation energy (6.97 kcal/mol) and reaction time (17.0 min) were lower than the average value of the individual fuels, confirming that a synergistic effect was observed in the co-processing of coal and petroleum coke.

Key words: Coal, Petroleum Coke, TGA, Gasification

INTRODUCTION

Gasification refers to a series of processes that produce synthesis gas, i.e., H_2 and CO from all substances containing carbon, such as coal, petroleum coke, heavy residual oil, wastes and biomass [1-3]. An Integrated Gasification Combined Cycle (IGCC) that produces synthesis gas for power generation is known to have higher energy efficiency than power generation from pulverized coal combustion and to satisfy the environmental regulations of the 21st century. The gasification process could be the most promising supplier of hydrogen for fuel cell technology, the power generation technology of the future. In addition, the gasification process is widely used in the oil refining industry, as well as the petrochemical industry. Typical examples are the heavy oil gasification process that supplies H_2 to the oil refining process, the coal gasification process that supplies H_2 for ammonia production, and the coal gasification process as a part of the acetic anhydride production process such as Eastman chemical plant. In recent years the concept of "polygeneration," which combines power generation, synfuel and chemicals production from synthesis gas, has been seriously regarded. If high oil prices continue, the gasification process spearheaded for polygeneration is expected to receive more popular attention.

The advantages of petroleum coke are that it has a high calorific value, and it is cheaper than coal; however, its high sulfur and vanadium content puts it in a very disadvantageous position from an environmental perspective, as compared to coal. In particular, vanadium oxide (V_2O_5) causes slagging of boiler pipes. V_2O_5 can be accumulated in the SCR NOx removal catalyst, and serves as an oxidation catalyst, thereby oxidizing SO_2 into SO_3. SO_3 then forms deposits in the downstream process together with ammonia. As the deposited V_2O_5 increases, the production quantity of SO_3 continues to increase, thereby necessitating frequent replacement of the SCR

catalyst. Therefore, a gasification process not emitting SOx and NOx and yet capable of generating power and producing new chemical materials is the best process for utilizing petroleum coke [4,5].

In recent years, various attempts have been made to produce synergistic effects by co-processing of fuels. Kinetic research on polypropylene and oil shale mixtures was carried out by Gersten et al. [6]. The pyrolytic characteristics of a coal and biomass blend were reported by Jones et al. and Moghtaderi et al. [7,8]. Suelves et al. studied the synergistic effect in a coal and petroleum residue blend and observed the unfavorable characteristics of aromatic compound production during co-pyrolysis [9].

The combustion characteristics, chemical elements, and technical analysis of the fuel fed into the gasification reactor help to set up the operating conditions of gasification, and to find solutions to potential problems. Accordingly, to optimize the operating conditions of the gasification process and to prevent operational problems, the basic operating parameters such as the combustion characteristics of coal, petroleum coke and their mixed fuel in the gasification conditions must be understood. Moreover, the partial oxidation reaction of the fuel is considered one of the important reactions in gasification. Therefore, TGA experiments will reflect the gasification reaction characteristics.

This study is a preliminary investigation into the gasifying of anthracite coal, which has limited use due to low calorific value and high ash content mixed with petroleum coke, which has high calorific value, low ash content, and a high content of vanadium. The combustion characteristics of anthracite coal, petroleum coke and their mixture were examined by means of TGA at various temperatures.

EXPERIMENTAL

Anthracite coal and petroleum coke obtained from Jangseong deposits in Korea and Hyundai Oilbank Co. with a particle size range of 20-50 μm were chosen for this study. Table 1 shows the results of proximate, ultimate and calorific value analysis of anthracite and petroleum coke.

A TGA (SETARAM TG/DTA 92-18) analyzer was used to in-

Table 1. Proximate, ultimate and calorific value analysis of anthracite and petroleum coke

	Coal (anthracite)	Petroleum coke
Proximate analysis (wt%)		
Moisture	9.36	7.59
Volatile matter	7.22	10.46
Ash	47.26	0.25
Fixed carbon	36.16	81.70
Ultimate analysis (wt%)		
Carbon	50.05	87.16
Hydrogen	1.31	3.75
Nitrogen	0.52	0.98
Oxygen	0.25	0.02
Sulfur	0.61	7.84
Calorific value (kcal/kg)	4,060	8,550

vestigate the combustion characteristics of anthracite, petroleum coke and the mixture of these two fuels used in the experiment on their gasification. The initial weight of the samples in the TGA basket was on average 19-20 mg. Sample weight did not affect the TGA result. The precision of sample weight and temperature measurements was 0.01 mg and 0.01 °C, respectively. TGA experiment temperature levels were 1,100, 1,200, 1,300 and 1,400 °C, the temperature range used in the mixed fuel gasification experiment. The heating rate and the nitrogen and oxygen flow rate were fixed at 15 °C/min and 100 ml/min, respectively, for all experiments. The weight changes of the samples were measured at intervals of 2.6 seconds with a computerized digital scale, and the data stored. To measure the ignition temperature and ignition time for coal and petroleum coke, samples were burned at the 15 °C/min heating rate up to 1,200 °C, while air was supplied. To understand the combustion characteristics of the char relating to the three sample types, the experiment was conducted at a 15 °C/min heating rate at four different reaction temperature levels (1,100, 1,200, 1,300 and 1,400 °C). In order to remove moisture and volatile matter, nitrogen was supplied until the reaction temperature specified for the generation of char was reached. Subsequently, air was supplied for two hours and the combustion of the char was induced and measured.

RESULTS AND DISCUSSION

The kinetics of the combustion reactions of local anthracite and petroleum coke can be interpreted by using various kinetic expressions commonly used in gas-solid reactions, such as a simple nth order reaction as the following.

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

Here t is time, k is the reaction rate constant, X is the conversion rate of char at time t and n is the degree of reaction.

The temperature dependency of the reaction rate constant is represented in the following Arrhenius expression.

$$k = A\exp\left(\frac{E}{RT}\right) \tag{2}$$

In the case of anthracite, ash remains after the combustion reaction in TGA, while most of the moisture and volatile matter contained devolatilize before the combustion reaction. Therefore, excluding the moisture and ash contained in the anthracite, the conversion rate at a given time is represented in the following expression (3).

$$X = \frac{W_O - W_{H_2O} - W}{W_O - W_{H_2O} - W_{ash}} \tag{3}$$

Eq. (3) is substituted into Eq. (1) and the resulting kinetic model (Eq. (4)), was used to analyze the combustion reaction characteristics of local anthracite and petroleum coke.

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

To understand the ignition temperature and combustion characteristics of anthracite and petroleum coke, the weight reduction in air during 15 °C/min of heating time to 1,200 °C is illustrated in Fig. 1. In the case of anthracite, its weight was reduced by about 5% up to nearly 500 °C due to the small amount of moisture and volatile matter in the coal. Devolatilization of bituminous coals generally occurs near 300 °C, and char combustion takes place near 400 °C. Meanwhile, because the local anthracite used in this experiment has less volatile matter than bituminous coal, no salient devolatilization was observed. The results show that combustion of the anthracite started near 500 °C, and the weight remaining after the combustion reaction was about 47% meaning that the ash content was about 47%. The combustion characteristics of petroleum coke are known to vary by the place of origin and types of components. The TGA results for the petroleum samples used in this study show that the weight decreased up to 400 °C due to a very small amount of volatile matter and moisture, and then char combustion began. A very small amount of residue (close to 0%) remained after combustion.

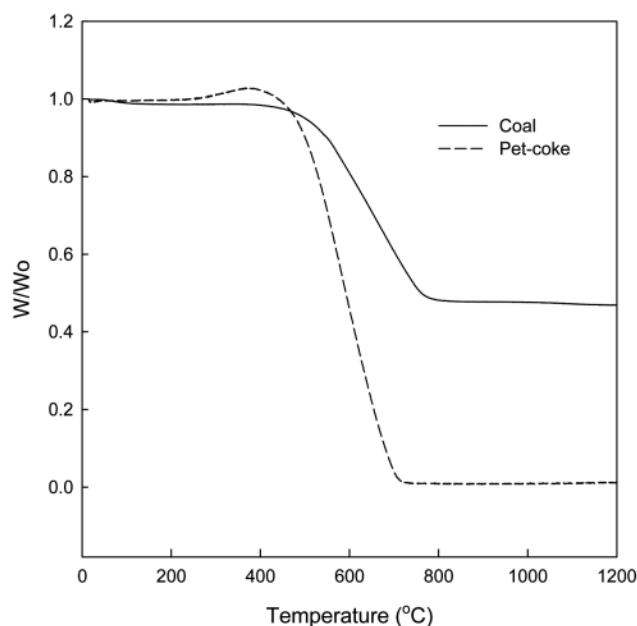To understand the pyrolysis and char reactions of anthracite and

Fig. 1. Combustion characteristics of anthracite and petroleum coke used in this study.
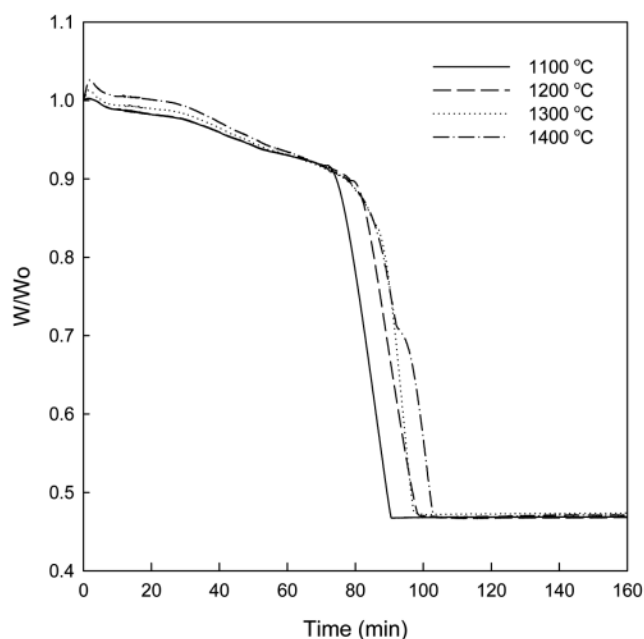
Fig. 2. Thermal gravimetric analysis of anthracite at different temperatures with a heating rate of 15 °C/min.
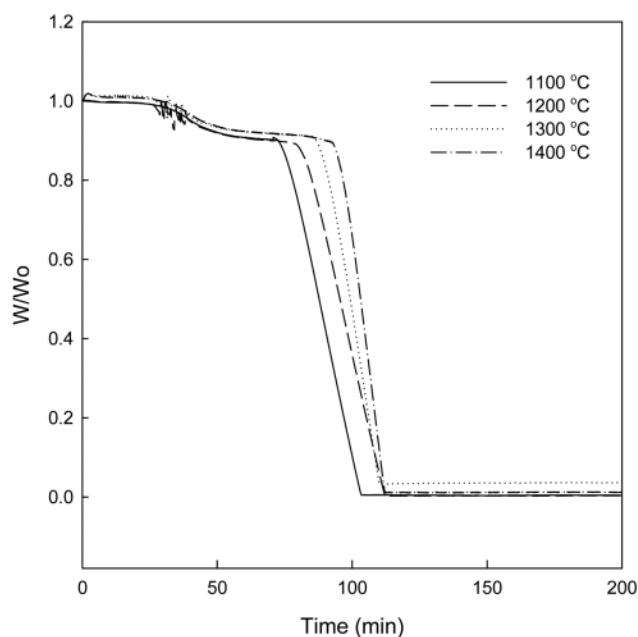

Fig. 3. Thermal gravimetric analysis of petroleum coke at different temperatures with a heating rate of 15 °C/min.

petroleum coke, the temperature was raised to a predefined temperature (1,100, 1,200, 1,300 and 1,400 °C) at a 15 °C/min heating rate in a nitrogen atmosphere. Nitrogen was replaced with air once a constant temperature was reached, and combustion took place for about two hours. The results are shown in Figs. 2 through 4. The combustion reaction starts from steeply decreasing point of sample weight. In the case of local anthracite, as shown in Fig. 1, about 10% of the weight was reduced due to the devolatilization of the moisture and volatile matter in the coal in the pyrolysis condition up to the specified temperature. The results show that the point where rapid weight reduction occurs is when combustion takes place as nitrogen is replaced with air. Comparing the four other constant temperature combustion conditions, the temperature of completion shows little variation, while the residual amount after pyrolysis at the respective temperatures (1,100, 1,200, 1,300 and 1,400 °C) was about 90%. As the final temperature increased, the amount of the residual char showed no difference. In addition, the amount of ash remaining after the combustion was the same at the various temperatures. That is, the completion temperature and the weight reduction at the different temperature do not seem to affect the formation of char. As for the trends in temperature, in general, as the combustion temperature rose, the slope of weight reduction versus time became steeper, meaning that as temperature increases at the four temperature conditions applied in this experiment, the time it takes to burn the same amount of char decreases. So, as the combustion temperature rises, the reaction rate of char increases. Fig. 3 shows combustion characteristics for petroleum coke at different temperatures. The result of this experiment shows that in the case of petroleum coke, there was some difference depending on temperatures. Similar to coal, about 10% of moisture and volatile matter devolatilized in the pyrolysis zone, and about 90% of char remains. Afterwards, 0-3% of residue is generated through combustion in the air atmosphere. TGA results of anthracite and petroleum coke mixed fuel at a mass ratio
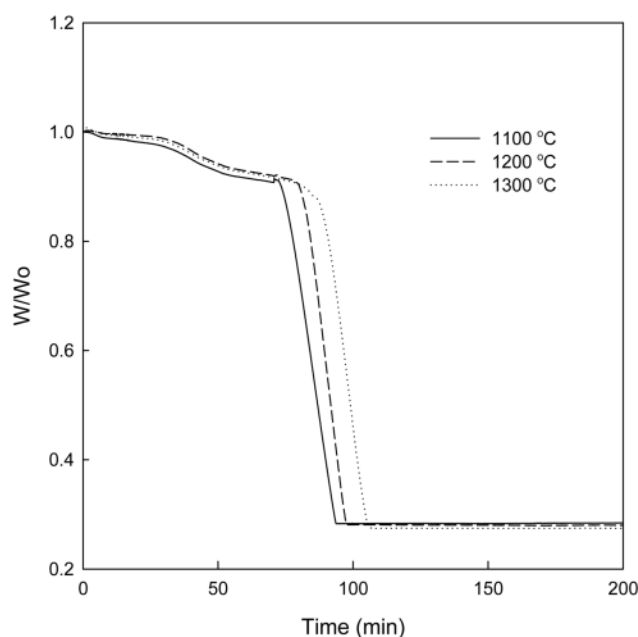

Fig. 4. Thermal gravimetric analysis of anthracite/pet-coke 1 : 1 mixed fuel at different temperatures with a heating rate of 15 °C/min.

of 1 : 1 are illustrated in Fig. 4 as a function of temperature. In this result, an average of each pure sample is seen, with about 90% char produced and 27% residue was remaining after combustion. The reaction time, however, did not yield an average value of the pure samples. The combustion reaction of the char for the case of mixed fuel was completed in about 17.0 min, which is lower than the average value (21.4 min) of anthracite (15.8 min) and petroleum coke (27.0 min). This may imply a synergistic interaction between coal

and petroleum coke, as in the case of a blend of low ranked coal with vacuum residue, plastics and/or biomass [9-12].

Figs. 2 through 4 show the reaction characteristics according to temperature of the anthracite, petroleum coke and mixed fuel used in this study. To obtain the char combustion characteristics and activation energy (E), and the frequency factor for each fuel, we used the volumetric reaction model proposed by Levenspiel and Ishida and Wen in relation to nonuniform gas-solid reactions, the shrinking core model, and the modified volumetric model proposed by Kasaoka et al. [13-15].

The reaction kinetics according to the shrinking core model is as follows.

$$\frac{dX}{dt} = k_r(1-X)^{2/3} \tag{5}$$

After integral calculus of the above expression, the relationship between the reaction time and the conversion rate is shown in expression (6).

$$k_r t = 3\{1-(1-X)^{1/3}\} \tag{6}$$

Accordingly, the reaction rate constant k_r can be obtained by multiplying the slope of $1-(1-X)^{1/3}$ at time t by 3. Time τ until the conversion rate becomes 1 or 0 as the reaction is complete has the following relationship.

$$k_r = \frac{3}{\tau} \tag{7}$$

The reaction kinetic expression according to the volumetric reaction model can be described as follows.

$$\frac{dX}{dt} = k_v(1-X) \tag{8}$$

After the integration of the above expression the relationship between the conversion rate and time can be described as follows.

$$k_v t = -\ln(1-X) \tag{9}$$

The reaction rate constant k_v can be obtained from the slope of $-\ln(1-X)$ at time t.

In addition, the reaction kinetic expression according to the modified volumetric model is as follows.

$$\frac{dX}{dt} = a^{1/b}b[-\ln(1-X)]^{(b-1)/b}(1-X)^n = k_m(1-X)^n \tag{10}$$

Here the conversion rate X is as follows.

$$X = 1 - \exp(-at^b) \tag{11}$$

The reaction rate expression according to the modified volumetric

model can be determined after obtaining the integral of the speed constant expression from each conversion value as shown below, or since the value of ks with the conversion rate of 0.5 is not different from the mean k_m, the following expression can be used in- stead.

$$k_m = \int_0^1 k_s(X)\,dX \tag{12}$$

$$k_m \approx k_s|_{X=0.5} = a^{1/b}b(\ln 2)^{(b-1)/b} \tag{13}$$

Here, a and b are constants obtained by curve-fitting the experimental data of X and time t in the least square method.

The conversion rate data according to the temperature of the char of the anthracite, petroleum coke and 1 : 1 mixed fuel used in this study are applied on the basis of the above-mentioned shrinking core model, volumetric reaction model, and modified volumetric model reaction expression. After analyzing the results, it was found that the experimental data were best fitted with the modified volumetric model, followed by the shrinking core model, and fitted poorly to the volumetric reaction model. Accordingly, this study used the modified volumetric model and the shrinking core model to obtain the kinetic parameters. The reciprocal relationship between the combustion rate constant k and the reaction temperature (1/T) of the char of the anthracite, petroleum coke and anthracite/pet-coke 1 : 1 mixture obtained by the two models at temperatures ranging from 1,100 and 1,400 °C, was Arrhenius-plotted as illustrated in Figs. 5
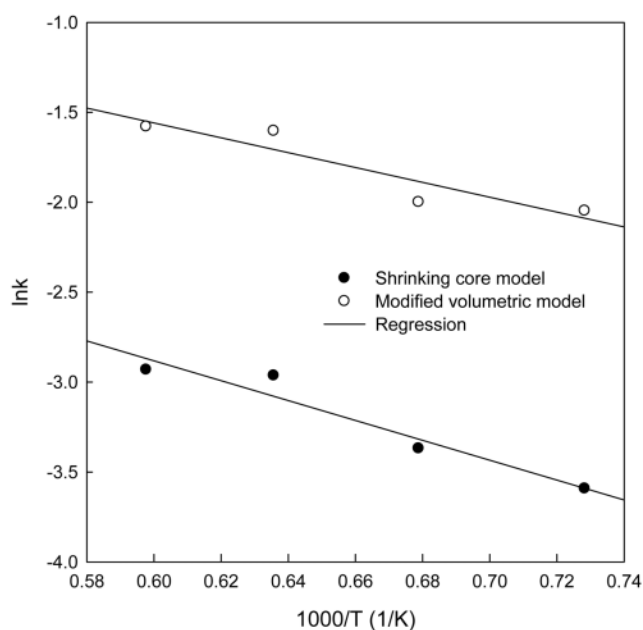

Fig. 5. Arrhenius plot of the coal-char.

Table 2. Activation energy and frequency factor of anthracite and petroleum coke

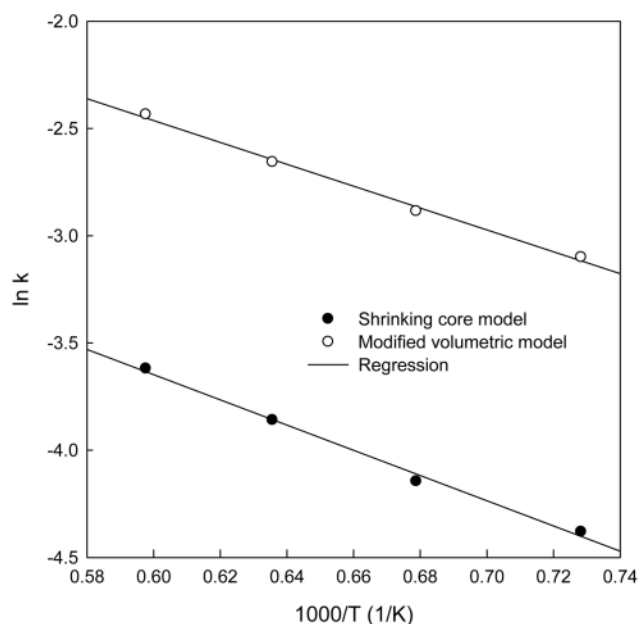|	Shrinking core model		Modified volumetric model	
	Activeation energy (kcal/mol)	Frequency factor	Activation energy (kcal/mol)	Frequency factor
Anthracite	10.940	1.544	8.175	2.507
Petroleum coke	12.843	1.297	11.001	2.419
Anthracite/Pet-coke 1 : 1 mixture	5.874	0.224	8.057	1.667

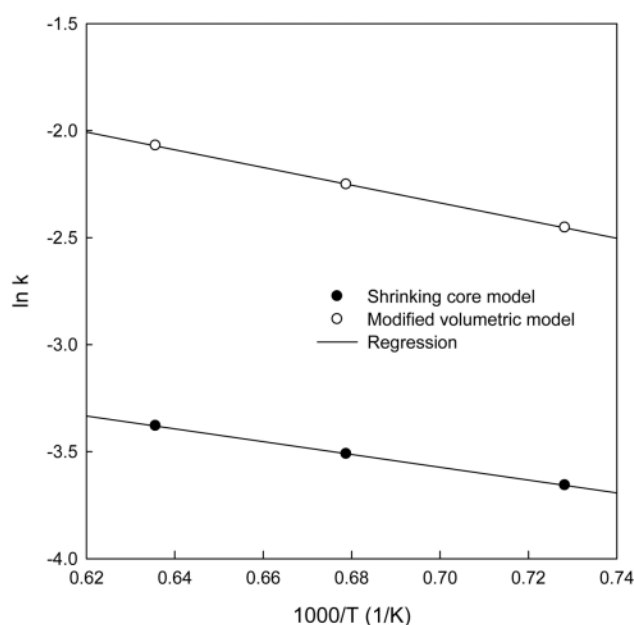Fig. 6. Arrhenius plot of the petroleum coke-char.

Fig. 7. Arrhenius plot of the coal and pet-coke 1 : 1 mixed fuel-char.

through 7. As a result of calculating on the basis of the slope and the intersection, the activation energy and frequency factor were obtained according to the shrinking core model and the modified volumetric model as summarized in Table 2. From the results, petroleum coke had greater activation energy than coal, which indicates that the reactivity of petroleum coke was lower than that of coal. Especially in the case of the coal/pet-coke mixed fuel, the activation energy shows a lower value than the average value of coal and petroleum coke. Along with the shortened reaction time mentioned above, this supports the conclusion that synergism occurred by mixing coal and petroleum coke. This kind of synergistic effect has been observed in the literature in studies on the co-processing of coal

Table 3. Reaction rate equation of anthracite and petroluem coke

Fuel	Reaction rate equation
Anthracite	$\dfrac{dX}{dt} = 1.544 \exp\left(-\dfrac{10.94}{RT}\right)(1-X)^{2/3}$
	$\dfrac{dX}{dt} = 2.507 \exp\left(-\dfrac{8.175}{RT}\right)(1-X)$
Petroleum coke	$\dfrac{dX}{dt} = 1.297 \exp\left(-\dfrac{12.843}{RT}\right)(1-X)^{2/3}$
	$\dfrac{dX}{dt} = 2.419 \exp\left(-\dfrac{11.001}{RT}\right)(1-X)$
Anthracite/Pet-coke 1 : 1 mixture	$\dfrac{dX}{dt} = 0.224 \exp\left(-\dfrac{5.874}{RT}\right)(1-X)^{2/3}$
	$\dfrac{dX}{dt} = 1.667 \exp\left(-\dfrac{8.057}{RT}\right)(1-X)$

with other fuels [1,2,4,5]. During coal and petroleum coke pyrolysis, various species of radicals such as aromatic, hydroaromatic, alkyl and heteroaromatic based radicals along with H, CH_2, OH, etc., are produced and stabilization of the radicals results in the production of lighter products than char. Therefore, it is expected that the radicals or reactive species produced from petroleum coke may stabilize the radicals from coal. Finally, kinetic equations of char production from anthracite and petroleum coke used in this study can be expressed in Table 3.

CONCLUSION

As a preliminary investigation of gasification of coal and petroleum coke mixture, the combustion characteristics based on TGA were studied. The TGA results at various temperatures were analyzed on the basis of the shrinking core model and the modified volumetric model. The results showed that the activation energies of the anthracite and petroleum coke used in this study were 9.56 and 11.92 kcal/mol, respectively, with the reactivity of petroleum coke lower than that of anthracite. Moreover, a synergistic effect was found in the lowering of the reaction time and activation energy in co-processing of coal and petroleum coke.

ACKNOWLEDGMENT

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