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Effect of oxydesulphurization on the combustion characteristics of coal

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Abstract

Desulphurization of a Turkish lignite by oxydesulphurization using dilute alkaline solutions, obtained by the extraction of fly ash with water, was carried out under 0–1.5 MPa partial pressure of oxygen at temperatures between 403 and 498 K for 30–90 min time intervals. TGA was performed to compare the combustion characteristics of original and desulphurized lignite samples. DTG curves were derived and the effects of desulphurization conditions such as temperature, partial pressure of oxygen and time on coal reactivity were studied considering ignition temperature, maximum combustion rate, combustion period, and the end temperature of combustion. Relations between coal reactivity and removals of sulphur and ash contents were also studied. © 1997 Elsevier Science B.V.

Keywords: Coal; Reactivity; Combustion characteristics; Oxydesulphurization

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1. Introduction

Physical coal cleaning techniques have been applied for long times in coal industry. These techniques provide high desulphurization ratios only when the sulphur content of coal is mainly in the pyritic sulphur form and the particle size of coal is sufficiently small. In case of coals having high contents of organic sulphur and finely disseminated pyritic sulphur, physical coal cleaning techniques are incapable of supplying satisfying desulphurization yields. In such cases chemical desulphurization methods must be applied. These methods based on the direct removal of sulphur compounds via reactions with some reagents or conversion of them to different structures which are easy to eliminate from coal. Besides, some variations are formed in both the organic coal matrix and the mineral constituents of chemically desulphurized coals [1]. Especially some chemical desulphurization methods in which severe conditions such as elevated temperatures, high pressures and strong chemicals are applied to coal cause considerable degradations in the organic matrix. This leads to a decrease in the combustible parts of coal and consequently a loss in heating value [2,3]. On the other hand, some mineral constituents are inert to process conditions and others are extremely sensitive. In the latter case, coal cannot conserve its original inorganic structure. These variations in coal structure are the main reason for the differences occurring in some properties of chemically desulphurized coals.

When coal is slowly heated in the presence of oxygen, the loss in the mass after moisture release represents the ignition of coal. The rate of this loss in

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mass increases up to a maximum and then begins to decrease and finally mass remains invariable. At the temperature at the end of combustion (TEC), loss in mass decreases to zero. Ignition temperature is a measure of thermal reactivity of coal; in other words, low ignition temperature indicates high thermal reactivity. Since reactive coals burn with high combustion rates, their combustion takes short times and finishes at low temperatures.

Determination of the extent of variations occurring in the combustion properties of coal is an important subject in the design and operation of combustion systems. Information about combustion characteristics of coal can be obtained using TGA technique. Application of this technique to original and treated coals and the comparison of the obtained data reflects the variations in the combustion characteristics of coal as a result of the treatment. Relations between the removal of pyritic and/or organic sulphur forms and the combustion properties of high sulphur coals should be taken into account. Moreover, it is necessary to determine the effect of desulphurization conditions on the thermal reactivity of chemically desulphurized coals.

2. Experimental

The experiments were performed in a 1 l magnetically stirred Parr autoclave made of Type 316 stainless steel. The autoclave was furnished with a removable liner made of nickel, an electrically heating jacket, a temperature control unit, and a pressure gauge.

In the experiments, a hard lignite sample from Gediz area (from western Turkey) was used. The analysis of the lignite sample is shown in Table 1. The particle size of the used lignite sample is $-250\,\mu m$. Solution used in oxydesulphurization was obtained by extraction of 5 g of fly ash with 200 ml of distilled water and the insoluble matters were filtered. The composition of this solution was 15.6 mg l^{-1} of Na^+, 26.5 mg l^{-1} of K^+, 35.2 mg l^{-1} of Ca^{++}, 0.8 mg l^{-1} of Mg^{++} and 91.4 mg l^{-1} of SO_4^{2-} and its pH value was 10.5.

For each experiment, 10 g lignite sample and 200 ml extraction solution were filled into the reactor and the reactor was sealed. The heating was started after the partial pressure of oxygen was established. While stirring, the autoclave was held at the desired temperature for a given period. After this period, the stirring was stopped, pressure was decreased and the autoclave was cooled using pressurized air. The autoclave content was filtered and washed with the hot distilled water until the washings get a neutral pH. The extracted coal was dried in a vacuum oven under nitrogen atmosphere at 373 K for 24 h. After weighing, total-, pyritic-, and sulphate-sulphur contents and ash content were determined according to ASTM Standards. Organic sulphur content was calculated by subtracting the sum of the pyritic- and sulphate-sulphur contents from the total sulphur content.

Thermal data was obtained using a Shimadzu TG 41 thermal analyzer. 20 mg samples after grinding to pass a 250 μm sieve, were spread uniformly on the bottom of the crucible made of alumina. The samples were oxidized in a dynamic dry air atmosphere of 40 ml min^{-1}. Temperature was raised from ambient to 1223 K at a heating rate of 10 K min^{-1}.

3. Results and discussion

Fig. 1 illustrates the DTG burning profile of the original lignite sample. Some critical results were placed on this figure to give an instance for the interpretations about the DTG burning profiles. The mass of the sample was inert to heating upto 608 K. However, apparent losses were observed after 608 K

Table 1
Analysis of the Gediz lignite sample

Moisture (%)	Moisture free									
	Volatile matter (%)	Fixed carbon(%)	Ash (%)	Calorific value (MJ kg^{-1})	C (%)	H (%)	S_T (%)	S_P (%)	S_O (%)	S_S (%)
1.8	30.7	37.4	31.9	22.9	64.7	5.0	7.38	2.85	4.16	0.37

S_T: Total sulphur; S_P: Pyritic sulphur; S_O: Organic sulphur; S_S: Sulphate sulphur.

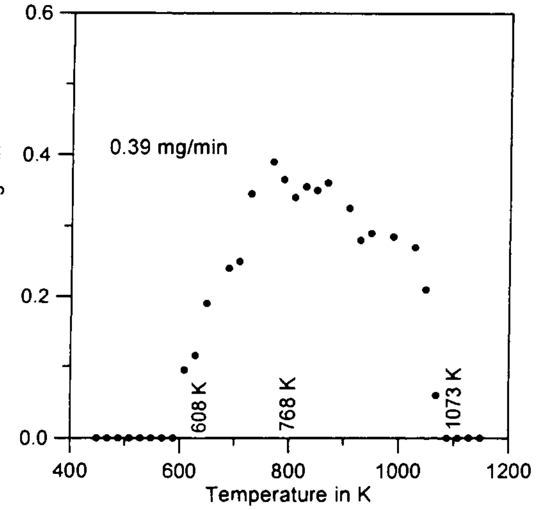

Fig. 1. DTG burning profile of the original lignite sample.

and so, this temperature was allowed as the ignition temperature of the original sample. The amount of the remaining coal decreased with combustion at different rates at different temperatures. The maximum combustion rate and the temperature at which this rate took place were determined as 0.39 mg $\min^{-1}$ and 768 K, respectively. Lower combustion rates were detected at temperatures over 768 K and it decreased to zero at 1073 K. Further heating did not cause any further decrease in the mass of the combusted bulk. Therefore, 1073 K was described as the TEC of the original lignite sample. It was calculated that 46.6 min was required to ensure complete combustion of the sample under the above mentioned experimental conditions.

Some desulphurization experiments were performed under 1 MPa partial pressure of oxygen for 30 min to investigate the effects of the desulphurization temperature on the DTG burning profiles of the treated samples. In these experiments, temperature was changed between 403 and 498 K. DTG burning profile of the sample treated at 403 K is given in Fig. 2. As it can be seen that, this treatment decreased both the ignition temperature and the TEC to 583 K and 1028 K, respectively. Maximum combustion rate was determined as 0.41 mg $\min^{-1}$ and this rate was measured at 753 K.

Fig. 3 illustrates the DTG burning profile of the sample desulphurized at 423 K. It was determined that ignition temperatures were the same for this sample

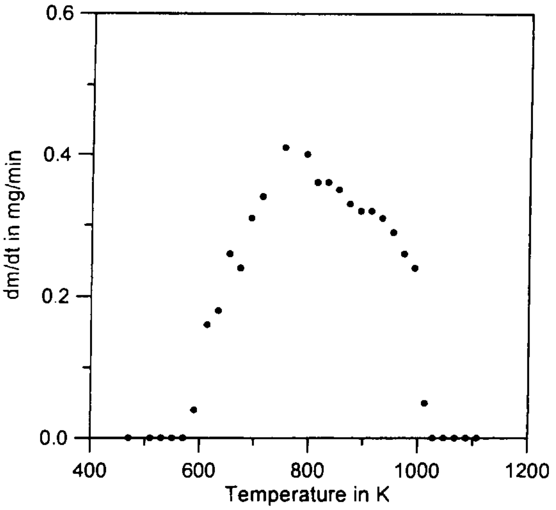

Fig. 2. DTG burning profile of the lignite sample desulphurized at 403 K.

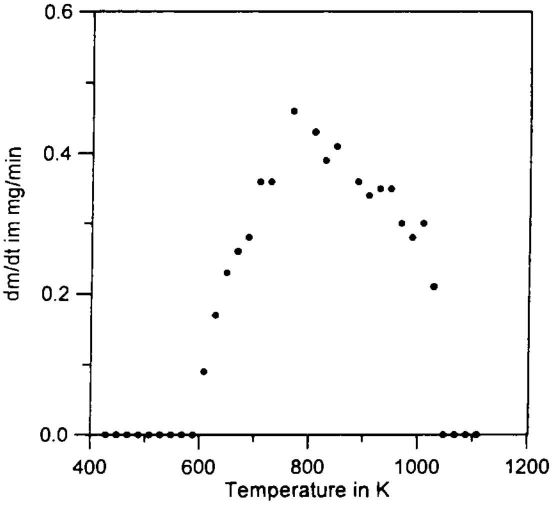

Fig. 3. DTG burning profile of the lignite sample desulphurized at 423 K.

and the original sample. However, TEC decreased to 1040 K after the treatment. Combustion reached to the maximum rate of 0.46 mg $\min^{-1}$ at 768 K.

Increase of the desulphurization temperature to 448 K decreased the ignition temperature to 583 K and reduced the TEC to 1068 K. Maximum rate of combustion was 0.44 mg $\min^{-1}$ and this rate was detected at 788 K (Fig. 4).

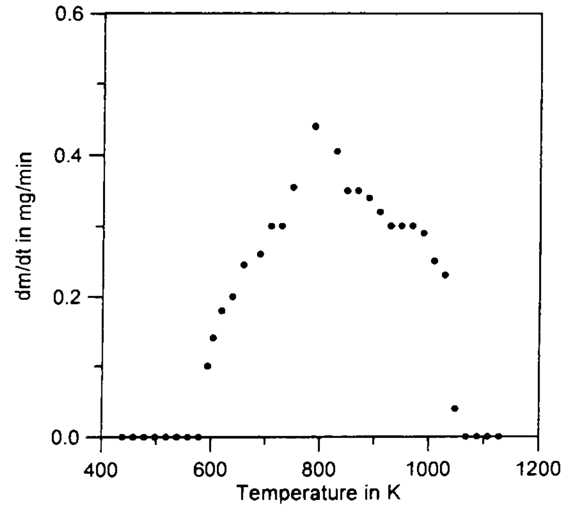

Fig. 4. DTG burning profile of the lignite sample desulphurized at 448 K.

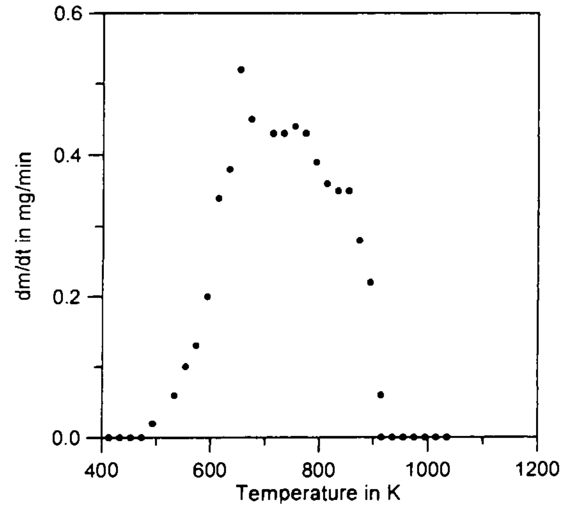

Fig. 6. DTG burning profile of the lignite sample desulphurized at 498 K.

Important variations were observed in the thermal properties of the desulphurized samples when desulphurization was carried out at higher temperatures such as 473 or 498 K (Figs. 5 and 6). Ignition temperatures were determined as 528 K for the desulphurized sample at 473 K and 503 K for the desulphurized sample at 498 K. TEC was also effected from these high temperatures. TEC values were 993 K for 473 K and 918 K for 498 K, whereas it was 1073 K for the original sample. Maximum combustion rate increased to 0.46 mg min^{-1} when the sample was desulphurized at 473 K. Increasing the desulphurization temperature to 498 K increased the maximum combustion rate to 0.52 mg min^{-1} showing a significant augmentation and this rate was detected at a very low temperature of 653 K.

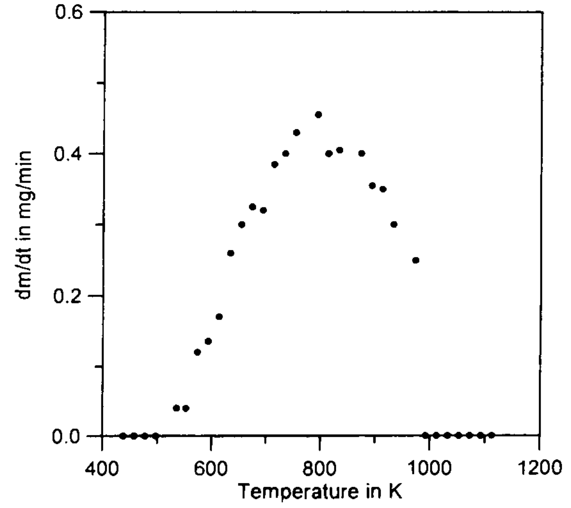

Fig. 5. DTG burning profile of the lignite sample desulphurized at 473 K.

The variation of the maximum combustion rate depending on desulphurization temperature is shown in Fig. 7. Increase of the desulphurization temperature from 403 K to 473 K increased the maximum combustion rate linearly but increase from 473 K to 498 K accelerated this increase.

Ignition temperature slowed down concerning the increase of desulphurization temperature. Especially temperatures over 448 K caused a considerable decrease in the ignition temperature (Fig. 8).

The original lignite sample took 46.5 min for complete combustion, whereas 44.5, 43.2 and 41.5 min were sufficient for the desulphurized samples at temperatures 403, 423 and 498 K, respectively. These results indicated that the desulphurized samples began to burn at lower temperatures, their combustion ended at lower temperatures and they had higher combustion rates in comparison with the original sample. Furthermore, among the desulphurized samples, high reactiv-

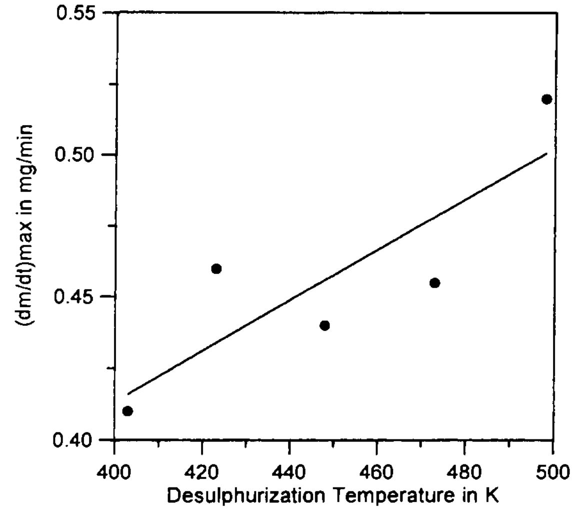

Fig. 7. Relation between maximum combustion rate and desulphurization temperature.

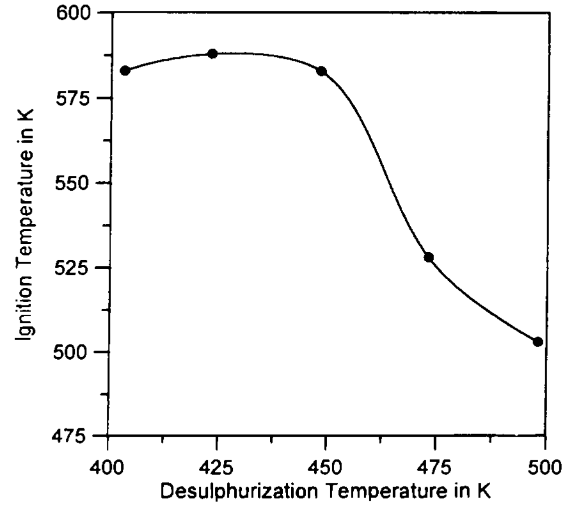

Fig. 8. Relation between ignition temperature and desulphurization temperature.

ities appeared when desulphurization temperature was held over 448 K.

In addition to the severity of treatments applied, it was found out that the removals of the sulphur compounds and ash content also had effects on the combustion period. Pyritic sulphur removals were 63.6%, 75.2%, 88.3%, 91.5% and 91.7% regarding desulphurization under 1 MPa partial pressure of oxygen at temperatures of 403, 423, 448, 473, and 498 K, respectively. Removal of ash content varied within a narrow range of 12.9–15.2%. Organic sulphur removals exponentially varied between 0.1% and 42.6% with increasing temperature. Increase of temperature tends to decrease the contents of pyritic- and organic-sulphur contents in coal and therefore, the reactivity of such treated samples should be expected as lower than that of the original sample. However, the increasing effect of the heat applied during desulphurization on the thermal reactivity was compensated with the mentioned decreasing effects. Hence, combustion period did not show important changes and it varied between 41.5 and 48.5 min.

The complete combustion of the lignite sample desulphurized without oxygen took 39 min. This treatment provided the removal of only 25.7% of pyritic sulphur content from the sample. The reactivity of the sample considerably increased after treatment since desulphurization was carried out at 473 K, and an important part of pyritic sulphur remained in coal in spite of the treatment. It is well known that some ash forming inorganic constituents are one of the fundamental factors determining the thermal reactivity of coal [4]. A great difference took place between the reactivities of original and desulphurized samples although ash content was not changed and the removal of organic sulphur content was only at the level of 9.5%. It can be concluded that the variation of the reactivity was mainly from the thermal treatment in the presence of oxygen.

DTG burning profiles of the samples treated without oxygen and under 1.5 MPa partial pressure of oxygen at 473 K for 30 min are illustrated in Figs. 9 and 10. It was determined that desulphurization performed without oxygen did not have any effect on the ignition temperature of the lignite sample, but it caused to decrease the TEC to 998 K. Under these conditions combustion rate reached to its maximum value of 0.44 mg min^{-1} at 773 K. Considerable changes were taken place in the combustion properties of the desulphurized sample by addition of oxygen at a partial pressure of 1.5 MPa. The desulphurized sample became so reactive that its ignition temperature was only 498 K and its TEC value was 978 K. Maximum combustion rate was observed as 0.43 mg min^{-1} at 758 K. Ignition temperatures of the samples treated at 473 K and under oxygen pressures of 0, 1, and

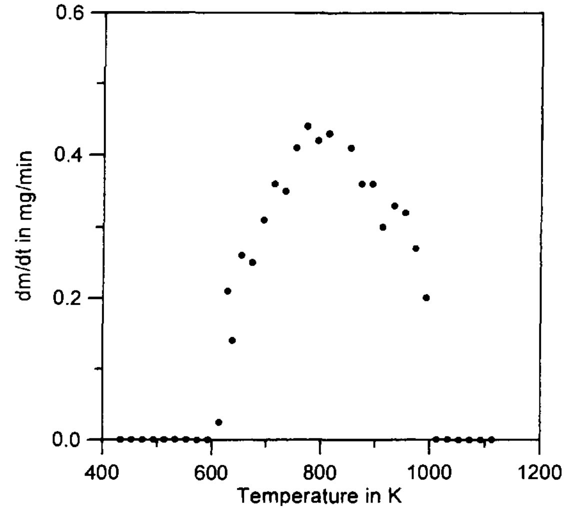

Fig. 9. DTG burning profile of the lignite sample desulphurized without oxygen.

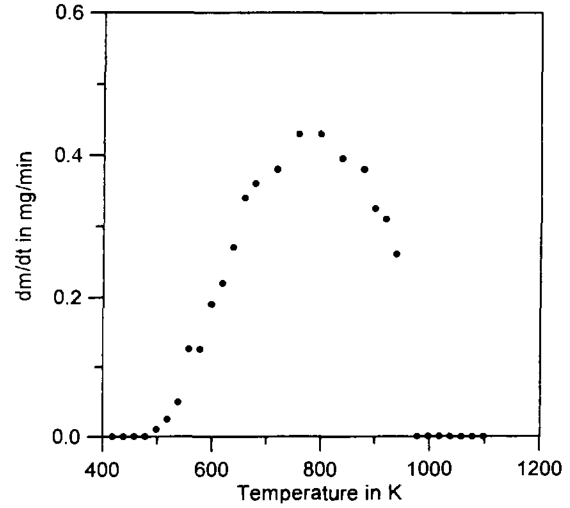

Fig. 10. DTG burning profile of the lignite sample desulphurized under 1.5 MPa partial pressure of oxygen.

1.5 MPa were determined as 608, 528 and 498 K, respectively. These results showed that thermal reactivity of the samples which subjected to oxydesulphurization increased due to the increase of the partial pressure of oxygen. High oxygen pressures resulted in the formation of new functional groups containing oxygen and the structures of aldehydes and ketones on the organic coal matrix [3]. These new groups and structures contributed to increase the reactivity after treatment with oxygen. TEC values pertaining to the increase of partial pressure of oxygen, had the tendency to decrease to some extent so that they were 998, 993 and 978 K under mentioned conditions.

Complete combustion of desulphurized samples under oxygen pressures took longer times than that of the sample desulphurized without oxygen. For instance, times of 46.5 and 48.0 min were required to ensure the complete combustion of desulphurized samples under partial pressures of 1 and 1.5 MPa, respectively. Thermal reactivity of the sample decreased with respect to the removals of 91.5% and 89.7% of pyritic sulphur content under these pressures. Both the decreasing effect of the pyritic sulphur removal and the increasing effect of the desulphurization temperature determined the level of the thermal reactivity. On the other hand, 50.4% of total sulphur content, 21.5% of organic sulphur content and 15.2% of ash content were removed under 1 MPa partial pressure of oxygen. Under 1.5 MPa partial pressure of oxygen, 56.9% of total sulphur content, 34.1% of organic sulphur content and 11.8% of ash content could be removed. Although ignition temperature was relatively low, combustion rates were not sufficiently high. Therefore longer periods were required to complete the combustion.

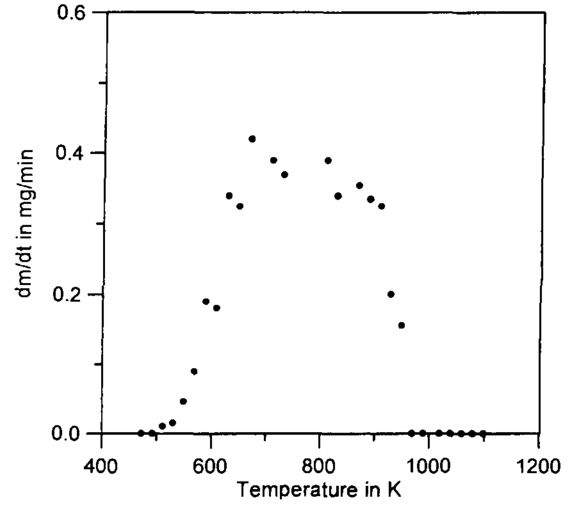

Fig. 11. DTG burning profile of the lignite sample desulphurized for 90 min.

After desulphurization under conditions of 1 MPa partial pressure of oxygen, 473 K and 90 min, some indications of thermal reactivity such as ignition temperature, TEC, and maximum combustion rate were detected as 515 K, 958 K and 0.42 mg min^{-1}, respectively (Fig. 11). These results can be interpreted that ignition temperature was not changed considerably whether the desulphurization time was 30 or 90 min. However, TEC and maximum combustion rate were slightly lower and combustion period were quite shorter for 90 min in comparison with the results for 30 min. This led to the conclusion that increase in the desulphurization time from 30 min to 90 min caused negligible variations in coal reactivity.

4. Conclusion

Thermal reactivity which is one of the important properties of coal obviously increased concerning the effects of oxydesulphurization method. This increase became more clear depending on the severity of the conditions applied. Particularly, at temperatures over 448 K, some properties indicating the level of the thermal reactivity (ignition temperature, TEC, maximum combustion rate, combustion period, etc.) were considerably affected. Especially, important variations took place in the ignition temperature and maximum combustion rate as a result of the increase in the desulphurization temperature. The formation of new functional groups containing oxygen and the structures of aldehydes and ketones on the organic coal matrix also had effects on the thermal reactivity. It was determined that, the lower the pyritic sulphur content, the lower will be the thermal reactivity. Ash- and organic sulphur-content showed secondary effects on the variation of thermal reactivity after desulphurization. In case of removal of most of the pyritic sulphur content under mild conditions, thermal reactivity decreased significantly. In case of severe conditions, however, the lowering effect of the pyritic sulphur removal on thermal reactivity was compensated with the increasing effect of the desulphurization conditions.

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