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# THE EFFECT OF OXIDATION ON THE STRUCTURE PROPERTIES AND CALORIFIC VALUES OF LIGNITES

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## ABSTRACT

Information on the change of oxygen functional groups in the oxidizing coal is important to coal utilization particularly for lower rank coal which has high oxygen content. In this work, effect of oxidation on the structure properties and calorific values of lignites was investigated by using two different Turkish lignites. Lignite samples were oxidized by air circulation and in aqueous media, solution of hydrogen peroxide (5%$H_2O_2$). FT-i.r. technique was applied to the original and oxidized lignite samples to investigate functional group analyses. The results indicated that oxidation reaction caused a decrease in the aliphatic C-H stretching bands, whereas it lead to a significant increase in the C=O, C-O, and -OH stretching absorption bands.
**Keywords:** Coal, oxidation, $H_2O_2$, air circulation

## LİNYİTLERİN YAPISAL ÖZELLİKLERİ VE ISIL DEĞERLERİ ÜZERİNE OKSİDASYONUN ETKİSİ

## ÖZET

Oksitlenmiş kömürlerde bulunan oksijen bağlı fonksiyonel grupların değişimi, özellikle yüksek oksijen içeren düşük ranklı kömürlerin kullanımı için önemlidir. Bu çalışmada, oksidasyonun linyitlerin yapısal özellikleri ve ısıl değerleri üzerine etkileri, iki farklı Türk linyiti kullanarak araştırılmıştır. Linyit numuneleri, hava sirkülasyonu ve hidrojenperoksit çözeltisi (5%$H_2O_2$) ile muamele edilerek oksitlendirilmiştir. FT-i.r tekniği kullanılarak orjinal ve oksitlendirilmiş linyit numunelerinin fonksiyonel grup analizleri yapılmıştır. Sonuçlar, oksidasyon reaksiyonlarının alifatik C-H absorbsiyon bandlarında azalmaya, C=O, C-O, -OH absorbsiyon bantlarında önemli derecede artışa neden olduğuna işaret etmektedir.
**Anahtar Sözcükler:** Kömür, oksidasyon, $H_2O_2$, hava sirkülasyonu

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## 1. INTRODUCTION

Oxidation studies have been carried out in three basic areas. First area is interested in the occurrence of autoignition. Some coals have tended to autoignite when exposed to in storage pile. These properties of coals cause to some problems during industrial process. A second area of interest has been destructive oxidation of coal as a method for gathering structural information. A third type of coal oxidation work has to do with the conversion of coal-to-coal acids. (e.g. aromatic polycarboxylic acids) or humic acids, intended for use as fertilizer. Oxygen in aqueous alkaline media or alkaline oxygen oxidation has been the principal method for converting coal to

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acids. In this process, generally nitric acid ($HNO_3$), electrolytic oxidation, permanganate, hydrogen peroxide and chromic acid have been used. After this treatment, coal acids (or humic acids) have separated as water soluble and insoluble fractions [1,2].

It is well known that oxidation changes physical and chemical properties of coals such as calorific value, combustion properties, surface structure, cleaning, pyrolysis and carbonization properties [3].

Oxidation by means of dissolved oxygen is one of the influential methods, in which oxygen is applied to a suspension in the liquid phase, converts sulphur compounds into soluble sulphates. Desulphurization of coals by means of hydrogen peroxide has been most frequently studied due to its strong agent. The treatment with this solution is cheap because of the moderate temperature and atmospheric pressure. On the other hand, aerial oxidation has a negative effect on industrial usage of coal such as transportation and storage. For these reasons, air circulation is an important process [4].

The mechanism of coal oxidation has been the subject of considerable study [5]. It is generally accepted that the initial stage of oxidation involves the attack of molecular oxygen on certain aliphatic species, generally methylene groups to aromatic ring or to –OR groups, producing peroxides and hydroperoxides which decompose to form oxygenated groups [6]. In the initial step of oxidation, oxygen diffuses into pores of coals and fills the apertures by physical means. Then, as oxidation proceeds, this adsorbed oxygen is combined with the coal matrix chemically. Further oxidation converts chemisorbed oxygen into surface oxides [7].There has been detailed information about structural changes resulting from oxidation of bituminous coals, but for lower rank coals information is limited.

The aim of this paper is to present some information about changes in the calorific value and chemical composition of lignite samples as a result of oxidation with aqueous solution of medium, hydrogen peroxide and weathering.

## 2. EXPERIMENTAL

### 2.1. Coal samples

In this work, two different Turkish lignite samples, Tunçbilek and Seyitömer, were used. The coal samples were dried in an oven at 105$^oC$ for 2h and then the samples were ground and sieved to a particle size < 0,2 mm. Their proximate and ultimate analyses were performed according to ASTM standards (ASTM D3174, 3175, 3176) [8,9,10]. Results are given in Table 1.

**Table 1.** Proximate and ultimate analysis of raw coals

| | Tunçbilek | Seyitömer |
|---|---|---|
| Proximate analysis (wt.%) | | |
| Moisture (ad) | 10 | 29 |
| Ash(db) | 19 | 35 |
| Fixed carbon (db) | 46 | 25 |
| VM(db) | 35 | 40 |
| | | |
| Ultimate analysis (wt.%db) | | |
| C | 61.24 | 39.26 |
| H | 4.52 | 3.94 |
| N | 2.69 | 0.86 |
| S | 1.91 | 1.97 |
| O (by differences) | 29.64 | 53.97 |

## 2.2. Oxidation

Oxidation of the lignite samples was carried out by two different methods, aerial oxidation and treatment with aqueous solution of hydrogen peroxide. Aerial oxidation of the lignites was performed at 200°C for 5 h in the oven with forced circulation of air at 4 lt/min. In the oxidation method carried out with solution, solid/liquid ratio was used as 1/8 (wt/wt) and lignite samples and solution were loaded into the reactor immersed into a water bath circulation at constant temperature, 30°C. Peroxide concentration was selected as 5% (wt/wt) during the leaching period. The mixture was stirred for 3 h and then the mixture was filtered. The treated lignite was dried in an oven at 105°C for 2h for analyzes.

The raw and oxidized lignite were analyzed by FT-i.r. technique. Spectra of the lignite samples were obtained using a Mattson 1000 Series FT-i.r. spectrometer. 100 mg of KBr pellets containing 1 wt% lignite were dried at 105°C for 2 h and spectra were obtained at a resolution of 8 $cm^{-1}$. The peak assignments in this paper are based on information in Table 2 [11]. Also, calorific values of the raw and the oxidized lignites were determined using a bomb calorimeter which had been calibrated using benzoic acid as a standard The bomb was pressurized to 24 atm with $O_2$.

**Table 2.** Band assignments in FT-i.r. spectra of coal [11]

| Bands ($cm^{-1}$) | Assignments |
|---|---|
| 3420-3320 | -OH stretching |
| 3050-3030 | Aromatic CH strertching |
| 3000-2800 | Aliphatic CH stretching |
| 1700 | Aromatic carbonyl/carboxyl C=O stretching |
| 1610-1560 | Aromatic C=C ring stretching |
| 1510 | Aromatic C=C ring stretching |
| 1450 | Aliphatic CH deformation |
| 1430-1420 | Aromatic C=C ring stretching |
| 1370-1360 | Aliphatic $CH_3$ deformation |
| 1317-1315 | Aliphatic $CH_2$ deformation |
| 1270-1250 | Aromatic CO-and phenolic-OH stretching |
| 1060-1030 | Aliphatic ether C-O-and alcohol C-O stretching |
| 870 | 1 adjacent H deformation |
| 810 | 2 adjacent H deformation |
| 780-770 | Aliphatic $CH_2$ deformation |
| 750 | 3-4 adjacent H deformation |

## 3. RESULTS AND DISCUSSION

Figures 1a-c show FT-i.r. spectra of (a) original Seyitömer lignite (b) Seyitömer lignite oxidized in air at 200°C and (c) Seyitömer lignite oxidized by hydrogen peroxide. The F.T.i.r. spectra of Tunçbilek lignite samples are drawn out in Figure 2a-c. (a) original Tunçbilek lignite (b) Tunçbilek lignite oxidized in air at 200°C and (c) Tunçbilek lignite oxidized by hydrogen peroxide.

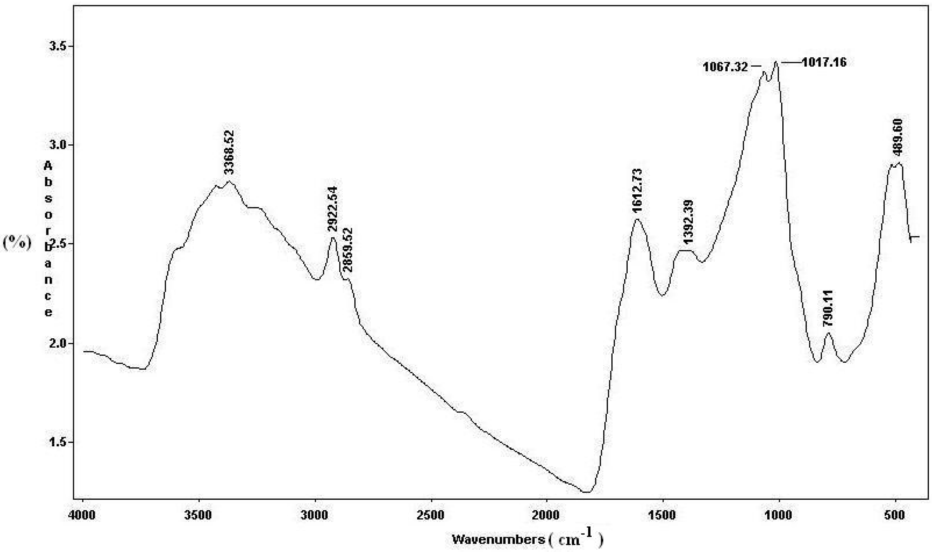

**Figure 1a.** FT.i.r. spectra of original Seyiömer lignite

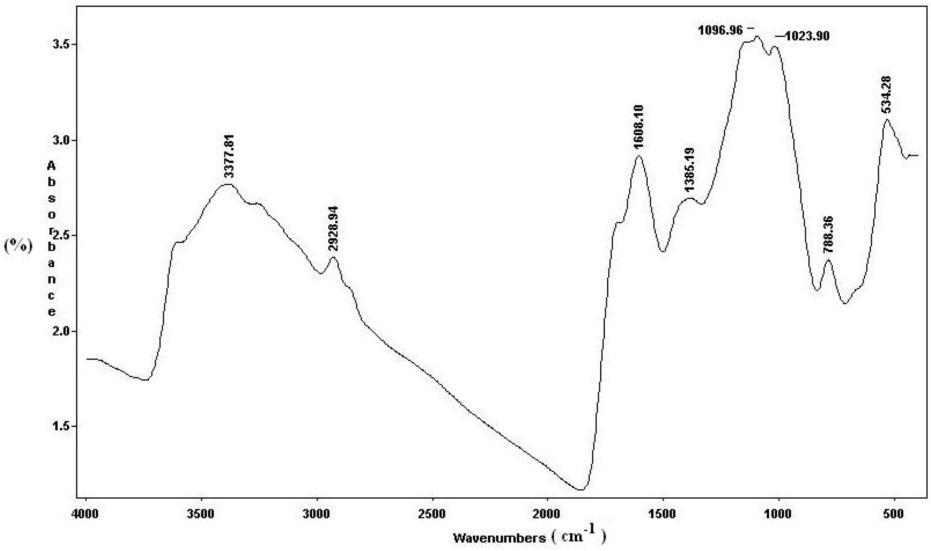

**Figure 1b.** FT.i.r. spectra of Seyitömer lignite which oxidized by air

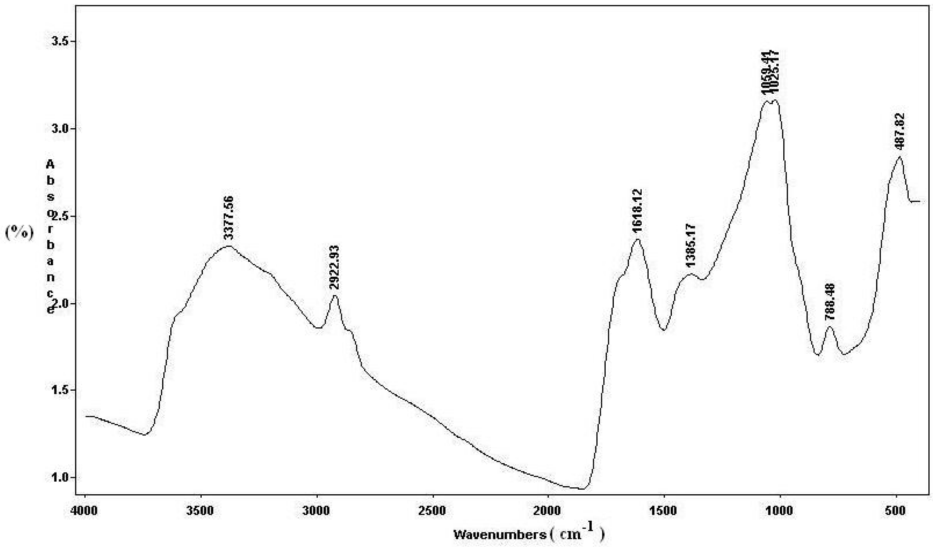

**Figure 1c.** FT.i.r. spectra of Seyitömer lignite which oxidized by $H_2O_2$ solution

It can be seen in Fig.1a that the FT-i.r spectra of Seyitömer raw coal consist of six-peak region. The IR peak of 3600-3100 $cm^{-1}$ indicate that the phenolic groups or free hydroxyl groups –OH. The absorption bands in 2860-2900 $cm^{-1}$ from the symmetric and asymmetric stretching vibration of C-H, all these $CH_2$ are in aliphatic hydrocarbon and saturated aliphatic cyclic hydrocarbon. The IR peak of 1600 $cm^{-1}$ indicates aromatic stretching. Other absorbtion bands in FT-i.r. spectra of the lignite were at 1400 $cm^{-1}$ (the asymmetric $CH_3$ and $CH_2$ bending bands), 1010-1070 $cm^{-1}$ (etheric bands, C-O groups) and 740-490 (mineral particularly calcite (Fig.1a).

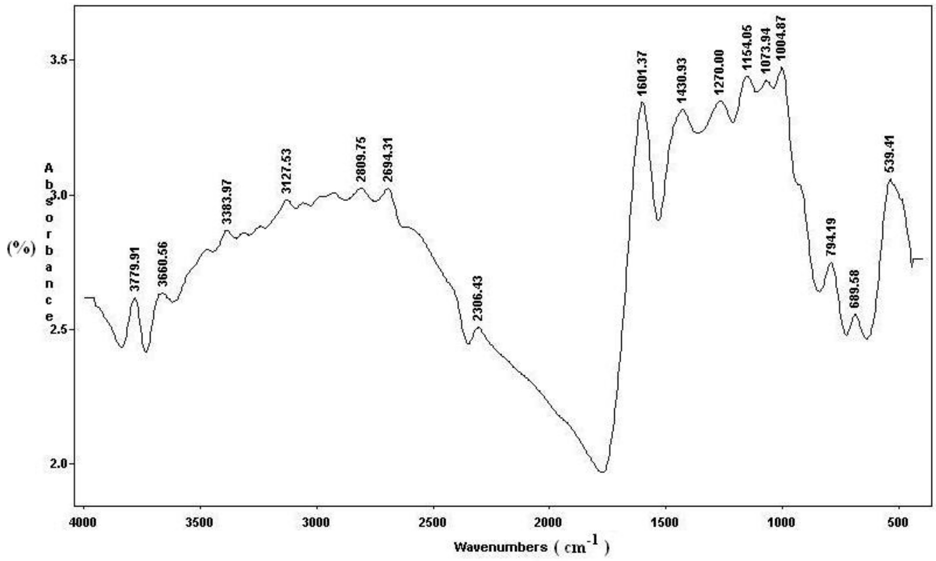

**Figure 2a.** FT.i.r. spectra of original Tunçbilek lignit

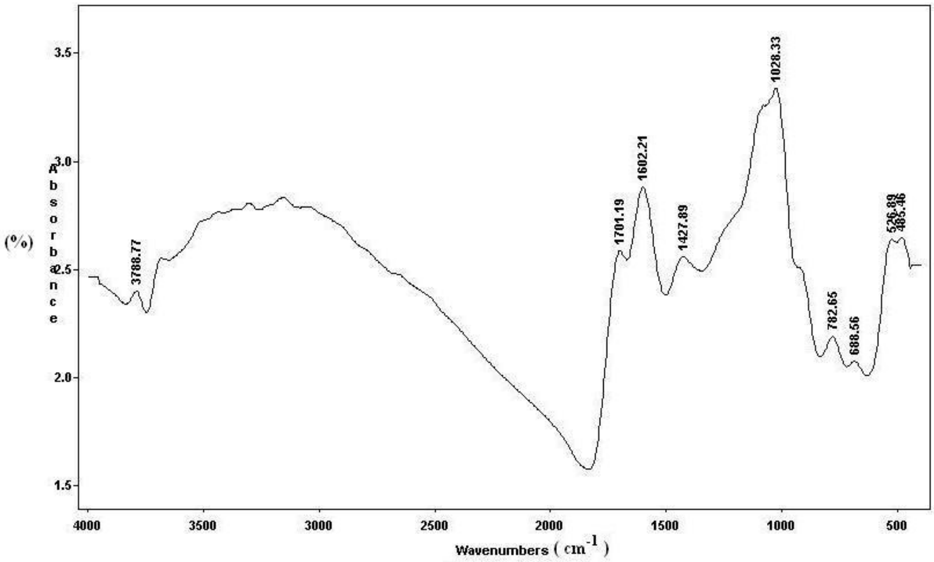

**Figure 2b.** FT.i.r. spectra of Tunçbilek lignite which oxidized by air

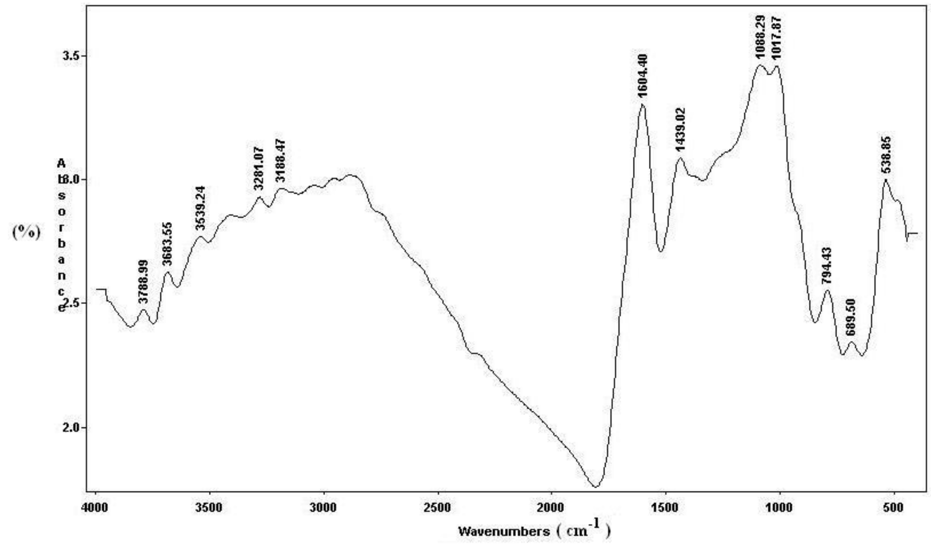

**Figure 2c.** FT.i.r. spectra of Tunçbilek lignite which oxidized by $H_2O_2$ solution

The FT-i.r. spectra of the oxidized by air and peroxide solution Seyitömer lignite are shown in Fig.2b and Fig.2c, respectively. Both of figures showed similar trends in the oxidation reactions. The absorption bands at 2859 cm$^{-1}$ changed with oxidizing treatment, which point to the presence of aliphatic hydrocarbon species. FT-i.r. spectra of raw Tunçbilek lignite has some differences in absorption bands. The main differences are present in the regions, 2300 cm$^{-1}$, 1430 cm$^{-1}$, 1000-1200 cm$^{-1}$ due to C=C, $CH_2$ groups, C-O in alcohol or ether bands respectively

(Fig.2a). FT-i.r. spectra of oxidized by air showed different trend in according to spectra of original and oxidized by peroxide solution of Tunçbilek lignite. The band at 1700 cm$^{-1}$ (aromatic carbonyl or carboxyl C=O stretching) shown to oxidized of lignites with air. In addition to, the intensity of the C-O bands (1120-1160cm$^{-1}$), -OH bands (3600-3100 cm$^{-1}$) increased significantly during the oxidation process.

**Table 3.** Calorific values of raw and oxidized lignite samples (Kcal/kg)

| Lignite Samples | Original Samples | Oxidation with air | Oxidation with hydrogen peroxide (5%) |
|---|---|---|---|
| Seyitömer | 3441 | 3216 | 3174 |
| Tunçbilek | 5886 | 4611 | 5802 |

## 4. CONCLUSIONS

It is concluded that lignite structures are sensitive to oxidation. In aerial oxidation, oxygen adsorbed on the surface on the lignite samples by physically and then it chemically sorbed on the lignite matrix. Formation of gases such as $CO_2$, $H_2O$, CO, $C_xH_y$, $H_2$ occurred resulting from oxidation. For this reason, carbon and hydrogen content decreased in coal structure. Treatment of coal with hydrogen peroxide with coal led to formation of acidic functional groups such as –OH, -COOH, C=O, C-O, while aliphatic bond such as C-H, C=C decreased at the end of oxidation with aqueous solution. It is concluded that oxidation treatment of lignites caused an increasing of oxygen-containing functional groups in structure and led to a decreasing of calorific values of lignite samples.

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