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Feasibility studies of de-sulfurization and de-ashing of low grade medium to high sulfur coals by low energy ultrasonication

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HIGHLIGHTS

- A partially green method for de-sulfurization and de-ashing of low grade coals is proposed.
- The removal of organic sulfur is revealed by quantitative FT-IR spectroscopy.
- TG-DTG analysis shows the improvement in the combustion efficiencies of the clean coals.

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ABSTRACT

The present paper reports an attempt of using low ultrasonic energy (20 kHz) to clean some low rank medium to high sulfur coal samples from northeast India in the presence of H_2O_2 solutions. The study shows satisfactory removal of all the forms of sulfur and mineral matters (ash) from the coal samples. The physico-chemical characterizations of the raw and ultrasonicated coal samples were carried out by using Fourier Transformation Infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Thermogravimetry-Derivative Thermogravimetry (TG-DTG) techniques to evaluate the final product quality. The quantitative FT-IR spectroscopic analysis demonstrated the formation of oxidized sulfur species (S=O and —SO_2) and their subsequent removal from the coal samples during ultrasonication. The XRD profiles supported the partial removal of some minerals from the coal including their de-ashing. The TG-DTG profiles of the beneficiated coal revealed their improved quality for use in thermal plants with better combustion efficiency.

1. Introduction

Coal is one of the world's most abundant fossil fuel resources. However, it causes significant environmental pollution by emitting particulate matters and toxic gases during its utilization [1]. Sulfur compounds present in coal are one of the major contaminants, which produce sulfur dioxide during combustion. The mineral matter in coal is also a serious drawback and creates environmental problems in comparison to other gas and liquid fuels. The sulfide minerals present in coal when exposed to atmospheric oxygen and water, results in the acid mine drainage [2]. During combustion, the mineral matter transforms to ash and causes several disadvantages during coal processing including leaching of potentially hazardous elements during its disposal. The ash disposition on power plant also leads to the deterioration of turbine blades and boiler tubes. Thus, de-sulfurization and de-ashing are essential for sustainable utilization of the low rank high sulfur coals used in different industries [2–4]. Moreover, clean coal technology is needed to reduce harsh environmental effects during coal processing. There are several methods in literature for the removal of mineral matter, total sulfur and different forms of sulfur from coal and are mainly subdivided into physical and chemical methods [3–5]. The physical methods can remove the soluble sulfates and coarse pyrite. The organic sulfur remains largely untouched by physical method. On the other hand, chemical methods can remove a portion of the organic sulfur from coal. However, the chemicals used in the majority of the coal beneficiation processes are mostly lethal to humans.

The high sulfur coal reserves are mostly found in China, US, Russia, Australia, Ukraine, Brazil, India, etc. [6]. However, the amount of total sulfur and the forms of sulfur in different coals throughout the world is highly variable, depending on the geologic conditions [7]. The sulfur abundance in coals is controlled mostly by depositional environments. The sulfur isotopic evidence indicated the seawater source for sulfur in high-sulfur coal [8]. Chou (1990) indicated that the most of the sulfur in coals with <1% comes from the original vegetation [9]. For coals with more sulfur, an increasing proportion comes from marine strata. Price and Shieh (1979) using sulfur isotope data found that 63% of the sulfur in high sulfur coals

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is derived from sea water by sulfate reduction and the rest is derived from the original vegetation [10]. Organic sulfur species in coals are mainly thiols, sulfides, disulfides and thiophene and its derivatives. The organic sulfur species in coal evolve during the history of coal formation. The different aspects of geochemical characterization on high organic sulfur coals were carried out by several authors [11–17]. High sulfur Chinese coals (OS > 0.8%) are also found at late Carboniferous and late Permian in southern China [14]. Dai et al. (2008) reported the occurrence of some super high-organic-sulfur (SHOS) coal of late Permian age in Yanshan Coalfield, southwestern China [15]. Thus, it is incredibly important to study on various issues of high-sulfur coals and their beneficiation.

1.1. Ultrasonication of coals

Ultrasonication has a great potential in the processing of liquids and slurries, by improving the mixing and chemical reactions in various fields of applications including ultrasonic cleaning as it produces high energy ultrasound with high intensity [18,19] causing cavitations bubbles in liquids and slurries [20,21]. Ultrasound assisted coal de-sulfurization and de-ashing have been recently studied by some researchers [22,24,26,27,30] but the removal of sulfur components was not studied completely. The suitability of the coals for thermal applications was also not investigated by any researchers. Ultrasound promoted desulfurization of low rank coal with a dilute solution of sodium hydroxide (0.025–0.2 M) at 30–70 °C was reported [22]. The shear forces produced by the ultrasound energy are responsible for exposing the finely disseminated sulfur sites during coal oxidation. Sono-chemical degradation of organic compounds present in water was also investigated during oxidation [23]. The studies on de-sulfurization and de-ashing of coals by 20 kHz frequency and 200 W powers was investigated and reported that power ultrasound can drive physical separation of pyrite from coals [24]. Wang and Yang [25] used several carbon based sorbents for de-sulfurization of model jet fuels. The amount of sulfur desorbed was found to be higher by using ultrasound. Grobas et al. [26] investigated hydro-de-sulfurization of benzothiophene in the presence of formic acid and Pd/C catalyst under ultrasound irradiation and found that the use of formic acid in the presence of ultrasonic irradiation was effective in desulfurization. Ambedker et al. [27] reported the aqueous-based ultrasonic coal desulfurization method, where OH, H_2O_2, HO_2, O_2 and ozone were produced. The evidence of formation of free radicals during aqueous ultrasonication was also reported [28]. Shen et al. [29] thoroughly investigated a rapid desulfurization method for coal water slurry using ultrasound assisted metal boron hydride (KBH_4, $NaBH_4$). Mello et al. [30] 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.

1.2. Ultrasonication and Indian coals

The Northeast parts of India provide a large amount of coal energy with an increase in various thermal plants envisaged in the near future. However, the use of ultrasonic energy to any Indian low rank coals has not been done so far. The northeast Indian coals contain low ash and medium to high sulfur (2–8%) with mainly 75–90% in organic form. So, it could not be directly used in the thermal plants without de-sulfurization and de-ashing due to stringent environmental regulations. The coals are generally termed as low sulfur (<1% sulfur content), medium sulfur (1 to <3% sulfur content) and high sulfur coals (>3% sulfur content) based on their sulfur contents [8]. The use of different types of chemicals in de-sulfurization and de-ashing of high sulfur Indian coals was reported by Baruah and Khare [3]. But, the use of green chemicals and methods in coal cleaning will regulate the related environmental issues in coal preparations. Thus, our present investigation deals with a green approach for removing the forms of sulfur and mineral matters from low rank high sulfur Indian coals by ultrsonication in water and H_2O_2. It is our prime interest to see the effect of ultrasonication (and H_2O_2) on these low rank coals and their possible combustion efficiencies after ultrasonication. The use of cost-effective and environment friendly hydrogen peroxide along with low ultrasonic energy makes the process partially green. Moreover, improvement in coal quality also reduces the cost of transportation fuel because less moisture and ash is transported to consumer.

2. Experimental sections

2.1. Medium to high sulfur coal samples

The representative of medium to high sulfur coal samples (run-of-mine) were collected from the Assam (T2) and the Meghalaya (SCF, B and MK2) coalfields of northeast India by following standard ASTM procedure [31]. The sub-sampling of each coal samples were performed by coning and quartering method. Then, 1 kg of each samples were ground to 0.211 mm sizes and preserved in air tight container for further experiments.

2.2. Physico-chemical characterizations

The proximate analysis of the raw and treated coal samples were done in the 'Proximate Analyser' (Model: TGA 701; Leco Corporation, USA) by following ASTM method [32]. The carbon, hydrogen and nitrogen were estimated by using 'Elemental Analyser' (Model: Perkin–Elmer 2400) and total sulfur by 'Sulfur Analyser' (Leco Corporation, USA) by following ASTM methods [33]. The forms of pyritic sulfur and sulfate sulfur were determined by following the ASTM method [34]. The percentage of organic sulfur was calculated by the difference. The gross calorific values were

Table 1
A summary of physico-chemical characteristics of raw and ultrasonicated coal samples (as received, wt.%).

Coal samples	M	Ash	VM	FC	TS	PS	SS	OS	PS removed	SS removed	OS removed	TS removed	Ash removed	GCV (kcal/kg)
T2 raw	2.07	3.51	43.08	51.34	3.28	0.41	0.21	2.47	–	–	–	–	–	7921.30
T2 + H_2O_2 + US	1.95	2.37	39.5	56.10	2.63	0.20	0.11	2.37	51.21	47.61	4.05	19.81	32.47	8452.12
MK2 raw	4.11	13.95	44.78	41.27	2.47	0.56	0.24	2.71	–	–	–	–	–	7135.70
MK2 + H_2O_2 + US	3.82	12.20	40.70	43.50	1.96	0.39	0.15	1.42	30.35	37.50	47.60	20.64	12.54	7438.98
SCF raw	4.07	25.9	31.80	38.30	4.47	0.87	0.18	3.44	–	–	–	–	–	7056.58
SCF + H_2O_2 + US	1.90	23.7	32.20	40.20	3.08	0.70	0.10	2.28	19.54	44.44	33.72	31.09	7.78	7256.32
B raw	4.30	17.8	33.70	44.00	3.47	1.08	0.67	1.72	–	–	–	–	–	7658.76
B + H_2O_2 + US	4.11	15.9	33.20	45.79	2.50	0.90	0.45	1.35	16.66	32.83	21.51	27.95	10.67	7804.94

(US: ultrasonicated coal; M: moisture; VM: volatile matter; FC: fixed carbon; TS: total sulfur; PS: pyritic sulfur; SS: sulfate sulfur; OS: organic sulfur; and GCV: gross calorific value).