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DEMINERALIZATION OF ZONGULDAK HARD COAL BY SEQUENTIAL APPLICATION OF FLOTATION, HCl AND NaOH LEACHING

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Abstract: In all regions of the world, energy demand has grown in last decades. Fossil fuels, whether in solid, gas or liquid form, have been used as the main source of energy for years. The world's fossil fuel reserves are finite and non-renewable. The threat of eventual depletion of fossil liquid fuels has made the development of alternatives necessary to reduce the dependency and consumption rates of these fuels. The research studies about the production of coal-water slurries as an alternative to the liquid fossil fuels has been ongoing for many years. In this period, a significant amount of development has been achieved for the substitution of liquid fossil fuels in internal combustion engines and power plants. This study considers production of a high calorific value coal concentrate with low ash and low sulfur from Zonguldak hard coal to be used in the preparation of coal-water fuels. Flotation and leaching techniques were used to achieve this goal. At the end of the studies, a clean coal concentrate containing 1.18% of ash and 0.53 % of sulfur with 8188 kcal/kg calorific value was obtained from 14.43% of ash hard coal.

Keywords: *coal, flotation, leaching, coal-water slurry*

Introduction

Coal has been used as an energy source for the centuries. As of today, it is the second source of primary energy with a share of 28.9% in the world total primary energy supply (International Energy Agency, 2015). Its share in global power generation was over 40% in 2013. Although some developed countries are trying to shift to alternative sources of energy, coal seems to keep its vital role in facilitating economic growth in the developing world. At the production levels of 2011, proven coal reserves are estimated to last 118 more years, and proven oil and gas reserves should last around 56 and 60 years, respectively (World Energy Resources, 2013). Different fuel alternatives have been studied during recent years to reduce dependency on oil and gas

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resources. Coal has always been a valid option in the search studies for the development of a widely available, safe, reliable, and relatively low cost fuel.

The quality of the coal mined has steadily declined over the recent years due to depletion of the higher grade coal reserves. Despite the problems associated with their utilization, the reliance on lower quality coals has been growing increasingly in many countries. The operating expenses of mining are lower for this type of coal deposits as a consequence of using large scale surface mining methods. Studies have indicated that low quality coals can be upgraded to improve their properties. However, cleaning of a low quality coal is more expensive compared to high-quality coals. N various novel upgrading processes are still being studied to develop a high efficiency and low cost coal cleaning technique (Mills, 2011).

Coal-water slurry (CWS) has been a research subject as a potential substitute for fuel oil since 1970s. Several studies have been conducted to produce a feasible alternative to diesel oil after the development of coal burning internal combustion engines. CWS is composed of finely pulverized coal, water and chemical additives (Cheng et al., 2008). The impurity content, coal particle size and concentration, viscosity, and stability are significant properties of the CWS for its utilization in different areas. Chemical additives are used to maintain the stability of the suspension while water content is important to adjust the apparent viscosity for spraying in combustion (Zhou et al., 2008). A practical CWS should have a high coal concentration (60-75%) for heat value and economical use, and a low apparent viscosity to accommodate CWS’s spray for combustion (Dincer et al., 2003).

Higher quality coal water slurries can be obtained by using the clean coals with low ash and sulfur content. It is obvious that a higher efficiency of combustion and longer life time can be expected for the engines working with low ash coals. Several research studies have been conducted on the production of ultra-clean coal in the past. Flotation and acidic/basic leaching techniques were determined as promising methods of cleaning for this purpose.

Jena et al. (2008) used flotation technique on a coal sample with 14% of ash, and able to produce a clean coal concentrate having 10% of ash with 81% combustible recovery (Jena et al., 2008). Atesok et al. (2001) were able to obtain a clean coal concentrate with 8.3% of ash and 81% combustible recovery from a feed coal having 16.3% of ash using flotation (Atesok et al., 2001). Stonestreet and Franzidis (1988) have been succeeded to reduce the ash content of a high ash coal (54%) to 12% by using indirect flotation (Stonestreet and Franzidis, 1988). Gupta et al. (2007) reported that a clean coal concentrate with 11% of ash was obtained from 24.5% ash containing feed material using flotation technique successfully (Gupta et al., 2007). Waugh and Bouling (1984) employed NaOH pressure leaching at 200 ^{o}C temperature, and removed 90% of mineral matter of coal successfully (Waugh et al., 1984). Wang et al., (1986) studied NaOH pressure leaching at 187 ^{o}C temperature, and able to reduce the ash content to 2.2% using a 15.5% ash containing feed coal (Wang et al., 1986). Muknerjee and Borthkur (2001) applied NaOH and HCl leaching for coal demineralization and desulfurization. They were able to remove 43–50% of the ash by the application of leaching with sodium hydroxide followed by hydrochloric acid leaching.

Internal combustion engines are typically fed with fossil fuels like natural gas or petroleum products. They can be designed to burn coal/water and/or coal/fuel oil mixture. The most important problem regarding the use of coal as a substitute for petroleum oils is excessive and rapid engine parts wear (Patton et al., 2010) due to mineral matter content. For this reason, the coal used as fuel should contain very low ash and has a high calorific value. In this purpose, the aim of the study was to obtain a coal product with ash content below 1%, which was suitable to make superior quality coal/water and/or coal/liquid fuel mixtures to be used for internal combustion engines.

Materials and methods

The clean coal product of Zonguldak/Turkey coal washery was used for this study. The sample was a bituminous coal in the size range of 10–0.5 mm with 12.5% moisture. The sample was initially dried at 80 ^{o}C and then ground below 150 μm using a rod mill. The particle size distribution of the ground coal was presented in Table 1. The proximate analyses of coal and composition of coal ash are given in Table 2.

Table 1. Particle size distribution of the coal sample after grinding below 150 μm

Particle size (μm)	Weight (%)	Cumulative undersize (%)	Cumulative oversize (%)
+150	4.46	100.00	4.46
-150+106	3.52	95.54	7.98
-106+75	14.31	92.02	22.28
-75+45	43.68	77.72	65.97
-45	34.03	34.03	100.00
Total	100.00	100.00	

Table 2. Proximate analysis of coal and composition of the coal ash

Coal, dry basis	Fixed carbon (%)	Volatile matter (%)	Ash (%)	Total sulfur (%)	Higher calorific value (kcal/kg)
	61.75	31.04	14.43	0.51	6907

Components of ash	SiO_2	MgO	Fe_2O_3	CaO	Al_2O_3	Na_2O	K_2O	SO_3	TiO_2	MnO
(%)	51.23	2.34	7.31	11.29	20.84	0.20	0.25	3.09	0.80	0.15

A three-stage flowsheet was applied to produce an ultra-clean coal concentrates. The flotation method was used as the first-stage beneficiation method. After the grinding of the flotation concentrate to below 45 µm, HCl and NaOH leaching were applied, sequentially.

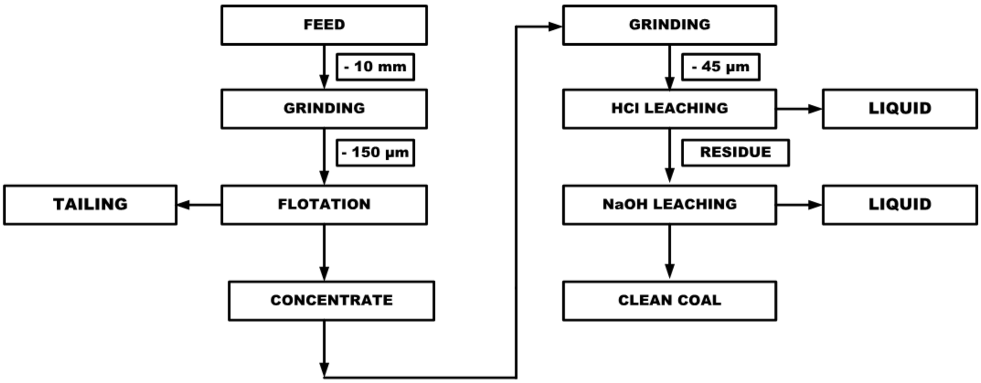

Fig. 1. Flowsheet of the experimental procedure

X0-800S ultrasonic homogenizer with 800 W power and 20 kHz wave length was used for the preparation of kerosene/water emulsions (Fig. 2).

Fig. 2. XO-800S Ultrasonic homogenizer

Results and discussion

Flotation tests

The flotation tests were performed according to the flowsheet given in Fig. 3. Kerosene was used to improve the floatability of the coal particles. Ultrasonic pre-treatment method was employed in emulsification of kerosene in water to reduce the consumption and to enhance the flotation selectivity. It is reported that ultrasonic pulses help to reduce the droplet size of the kerosene and enhance the attachment of these droplets to the coal surfaces (Atesok et al., 2001).

The flotation tests were conducted at natural pH of the sample (8.4) and 10% of solid/liquid solid/liquid ratio. 4000 g/Mg Na_2SiO_3 (depressant/dispersant for quartz and kaolinite), 5 g/Mg MIBC (frother), and 15 g/Mg kerosene (collector) were used at rougher flotation stage. The consumption rates of the flotation reagents at different stages are presented in Table 3.

Table 3. Flotation reagent consumption rates

	Addition points	Na_2SiO_3 (g/Mg)	MIBC (g/Mg)	Kerosene (g/Mg)
Rougher Flotation	1	4000	5	14.6
Cleaning Flotation	1	-	-	5.8
	2	-	-	5.8
	3	-	-	5.8
Scavenging Flotation	1	-	2	2.9
	2	-	2	2.9
	3	-	2	2.9
Total		4000	11	40.7

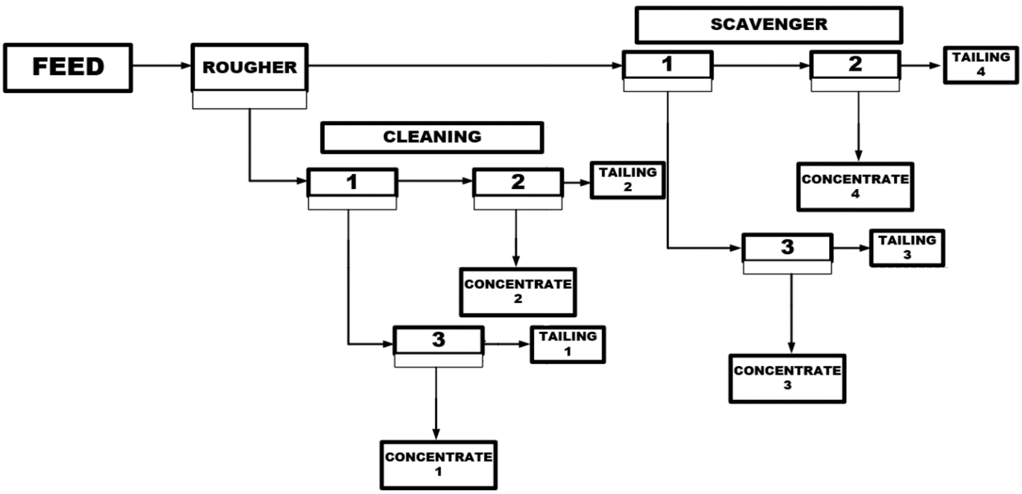

Fig. 3. Flowsheet of flotation tests

The results of the flotation tests are presented in Table 4 and Fig. 4. The cleanest concentrate was obtained with 2.78% of ash and the combustible matter recovery of 16.81%. The results showed that the flotation alone without the leaching produced concentrate which was not suitable for the preparation of coal-water slurries due to relatively high ash content.

Table 4. The results of flotation tests

Product	Weight (%)	Ash (%)	High heating value (HHV) (kcal/kg)	Cumulative weight (%)	Cumulative ash content (%)	Cumulative combustible recovery (%)
Concentrate (1)	15.0	2.78	8090	15.00	2.78	17.48
Concentrate (2)	3.19	3.69	8026	18.19	2.94	21.02
Concentrate (3)	5.07	4.12	7978	23.26	3.20	26.85
Concentrate (4)	8.05	6.67	7771	31.31	4.09	35.86
Tailing (1)	9.20	4.22	7978	40.51	4.12	46.43
Tailing (2)	23.46	6.76	7605	63.97	5.09	72.12
Tailing (3)	4.74	7.65	7503	68.71	5.26	77.24
Tailing (4)	31.29	34.55	5050	100.0	14.43	100.0
Total	100.0	14.43	6954			

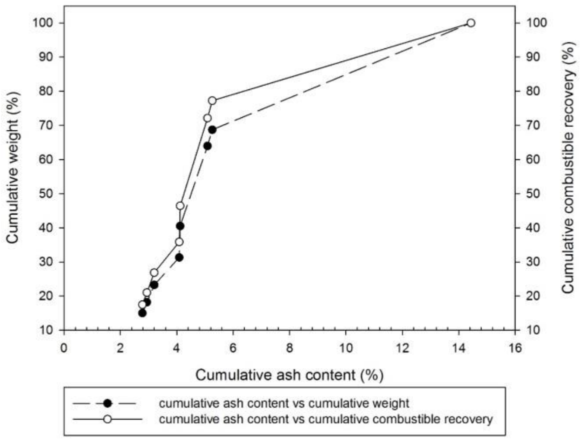

Fig. 4. Cumulative weight and cumulative combustible recoveries versus cumulative ash content of the coal concentrates

Leaching tests

The flotation products were evaluated based on the ash content and weight, and recoveries to determine the optimum feed material for the leaching tests. As a result, it was decided to combine concentrate 1, concentrate 2, concentrate 3 and tailing 1 to compose the feed material containing 3.48% of ash and 0.55% sulfur with 32.46% weight and 44.77% combustible matter recovery. The leaching tests were planned to remove carbonates, iron oxides, sulfur, and silicates from the composed flotation product.

HCl leaching

The HCl leaching was conducted to remove carbonates and iron oxides from the feed material. The feed material was ground below 45 μm using a ball mill prior to the leaching tests. 25 g of ground sample was weighted, and 250 dm^3 of distilled water was added into an Erlenmeyer flask to reach a solid/liquid ratio of 1/10. A 2 mol/dm^3 HCl solution was used in atmospheric leaching test. The flasks were put into a water bath at 80 ^oC and shaken for 6 h.

The leachate was removed by filtering. The solid was washed on a Buchner funnel with distilled water until the supernatant reached a pH of 5–6 and dried at 80 °C in a drying oven. The residue of the HCl leaching was subjected to chemical analysis. The results showed that 40% of ash could be removed by HCl leaching from the flotation concentrate, a coal concentrate containing 2.08% of ash and 0.51% of sulfur with a *HHV* (high heating value) of 8122 kcal/kg was obtained.

NaOH leaching

The NaOH leaching was applied to the residue of the HCl leaching to remove SiO_2 and sulfur contents. A Parr titanium autoclave was used for the NaOH leaching tests. 20 g of the HCl leaching residue was weighted and subjected to pressure leaching at 200 °C for 3 h using 250 dm^3 4 mol/dm^3 NaOH. The leachate was removed by filtering. The solid was washed on a Buchner funnel with hot distilled water followed by repeated dilute HCl washes. The solid residue was dried at 80 °C in a drying oven and subjected to the chemical analysis.

The results presented in Table 5 showed that a clean coal product containing 1.18% of ash, 0.53% of sulfur, 30.79% of volatile matter and 86.55% of fixed carbon with a HHV of 8188 kcal/kg could be obtained.

The feed material and the products of the flotation and the NaOH leaching test were subjected to SEM analysis using JEOL JXA 733 Superprobe (SEM+ EDS) equipment to find out the morphological changes on the samples. As can be seen from Fig. 5, the surface of the particles were intact in the feed and flotation product, whilst some traces of demineralization and surface disintegration were detected in the NaOH leaching product (Fig. 5c).

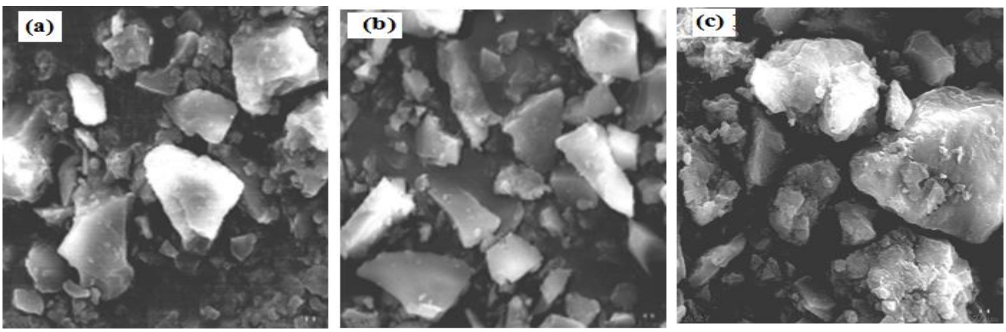

Fig. 5. SEM images of (a) feed coal, (b) flotation, (c) NaOH leaching products

Table 5. Summary of the final results of the study

Product	Ash (%)	S (%)	High heating value (kcal/kg)	Volatile matter (%)
Feed Coal	14.43	0.51	6907	31.04
Flotation concentrate	3.48	0.55	8030	30.88
HCl leaching product	2.08	0.51	8122	30.43
NaOH leaching product	1.18	0.53	8188	30.79

A Rigaku Miniflex II XRD equipment was used to investigate the mineralogical changes on the same samples. The trace of the demineralization process can easily be seen in the XRD patterns given in Fig. 6. The signals of the minerals consisting of mineral matter content of the feed coal almost diminished after the NaOH leaching.

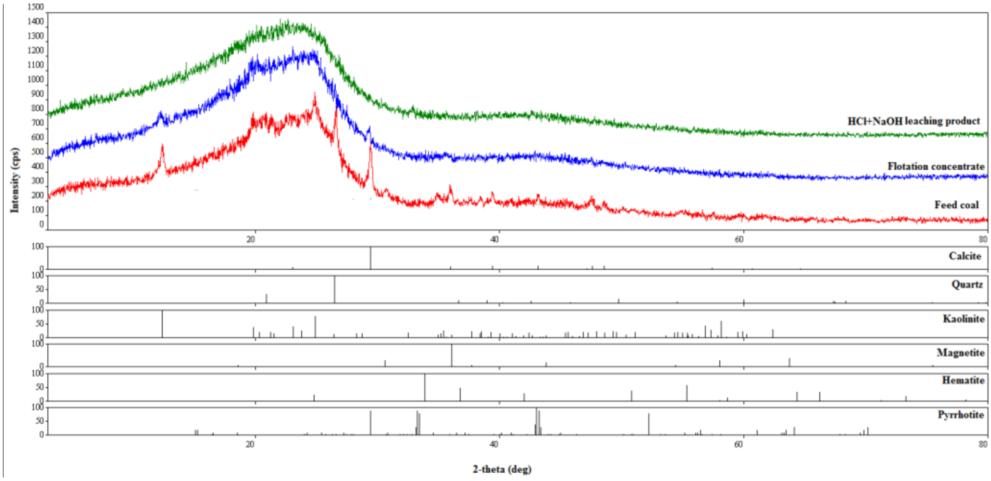

Fig. 6. XRD patterns of feed coal, flotation, and NaOH leaching products

Conclusions

An ultra-clean coal concentrate assaying 1.18% of ash and 0.53% sulfur was produced from 14.43% ash containing Zonguldak hard coal by flotation followed by HCl and NaOH leaching. Coal ash content was reduced by 91%. However, the sulfur content could not be reduced due to its organic origin.

The XRD analyses showed clearly that the flotation was very effective for removing bulk inorganic materials such as quartz, clay, iron oxides, and calcite. The remaining clay and calcite were removed in the leaching stages.

Disintegration of the surfaces of coal particles determined by SEM analyses suggested that the coal particles have still some inclusions (interlocking) of inorganic matters. Thus, it can be expected that the ash content could be further reduced when finer feed would be used for the leaching stages.

The final product with 34.28 MJ/kg HHV seems to be suitable to be used for the preparation of superior quality coal-water and/or coal-liquid fuel mixtures, which could also be used for burning in specially designed internal-combustion engines.

The findings from this study well demonstrated that it is technically possible to obtain an ultra-clean coal product from Zonguldak bituminous coal by the multi-stage process applied. The costs of coal beneficiation and coal-water slurry preparation are the major factors limiting the economic competitiveness of the coal-water fuels. Today, the oil prices do not allow coal-water fuels to compete economically with petroleum oils. However, the increasing prices and decreasing reserves of the petroleum oils in near future would let this alternative fuel be economically feasible.

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