Ultrasonic Desulfurization of Low Rank Turkish Coal Using Various Chemical Reagents

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***Abstract*—This paper investigates the use of ultrasonic energy (24 kHz, 400 W) to clean a low rank-medium sulfur lignite coal in the presence of various chemicals (Methanol, ethanol and sodium hydroxide (NaOH)). The tests were performed at different coal sizes (-300 µm and -150 µm), and ultrasonic treatment time (5 min), reagent concentration (0.5 M) and solid ratio of slurry (40 g/L). Results indicate that methanol has a significant effect on the clean coal yield (89.5%) and sulfur reduction (41.1%).**

***Keywords*— Coal; Ultrasonic; Chemical reagents; Desulfurization**

I. INTRODUCTION

Sulfur compounds present in coal are one of the major contaminants, which produce SO_2 during combustion. In Turkey, coal constitutes the most important primary energy source. The total sulfur content of Turkish coals varies between 0.5 and 15.0 wt% (Table 1) (1).

Table 1: Ranges of composition (wt%) of Turkish coals (1).

	Range
Moisture	0.5-50.0
Volatile matter	20.0-45.0
Ash	5.0-40.0
Fixed carbon	10.0-60.0
Total sulfur	0.5-15.0

Sulfur in coal occurs in the forms of inorganic and organic. The inorganic sulfur is present mainly in two forms, disulfides and sulfate. The organic form, which is bound directly to the organic coal matrix, generally occurs in forms of thiols, sulfides, disulfides, thiophenes, and cyclic sulfides (2). De-sulfurization is very essential for sustainable utilization of the low rank high sulfur coals used in different industries (3-5). Under the influence of ultrasound, normal leaching occurs, but several additional factors contribute toward improvements in the efficiency. These include the following: i-Asymmetric cavitation bubble collapse in the vicinity of the solid surface, leading to the formation of high-speed micro jets targeted at the solid surface. The micro jets can enhance transport rates and also increase surface area through surface pitting, ii-Particle fragmentation through collisions will increase surface area, iii-Cavitation collapse will generate shock waves which can cause particle cracking through which the leaching agent can enter the interior of particle by capillary action, iv-Acoustic streaming leads to the disturbance of the diffusion layer on the surface and v-Diffusion through pores to the reaction zone will be enhanced by the ultrasonic capillary effect (6).

On the other hand, ultrasound assisted coal desulfurization has been recently studied by some researchers. Ultrasound promoted desulfurization of low rank coal with a dilute solution of NaOH (0.025–0.2 M) at 30-70^{o}C was reported by Zaidi (7). The studies on de-sulfurization of coals by 20 kHz frequency and 200 W power were investigated and reported that power ultrasound can drive physical separation of pyrite from coals (8). Ambedkar et al. (9), reported the aqueous-based ultrasonic coal desulfurization method, where OH, H_2O_2, HO_2, O_2 and ozone were produced. Shen et al. (10), thoroughly investigated a rapid desulfurization method for coal water slurry using ultrasound assisted metal boron hydride (KBH_4, $NaBH_4$). Mello et al. (11), optimized the conditions for ultrasound assisted oxidative desulfurization, where the sulfur removal was about 95% after 9 min of ultrasonic irradiation using hydrogen peroxide and acetic acid, followed by extraction with methanol. Saikia et al. (12), investigated the use of ultrasound energy in water and mixed alkali (1:1 w/v NaOH and KOH solutions) for removal of different forms of sulfur from high sulfur Indian coals and showed the maximum removal of 18.8% of total sulfur, which was achieved within lower concentration, minimum treatment time and lowest alkali volume consumption upon low energy ultrasonication. The last investigation was reported a preliminary attempt of using ultrasonic energy (40 kHz) to clean some low rank high sulfur Brazilian power-coal samples in presence of H_2O_2 solution by Saikia et al. (13). This study showed maximum removal of 87.52% total sulfur, which was achieved within lower concentration with minimum treatment time upon low-energy ultrasonication.

In this present investigation, the effect of coal particle sizes (-0.300 mm, -0.150 mm) on the desulfurization efficiency and calorific value from low rank Turkish lignite coal by ultasonic treatment is reported.

II. MATERIALS AND METHODS

A. *Materials*

Low rank coal from the Afsin-Elbistan coal plant in Turkey was used for the experiment. By screening, the coal sample with easily prepared granulometry of -0.300 mm and -0.150 mm was chosen as the experimental sample. The proximate analyses, sulfur content and calorific value of untreated coal samples are shown in Table 2. Reagents (ethanol, methanol and NaOH) used in this experiment was purchased from Merck KGaA, Darmstast Germany.

Table 2: Proximate analysis (wt%), total sulfur content (wt%) and calorific value of coal sample.

Proximate analysis			Total sulfur content	Gross calorific value kcal/kg
Moisture	Ash	Volatile matter		
3.51	42.40	37.26	1.85	1,345

B. Methods

A 400 W ultrasonic processor (Hielscher Ultrasonics GmbH, Germany) (Fig. 1), working at a constant frequency (24 kHz) was used with a 22-mm-dia probe with a vibrating titanium tip attached to transducer in this study.

Figure 1: Ultrasonic processor

The manufacture specifications report the maximum ultrasonic power (acoustic power density) (Table 3) was 85 W/cm^2, and maximum amplitude was 100 µm (14). Technical properties of ultrasonic processor were given in Table 4.

Table 3: Performance data for sonotrod (H22) used.

Max. submerged depth (mm)	Tip diameter (mm)	Max. amplitude (µm)	Acoustic power density (W/cm^2)
45	22	100	85

Table 4: Technical properties of ultrasonic processor.

Specification	
Efficiency	>90%
Working frequency	24 kHz
Control range	±1 kHz
Output control	20% … 100%, steplessly adjusted
Pulse-pulse mode factor	10% … 100% per second, steplessly adjusted
Usable/nominal output	UP400S: 400 W

The amounts of sulfur and ash reductions were calculated by following formulae:

Sulfur reduction (wt.%) = $100[x_1-x_2(m_2/m_1)]/x_1$ (1)

Clean coal yield (wt.%) = $100m_2/m_1$ (2)

where x_1 denotes the sulfur percentage in the original sample, x_2 represents the sulfur percentage in the sample obtained from clean coal, y_1 is the ash percentage in the original sample, y_2 denotes the ash percentage in the sample obtained from clean coal, m_1 is the weight of the original dried sample, and m_2 represents the weight of the dried sample of clean coal.

The proximate analysis, sulfur determination and calorific value of the raw and treated coal samples were determined on a LECO-AC 500 (Leco Corporation, USA) by following the ASTM D5865, ISO 1928 standard procedures.

III. RESULTS AND DISCUSSION

A. Effet of particle size on coal yield and sulfur reduction

The maximum total sulfur removal (32.7%) was obtained for the coal sample (-300 mm) in 0.5 M NaOH. Moreover, total sulfur removal (38.4%) was obtained for the coal sample (-150 mm) in 0.5 M NaOH. This results were the same as other chemicals such as methanol and ethanol. It can be stated that particle size plays a major role in ultrasonic coal desulfurization. Table 5 and Table 6 show that the desulfurization efficiency increased with the decrease of coal particle size from -300 µm to -150 µm with ultrasound-assistance. Shen et al. (10) also showed that the delsulfurization efficiency increased with the decrease of coal particle size with ultrasound-assistance.

Table 5: Characterization of ultrasound treated coal samples (-300 µm) [a]

Parameters	Methanol reduction	Ethanol reduction	NaOH reduction
Total sulfur content	1.51 *(-6.8%)*	1.18 *(-27.2%)*	1.09 *(-32.7%)*
Calorific value (kcal/kg)	1,556 *(+5.8%)*	1,494 *(+1.6%)*	1,555 *(+5.7%)*

[a] Process conditions: 5 min ultrasonic time, 25 KHz ultrasonic frequency, 40 g/L slurry concentration, 0.5 M reagent concentration

B. Effect of chemical reagent on sulfur reduction and coal heating value

It was found that the maximum total sulfur removal was 40.0% and 38.4% for the coal sample (-150 µm) in ethanol and NaOH during ultrasonication to generate a favorable condition for increasing clean coal yields 88.9% and 87.7%, respectively (Table 7).

Table 6: Characterization of ultrasound treated coal samples (-150 μm) [b]

Parameters	Methanol reduction	Ethanol reduction	NaOH reduction
Total sulfur content	1.09 *(-41.1%)*	1.11 *(-40.0%)*	1.14 *(-38.4%)*
Calorific value (kcal/kg)	1,508 *(+9.5%)*	1,506 *(+9.4%)*	1,430 *(+3.8%)*

[b] Process conditions: 5 min ultrasonic time, 25 KHz ultrasonic frequency, 40 g/L slurry concentration, 0.5 M reagent concentration

Table 7: Summary of the desulfurization results for various chemicals

	Total sulfur (wt%)	Total sulfur removal (wt%)	Coal yield (wt%)	Heating value (kcal/kg)
0.5 M NaOH	1.14	38.4	87.7	1,430
0.5 M Methanol	1.09	41.1	89.5	1,508
0.5 M Ethanol	1.11	40.0	88.9	1,506

(Sonication time: 5 min) (coal size: -150 μm)

The results also showed that the maximum total sulfur removal (41.1%) was obtained for the coal sample (-150 μm) in methanol during ultrasonication. This can be attributed to the presence of methanol molecules, which can improve coal surface wettability, generate a favorable condition for increasing clean coal yield (89.5%). This result indicates that methanol has a significant effect on the clean coal yield and sulfur reduction.

The calorific value is also one of important indexes for coal. In order to observe the effect of desulfurization process on this property, the calorific value as well as yield of clean coal for -150 μm coal were determined after desulfurization. The results are also presented in Table 7.

IV. CONCLUSION

This study aimed to minimize the sulfur content of low rank coal via the ultrasonic treatment method. Ultrasound irradiation promotes desulfurization efficiency and increases calorific value of treated coal. It was found that the maximum total desulfurization (41.1%) was obtained for the coal sample in methanol during ultrasonication.

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