

Treatments of Çan Lignite with Some Mineral Acids after Sodium Hydroxide Washing

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Abstract

The fossil properties can be increased via enrichment process. It is the process that removes sulfur and mineral matter without changing the organic structure. In this study, Çan lignite was demineralized with some mineral free acid of 5% such as HCOOH and some mineral acids of 5% such as HNO₃, H₂SO₄, HCl, H₃PO₄ and HF after 5% NaOH washing. The best sulfur and mineral matter performed were obtained with NaOH plus HF treatment as approximately 44% and 45%, respectively. FTIR and X ray spectra of the samples were also drawn to determine the functional groups and mineral composition.

Keywords: Acid, Alkali, Lignite, Mineral matter, Sulfur

1. Introduction

Turkey has 8 billion lignite reserves. The estimated possible reserves are 30 billion tones. Although Turkey has such a big lignite reserves, most of them have low quality, high ash, volatile matter and sulfur ratio (Kaygusuz, 1997). Emissions of fossil fuel combustion are the major source of air pollution. The effect of this pollution on human health is a serious problem especially in the weather quality (Alonso, 2005).

The quality of fossil fuel is related to its structure. So, the mineral composition depend on the place, time and formation conditions (Sharma & Gihar, 1991). The fossil fuels that have high mineral matter can be enriched applying for some chemicals.

For demineralization purposes; acidic, basic solutions or some chemicals such as peroxide, alcohol can be used (Kusakebe, et al., 1989). The carbonaceous parts are separated from the body. Later ash minerals are extracted and finally some elements such as (Na, K, Ca) in the organic body are leached (Yang, et al., 1985).

Several authors tried to extract those undesired parts in order to increase fossil quality. Chen et al tried the coal with some acids to remove the pyrite from HM lignite (bulianta coal mine, Shandong-China) and YZ bituminous coal (Yanzhou of Shandong-China). For this purpose, nitric acid and combination of hydrofluoric and hydrochloric acids were used. Although nitric acid is very effective for removing pyrite, it is also cause slight oxidation of organic part of the coal. The total sulfur amounts of HM and YZ coals were 2.40 and 2.93 at the beginning. The sulfur ratios of HF treated coals were found as 2.00 and 2.95. With CrCl₂/HCl application, those results were changed as 1.63 and 1.96 (Chen, et al., 1999).

Gülen et al studied some 5% and 10% acidic solutions of HCl, HNO₃ and H₂SO₄ for Silopi-Harput asphaltite. Maximum extraction degree of 40% was obtained with HCl acids of 5 and 10% (Gülen, et al., 2005).

Wang and his colleaques tested Australian coal with Ca(OH)₂ plus HCl washing. They managed to extract 90% of the inorganic mater (Wang, et al., 1997).

Doymaz et al studied the combination of acid and alkali effects. They treated asphaltite with NaOH of 5% plus acids of HNO₃, HCl, H₂SO₄ of 10% and HF of 40%. Approximately 60% extraction was performed with 5% NaOH plus 10% H₂SO₄ and 40% HF acids (Doymaz, et al., 2007).

Murkherjee and Borthakur leached Assam coal in India with NaOH followed HCl treatment. They managed to extract approximately 50% ash and inorganic sulfur and 10% of organic sulfur (Mukherjee & Borthakur, 2003).

Steel and Patrick studied the HF acid alone and HF and HNO₃ together for UK coal. The ash level was decreased from 7.90% to 2.6% with HF alone and from 2.8% to 0.6% with 3.51 M HF and 1.26 M HNO₃ together (Steel & Patrick, 2001).

In this study, Çan lignite was treated with 5% NaOH plus 5% HNO₃, HCOOH, H₂SO₄, HCl, H₃PO₄ and HF acids for removing undesired parts.

2. Experimental

2.1 Materials

The materials have been grounded and sieved to pass 0.250 µm sieve. The proximate analyses are shown in Table 1. Those analyses were suite with ASTM standards (ASTM, 1983).

2.2 Methods

The high sulfur amount of Çan lignite was tried to decrease with basic 5% NaOH and later some 5% acidic solutions. These concentrations were chosen being studied at very diluted medium. 4 g lignite samples were stirred with 5% NaOH solution for 20 minutes. This sample was filtered, washed hot distilled water and dried in the oven at 105°C. Later, dried samples were stirred the aqueous acidic solutions for 20 minutes, filtered, washed and dried in the oven. Total sulfur amount of Çan lignite was found as 3.80%. The sulfatic, pyritic and organic ones were 0.75%, 1.03%, 2.02%, respectively. The sulfur results of Çan lignite treated with chemical agents are seen in Table 2.

Mineral matter of Çan lignite was decreased by applying 5% acidic solutions after affecting 5% alkali solution. Table 3 shows the ash values for demineralized samples.

The variations in calorific values after treated with those chemicals are shown in Table 4.

FTIR and Xray spectra of original and chemical treated samples were also drawn with Perkin Elmer and Rigaku Xray spectrometers, respectively. FTIR tablets were at the ratio of 1:100 (w/w) fuel and KBr. X ray diffraction pattern were collected at 0-70° 2θ.

Figure 1 and 2 show the FTIR and Xray spectra of Çan and chemical treated samples.

3. Results and Discussion

The results indicate that maximum sulfur reduction was obtained with 5% NaOH plus 5% HF as 43.95% yield (Table 2). The second best result was found with H₃PO₄ treatments as 32% sulfur removal. HF was very effective for decreasing mineral parts from the body. The result was 44.48% yield (Table 3). The second important agent was HCl. It is suggested that smaller molecules can more easily diffuse into particle according to Sharma and Gihar. So, 43.60% demineralization was performed with HCl treatment. Aqueous H₃PO₄ acid was supplied for 22.50% demineralization result.

Figure 1 (a, b) shows the functional structure of Çan and chemical treated samples as FTIR spectra. The samples were sequenced from bottom to top as original (A), NaOH (B), H₃PO₄ (C), HCOOH (D), HNO₃ (E), H₂SO₄ (F), HCl (G) and HF (H) treated.

In the original spectrum, the peaks at 474, 536, 598, 801 cm⁻¹ show the mineral matter of lignite. These areas are the areas of print finger and those peaks cannot be determined separately. And those peaks the evidence of mineral matter existence. 1033, 1097, 1122, 1199 cm⁻¹ bands are due to C-O stretching. 1401, 1435 cm⁻¹ also represent etheric oxygen group. 1401, 1435 cm⁻¹ which is a smaller shoulder peak and 1619 cm⁻¹ bands are aromatic C=C and C=O stretching. Aliphatic C-H groups give absorbance at 2846 cm⁻¹. 2923 cm⁻¹ show the presence of CH₃ and CH₂ groups in the body. 3395 cm⁻¹ peak is the indicator of O-H stretching. Beyond 3500 cm⁻¹, it is possible to expect the clay mineral existence.

After NaOH washing, the peak heights which show mineral matter existence are decreased.

Peaks at 1011, 1106 cm⁻¹ show C-O stretching. The bands at 1270, 1380, 1570 cm⁻¹ are C-O stretching, etheric oxygen and asymmetric symmetric carboxyl groups, respectively. The sharp end at 1400 cm⁻¹ which indicate C=C stretching was decreased after alkali washing.

Leaching with H₃PO₄, some mineral parts were removed. Peaks appeared at 468, 532 cm⁻¹ show mineral structure. C-O stretching bands are seen at 1034, 1111, 1270, 1610 cm⁻¹. 1401 and 1610 cm⁻¹ are for C=C and C=O stretching, respectively. The peak of aliphatic C-H group at 3153 cm⁻¹ was rounded with H₃PO₄ leaching.

With HCOOH effect, the peaks at 471, 528 cm⁻¹ were mineral matter. Bands shown at 1032, 1114 cm⁻¹ are C-O stretching. The double peaks at 1400 cm⁻¹ are aromatic C=C stretching. C=O stretching peak was shown at 1608 cm⁻¹. Peaks at 2841, 2921 cm⁻¹ are seen due to aliphatic C-H group and CH₃/CH₂ groups, respectively. Aliphatic C-H group at 3192 cm⁻¹ gives a wider shoulder peak.

With HNO₃ treatment, peaks seen at 536, 821, 872, 911 are due to mineral matter. C-O stretching peaks at 1384

cm^{-1} was increased. The peak at 1603 cm^{-1} was decreased. 2841, 2921, 3153 peaks are aliphatic C-H, CH_3/CH_2 groups and aliphatic C-H groups, respectively.

With H_2SO_4 acid extraction, the peaks which indicate mineral matter was very small. 1034, 1280 and 1598 cm^{-1} peaks show C-O stretching and C=O stretching. 2841, 2920, 3178 cm^{-1} peaks are similar the spectrum of HNO_3 .

When HCl was applied, the peaks at 466, 540, 793 cm^{-1} show mineral parts of lignite. 1032, 1114, 1263 cm^{-1} bands are C-O stretching. The peaks at 1401 and 1607 cm^{-1} show C=C stretching and C=O stretching. 2841, 2921, 3153 peaks are aliphatic C-H, CH_3/CH_2 group, aliphatic C-H group, respectively.

With HF washing, a sharp peaks at 483 and 741 cm^{-1} and a small one at 590 cm^{-1} are mineral parts. Bands seen at 1275, 1396 and 1608 cm^{-1} show C-O stretching. 1438 and 1608 cm^{-1} bands are aromatic C=C and C=O groups, respectively.

Figure 2 (a b) show the Xray spectra of Çan and other chemical treated samples. The bottom spectrum was original Çan lignite (A). The others were NaOH (B), HNO_3 (C), H_2SO_4 (D), HCl (E), H_3PO_4 (F), HF (G), HCOOH (H) treated samples from bottom to top.

The original Çan lignite gave peaks at $2\theta = 13.780, 23.099, 34.200$ as Nesquhomite; $2\theta = 23.962, 33.162, 40.858, 43.436, 49.498, 54.158, 62.522$ as hematite; $2\theta = 24.521, 31.338, 38.582, 52.352, 57.717$ as anhydride groups.

With NaOH treatment, quartz and hematite groups left. They gave peaks at $2\theta = 20.882, 26.661, 39.517, 40.438, 45.837, 50.194, 59.998, 64.201, 67.877, 68.342, 75.664$ and $2\theta = 24.184, 33.181, 35.682, 40.960, 43.537, 49.557, 54.178, 57.701, 62.514$, respectively.

When we applied HNO_3 acids those groups were found at the following. The peaks at $2\theta = 20.664, 26.700, 36.616, 42.556, 50.142, 60.033, 64.216, 67.818, 68.421$ quartz ones, $2\theta = 24.331, 33.258, 35.737, 41.074, 49.659, 54.162, 62.697$ hematite groups and $2\theta = 21.318, 23.162, 28.156, 29.720, 38.463$ gerdonite minerals.

The peaks at $2\theta = 24.578, 28.716, 31.396, 40.878, 43.281, 59.038$ were due to anhydride groups after H_2SO_4 treatment. Also, ternardite gave peaks at $2\theta = 19.074, 23.123, 28.037, 32.139, 35.696, 38.519, 48.839, 49.462$.

With HCl washing, the peaks shown at $2\theta = 20.919, 26.664, 36.561, 39.502, 42.502, 45.841, 50.217, 60.001$ and $2\theta = 24.235, 33.221, 35.663, 49.501, 54.261, 62.519$ correspond to quartz and hematite groups, respectively.

With H_3PO_4 leaching, the peaks at $2\theta = 20.318, 21.659, 22.656, 28.894, 30.745, 35.954, 39.517, 50.237$ and $2\theta = 20.824, 26.642, 36.576, 42.476, 59.943, 67.724, 68.314$ suite nacrite and quartz groups, respectively.

HF is very effective for clay especially siliceous minerals. Amesite, fluorite and williamite groups in the body gave peaks at $2\theta = 21.258, 25.579, 35.600, 52.597$; $2\theta = 28.315, 33.019, 47.019, 68.658, 87.400$; $2\theta = 38.862, 56.139, 70.376, 83.417$, respectively.

The top spectrum shows the HCOOH effect on the lignite body. The peaks at $2\theta = 23.804, 26.582, 36.534, 50.118, 55.460, 59.929, 64.077, 68.219$ were quartz; $2\theta = 21.240, 23.136, 24.149$ chalcoalumite and $2\theta = 30.362, 43.497, 54.120, 57.639$ were magnesiochromite groups.

4. Conclusions

In this study, chemical treatment of Çan lignite was performed with aqueous acids of HNO_3 , HCOOH, H_2SO_4 , HCl, H_3PO_4 and HF after alkali NaOH treatment. 5% HF is given the best result from the removal of sulfur and mineral parts. The enrichment yields were approximately 44% (Table 2, 3). Maximum calorific increment was found in HCl treatment as 12% (Table 4). The result of HF acid was 7%. Çan lignite has some organic constituents which is seen from C-H and C=O stretching vibrations of FTIR spectra. Original Çan lignite has some mineral groups such as hematite, anhydride, quartz, ternardite, nacrite, etc. Xray spectra show these mineral groups being left after demineralization treatment.

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Table 1. Proximate analyses of Çan lignite

Fixed carbon %	64.81
Volatile matter %	28.08
Sulfur %	3.80
Ash %	7.11
Moisture %	10.70
Calorific value	22 402 kJ/kg

Table 2. Sulfur variation values of Çan lignite and chemical treated samples

Sample	NaOH 5 %	Sulfur removal %
Çan (A)	3.09	18.68
(A)+HNO ₃	3.73	1.84
(A)+HCOOH	2.98	21.58
(A)+H ₂ SO ₄	2.89	25.0
(A)+HCl	2.66	30.0
(A)+H ₃ PO ₄	2.57	32.37
(A)+HF	2.13	43.95

Table 3. Ash removal and demineralization variations of Çan lignite and chemical treated samples

Sample	NaOH 5 %	Demineralization %
Çan (A)	6.58	7.45
(A)+H ₃ PO ₄	5.51	22.50
(A)+HCOOH	5.1	28.27
(A)+HNO ₃	4.48	36.99
(A)+H ₂ SO ₄	4.36	38.68
(A)+HCl	4.01	43.60
(A)+HF	3.94	44.48

Table 4. Calorific values of Çan Lignite and chemical treated samples

Sample	NaOH (kJ/kg)	Variation in calorific value %
Çan (A)	22 401.6	--
(A)+H ₃ PO ₄	23 354.6	4.2
(A)+HCOOH	23 532.6	5.04
(A)+H ₂ SO ₄	23 709.9	5.8
(A)+HF	24 059.6	7.4
(A)+HNO ₃	25 036.2	11.8
(A)+HCl	25 159.2	12.3

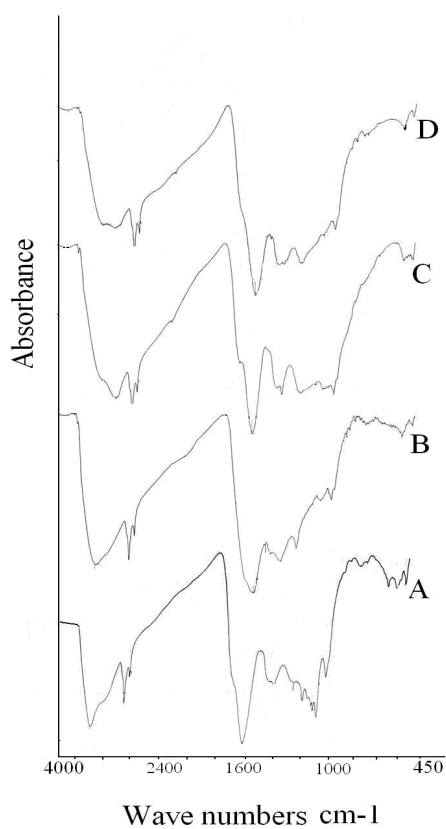


Figure 1 (a)

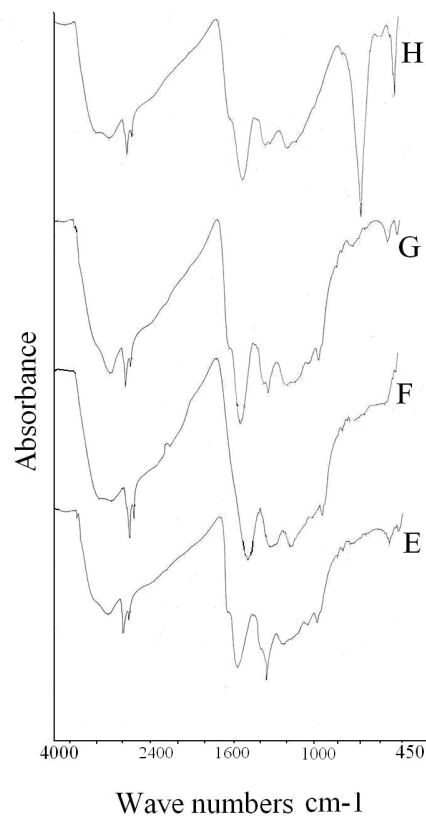


Figure 1 (b)

Figure 1. (a, b) FTIR spectra of Çan lignite and other chemical treated samples (A=Original Çan lignite, B=(A)+5%NaOH (B), C=(A)+(B)+5%H₃PO₄, D=(A)+(B)+5%HCOOH, E=(A)+(B)+5%HNO₃, F=(A)+(B)+5%H₂SO₄, G=(A)+(B)+5%HCl, H=(A)+(B)+5%HF).

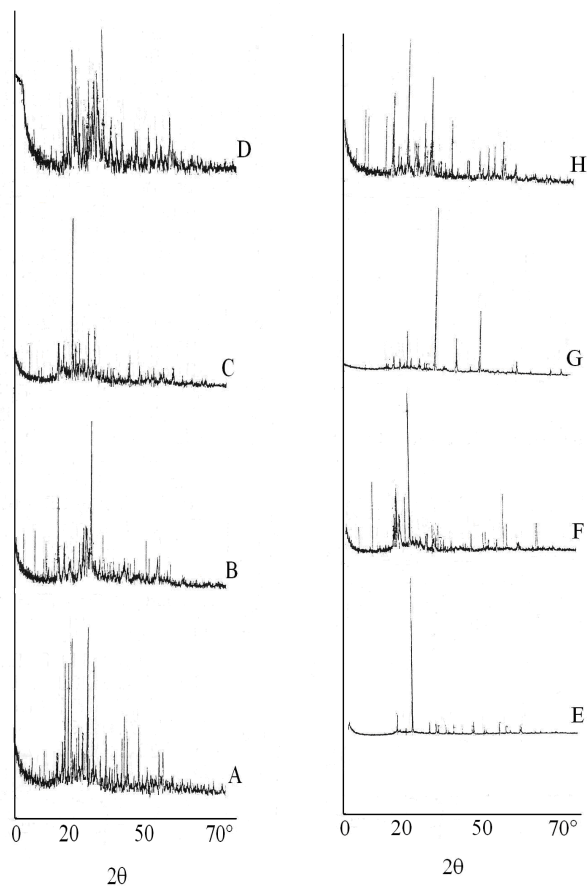


Figure 2 (a)

Figure 2. (b)

Figure 2. (a, b) X ray spectra of Çan lignite and other chemical treated samples (A=Original Çan lignite, B=(A)+5%NaOH(B), C=(A)+(B)+5%HNO₃, D=(A)+(B)+5%H₂SO₄, E=(A)+(B)+5%HCl, F=(A)+(B)+5%H₃PO₄, G=(A)+(B)+5%HF, H=(A)+(B)+5%HCOOH).