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Producing low-ash coal by microwave and ultrasonication pretreatment followed by solvent extraction of coal

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ABSTRACT

Low ash clean coal was produced from Indian coking coal through microwave irradiation or ultrasonication followed by solvent extraction in N-methyl-2-pyrollidone (NMP) containing smaller amount of Ethylenediamine (EDA) or Monoethanolamine (MEA). Pretreatment by ultrasonication followed by extraction with only NMP gave 10–15% higher clean coal yield of (56–58%) than extraction with only NMP (without pretreatment). Effect of using up to 10% EDA as cosolvent in NMP led to maximum clean coal yield. However use of EDA concentration beyond this showed decrease in clean coal yield and increase in ash contents. Clean coal yield increases because EDA is a strong polar solvent and strong base, which disrupts coal interactions and breaks bonds in coal by acid-base interactions. The extraction yield with and without pretreatment and microwave irradiation led to the enhancement in the yield of clean coal and was found to be in the range of 66–70% with microwave irradiation, which was 3–4% higher than without pretreatment. Clean coal Free Swelling Index (FSI) was improved by one unit. This was demonstrated at lab scale. Subsequently, this process was scaled up to 40 kg/batch coal mini-pilot plant.

1. Introduction

Coal is most abundant fossil fuel resource available all over the world and in India. In fact about 89% of Indian coals are non coking in nature. These coals have high ash content, which can be utilized mostly in thermal power generation. The high ash content is difficult to remove as the ash content is disseminated in the organic matter of coal. Very less amount (about 11%) of coking coals are available in India. India is among top five largest producer of crude steel in the world and soon it is expected to become the 2nd largest producer of crude steel [1]. Higher growth in steel sector, lower quality of domestic coal, and inadequate availability of domestic coking coal have resulted in India's coal imports increasing to 169 million tonnes (MT) in financial year (FY) 14. It is reported that the coking coal import in India is expected to rise by 130 MT in FY 2020 [2,3]. India has around 34 billion tonnes of coking coal reserves (including proved, indicated, inferred), mostly which has high mineral matter contents [1]. There is a need to produce low ash coking coal from high ash yield Indian coals to meet the demand of coking coal in India.

In general, coal is being washed by two methods: (a) physical beneficiation and (b) chemical beneficiation. In physical beneficiation, mineral matter is removed on the basis of differences in their physical properties. Physical beneficiation is a cheaper process than chemical beneficiation but shows limited liberation and it cannot reduce the ash yield content beyond a certain percentage. In India, physical beneficiation is used for reducing the ash content of coking coal from 30-35% to 15–16%. Because of its limitations, chemical beneficiation route is being explored which gives substantially higher yield of clean product having lesser ash content. Chemical beneficiation is carried out by chemical leaching of mineral matter present in coal with admixture of aqueous solutions of nitric acid (HNO_3), hydrochloric acid (HCl), ammonia (NH_3), hydrofluoric acid (HF), caustic soda (NaOH) etc. or through solvent extraction, by dissolving organic matter in various organic solvents. Chemical leaching study was done by Dash et al. [4–10]. Sharma et al. [11–13] and his research group have used milder atmospheric pressure conditions for the demineralization of coals. Steel et al. [7–10] reported extensively on chemical demenralization of coal using hydrochloric and hydrofluoric acids. Similarly, work has been carried out by Sharma et al. [14–16] on the parallel approach of the solvent extraction of coals to recover and separate out the organic matter from coal having lower ash contents using solvent extraction of coal process i.e., organo-refining of coals. Author's [17] reported the results on solvent extraction of the coking coals having difficult physical washability characteristics. The process intensification studies on

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the solvent extraction i.e., organo-refining of coals showed that maximum extraction yield was obtained after 1 h extraction time and 1:12 coal to solvent ratio using NMP as main solvent with small amount of EDA as the cosolvent. The maximum extraction yield obtained was 55% of the clean coal having 6% ash from the raw coal feed having 29% ash yield coal at optimum conditions. The bench scale study of solvent extraction process of Indian coal was also reported by author's[18]. Nag et al. [19] reported characterization study of solvent extracted Indian coals. Solvent extraction of coal may also help in improving the caking characteristics in the super clean coals (SCCs) obtained and this may also help in obtaining the SCCs from the non coking coals which may have caking properties [16]. The advantage of extraction over leaching is production of ultra low ash coal from very high ash yield coal, and ease of handling solvents and their easy recovery and also in obtaining ash free reductants and the SCCs having caking properties from the non coking coals. Recently, Sharma and Giri [20] have reported on the advantages of organo-refining of coals in the gasification of non coking coals and subsequent integrated gasification combined cycle power generation and advanced cleaner power generation system which would afford a convenient and cheaper CO_2 concentration sequestration.

Masaki and Yoshida et al. [21,22] developed the process of "HyperCoal" having zero ash contents i.e., an ash free coal. They extracted the coal by organic solvents such as 1-methylnaphthalene, qunoline, tetralin etc. under high pressure at elevated temperature. Yoshida et al. [22] reported that more than 60% extraction yield was obtainable from bituminous coal at higher temperature using nonpolar solvents 1-methylnaphthalene and light cycle oil. Miura et al. [23] reported the extraction of coal using a flow type reactor with solvents such as tetralin and 1-methylnaphthalene, obtaining more than 65% yield. Iino et al. [24,25] reported that bituminous coals were extracted by 1:1 mixture of carbon disulphide (CS_2) and N-methyl-2-pyrollidone (NMP) and achieved more than 60% extraction yield at room temperature. NMP is stable industrial solvent and also most commonly used solvent for coal extraction. In fact, the use of NMP: EDA (1:1) mixture at room temperature also leads to the organo-dissolution of coals though one has to use a larger solvent to coal ratio. NMP is a strong polar solvent [26]. Renganathan et al. [27] reported that more than 70% yield of cleaner coal was achieved having as little as 0.1% ash under mild conditions. Few coals showed extremely poor clean coal yields in NMP. Hence, there was a need for the use of a promoter cosolvent for enhancing the extraction of such coals in the NMP. Pande and Sharma [16] reported that the use of EDA as a cosolvent along with NMP synergises in breaking the intermolecular forces such as van der Waals forces, H-bondings, London forces, π-π interactions, charge – transfer interactions etc. present in the coal macromolecules in the solid form, by swelling the coals. In fact, this then paves the way for enhancing the extraction of coal molecules from the three dimensional cross-linked gel network structure of coals by the NMP under milder ambient pressure conditions. However, the extent of extraction enhancement differed for different coals in the EDA assisted NMP extractions. This showed that there is a scope for studying the use of pretreatments for enhancing the further extractions of coals. Kinetics of a swelling of a coal in different combinations of NMP and EDA was reported by Pande and Sharma [28].

Earlier, researchers focus was on chemical leaching and solvent extraction of coal without any pretreatment. However in recent years, many researchers all over the world have reported work on pretreatment of coal by ultrasonication (USN) and microwave irradiation (MI). These pretreatments would also break the intermolecular forces present in the coal macromolecules which hold the solid structure of three dimensional cross-linked gel network structure of coal macromolecules. In the present study author's approach is to remove the ash content and improve the yield by pretreatment with microwave and/or ultrasonication followed by solvent extraction, i.e., organo-refining. It is the prime interest presently to see the effect of microwave and ultrasonication treatment on the high ash yield Indian coal. Author's filed a patent on process flow sheet for pretreatment of high ash coal followed by solvent extraction to produce clean coal [29]. In the present study, a high ash yield Indian coal was tested for this purpose. Microwave irradiation and ultrasonication treatment was done separately in organic solvent. Subsequently, pretreated coal was subjected to solvent extraction method for ash removal. The effect of solvent-to-coal ratio, ultrasonication time, microwave heating period, and addition of EDA/MEA in NMP on extraction yield was investigated. Fourier Transform infrared spectroscopy (FTIR) was done for feed and extracted coals. Results were compared with and without pretreatment to see the pretreatment effect.

2. Irradiation

2.1. Microwave irradiation of coal

The advantages of using microwave energy for coal processing are its easy penetration inside the particle, heat all particles simultaneously, controllably and this can be turned on and off instantly. It is a non contact technology, it provides uniform energy distribution, it reduces processing time [30]. Sonmez et al. [31] has produced ash-less coal extracts by microwave irradiation using NMP, NMP/ethylenediamine (EDA) mixture and NMP/tetralin mixture. They produced clean coal with as low as 0.11% ash. They concluded that ash removal is better in case of microwave extraction than with thermal extraction. Review papers on microwave coal processing [32] and microwave energy for mineral treatment processes have been published [33]. Binner et al. [32] reported that microwave irradiation has the potential in coal cleaning and comminution, coking, liquefaction, enhancing fluid flow in coal beds and coal characterisation. Haque [33] reported that microwave irradiation has potential in mineral treatment such as heating, drying, leaching and pretreatment of gold ores. They also mentioned that fundamental understanding of microwave interaction with minerals has to be understood during research work. Srikant et al. [34] reported on various prospects about the application of microwave energy in coal processing and utilization. Kingman et al. [35] considered many different applications including heating rate studies, microwave treatment of coal, microwave assisted grinding in their review paper. The effect of microwave pre-heating on different coals were studied by Laster et al. [36] and the author's investigated different properties such as moisture content, fuel ratio, petrography and intrinsic reactivity. Monsef-Mirzai et al. [37,38] reported work on the use of microwave heating for the pyrolysis of coal. Tao et al. [39] reported on the progress on coal desulfurization techniques using microwave. Microwave assisted extraction of oils using bituminous coal and other biomass material was reported by Voon [40]. It is essential to break the intermolecular forces present between the coal macromolecules and the use of microwaves can dis-associate these associative intermolecular forces. This would thus help in the extraction of coals by different solvents in the extraction disrupted free molecules from coals.

2.2. Ultrasonication of coal

In recent years, use of ultrasonication technology in mineral processing has been reported and applied for the extraction, leaching, desulfurization, and flotation of coal [41–44]. There is a great potential in the processing of liquids and slurries by ultrasonication as it produces high energy ultrasound waves. The advantage of using ultrasonic wave energy is that these can penetrate the coal particles and disassociate the intermolecular forces such as van der Waals forces, London forces, H-bondings, π-π interactions, charge transfer interaction and other intermolecular forces holding coal molecules as associative forces. Feasibility studies of coal desulfurization and deashing of low grade medium to high sulfur coals have been reported by Saikia et al. [41]. They used low ultrasonic energy (20 kHz) to remove ash and sulfur