

LOW TEMPERATURE OXIDATION OF TURKISH AŞKALE LIGNITE: EFFECTS OF PARTICLE SIZE AND TEMPERATURE

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ABSTRACT

The chemical changes occurring during the low-temperature oxidation of Aşkale lignite (Turkey) in air has been investigated with both wet chemical analysis and FT-IR spectroscopy. The oxidation tests were carried out at elevated temperatures, 40, 70, 120, 170, 200, 250 and 300 °C for the samples with three different particle sizes, which were -125, 125-250 and 250-710 µm size fractions. There were changes in the hydroxyl and the carboxyl contents, depending on the temperature of oxidation.

Keywords: Oxygen-containing functional groups, FT-IR Spectroscopy, Wet chemical analysis

TÜRK AŞKALE LİNYİTİNİN DÜŞÜK SICAKLIK OKSİDASYONU: PARTİKÜL BOYUTU VE SICAKLIĞIN ETKİSİ

ÖZET

Aşkale Linyitinin (Türkiye) düşük sıcaklık oksitlenmesi sırasında meydana gelen kimyasal değişiklikler, hem ıslak kimyasal analizler hem de FT-IR spektroskopisi ile incelenmiştir. Oksidasyon testleri, -125, 125-250 ve 250-710 µm partikül boyutuna sahip, üç farklı partikül boyutlu numuneler için 40, 70, 120, 170, 200, 250 ve 300 °C'lerde yükseltilmiş sıcaklıklarda yürütülmüştür. Oksidasyon sıcaklığına bağlı olarak, hidroksil ve karboksil muhtevalarında değişiklikler olmuştur.

Anahtar Kelimeler: Oksijen İçeren Fonksiyonel Gruplar, FT-IR Spektroskopisi, Islak Kimyasal Analizler

1. INTRODUCTION

When freshly mined coal is exposed to an oxidizing atmosphere, exothermic oxidation reactions releasing large amounts of heat occur.

Such a heat release may lead to a temperature rise, which can result in the spontaneous combustion, if it isn't removed [1-3]. The use of more and more coal ever increasing as an energy source has urged the improvement in technology in order to predict and prevent the spontaneous combustion during storage and transport [3]. For this reason, an understanding of the oxidation reactions of coals at low temperature is fundamentally important for predicting self-heating and spontaneous combustion.

The products of the oxidation reactions of coal at low temperatures are carbon monoxide, carbon dioxide, water vapour and carbon-oxygen surface complexes on the coal, which eventually transform into stable structures of oxygen-containing functional groups [4, 5]. Oxygen-containing functional groups in coal have been categorized into five groups: carboxyl, hydroxyl, carbonyl, methoxyl and residual oxygen [7, 8]. The residual oxygen is mainly in ether and alcohol forms. The first three groups are particularly predominant in low-rank coals. These groups in the coals affect the technological properties of coal such as coking and caking behaviour [9], extractability [10], liquefaction [11], the hydrophilic nature of coal [12], instability and susceptibility to oxidation [12, 13], autogenous heating [9,12], coal flotation and agglomeration [14].

The oxidation of coal in air increases the oxygen-containing functional group content, in particular the polar functional groups (-COOH, -OH). The formation and/or destruction of these oxygen-containing polar functional groups cause some changes in the chemical nature of the coal surface. These polar groups have a tendency to make the surface more hydrophilic thereby increasing the capacity to reabsorb moisture [15, 16]. Consequently, the coal's hydrophilicity and wettability increases, and thus the spontaneous combustion reactivity and liability of the coal increases [6]. Besides, the low-rank coals are oxidized during the drying processes applied for increasing their calorific values per mass in industry and then with the spontaneous combustion problems may occur.

In the last fifty years, much progress in the methods used for the hydroxyl and carboxyl content determinations has been made. In addition, some new methods have been developed by numerous investigators. It will be shown that the agreement between the results obtained with the different methods is rather satisfying [6]. The used techniques were mostly based on the ion-exchange properties of the total and carboxyl acidity groups [28]. The total acidity (phenolic hydroxyl+carboxyl) was calculated from the decrease in concentration of a barium hydroxide solution used to exchange acid groups. The phenolic hydroxyl content was taken as the difference between the total acid-group content and the carboxyl content [19, 29, 30]. Schafer determined the carboxylate content from the amount of acid needed to convert the carboxylate groups to the acid form [39]. Later on, he recommended that acid extraction should be used prior to ion-exchange for the accurate determination of the total carboxyl content in brown coals [40].

Blom and co-workers used the standard-acetylation method for -OH determination and the method based on the reaction with calcium acetate by estimation of the generated acetic acid titration with alkali for the carboxyl groups' determination [19].

T.P. Maher determined acidic functional groups in five low-rank coals by aqueous ion exchange and non-aqueous titration procedures. The values for carboxyl and total acid group contents obtained by the non-aqueous titration procedure were higher than those obtained by ion exchange [31]. O.V. Nechaeva specified a method for the most complete determination of hydroxyl groups in coal by the reaction leading to the trimethylsilyl ester formation. The results obtained by this method exceeded that found by the barium oxide method [32]. U.Lenz described another method for the quantitative determination of hydroxyl groups in lignites by means of activated triethylborane [33].

Total acidity of the initial and heat-treated coals was determined by the barite technique and the content of carboxyl groups by the reaction with sodium acetate. The thermal and thermo-oxidative destruction of the

lignite was compared. The composition of the solid residues obtained at various temperatures was studied by infrared spectroscopy [26].

Snyder demonstrated that the combination of FT-IR and solid state ^{13}C NMR spectroscopy with this acetylation procedure was potentially a technique that could distinguish between alkyl and phenolic OH groups. In the infrared spectra, three separate bands, assigned to acetylated phenolic OH, alkyl OH and NH groups could be identified. Infrared spectroscopic methods have relied principal on the measurement of individual bands, usually the O-H stretching mode near 3400 cm^{-1} . The proportion of phenolic to alkyl OH was approximately constant for the coals used in this study [34].

Six Turkish lignites were treated with solutions of HCl or EtONa at ambient temperature or at $150\text{ }^{\circ}\text{C}$. The effects of the treatment on certain structural components of the lignites varied from one lignite to another. FT-IR Spectroscopy provided some additional evidence regarding the changes in lignite structure due to the treatments. It showed characteristic bands of carboxylate species around $1600\text{-}1440\text{ cm}^{-1}$, the band corresponding to C=C in aromatic structures around 1610 cm^{-1} and the O-H stretching band centred around 3400 cm^{-1} [36].

The use of quantitative FT-IR spectra was offered as a method of estimating the hydroxyl content of a coal by P.R.Solomon. The hydroxyl O-H stretch absorbance appeared to be a broad band stretching from $3600\text{ to }2000\text{ cm}^{-1}$ [37].

Osawa and Shih used the absorption of the O-H stretch at 3450 cm^{-1} in the infrared measurement of the hydroxyl concentration of coals [34]. Another IR method based on intensity measurements of the 1710 cm^{-1} carboxylic acid C=O stretching mode was reported [38].

The rate of oxidation is believed to depend on factors such as oxygen reactivity of the coal, the extent of previous oxidation, temperature, oxygen concentration in the ambient air, particle size and coal rank [3, 6].

The paper of O.I. Ogunsola is one study the effect of oxidation rate by thermal treatment in the literature. O.I. Ogunsola evaluated the effect of an evaporative thermal treatment on the distribution of the oxygen-bearing functional groups in lignite. The lignite was thermally treated at varying temperatures (200-500 °C) in three different process media (nitrogen, steam and products of combustion in 15 % excess air). The effect of the treatment on the oxygen functional groups was performed by wet chemical techniques. Steady decreases in -OH and -COOH groups with increases in treatment temperature, with a relatively small change in the >C=O group were observed [8]. On the other hand, neither Ogunsola nor others studied the effect of particle size. The relationship between oxygen functional group distribution and particle size ought to be known since coal particle size is one of the most important parameters affecting to spontaneous combustion.

As can be understood from the literature, a lot of quantitative analytical methods for polar functional groups analysis have been performed. There are no clear differences between the results obtained with the different methods. On the basis of this view, two methods, the Calcium-acetate and the Acetylation Methods, were selected for oxygen functional analysis under current conditions. Except for one study, the effect of the oxidation extent by thermal treatment has been not studied in detail. In light of all this literature, we performed both qualitative and quantitative analyses of oxygen functional groups under oxidation conditions varying with particle size at large temperature intervals [17]. Aşkale lignite was used for our study, thanks to its tendency to undergo spontaneous combustion [23-25].

Finally, the purpose of the present study was to investigate the effect of the low temperature oxidation at various temperatures for different particle sizes on the carboxyl and hydroxyl contents from oxygen functional groups in coal. The carboxyl and hydroxyl contents were analysed with both wet chemical methods and by FT-IR spectroscopy for evaluating the oxidation characteristic of Aşkale lignite from Turkey.

2. MATERIALS AND METHODS

According to the standard methods of collecting samples, the coal samples used in this investigation were collected from Aşkale coal mines in Turkey. The samples were carefully crushed, ground and then sieved to give the size fractions of -125, 125-250 and 250-710 μm using ASTM standard sieves. The analysis performed by ASTM methods for the coal samples are given in Table 1.

Table 1- Composition of different particle size fractions of Aşkale coal samples. Results are averages of duplicate analyses (as received).

Particle Size (μm)	Proximate analysis (wt%)				Sulfur distribution (wt%)				Fraction	Heating value (cal/g)	Surface Area (m^2/g)
	Ash	Volatile matter	Fixed carbon	Moisture	Total	Sulfate	Pyritic	Organic			
250-710	26.99	35.25	36.04	1.72	5.70	0.02	3.27	2.40	41.23	5974	1.16
125-250	20.24	37.06	40.98	1.72	4.70	0.24	2.68	1.78	24.67	6413	1.30
-125	21.52	35.79	41.24	1.45	4.30	0.16	2.35	1.79	34.10	6503	2.13

The coal samples were oxidized with air in a furnace at various temperatures (40, 70, 120, 170, 200, 250 and 300 $^{\circ}\text{C}$) for 1 h. The oxidized coal samples were stored in nitrogen filled containers. This step was taken so that the oxidation could be prevented. Before analysis, the samples were also protonated and demineralised, as follows. About 4 g

of each prepared sample was soaked overnight in 60 mL of 2 N HCl. The sample was washed in order to remove acid with rinsing until the effluent was negative to the AgNO₃ test. The sample was dried in vacuum at 100 °C for 20 h, and after which it was cooled down in an air-tight container filled with nitrogen [8, 24].

The carboxyl and hydroxyl contents of oxidized and raw coals were determined by means of wet chemical methods. The concentrations of hydroxyl (-OH) were determined by the method similar to those used by Angle [18] and Ogunsola [8]. Briefly, for the hydroxyl group determination, the mixture of acetic anhydride and pyridine was added to protonated coal samples. This was refluxed about 20 hours, and then left to cool. It was diluted with 100 mL of water. It's then filtered and washed with water till the effluent is free of acid. The sample was dried at 100 °C in a vacuum and cooled. CH₃OH and Ba(OH)₂ dissolved in 40 mL were added water to the dried coal. This content was refluxed for 20 hours, and then filtered. The filtrate was passed through an ion-exchange column; and was then titrated with 0,1 M NaOH. From this titration the total hydroxyl content can be calculated according to Blom et al [19].

The used method for determining the carboxyl content was also similar to that developed by Blom and others [19] as well. Basically, in the carboxyl determination method, aqueous calcium acetate solution and 50 mL water were added the protonated coal in a flask. The content was stirred with a magnetic stirrer for about 20 hours. After filtering and washing, the filtrate was titrated with standard NaOH (0,02 N). The concentrations of total carboxyl groups were calculated as equiv. carboxyl per gram. Other detailed descriptions of these methods can be found elsewhere [8, 18, 19]. Then, the spectra of the oxidized and initial samples were obtained using an FT-IR spectrophotometer.

FT-IR spectral data of coals were collected using KBr disc techniques. Mixtures of 1 mg sample and 300 mg KBr were finely ground for at least 15 minutes to assure the optimum measurement and then pressed under vacuum with a load of 800 kg. Then, the discs were dried at 100 °C under

vacuum for 24 h and analysed immediately. The FT-IR spectra were recorded between wave numbers 400-4000 cm^{-1} .

3. RESULTS AND DISCUSSION

It is generally accepted that air oxidation at low-temperature alters the organic and the inorganic composition of coals. These changes have important impacts on both physical and chemical properties [7, 20]. Therefore, the oxidation affects the technological properties of coals and coking and caking behaviour, extractability, tar yields, softening and swelling behaviour, heats of combustion and calorific values of the coals decrease sharply. The carbon and hydrogen contents fall in elemental composition, the oxygen content rises, and the macromolecular structure reorientates itself during oxidation. Air oxidation also causes the formation of ether or ester cross-links, which affect the fluid properties of the coal [21].

As mentioned before, the oxidation products of coals at low-temperature are CO, CO₂, water and oxygen functional groups formed on the surface in the result of the oxidation reaction of the coal. The contents of the carboxyl and hydroxyl groups, which are the two oxygen-containing functional groups produced on the surface with air oxidation at low-temperature were examined with both chemical analysis and by FT-IR spectroscopy. In this study, the results determined by two methods are in good accordance with the literature data obtained from different lignite's. It was determined that the analysed carboxyl and hydroxyl contents show rather different tendencies with increasing temperatures. It is shown in Table 1 that three different fractions (-125, 125-250 and 250-710 μm) of the Aşkale lignite were used in this study. The compositions of these fractions were highly different from each other. In addition, the elemental compositions contained moisture, ash, volatile matter, fixed carbon, pyritic, organic and sulphate sulphur contents were also rather different from each other. Therefore, it will be convenient to think these three fractions to act differently. Different components have different physical and chemical properties. For this reason, it is accepted that

different components have also different grinding properties. As a result, the fractions with different particle sizes have also rather different oxygen functional group concentrations.

Table 2- The oxygen functional group contents of untreated and oxidized Aşkale coal samples.

Particle Size (μm)	Oxidation Temperature ($^{\circ}\text{C}$)	Hydroxyl Content (mmol g^{-1})	Carboxyl Content (mmol g^{-1})
250-710	Untreat	12.05	0.12
	40	23.91	0.19
	70	24.51	0.16
	120	12.47	0.29
	170	24.77	0.43
	200	32.49	0.33
	250	35.53	0.22
	300	10.65	0.08
	125-250	Untreat	7.25
40		21.66	0.17
70		22.30	0.14
120		5.31	0.21
170		16.98	0.42
200		23.12	0.48
250		22.93	0.25
300		10.93	0.12
-125		Untreat	4.79
	40	21.42	0.15
	70	21.27	0.11
	120	5.06	0.21
	170	16.42	0.41
	200	21.73	0.53
	250	11.06	0.50
	300	22.34	0.14

The contents of oxygen-containing functional groups (carboxyl and hydroxyl) are showed in Table 2. A decrease was observed with decrease in particle size at oxidation temperatures under 250 °C and an increase with decrease in particle size at temperatures above 250 °C for hydroxyl group content. During the transition from untreated coal to oxidized coals at temperatures between 40-70 °C, the hydroxyl content increases. The content decreases considerably at temperatures above 70 °C as shown in Figure 1. An increase was observed in the total oxygen content of each sample oxidized at 45 °C and the same trend was also displayed at 35 °C and 55 °C [22]. A decrease was determined in hydroxyl content after 70 °C and the increase was continued to 120 °C. An increase again was shown in the temperature range of 170-200 °C, after 120 °C. A considerable reduction was shown in transition from 200 °C to 300 °C. The reductions in this temperature range are also noticed in literature. The cause of this reduction at the temperatures of 300 °C and above is probably due to slowing of the oxidation with release of tar occurring with moisture, which blankets the coal [8]. This concept may be thought as the cause of the loss in hydroxyl content. This was also supported by the concept that a beginning of softening in Aşkale lignite is about 300 °C [23, 24]. However, an opposite tendency appears in the oxidization of the particle size of -125 µm at about 250 °C. The cause of these tendencies regarding a decrease at this temperature and an increase again at 300 °C in hydroxyl content still has not been fully understood.

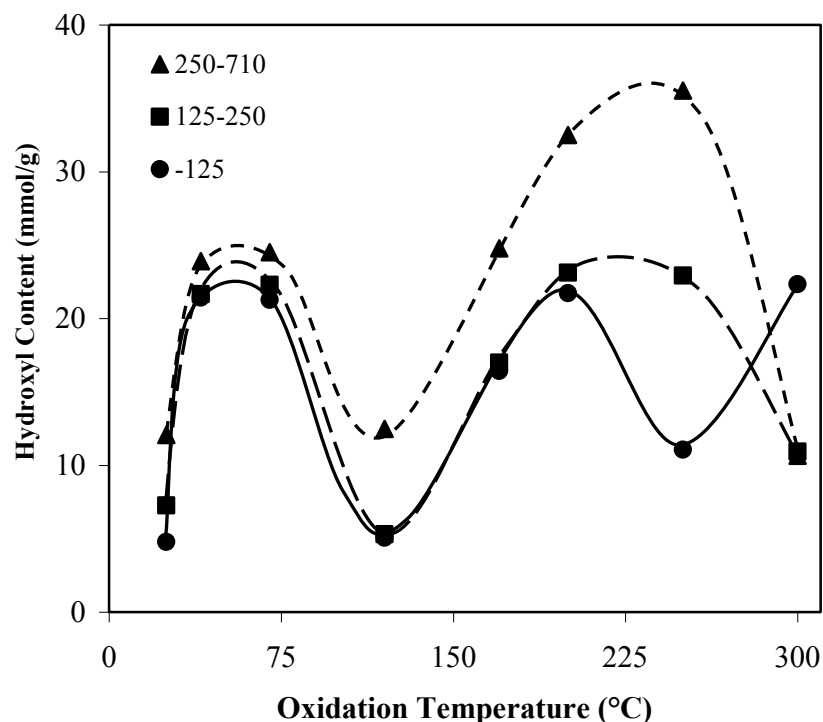


Figure 1- Changes in the hydroxyl group contents for Aşkale lignite of 250-710, 125-250 and -125 μm size fractions between 40-70 °C at increasing oxidation temperatures.

The initial stage of oxidation involves the attack of molecular oxygen on certain aliphatic moieties in which the methylene is generally transformed to aromatic rings or to $-\text{OR}$ groups to produce peroxides and hydro peroxides [21]. In the first stage, the formation of the functional groups is the result of breaking the intermolecular hydrogen bonds and the bonds of an ether type in the bridges joined to aromatic rings [26]. It has been determined that alkoxy and hydroxyl radicals are produced by the hemolysis of peroxides at temperatures between 20 °C and 60 °C and the stable gaseous and solid products of coal oxidation are produced also by further reaction of these free radicals. The experimental results show that the oxygen reactivity of coal is related to its free radical concentration. Drying in air reduces the free radical concentration and the oxygen reactivity of coal, whereas the thermal dewatering increases the free radical concentration of coal and its oxygen reactivity [22].

The carboxyl group content decreases with reduction in particle size at temperatures to 200 °C and increases with decrease in particle size at temperatures above 200 °C as shown in Table 2. The carboxyl group content as a function of oxidation temperature is represented graphically in Figure 2. An increase was shown during the transition at temperatures from untreated coal to 40 °C and then a decrease at temperatures from 40 °C to 70 °C. The temperature of untreated coal for both figures was also given as room temperature in 25 °C. Peroxides and hydro peroxides are produced with the attack of molecular oxygen on certain aliphatic moieties in the initial stage of the oxidation. It is generally accepted in the literature that hydro peroxides and peroxides are unstable and decompose above 70 °C to form oxygen-containing functional groups such as hydroxyl, carbonyl and carboxyl. Moreover, an overall increase was observed in carbonyl and carboxyl groups of coal and the loss in aliphatic groups during the oxidations at 60 °C and 140 °C. Carboxyl groups were formed and the aliphatic groups were lost during the oxidation of coal at 150 °C [21]. Figure 2 illustrates a sudden increase in carboxyl content at temperatures above 70 °C. The increase continues to 200-250 °C and a sharp decrease is observed to 300 °C. As a result of this decrease, the formation of tar may be indicated as mentioned before. Pyrite is well known to be a sensitive mineral to oxidation even at low temperatures. In addition to this situation, the ferrous (II) sulphate, which is the main product of pyrite oxidation, is formed in air at 50 °C. It was observed particularly at the early times of the process that the formation of iron (II) sulphate prevented the oxidation of aliphatic CH₂ and CH₃ groups. These groups caused the reaction with molecular oxygen to yield carboxyl-containing functional groups [21]. It is quite interesting that the curves in three different particle sizes indicate similar tendencies in graphics concerning hydroxyl and carboxyl group contents.

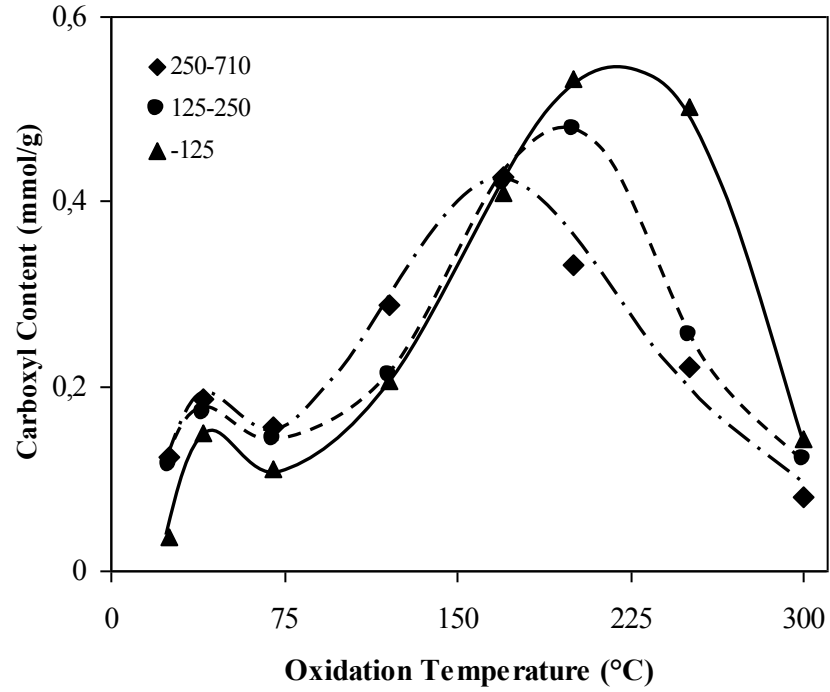


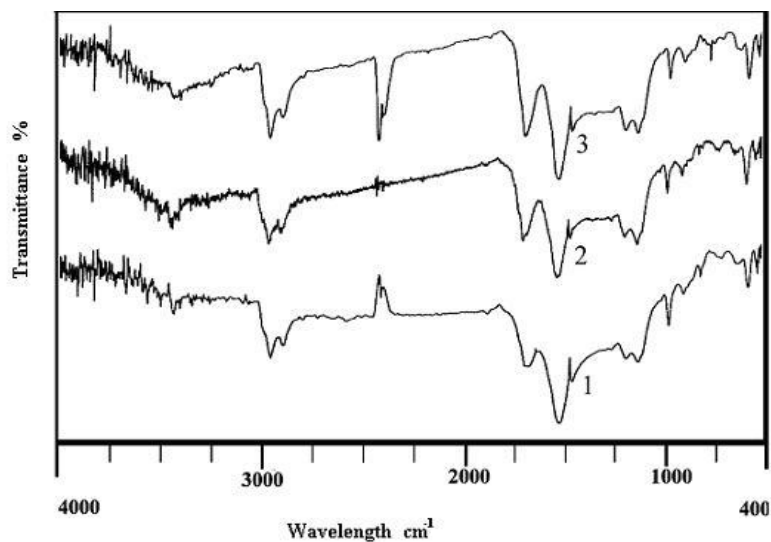
Figure 2- Changes in the carboxyl group contents for Aşkale lignite of 250-710, 125-250 and -125 μm size fractions between 40-70 °C at increasing oxidation temperatures.

The averages of standard deviations (SD) and the averages of relative standard deviations (RSD) calculated from variations of $-\text{OH}$ and $-\text{COOH}$ group content values are given for three different particle sizes in Table 3.

Table 3- The averages of standard deviations (SD) and the averages of relative standard deviations (RSD) from variations of -OH and -COOH group content values.

		Particle Size (μm)		
		250-710	125-250	-125
Hydroxyl	SD	2.10	1.05	1.30
	RSD (%)	9.73	5.13	6.00
Carboxyl	SD	0.01	0.03	0.02
	RSD (%)	3.65	5.00	4.36

According to the results obtained from IR spectroscopic determinations performed for the same coal, similar peaks occurred for three different fractions in spectra showing the changes in functional groups for the untreated coal and oxidized coals at temperatures between 40 °C and 300 °C.

**Figure 3-** IR-Spectra of untreated coals in 250-710 (1), 125-250 (2) and -125 (3) μm size fractions.

There is not much difference among the peaks observed for three different particle sizes of unoxidized raw coals. There is a very slight decrease in intensity of phenolic –OH peaks determined in the region of about 3400 cm^{-1} while the particle size falls, as represented in Figure 3. There is no considerable difference in aliphatic C-H groups in the region of $2900\text{-}2800\text{ cm}^{-1}$. Carboxyl peaks in the range $1600\text{-}1550\text{ cm}^{-1}$ did not show too much change, since carboxyl groups appeared in the highest oxygen-containing coals. It is known that the presence of carbonyl peaks are shown by absorptions at $1700\text{-}1600\text{ cm}^{-1}$, aromatic C-H groups at $900\text{-}800\text{ cm}^{-1}$ and CH_3 deformations at $1500\text{-}1400\text{ cm}^{-1}$.

For the fraction of $250\text{-}710\text{ }\mu\text{m}$, the graph for spectra for all oxidation temperatures is shown in Figure 4. The graph for the $125\text{-}250\text{ }\mu\text{m}$ fraction is shown in Figure 5, which of $\text{-}125\text{ }\mu\text{m}$ is given in Figure 6. As shown in these three graphs, the phenol hydroxyl groups had appeared in region $3600\text{-}3400\text{ cm}^{-1}$. At the same time, it is observed that the peaks of these groups are found little amounts in the untreated coal (in Table 2). In addition, these peaks increase during the oxidation temperatures at $40\text{ }^\circ\text{C}$ and $70\text{ }^\circ\text{C}$ and again decrease at about $120\text{ }^\circ\text{C}$. The densities of –OH peaks at $170\text{-}200\text{ }^\circ\text{C}$ slightly increases and then an again decrease begins at $250\text{-}300\text{ }^\circ\text{C}$ in all spectrums. At low temperatures, it has been known that phenol hydroxyl and carbonyl groups accumulate [26]. Aliphatic C-H groups which have been determined in the region $3100\text{-}2800\text{ cm}^{-1}$ have diminished as oxidation temperature increases. It was determined that oxidation may be led to formation of carbonyl groups to be consumed of both aliphatic and aromatic groups such as the hydrogen's that form the bridge in hydrogen-bond functional groups. The formation of carbonyl groups at $2000\text{-}1600\text{ cm}^{-1}$ was noticed. It follows from these graphs that C-O-C and C-O groups at $1200\text{-}1000\text{ cm}^{-1}$ and aromatic substituted C-H groups at $800\text{-}700\text{ cm}^{-1}$ are decreased with an increase in oxidation temperature. Similar tendencies have been also shown for three different graphs. It is recorded that the region between 1200 cm^{-1} and 1800 cm^{-1} is the most affected region from oxidations.

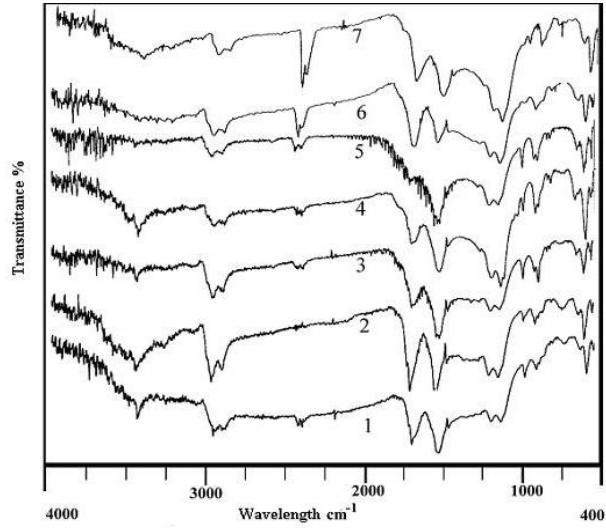


Figure 4- IR-Spectra of oxidized coals at 40 (1), 70 (2), 120 (3), 170 (4), 200 (5), 250 (6) and 300 (7)°C in 250-710 μm size fractions.

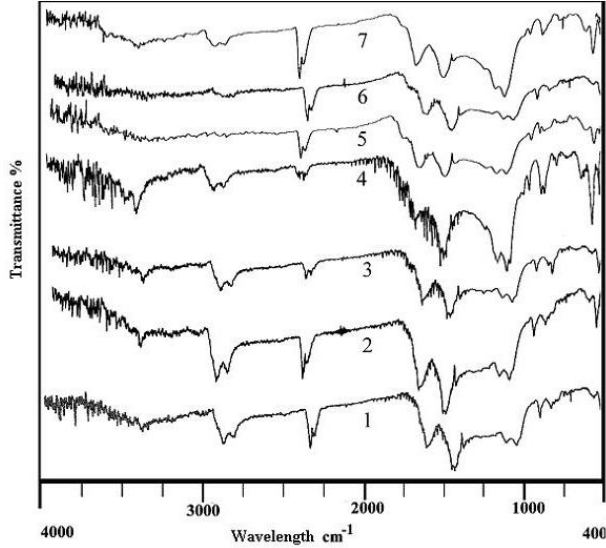


Figure 5- IR-Spectra of oxidized coals at 40 (1), 70 (2), 120 (3), 170 (4), 200 (5), 250 (6) and 300 (7)°C in 125-250 μm size fractions.

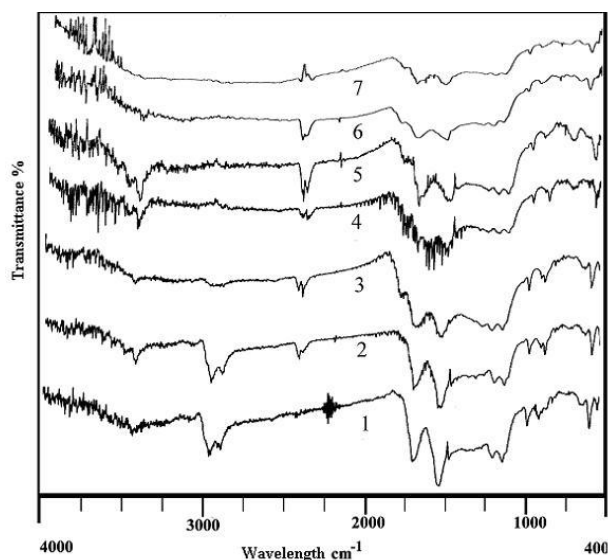


Figure 6- IR-Spectra of oxidized coals at 40 (1), 70 (2), 120 (3), 170 (4), 200 (5), 250 (6) and 300 (7)°C in -125 μm size fractions.

As seen in spectrums, it is verified that aromatic structures were not affected so much as aliphatic groups by the oxidation process during air oxidation at low-temperature. Thus, aliphatics seemed to be more active than aromatic groups. That is, aromatics seemed to be more stable than aliphatics during the oxidation process. The major changes in the oxidation spectrums were observed in the region 3000-2500 cm^{-1} that was determined to be the aliphatic region and in the 2000-1600 cm^{-1} known as the carbonyl region and in the region 1200-800 cm^{-1} that C-O-C, C-O and the aromatic C-H groups were presented [21]. Carbonyl groups at 1600 cm^{-1} could be observed to decrease fairly by which oxidation increases. The formation of carboxyl groups and the loss of aliphatic CH_2 and CH_3 groups were appeared at 150 °C and above this. In addition, it was recorded that the aryl and alkyl esters and anhydrides were formed at 1800-1700 cm^{-1} . Methyl peaks decrease about 1400 cm^{-1} while oxidation temperature increases. The aromatic C-H groups at 3100-2992 cm^{-1} and the aliphatic C-H groups at 2992-2795 cm^{-1} was determined. Moreover, it was observed that air oxidation at 200 and 250 °C affected the aliphatic carbons more than aromatics.

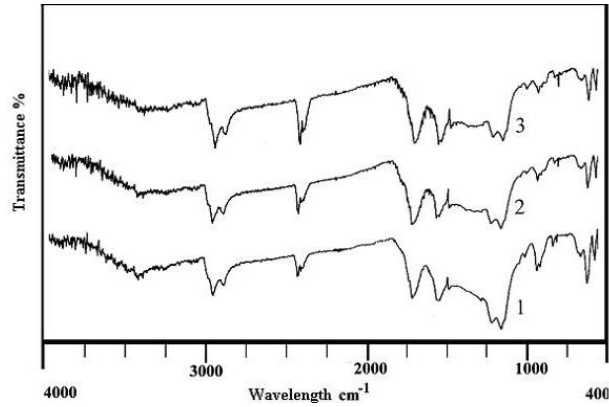


Figure 7- IR-Spectra of the demineralised and untreated coals in 250-710 (1), 125-250 (2) and -125 (3) μm size fractions.

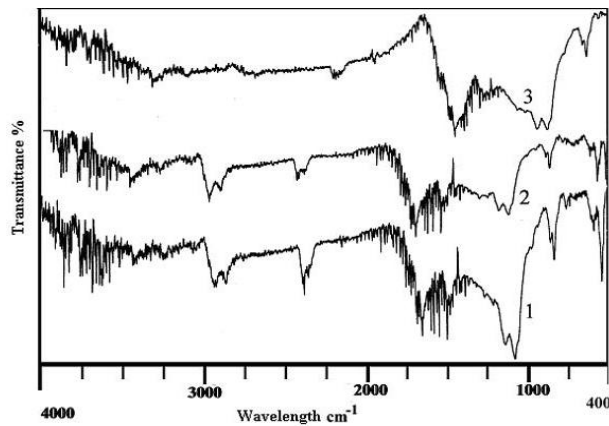


Figure 8- IR-Spectra of the demineralised and oxidized coals in 250-710 (1), 125-250 (2) and -125 (3) μm size fractions oxidized at 120°C.

Figure 7 and 8 is shown the spectrums of the demineralised untreated coal with HCl and the demineralised coal samples by oxidizing at 120 °C in three different fractions, respectively. By demineralisation of the coals is facilitated the access of oxygen to the coal structure and the ash content decreases and then it passes to solution. The remove of the mineral matter increases the oxidation. Aromatic structures were not affected significantly by demineralisation and aliphatic CH_2 and CH_3 groups

occurring at 1380, 1440, 2850, 2920 and 2970 cm^{-1} by air oxidation at 150 °C were decreased. Aliphatic C-H groups also decrease in graph of the protonated coal by oxidizing at 120 °C. It was especially found an increase in carboxyl and carbonyl groups [20]. In the aromatic bonds at 1610 cm^{-1} of the demineralised lignite's were not observed any changes [27].

4. CONCLUSIONS

At the results of applied analysis, it was observed that the amount of hydroxyl decreased with the reduction of particle size at the oxidation temperatures up to 250 °C but increased with increasing particle size at 300 °C. However, it was seen from obtained data that the amount of carboxyl has decreased with the reduction of particle size at temperatures up to 200 °C but it has reversibly increased at the temperatures above 200 °C. It was determined that these dissimilar liabilities observed at different particle sizes for both functional groups were also agreed with the analysis of FT-IR spectroscopy. Consequently, these two graphics obtained in this study are the ones, which illustrates to the all changes together occurred in the oxygen functional groups at a so large temperature interval until now.

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