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Influence of oxidative treatments on the thermal reactivity of lignites

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Abstract

Influence of wet oxidation on the burning profiles of lignites was investigated. For this purpose, five different Turkish lignite samples were treated with either 0.2 M sodium carbonate solution or distilled water at 423 K under 1.5 MPa partial pressure of oxygen for 60 min. TGA technique was applied to the original and treated lignite samples from ambient temperature to 1223 K under dynamic dry air atmosphere. Burning profiles of the original and treated lignite samples were derived from the thermogravimetric curves. In the case of alkaline conditions, some degradation took place in the organic matrix of the lignite samples. Loss of combustible part of the treated lignite samples led to important changes in the burning profiles of the treated lignite samples compared with those of the original lignite samples. The presence of sodium carbonate was detected from its decomposition peaks, predicting that some of sodium carbonate could not be eliminated from the treated lignite samples. Sulphuric acid forming as a result of the oxidation of sulphur compounds, removed some mineral species from the treated lignite samples, affecting burning profile. Oxidation of the lignite samples in either alkaline or acidic medium increased thermal reactivity. Consequently, the ignition temperature was decreased and burning rates increased. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Lignite; Thermal reactivity; Oxidation; Sodium carbonate

1. Introduction

Oxidative pretreatments have widely been applied to coal especially in order to reduce its sulphur content [1–3]. Turkish lignites contain high sulphur contents up to about 14% (on dry basis) [4]. There have been various investigations focused on the desulphurization of Turkish lignites via oxidative techniques [5,6]. The results of these investigations showed that every procedure applied to coal usually results in some changes in the physical and/or chemical characteristics of coal. On the other hand, removal of the reagents from treated coal is very difficult and cannot be eliminated completely.

The thermal reactivity of coal has been widely investigated using thermogravimetric analysis (TGA) technique. By this method, some combustion characteristics such as ignition temperature, burning time and burning rate can be determined. DTG (derivative thermogravimetry) curve derived from TGA diagram is called the burning profile by which burning rates can be determined. When dried coal is heated in the presence of oxygen, at first combustible components of volatile matter ignites and then burning

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continues until the organic part burns thoroughly. Burning rate increases until reaching a maximum, beyond that it decreases and finally becomes zero.

There are a number of factors determining the thermal reactivity of coal. Mineral matter content of coal is one of the important factors affecting combustion properties of coal. It was determined using 21 Turkish lignites that there was a strong relation between the sum of the CaO, MgO, Na_2O and K_2O contents and DTA ignition temperature, and DTG maximum peak temperature [7]. The higher the content, i.e., the sum of these inorganic constituents, the lower the value of both thermal reactivity indications will be. On the other hand, it is well-known that low rank coals are thermally more reactive than high rank coals. Although coal has extremely complex structures and there are various distinguishing differences to rank coals, oxygen content of coal augments with decreasing rank and it can be allowed the most important factor determining the level of thermal reactivity. When coal is subjected to oxygen for sufficient period, some remarkable changes take place in its physical and chemical properties. Its physical structure becomes more fragile, and some oxygen containing functional groups emerge from its surface. These changes affect the thermal reactivity of coal [8]. The aim of this paper is to investigate the effect of oxidative treatments on the thermal reactivity of some Turkish lignites.

2. Experimental

In the experiments, five different Turkish lignite samples, Agacli, Bolluca, Tavsanli, Malkara, and Yenikoy, were used. The proximate analyses of the lignite samples were performed according to ASTM standards and results are given in Table 1.

Oxidation experiments were performed in a 1 l, magnetically stirred Parr autoclave made of 316 stainless steel. Inner surface of the autoclave was protected using removable nickel liner. For each experiment, 10 g of lignite having $-250\,\mu m$ particle size was completely wetted with $300\,cm^3$ of distilled water or $300\,cm^3$ of 0.2 N sodium carbonate solution. After sealing, 1.5 MPa of partial pressure of oxygen was established and the autoclave was heated to 423 K. During these period, autoclave content was not stirred. Stirring at 500 rpm was initiated when temperature reached 423 K. Autoclave was held at the fixed temperature with the stirring rate for 60 min. Oxidation of pyrite (FeS_2) and some organic sulphur compounds initiated the formation of sulphuric acid. In the presence of sodium carbonate solutions, sulphuric acid was rapidly neutralised. When the solution was distilled water, the reaction medium gradually turned to acidic as a result of formation of sulphuric acid. At the end of this batch process, autoclave was rapidly cooled and pressure released. Suspension was filtered and washed several times with hot distilled water. The extracted lignite was dried under nitrogen atmosphere in a vacuum oven at 383 K for 24 h.

Thermogravimetric analysis was performed using a Shimadzu TG 41 thermal analyser. 20 mg samples after grinding to pass a $250\,\mu m$ sieve, were spread uniformly on the bottom of the crucible made of alumina. The samples were oxidised in a dynamic dry air atmosphere of $40\,cm^3\,min^{-1}$. Temperature was raised from ambient to 1223 K at a heating rate of $10\,K\,min^{-1}$.

Table 1
Proximate analysis of the lignite samples

Sample	Moisture (%)	Dry basis			
		Volatile matter (%)	Ash (%)	Fixed carbon (%)	Gross calorific value (MJ/kg)
Agacli	28.6	54.9	11.8	33.3	24.5
Bolluca	39.7	55.3	9.9	34.8	22.6
Tavsanli	13.9	40.1	15.5	44.4	26.8
Malkara	31.1	46.5	13.7	39.8	23.6
Yenikoy	30.2	52.1	9.6	38.3	22.8

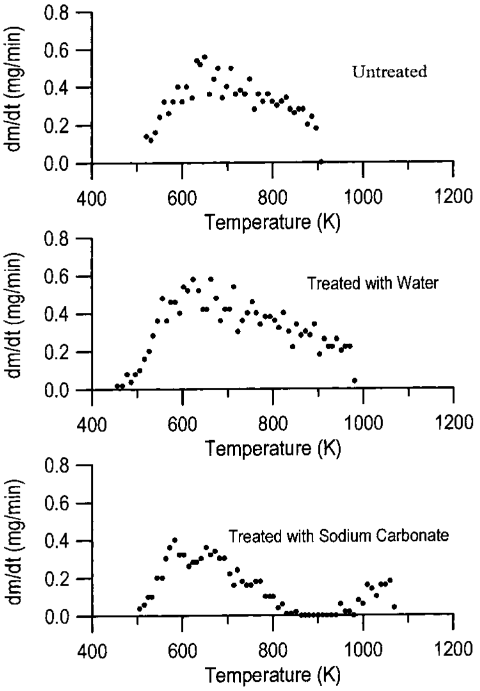

Fig. 1. Burning profiles of Agacli lignite sample.

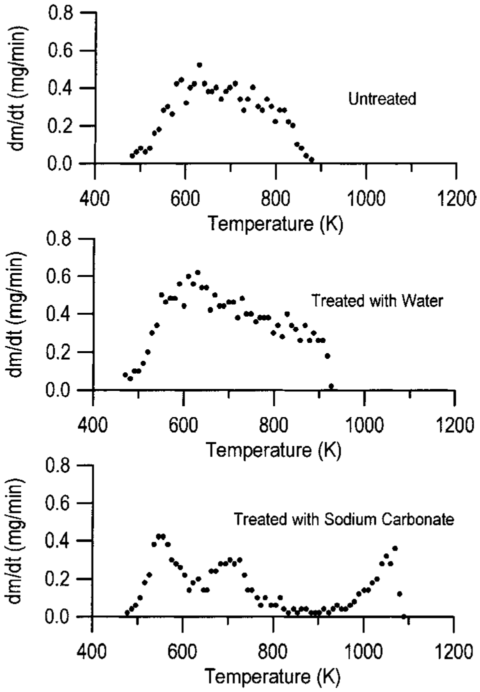

Fig. 2. Burning profiles of Bolluca lignite sample.

3. Results and discussion

The burning profiles of the original and treated lignite samples are shown in Figs. 1–5 and a comparison of some combustion properties of the lignite samples are given in Table 2. Ignition temperature (T_0), maximum burning rate (MBR), temperature at the maximum burning rate (T_{MBR}), and burn-out temperature (T_{BT}) values of the original lignite samples varied in large ranges, indicating that selected lignite samples have very different thermal properties. T_0 varied between 471 and 546 K, T_{MBR} between 618 and 694 K, T_{BT} between 871 and 1011 K, and MBR between 0.46 and 0.58 mg/min.

When the solution was distilled water, sulphuric acid spontaneously forming in the reaction medium extracted some mineral species of the lignite samples. Consequently, ash contents of the treated lignite samples decreased. The extent of the ash removals are shown in Table 3. Maximum ash removal was 39.4% for Bolluca lignite, and minimum ash removal was 14.2% for Tavsanli lignite. The fixed carbon content of Tavsanli lignite sample is high, is an indication of high carbonisation degree. Both porosity and pore diameter decrease with increasing carbonisation. The mean pore diameter of Tavsanli lignite sample was 0.64 μm, whereas that of Bolluca lignite sample was 1.62 μm. Removal of some inorganic species from the lignite samples led to concentrate the organic part and diminish the inorganic part relatively. This fact affected the shape of the burning profiles. The area under the curve became larger for treated lignite samples except Tavsanli lignite sample. The difference between burning profiles of original and treated Tavsanli lignite samples was not as important as the other lignite samples. On the other hand, it was determined that original Tavsanli lignite sample has the highest T_0 and T_{MBR} values, designating that Tavsanli lignite sample burns slowly and steadily.

Oxidation of the lignite samples in the suspension of distilled water caused to decrease the ignition temperature (T_0) . This decrease varied between 20 and 93 K. On the other hand, MBR increased for the treated lignite samples except for Tavsanli lignite sample. However, variations in T_{MBR} were negligible. T_{BT} for the treated lignite samples was higher than that

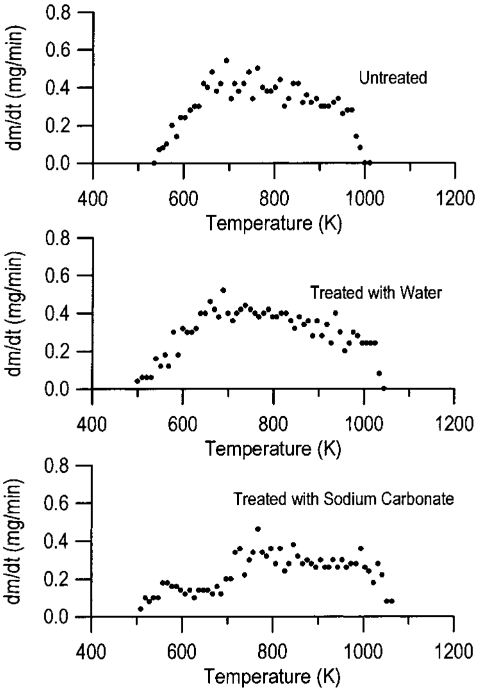

Fig. 3. Burning profiles of Tavsanli lignite sample.

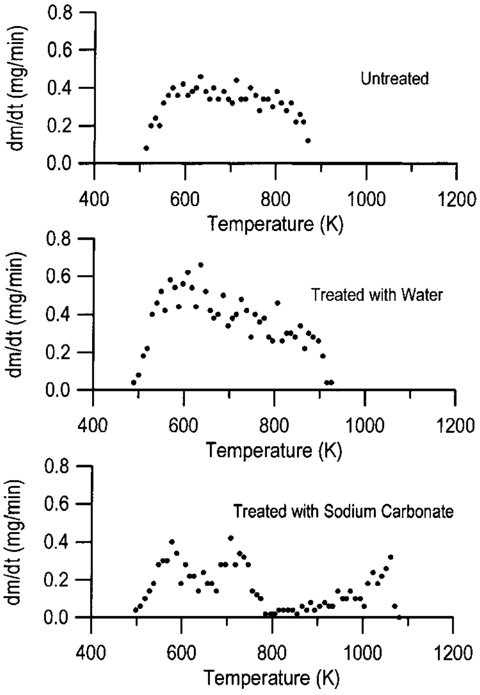

Fig. 4. Burning profiles of Malkara lignite sample.

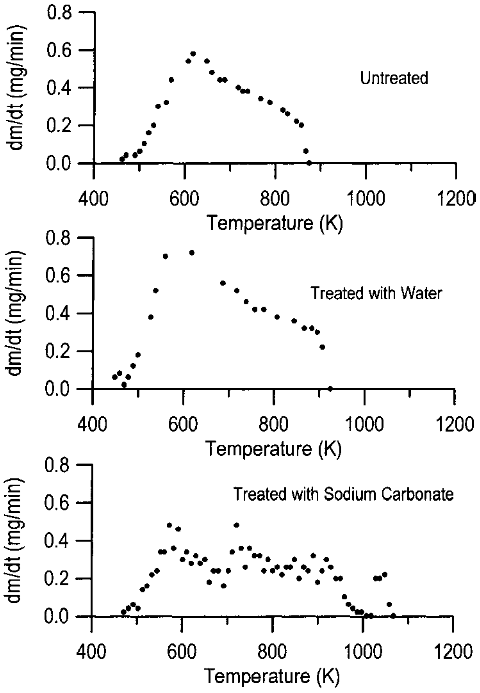

Fig. 5. Burning profiles of Yenikoy lignite sample.

for the original lignite samples. In that connection, lower T_0 , and higher MBR indicated that the treatment of lignite samples under oxidative conditions using water resulted in the increase of the thermal reactivity.

Since lignitic structure is highly sensitive to both oxidation and alkaline treatment, considerable organic part of the lignite samples could not be recovered after treatment with sodium carbonate. Recovery ratios of the lignite samples are presented in Table 4. Tavsanli lignite sample having highest calorific value and fixed carbon content, and lowest moisture content was recovered in the ratio of 58.2% (on dry basis). Whereas, recovery ratios of other lignite samples varied between 17.5% and 21.9%, indicating that most of their humic acids decomposed under alkaline conditions. As a result of that loss in the organic matrix, combustible part of these lignite samples declined considerably. Therefore, burning rates of the samples which were treated by sodium carbonate solution were lower than those of the original lignite samples.

TGA curve of anhydrous sodium carbonate shows weight loss at the temperature range of 900–1175 K

Table 2
Comparison of some combustion characteristics of the lignite samples

Sample	Ignition temperature (K)	Maximum burning rate (mg/min)	Temperature at maximum burning rate (K)	Burn-out temperature (K)
Agacli-original	531	0.56	650	908
Agacli-water	438	0.58	663	981
Agacli-sodium carbonate	505	0.40	583	840
Bolluca-original	491	0.52	630	879
Bolluca-water	471	0.62	630	927
Bolluca-sodium carbonate	488	0.42	556	854
Tavsanli-original	546	0.54	694	1011
Tavsanli-water	500	0.52	688	1044
Tavsanli-sodium carbonate	509	0.46	767	1063
Malkara-original	515	0.46	633	871
Malkara-water	490	0.66	636	926
Malkara-sodium carbonate	499	0.42	708	806
Yenikoy-original	471	0.58	618	875
Yenikoy-water	449	0.72	617	925
Yenikoy-sodium carbonate	471	0.48	720	1007

under static air atmosphere [9]. Decomposition of sodium carbonate retained in the lignite samples gave rise further decrease in the amount of the samples at this temperature range. Consequently, new peaks were appeared in the burning profiles of the samples except for Tavsanli lignite sample. Since, the highest burn-out temperature (T_{BT}) belonged to Tavsanli lignite sample, the phenomena of decomposition was begun before the completion of the burning. For other lignite samples, DTG diagrams could be easily divided into two regions as burning of the combustible part and then the decomposition of the retained sodium carbonate.

T_0 of the lignite samples except for Yenikoy lignite decreased owing to the treatment with sodium carbonate solutions under oxidative conditions. Lignite samples have high tendency toward oxygen uptake. When oxidation process takes place in an alkaline medium, the oxygen uptake accelerates and the surface of the lignite sample is covered with oxygen containing functional groups such as carbonyl, carboxyl, ether, etc. These groups can be allowed to increase the thermal reactivity of the lignite samples. Removal of humic acids became the treated lignite poor in organic constituents and relatively rich in the mineral matter. Therefore, T_0 of the lignite samples

Table 3
Ash removals from the lignite samples via treatment with distilled water

Sample	Ash removal (%)
Agacli	27.1
Bolluca	39.4
Tavsanli	14.2
Malkara	31.4
Yenikoy	30.2

Table 4
Recovery ratios of the lignite samples after treatment with sodium carbonate solution

Sample	Recovery ratios (%)
Agacli	17.5
Bolluca	21.9
Tavsanli	58.2
Malkara	19.1
Yenikoy	17.9

treated under alkaline conditions was not so low as the T_0 of lignite samples treated under acidic conditions.

4. Conclusion

Thermal reactivity of lignite is extremely susceptible to the wet oxidation regardless the medium is acidic or alkaline. Oxidation under alkaline conditions has a big decomposing effect on the organic coal matrix. Since most of the humic acids become soluble under alkaline conditions, only small portion of the organic part and almost all of the mineral matter can be recovered.

In case of the absence of alkalinity, oxidation of pyrite and some organic sulphur compounds yielded to the formation of sulphuric acid, which can extract some mineral matter constituents. Consequently, organic part became relatively concentrated and the area under DTG diagram became larger. Likewise, MBR generally increased when lignite is treated under acidic conditions. Oxidised lignite can be ignited at lower temperatures. Easier ignition and higher MBR values indicated that lignite samples become more reactive when they oxidised in aqueous acidic or alkaline medium.

Sodium carbonate retained in the lignite samples appears in the burning profile of lignite samples as a discrete peak or associated with the combustion peak depending on the burn-out temperature of the lignite samples.

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