

Effect of Acid Treatment on Volumetric Swelling Ratios of Coals

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To remove Ca^{2+} ions, six low rank coals and one coking coal were treated with 0.1 and 1.0 N HCl for 24 h. IR spectra and proximate analysis of the lignites indicated that only slight structural changes had occurred during acid treatment. The swelling ratios of parent and acid-treated coal samples showed that removal of Ca^{2+} resulted in an increase in the swelling ratios. Higher swelling ratios were obtained with acid-washed coal samples. While the highest swelling ratios of the parent lignites were obtained in ethylenediamine, those of acid-treated samples were obtained in pyridine and dimethylformamide.

Introduction

Their low costs and high reserves suggest low rank coals may be suitable feedstocks for liquefaction processes. The behaviour of low rank coals towards solvents has therefore been investigated.

According to recent models of coal structure, the organic matrix of coal has a three-dimensionally cross-linked, macromolecular structure¹⁻². The macromolecular network consists of groups of aromatic and hydroaromatic ring structures containing hetero atoms in various functional groups³⁻⁴. The predominant functional groups in coal are those containing oxygen such as carboxylic acids and phenolic hydroxyl⁵. These polar functional groups are able to form hydrogen bonds⁶. Lower rank coals contain substantially more organic oxygen than bituminous coals. Thus, the reactivity of low rank coals depends largely on their carboxylic acid and phenolic hydroxyl contents.

On the other hand, the reactivity of coals in liquefaction depends on the content of inorganics which are both physically and chemically associated with the organic matrix of coal. Substantial amounts of inorganics are associated with the organic structure of low rank coals, as carboxylic acid salts: $-\text{COO}^- \text{M}^+$, $-(\text{COO}^-)_2 \text{M}^{++}$ where M is an alkali (K^+ , Na^+) or alkaline earth metal (i.e., mostly Ca^{2+}) which can be exchanged⁷⁻⁸. The effects of these exchangeable cations⁹⁻¹² on different conversion processes and product quality have been reported in the literature⁹⁻¹².

Since it has been indicated that both the rate and extent of liquefaction can be increased by using swollen coals¹³⁻¹⁴, in the present study, to investigate the behaviour of low rank coals toward solvents, their

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swelling ratios in different solvents were determined and the effect of the removal of Ca^{2+} on the swelling ratios was examined.

Experimental

Coal Samples

Four lignites (i.e., Mugla-Yatağan, Adıyaman-Gölbaşı, Bolu-Göynük and Kütahya-Seyitömer), two subbituminous coals (i.e., Soma-Merkez and Kütahya-Tunçbilek) and one coking coal (i.e., Zonguldak-Kozlu) were used in this study. The samples were grounded to (-0.4)-(-0.1) mm particle size and kept under nitrogen. Their proximate analyses and % C contents are presented in Table 1.

Table 1. Proximate Analyses and % C and % Volatile Matter Contents of The Coal Samples.

	Bolu Göynük	Kütahya Seyitömer	Muğla Yatağan	Adıyaman Gölbaşı	Soma Merkez	Kütahya Tunçbilek	Zonguldak Kozlu
Proximate Analyses (Air-Dried)							
Moisture	16.6	15.2	10.6	25.8	12.8	9.4	1.3
Volatile Matter	25.9	22.5	39.4	26.2	30.4	30.6	29.0
Fixed Carbon	31.7	25.5	33.7	24.4	41.1	44.4	59.7
Ash	25.8	36.8	16.3	23.6	15.7	15.6	10.0
% C Content (daf)	61.0	61.45	65.3	68.3	72.6	71.9	88.3
% Volatile Matter(daf)	45.0	46.9	53.9	51.8	42.5	40.8	32.7

Acid Treatment of Samples and Removal of Ca^{2+}

To remove Ca^{2+} , 100 g of each raw sample was mixed with 450 ml of 0.1 N HCl or 1N HCl solution at room temperature for 24 h with occasional stirring. The samples were then filtered on Black Ribbon (589¹) (Schleicher & Schuell) filter paper, washed with warm distilled water to remove HCl and air dried. The pale yellow acid filtrate was stored in a flask until its Ca^{2+} was determined.

Determination of Ca^{2+}

Determination of the Ca^{2+} content of untreated coal samples and of the acid filtrates was performed according to ASTM 2795¹⁵ standard. To facilitate comparisons between untreated and acid-washed coals, the results were calculated on a dry untreated coal basis and are presented in Table 2.

Coal Preswelling

Swelling ratio measurements were carried out essentially as described in the Literature¹⁶; 10 ml, cylindrical, 0.1 ml graduated glass tubes of 13 mm outer diameter with glass stoppers were used. 0.6 g of coal sample was placed in the tube and centrifuged for 5 min at 1725 rpm, and the height of the sample was measured (h_1). Then 3-4 ml solvent was added, the contents were shaken vigorously and left overnight and the height was then measured (h_2). Shaking and centrifuging were repeated every 24 h until the height of the swollen sample (h_2) was constant. The volumetric swelling ratio (Q) was calculated ($Q = h_2/h_1$).

Table 2. Ca²⁺ Content of Untreated and Treated Coals and The Amount of Ca²⁺ Removed.

	Bolu Göynük	Kütahya Seyitömer	Muğla Yatağan	Adıyaman Gölbaşı	Soma Merkez	Kütahya Tunçbilek	Zonguldak Kozlu
Untreated							
Ca ²⁺ (mg/g coal)	19.36	10.41	27.04	32.03	4.06	2.46	1.03
Washed with 0.1 N HCl							
Ca ²⁺ (mg/g coal)	15.60	8.34	20.33	26.52	3.17	1.46	0.62
(Removed)	3.76	2.07	6.71	5.51	0.89	1.00	0.41
Washed with 1 N HCl							
Ca ²⁺ (mg/g coal)	7.43	6.09	8.04	18.47	3.02	1.42	0.42
(Removed)	11.93	4.32	19.00	13.56	1.04	1.04	0.61

The solvents used for swelling are listed in Table 3¹⁷. While their electron donor and electron acceptor numbers are in the ranges of 0-55 and 0-41.5, respectively, all the solubility parameters were within the range 9.1-12.9. The swelling ratios of the original and treated samples are given in Table 3.

Results and Discussion

Table 3 summarizes the swelling ratios of the original coal samples in 14 solvents with different solubility parameters, and donor and acceptor numbers. As reported previously¹⁸, swelling ratios of coal samples increased with increasing donor number (DN) of the solvent. The highest swelling ratios are obtained with those solvents containing unshared electron pairs¹⁹. However, organic bases are more effective in modifying the swelling of lignites. As seen in Table 3 the highest swelling ratios of lignites are obtained with ethylenediamine. These results are in accordance with earlier reports¹⁹. Because of the presence of relatively large amounts of polar carboxyl and phenolic hydroxyl groups, ionic and hydrogen bonds play an important role in the swelling of lignites. On the other hand, solvents having a strong base character interact with ionic and hydrogen bonds and swell lower rank coals. Since as the carbon content increases, the number of polar groups decreases; a slight decrease in the swelling ratio of the higher rank coal samples in ethylenediamine was observed.

The calcium content of the untreated coal samples and the amount of Ca²⁺ removed are presented in Table 2. The Ca²⁺ contents of the coking coal and of the two subbituminous coals are considerably lower than those of the lignites. As seen in Table 2, although as the concentration of hydrochloric acid solution was increased from 0.1 N to 1 N HCl, the amount of removed Ca²⁺ increased, it was not possible to remove all the Ca²⁺ present in the samples by 1 N HCl treatment at room temperature. This might be due to the presence of Ca²⁺ ions associated with clay minerals which are only partially dissolved even in boiling hydrochloric acid solution²⁰.

As seen in Figure 1-3, in each IR spectra of the four 1 N HCl treated lignite samples there is a small carbonyl peak at 1730 cm⁻¹ attributable to carboxylic esters. Only a slight shoulder was recognizable in the corresponding spectra of 0.1 N HCl treated samples and the two 1N HCl treated subbituminous coals. The carbonyl stretching frequency of the carboxylic acids (at 1665-1700 cm⁻¹) present in low rank coals is obscured by the large absorption band centered at 1600 cm⁻¹ assigned to aromatic carbon-carbon linkages²¹ and does not appear in the IR spectra of the parent lignite samples. In view of these results, it would seem that during the 1N HCl treatment of low rank coals some ester linkages were formed between coal fragments.

Table 3. Volumetric Swelling Ratio of Coals and Solvent Characteristics.

Solvent	Donor Number	Acceptor Number	Solubility Parameter (cal/cm ³) ^{1/2}	Volumetric Swelling Ratios, $Q = h_2/h_1$								
				Muğla- Yatağan	Kütahya- Seyitömer	Adyaman- Göلبaşı	Bolu- Göynük	Soma- Merkez	Kütahya- Tunçbilek	Zonguldak- Kozlu		
				Q^1	Q^2	Q^3	Q^4	Q^5	Q^6	Q^7	Q^8	Q^9
Toluene	-	-	8.9	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
n-hexane	0	0	-	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Chlorobenzene	-	-	9.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Benzene	0.1	8.2	9.2	1.0	1.1	1.1	1.0	1.0	1.0	1.1	1.1	1.0
Methanol	19	41.3	12.9	1.0	1.2	1.3	1.4	1.3	1.3	1.4	1.1	1.2
1.4-dioxane	14.8	10.8	9.8	1.0	1.3	2.0	1.1	1.4	1.9	1.1	1.1	1.1
2-propanol	20	33.5	11.5	1.0	1.1	1.5	1.1	1.4	1.6	1.0	1.1	1.3
Dichloromethane	-	20.4	9.9	1.1	1.1	1.3	1.1	1.1	1.1	1.0	1.1	1.3
THF	20	8	9.1	1.2	1.4	2.4	1.4	1.4	2.0	1.1	1.4	2.0
MEK	-	-	9.45	1.2	1.2	1.9	1.2	1.2	1.4	1.0	1.1	1.3
Pyridine	33.1	14.2	10.4	1.5	1.9	2.8	1.8	1.9	2.2	1.3	1.7	2.4
DMF	26.6	16	11.5	1.8	2.2	3.0	1.8	2.1	2.2	1.2	1.7	2.9
EDA	55	20.9	11.5	2.2	2.3	2.4	2.1	2.3	2.3	1.8	2.2	2.6

¹) O ; Untreated Samples

²) 0.1 ; Treated with 0.1 N HCl

³) N ; Treated with 1 N HCl



Figure 1. IR Spectrums of Untreated samples. Absorption bands between 2000 and 1200 cm^{-1}

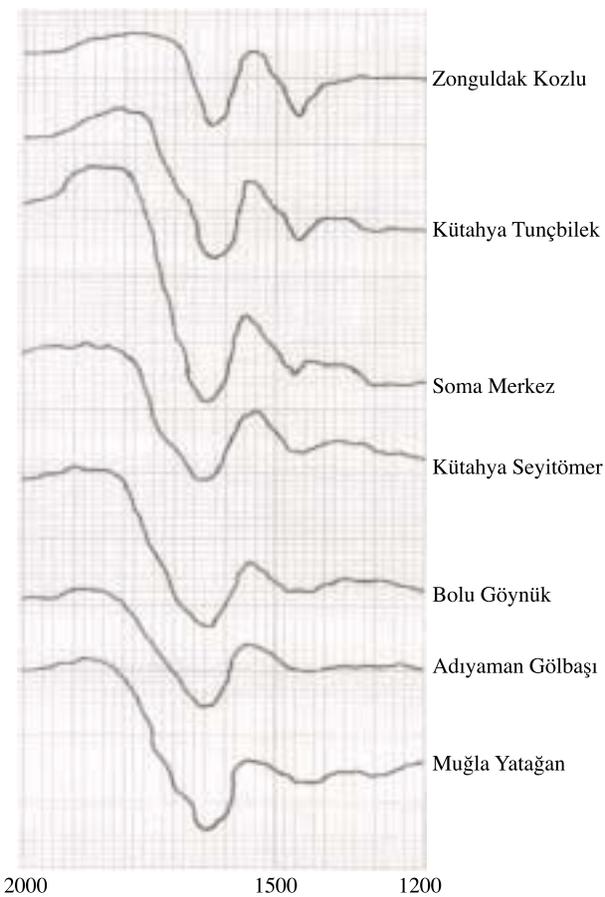


Figure 2. IR Spectrums of the samples treated with 0.1 N HCl. Absorption bands between 2000 and 1200 cm^{-1} .

In the IR spectra of 1N HCl treated coking coal, no carbonyl band was visible, which is in accordance with earlier reports on the smaller carboxylic acid content of bituminous coals².

It could also be noted that the strong absorption band observed at about 1100 cm^{-1} , attributed to kaolinite, is sharper in the IR spectra of acid washed lignite samples, probably due to the elimination of some of the other minerals. Although, according to the IR spectra of the parent and acid-treated coals, acid washing did not affect the aromatic structures of the coals, proximate analysis of the HCl treated samples indicated that acid washing of the lignites resulted in a decrease in the fixed carbon and that volatile acid washing of the samples for 24 h affected the organic matrix of the lignites.

As Table 3 shows, removal of Ca^{2+} improved the swelling properties of the coals. The swelling ratios increased as the acid concentration increased from 0.1 to 1 N. However, the increase in the swelling ratios of the acid-treated lignite was relatively higher than that of the subbituminous and bituminous coals.

Studies being carried out presently in our laboratory have indicated that addition of Ca^{2+} to the acid-treated lignite according to the procedure given in the literature⁷, resulted in a decrease in the swelling ratio.

It is also interesting to note that while the parent lignites gave higher swelling ratios in ethylenediamine, the swelling ratios of acid-treated lignites were higher in pyridine and dimethylformamide.

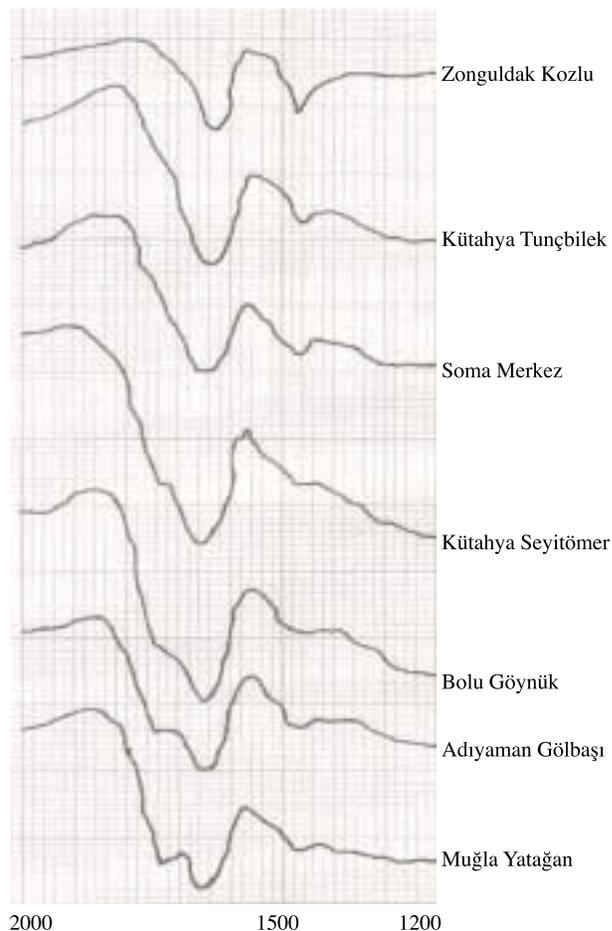


Figure 3. IR spectrums of the samples treated with 1 N HCl. Absorption bands between 2000 and 1200 cm^{-1} .

These results might be due to the removal of ionic cross-links by the acid treatment as was previously reported in the literature²². Although as was reported by Azık et al.²³ removal of some of the mineral matter may have resulted in a relaxation in the organic structure of lignite, which might have played a role in the increase in the swelling ratio of the coals.

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