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Reactivity study of combustion for coals and their chars in relation to volatile content

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Abstract−To determine the effect of volatile matter on combustion reactivity, the pyrolysis and combustion behavior of a set of four (R, C, M and K coals) coals and their chars has been investigated in a TGA (SDT Q600). The maximum reaction temperatures and maximum reaction rates of the coals and their chars with different heating rates (5-20 °C/min) were analyzed and compared as well as their weight loss rates. The volatile matter had influence on decreasing the maximum reactivity temperature of low and medium rank coals (R, C and M coals), which have relatively high volatiles (9.5-43.0%), but for high rank coal (K coal) the maximum reactivity temperature was affected by reaction surface area rather than by its volatiles (3.9%). When the maximum reaction rates of a set of four coals were compared with those of their chars, the slopes of the maximum reaction rates for the medium rank coals (C and M coals) changed largely rather than those for the high and low rank coals (R and K coals) with increasing heating rates. This means that the fluidity of C and M coals was larger than that of their chars during combustion reaction. Consequently, for C and M coals, the activation energies are lower (24.5-28.1 kcal/mol) than their chars (29.3-35.9 kcal/mol), while the activation energies of R and K coals are higher (25.0-29.4 kcal/mol) than those of their chars (24.1-28.9 kcal/mol).

Key words: Combustion of Coal and Char, Reactivity, Volatiles, TGA, Activation Energy

INTRODUCTION

The combustion behavior of coals depends on the characteristics of the coals such as volatile and ash content, surface area and active sites, minerals in ash and rank of coals as well as on the combustion conditions such as temperature, heating rate, oxygen concentration and so on [1,2]. It is generally accepted that the combustion of coal particles has a series of reactions that involve a pyrolysis stage in an oxygen lean atmosphere and a heterogeneous reaction stage of oxygen with the carbon-rich solid residue named char [3]. During the coal pyrolysis, the evolution and combustion of volatiles prevent oxygen from reacting with the surface of coal particles, and thus it is normally assumed and believed that the pyrolysis and combustion of the particles are consecutive processes with little interaction between them [3]. So, the reactivity studies of the combustion of coal particles have progressed in the two-reaction regime, pyrolysis and char combustion [4-6]. Of these reactivity studies, the determination of reactivity of char combustion by TGA (thermogravimetric analysis), which has proved to be a valuable tool in the assessment of the combustion reactivity of coals, is usually achieved by using char particles formed at a high temperate under inert atmosphere (N_2) [6-8]. However, the combustion of the char particles is influenced by petrographic characteristics of coals affected by release and combustion of volatile matter with oxygen in coal particles [1, 2,9].

In this study, the role of volatile matter during the combustion of coal particles has been investigated in the TGA experiments. To determine the reactivity of coal combustion with and without volatile matter, the TGA experiments for combustion of four kinds of coals and their chars in relation to volatile content have been carried out. Also, the change of combustion reactivity due to volatile matter of coal has been observed and discussed.

EXPERIMENTAL

Four coals (R, C, M, K-coal) are considered in this study on the basis of their different volatile and ash contents. R-coal is high volatile (43%) bituminous coal and C and M coals are medium volatile (9-11%) and high ash (34-51%) bituminous coals. K-coal is low volatile (4%) and high ash (27%) anthracite. The analyses of these coals are shown in Table 1. Coals were ground and sieved to 30-80 mm within the similar size range used in an industrial pulverized coal boiler. Chars from each coal were prepared at 900 °C under N_2 atmosphere at a range of heating rates (5-20 °C/min), which were in accord with the heating rates of coal combustion experimental conditions.

Combustion analyses of coals and their chars were performed by TGA (SDT Q600, TA) using a small amount (10-15 mg) of each coal and char samples. Coals and chars were heated to 900 °C at a different heating rate (5-20 °C/min) under air (100 ml/min). Coal pyrolysis was also carried out under N_2 up to 900 °C with the same heating rates of the combustion experiments.

To determine and compare the combustion reactivity, activation energy was calculated by the Eq. (1) proposed by Kissinger [10].

$$\frac{d\ln(\beta/T_m^2)}{d(1/T_m)} = -\frac{E_a}{R} \tag{1}$$

This method uses the fact that the temperature of the maximum reactivity (T_m) increases with increasing heating rate (β), so the method can be available to calculate activation energy (E_a) in a non-isothermal experiment. From this equation, activation energy could be calculated by determination of the slope of the plot for $\ln(\beta/T_m^2)$ versus $1/T_m$.

On the other hand, the surface and pore properties of the sample

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Table 1. Analysis of coals used in this study

Items		Unit	R-coal	C-coal	M-coal	K-coal
Ultimate analysis (Dry base)	C	wt%	76.00	56.73	39.40	68.79
	H	wt%	4.10	2.20	1.85	0.79
	N	wt%	1.69	0.66	0.52	0.43
	S	wt%	0.19	2.47	2.08	1.10
	O	wt%	9.60	2.78	4.24	0.83
	Ash	wt%	8.42	35.16	51.91	28.06
	H/C (O/C)	-	0.054 (0.126)	0.039 (0.049)	0.047 (0.108)	0.011 (0.012)
Proximate analysis (Air dry base)	Moisture	wt%	7.97	2.09	1.62	3.76
	VM	wt%	43.02	9.46	10.62	3.92
	FC	wt%	42.17	54.03	36.69	65.32
	Ash	wt%	6.84	34.42	51.07	27.0

particles were also measured to analyze their effects on the change of the combustion reactivity of coals and chars.

RESULTS

Information of the burning profiles of coals in the TGA can be used to estimate their combustion performance in an industrial combustor. The burning profiles of the coals used in this study are shown in Fig. 1. All combustion results obtained under air with increasing temperature up to 900 °C show the first weight losses at about 100 °C due to drying process of coals, and then show serious weight losses due to devolatilization and combustion, which start at different temperatures in relation to the volatile content of the coals. The evolution of volatile matter of R-coal, which has the highest volatile content, started at about 200 °C, but the devolatilization of K-coal began at about 500 °C. The temperature of the initial weight loss due to devolatilization was much lower with increasing volatile content of the coals. After the beginning of evolution of volatile matter, all coal particles were burned with oxygen. All profiles show these consecutive processes, but it is difficult to distinguish the pyrolysis from the combustion of coals. So, the reactivity studies have been usually performed in each reaction regime, which are the pyrolysis of coal

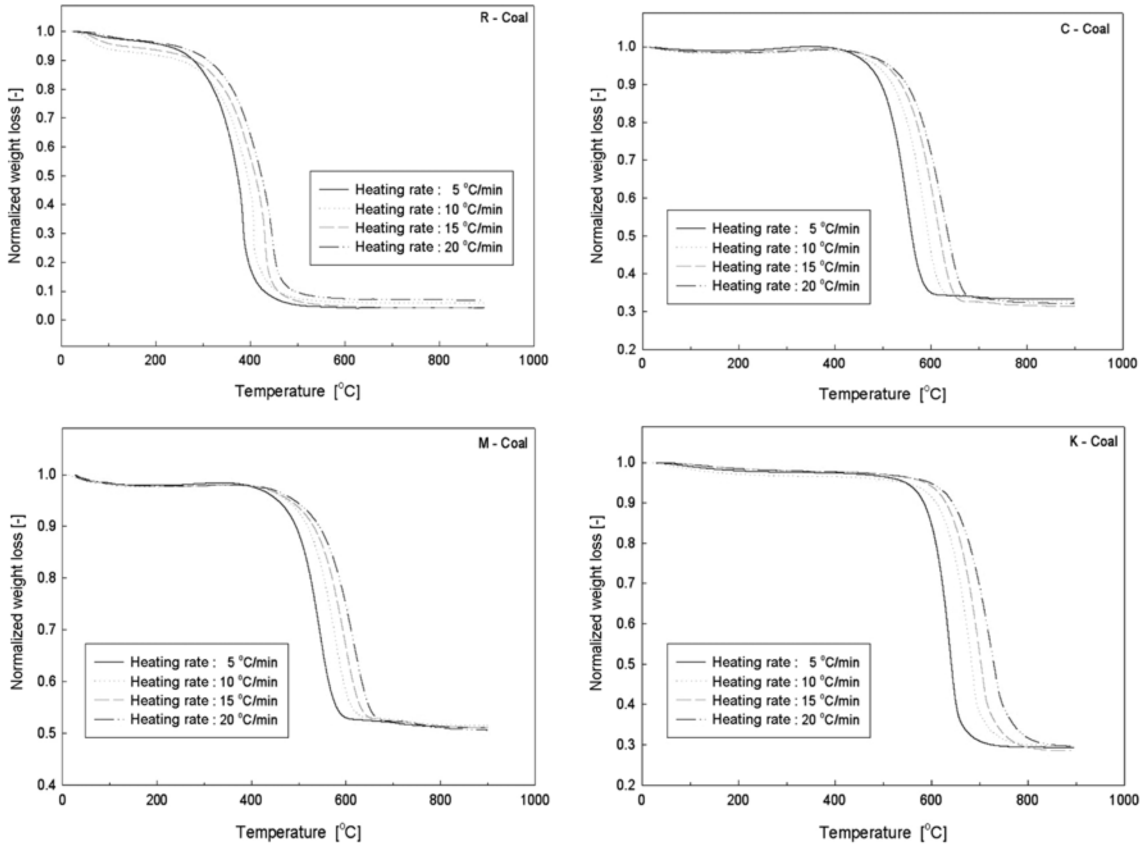


Fig. 1. Weight losses of four (R, C, M and K) coals with heating rates in combustion reaction (air atmosphere).

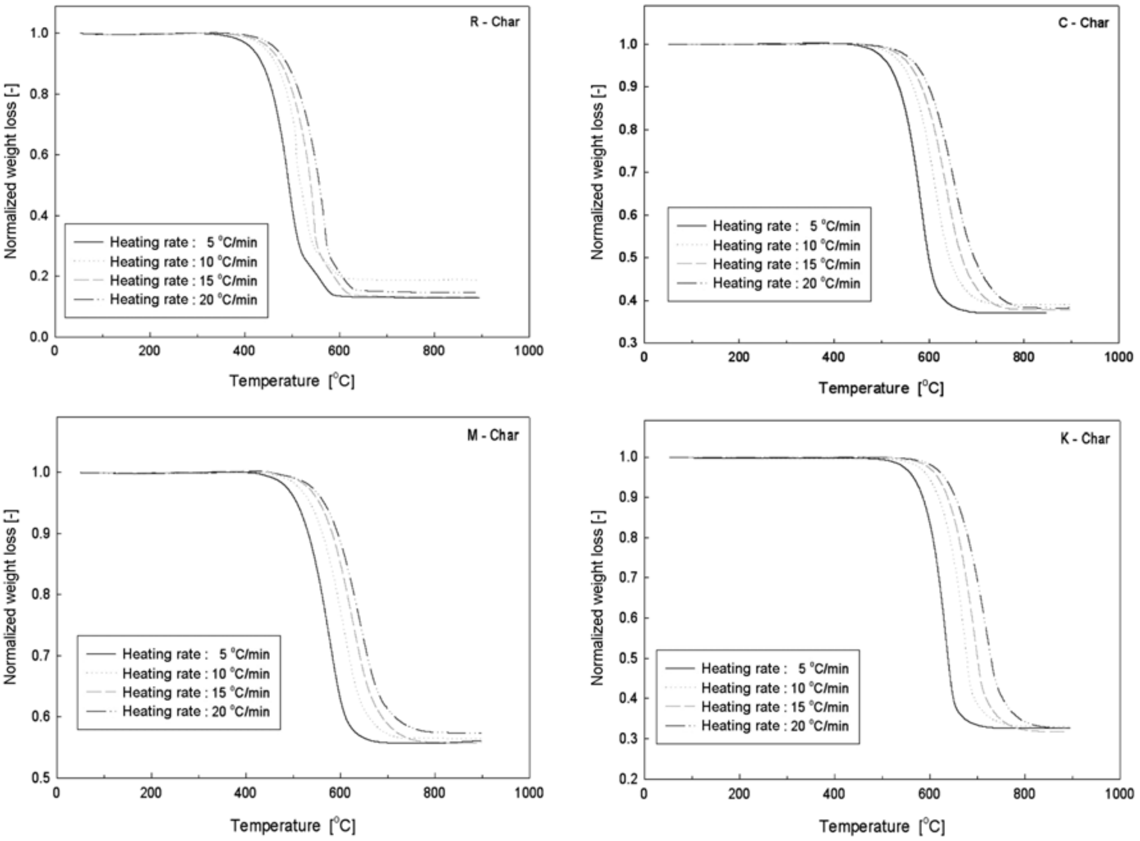


Fig. 2. Weight losses of four (R, C, M and K) chars with heating rates in combustion reaction (air atmosphere).

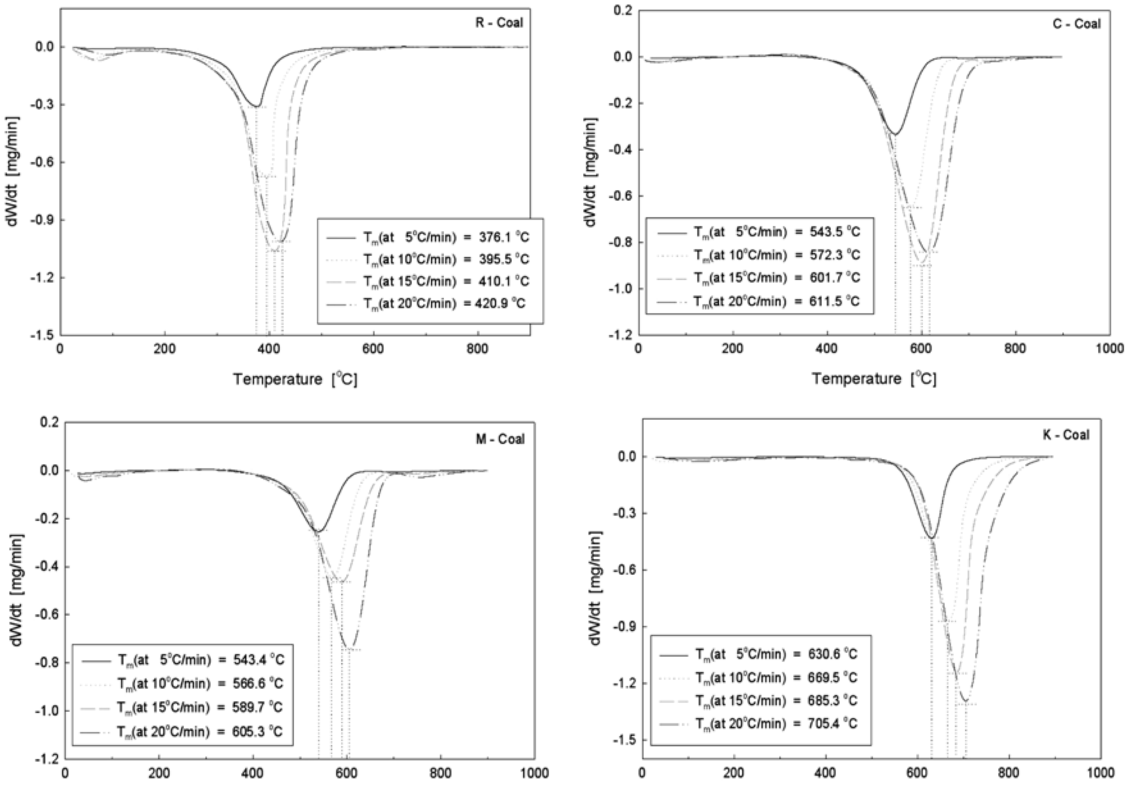


Fig. 3. Maximum reactivity temperature of four (R, C, M and K) coals with heating rates in combustion reaction (air atmosphere).

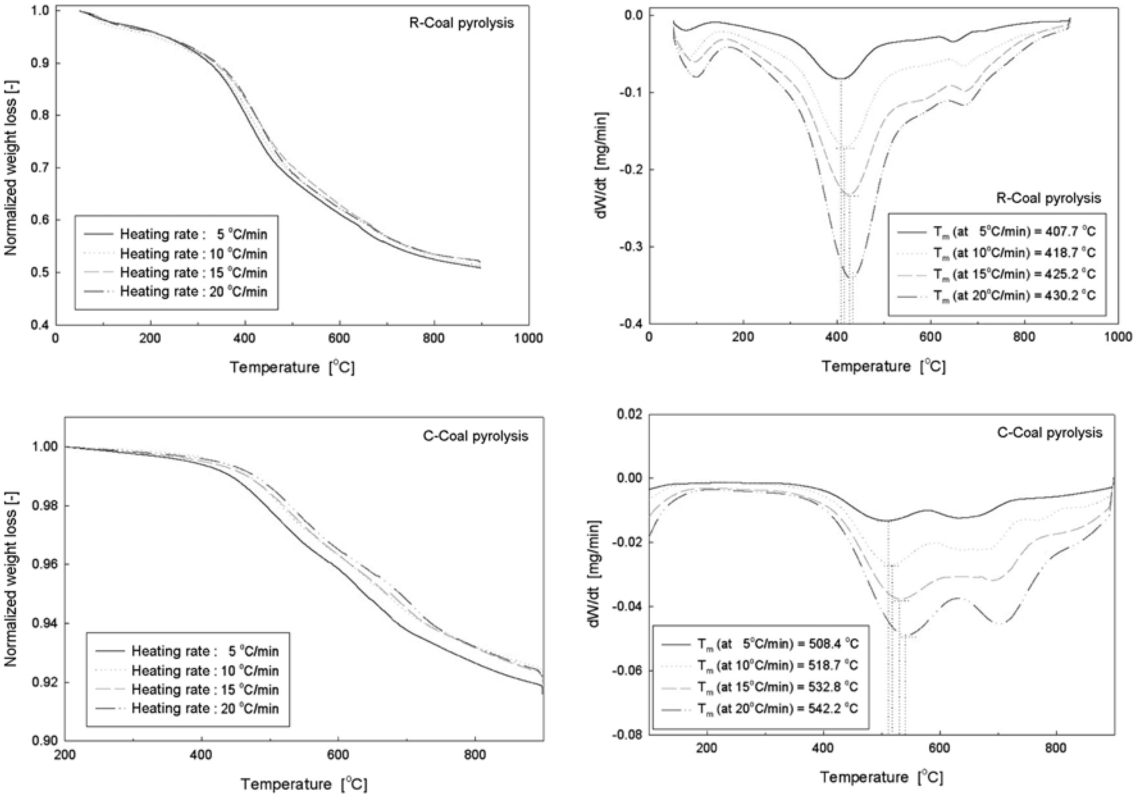


Fig. 4. Weight losses and maximum reactivity temperature of R and C coals with heating rates in pyrolysis reaction (N_2 atmosphere).

and the combustion of char [4-6,11].

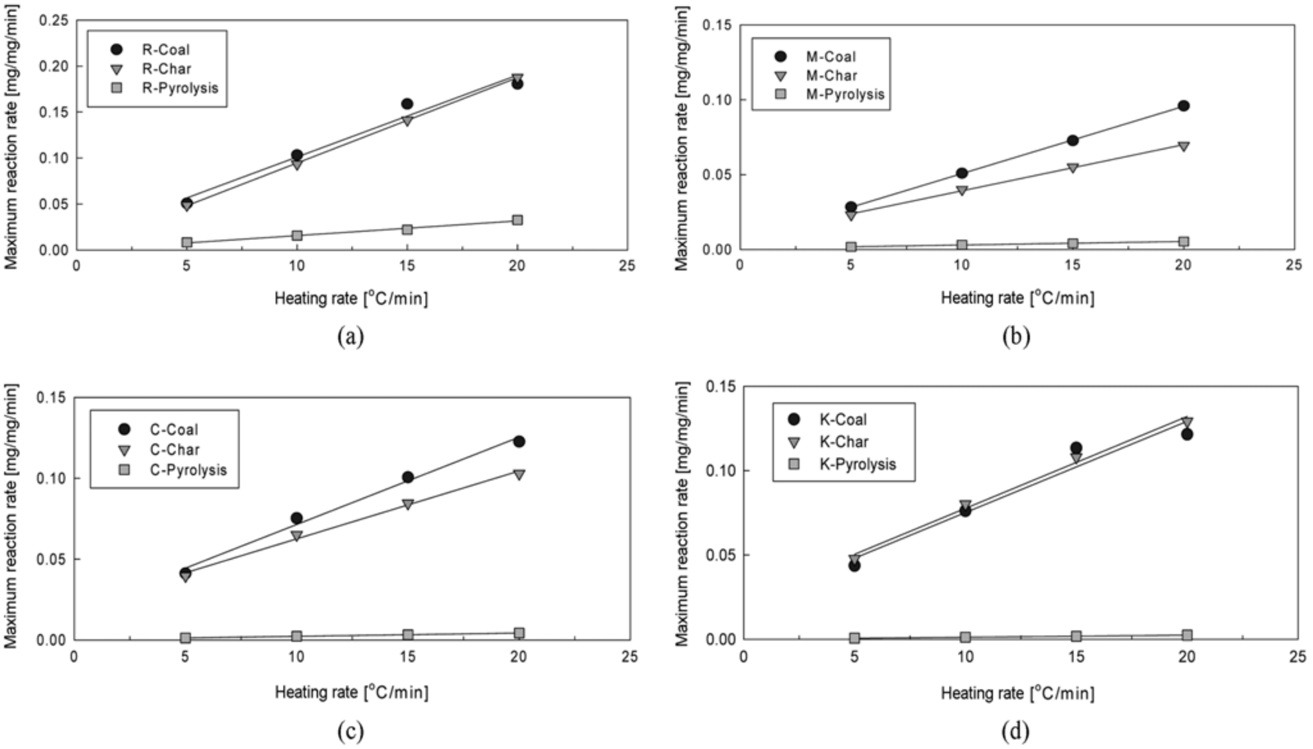
The profiles of the combustion of the chars at different heating rates under air are shown in Fig. 2. The profiles of the char combustion are similar to those of the coal combustion except including the processes of drying and pyrolysis. Also, the beginning of the initial weight losses due to combustion of chars has similar trends of that of coal combustion, although the beginning temperature of the initial weight loss of each char was shifted to higher temperature. This means that the initial burning temperature of the coal depends on the intrinsic material in the coal rather than the volatile content and its release, although the volatile content and its release correspond to the initial burning temperature [9,13].

Fig. 3 shows the maximum reactivity temperature with a range of heating rates for coals under air. The maximum reactivity temperature means the temperature having the maximum rate of the weight loss of the sample particles during the reaction. As shown in Fig. 3, the more volatile matter in coal, the lower temperature of the maximum weight loss rate during combustion. R-coal has the lowest temperature of the maximum weight loss rate, while K-coal has the highest temperature of the maximum weight loss rate. Also, the higher the heating rate to the coal particles, the higher the temperature of maximum weight loss rate. High heating rate results in a more extensive thermal fragmentation of coal's molecular structure and suppresses secondary reactions and the loss of fixed carbon [14,15]. Thus, a high heating rate may shift the reactions to a much higher temperature range [16,17].

On the other hand, during coal combustion, the pyrolysis of the coal occurs continuously up to 900 °C, as shown in Fig. 4. This means that the weight loss of the coal combustion shown in Fig. 3 includes both the devolatilization and the char combustion process for the whole weight loss period. The maximum weight loss rate of the pyrolysis is much lower than that of the combustion, so the weight loss rate of the pyrolysis does not seem to play an important role in the maximum weight loss of the coal combustion. Also, the maximum reactivity temperatures of the pyrolysis of R and C-coals, which are shown in Fig. 4, did not correspond to those of the combustion of R and C-coals. The maximum reactivity temperature of the pyrolysis of R-coal was higher than that of its combustion, but C-coal showed the contrary trend. It seems that pyrolysis does not directly

Table 2. Maximum reactivity temperature (T_m) with various reaction conditions

Species of coals	T_m [°C]			
	5 °C/min	10 °C/min	15 °C/min	20 °C/min
R-coal under air	376.1	395.5	410.1	420.9
R-char under air	488.6	506.6	529.9	548.5
R-coal under N_2	407.7	418.7	425.2	430.2
C-coal under air	543.5	572.3	601.7	611.5
C-char under air	573.8	608.2	624.1	639.3
C-coal under N_2	508.4	518.7	532.8	542.2
M-coal under air	543.4	566.6	589.7	605.3
M-char under air	573.8	601.9	615.9	627.2
M-coal under N_2	500.8	510.5	521.0	529.4
K-coal under air	630.6	669.5	685.3	705.4
K-char under air	627.4	662.5	679.9	703.4
K-coal under N_2	539.9	543.7	546.5	559.9



(a) (b)

(c) (d)

Fig. 5. Maximum reaction rate of combustion and pyrolysis of four coals and their chars.

increase the reactivity rate of the coal combustion.

The maximum reactivity temperature of the char combustion showed a similar trend of that of coal combustion and is summarized in Table 2. This increased with increasing heating rate and with decreasing volatile content of the coal. On the other hand, the maximum reactivity temperatures of R, C and M-char combustion were higher than those of their coals, but for K-char combustion, the temperature was lower than that of K-coal. It seems that the volatiles in R, C and M-coal have an influence on decreasing the maximum reactivity temperature of the coals. For K-coal, however, the volatile content was much lower than other coals, so the maximum reactivity temperature was affected by reaction surface area, which may be increased after devolatilization, rather than volatiles in the coal.

Fig. 5 shows the maximum reaction rates of the coals and their chars combustion and pyrolysis with variation of heating rate for a set of four coals. The maximum reaction rates of all reactions and all coals increased linearly at a given heating rate. This is why the heating rate has a crucial impact on the coal fluidity [18,19]. At relatively slow heating rates, both the maximum fluidity and the temperature range of the plastics region of the coal increase with increasing the heating rate [20]. On the other hand, the slopes of the maximum reaction rates of R and K coal combustion were similar to their chars combustion as shown in Fig. 5(a) and (d), but the slopes for C and M coal combustion were larger than those of their chars combustion with increasing the heating rate. This means that the heating rate has more influence on the fluidity during C and M coal combustion, although R-coal has the highest volatile content in the coal. In the case of K-coal, the maximum reaction rate of the char combustion was higher than that of its coal combustion. K-coal has

Table 3. Surface area and pore characteristics

Species	BET surface area [m^2/g]	Avg. pore size [nm]
R-coal	1.3371	15.57751
R-char	3.4289	3.38852
C-coal	59.9442	2.56746
C-char	127.2548	2.20397
M-coal	35.6232	3.16676
M-char	109.6795	2.29750
K-coal	4.3099	9.09387
K-char	6.2330	6.45463

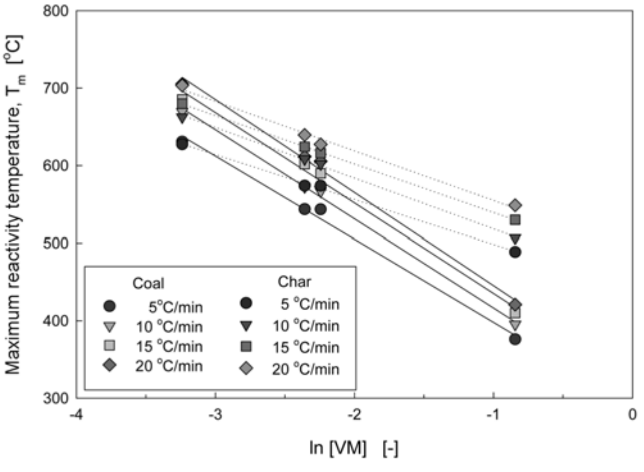


Fig. 6. Maximum reactivity temperature with volatile content of coals.

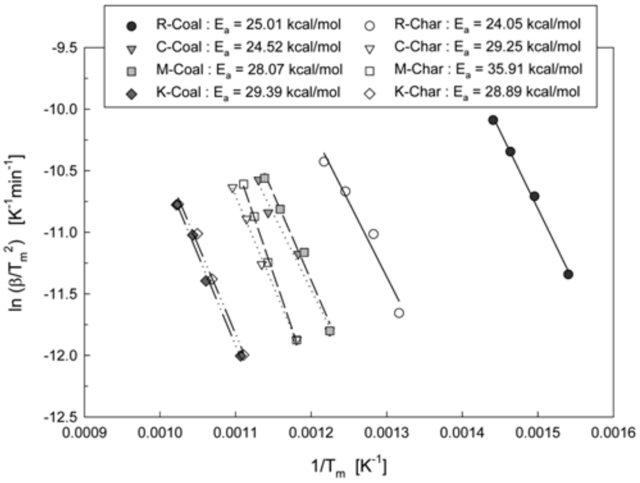


Fig. 7. Activation energy of combustion reaction for four coals and their chars.

least volatiles enhancing coal combustion, so this may be due to the increase of the reaction surface area after devolatilization as shown in Table 3.

Fig. 6 shows the maximum reactivity temperature with variation of volatile content and heating rate for coals and their chars. The maximum reactivity temperature increased as the heating rate increased and as volatile content decreased. This is also from the change of coals and chars fluidity and from the change of the cross linking temperature with volatile content and heating rate [19]. On the other hand, the temperatures linearly decreased against logarithms of volatile content for both coals and chars, that the change of the temperature was larger for the coal combustion and high heating rate. So, the maximum reactivity temperature seems to have more influence on coal combustion reaction and on higher heating rate.

Fig. 7 shows the activation energy for the combustion reaction of coals and their chars. The activation energy was obtained from Eq. (1) proposed by Kissinger [10]. The activation energies of coals ranged from 24.5 to 29.4 kcal/mol and those of chars from 24.1 to 35.9 kcal/mol. Generally, during the coal pyrolysis at low and medium heating rates under air condition, the evolution and combustion of volatiles prevent oxygen from reacting with the surface of coal particles, and the weight loss due to coal pyrolysis does not have a large effect on the overall reaction rate as shown in Fig. 5. Additionally, the surface areas of the char particles are larger than those of the coal particles, as summarized in Table 3. The activation energy of the coal is thus generally higher than that of its char in this reaction condition. However, as shown in Fig. 7, the activation energies of C and M-coals are lower than those of their chars. This may be due to the following reason [1,9]. When coal particulate samples are heated under an oxidizing atmosphere and at moderate heating rates, an outer rim of oxidized, highly crosslinked material will be formed first, while the inner core will keep its thermoplastic properties unaltered. The presence of a rigid oxidized outer rim will prevent the pyrolyzing coal particles from swelling under the pressure exerted by the volatiles generated. The higher pressure which must exist in the inner part of the coal particles has two main effects on the pyrolysis behavior of the core: i) a reduced volatile yield, and ii) an increased likelihood for repolymerization reactions to take place, which, in turn, also reduces the volatile yield [9]. Medium rank coals (C and M-coals) yield higher percentages of tar than low and high rank coal [21], and these are precisely the bigger molecules that are produced during pyrolysis. It is likely that the diffusional constraints of the volatiles to pass through the oxidation rim will be more important for these species. Besides, these retained tars are especially prone to undergo repolymerization/recondensation [1,9]. So, as shown in Fig. 7, for the C and M-coals when compared with their chars, the combustion reaction under an oxidizing atmosphere and at moderate heating rates occurs more easily due to high polyaromatic components, which might result in a more rapid combustion reaction of the coals. Consequently, the activation energies of C and M-coals are lower than those of their chars. Therefore, the combustion reactivities of the medium rank coals (C and M-coals) are higher than those of their chars, while the combustion reactivities of the low and high rank coals (R and K-coals) are lower than those of their coals.

CONCLUSION

To determine the effect of volatile matter on combustion reactivity, the combustion reaction of four (R, C, M and K coals) coals and their chars was investigated in TGA experiments. The volatiles had an influence on decreasing the maximum reactivity temperature of low and medium rank coals (R, C and M coals), which have relatively high volatile content, but for high rank coal (K coal) the maximum reactivity temperature was affected by reaction surface area rather than by its volatiles. On the other hand, the maximum reaction rates of R and K coals were similar to their chars, but C and M medium rank coals were more affected by volatiles with increasing heating rate when compared with their chars, which means that the fluidity of C and M coals was larger than that of their chars during combustion reaction. Consequently, for C and M coals, the combustion reaction under an oxidizing atmosphere and at moderate heating rates occurred more easily due to high polyaromatic components, which might result in a more rapid combustion reaction of the coals. The activation energies of C and M-coals were therefore lower than those of their chars, while the activation energies of R and K coals were higher than those of their chars.

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