

Literature Review

2.1 General Statement

The current research focuses on the characterization of Indian Permian coal from the Gondwana basin of peninsular India, studied by different analytical techniques. Numerous studies, directly and indirectly, related to the study's objective have also been reviewed. In addition to the traditional chemical analysis of coal, some advanced studies have also been adopted.

2.2 Coal as a Fuel

However, coal mining was only a later development in India after discovering its occurrence in Bengal in 1774. The first published reference to coal mining dates back to 1774 when shallow mines are reported to have been developed in the Raniganj coal fields in West Bengal (Govt. of India report, 1961). The first written records of pollution created by the burning of coal date back to the 12th century, when the English Queen Eleanor left Nottingham town (UK) because of smoke (Kovarik, 2021). Fifty years later came the first example of environmental legislation, in the reign of Edward I, when the use of coal in London for industrial and domestic purposes caused a great nuisance. However, the law proved impossible to enforce with any effectiveness. Increased reliance on coal to sustain industrial pollution has simultaneously brought environmental awareness among people at large in recent decades. The coal-burning associated air pollution with the development of humanity and the industrialization has gradually become a significant public health problem among the industrial nation's population worldwide. Coal combustion as a fuel in

different industries produces heat and energy for power generation and the growth of a nation. It is the most significant source of greenhouse gas (GHG) emissions and aerosol generation. Many Asian and European countries have experienced the damages to their environmental aspects and human health due to years of coal excavation, combustion, and related metallurgical processes (Kumar et al., 2015a; Medunić et al., 2018b; Naik, 2016). Notwithstanding the present situation of high energy requirements, coal remains a promising energy source. Based on information from the World Coal Association (WCA), proven total coal reserves are much larger and sufficient to supply energy for more than 100 years (Sati and Verma, 2021). The latest reports from WCA, noted that coal still makes up 29% of actual world energy production and 41% of electricity generation but the lack of pollution-control technologies hurts the environment (Chakraborty and Sarkar, 2005).

The Singrauli coalfield Basin located in central India was known as early as 1840. Mukhopadhyay and Adhikari (2004) worked on the integrated basin analysis of this coalfield. They classified the thick sedimentary packages of the basin into the Parsora Formation, Pali Formation, Raniganj Formation, Barren Measures, Barakar Formation, and Talchir Formation in descending order above the metamorphic basement. Coal is mainly restricted to the Lower Permian Barakar and Upper Raniganj formations. The Singrauli coal-bearing basin has been structurally divided into two basins; the Moher sub-basin in the northeast part and the Main sub-basin situated in the western portion. However, some scientific studies have dealt with petrological and chemical characteristics of Lower Gondwana coals from Moher Sub-basin by Misra and Singh, (1990). Singh et al. (2014) conducted the first detailed petrographic and geochemical study of the Lower Permian Barakar coals and their depositional environment in the Singrauli main sub-basin. Petrographic studies of

Barakar coal measures in the Moher sub-basin, also carried out by Chakrabarti (2001), and suggested a deltaic environment of deposition. Later, a fluvial-lacustrine condition for depositing Raniganj and Barakar coal seams was established by Singh et al. (2014). However, several coal samples from Turra and Purewa coal seams of the Barakar Formation (Singrauli coalfield) in the Moher sub-basin show deposition in deltaic conditions. They carried out petrological studies of different borehole samples drilled in the main sub-basin, and a deltaic environment of deposition for these Barakar coal seams was established. Rajeeva et al. (2012) studies about the sedimentation of Barakar sediment, which hosts the major seams in the Gondwana basin, have reported the dominance of SiO_2 and Al_2O_3 , along with Fe_2O_3 , MgO , Na_2O , and K_2O , which indicate that the sediment deposited during the Barakar formation is mainly derived from a mix of quartzose sedimentary and felsic igneous provenance. He also observed that radioactive minerals like uranium and thorium mainly attached to the surface of iron oxides (Fe_2O_3 , and FeO).

2.3 Chemical Characterization of Coal

The ultimate and proximate analyses have been required to investigate chemical reaction processes and predict coal quality and combustion characteristics (Nhuchhen, 2016). It gives information about the chemical compositions of coal and confirms its logical and reasonable use. Through the knowledge of the proximate and ultimate analyses, it is easy to predict different fuel-related parameters (Mathews et al., 2014). Neavel et al. (1986) proposed an equation to calculate VM using ultimate analysis for lower rank coal, and the elemental composition of coal can predict many physical properties and process responses. The proximate analysis can be used to calculate general characteristics and the fundamental structures of coal. Shen et al. (2010)

proposed correlations to estimate the ultimate analysis of coal using proximate results. The data considered by Parikh et al. (2007) are the contents of carbon, hydrogen, oxygen, VM, and FC, ignoring the effect of ash yield on the element compositions. However, there were no perfect correlations exist to evaluate the ultimate parameters of coal using the proximate values except for the relationship proposed by Li et al.(2004), which correlated with the effect of GCV on ultimate analysis. The nitrogen in coal was less than 0.5–1.8% and not correlated with the degree of coal maturation. Moreover, sulfur content depends on depositional conditions when coal is deposited. The nitrogen and sulfur content in coal is not taken into consideration.

Mishra, (2009) found that Permian coal contained low to medium moisture content, medium to high VM content, and high ash. The grindability of the coal samples is low, making them difficult to grind. The GCV of the coal varies between 3345 and 4703 kcal/kg. Some of the coals can be easily washed, but the degree of difficulty varies between the types and nature of the samples. Studied coal can be used for thermal purposes or in other small-scale factories for energy generation. However, suitable pollution control measures must be made since these coals are expected to give off a significant amount of CO₂ and other harmful pollutants during combustion because the ash percentage of the coal is very high.

Medunić et al., (2020a) studied the characteristics of Raša coals, mined out from the Istrian Peninsula situated in the Croatian Republic for 400 years till 1999, which had a very high level of organic sulfur content, and a very high level of heavy metals like selenium, uranium, molybdenum, vanadium, and others. Selenium (Se) is a potentially toxic element responsible for the loss of different faunal species in this

region. It is required for humans in a meager amount, but high concentrations can be deleterious for health.

Saikia et al.(2016) used ultrasonic energy in a hydrogen peroxide H_2O_2 medium to minimize coal's sulfur and ash content. They found that removal efficiency was up to 87.52%. They also defined other clean-coal technologies (CCT) with minimum energy consumption, treatment time, and limited use of reagents. Their suggested methodology may benefit larger industrial applications with high ash and sulfur-value coals.

Dai and Finkelman, (2018a) investigated coal's geochemical maturity. They found that coal is a good source of many REEs and other base metals like aluminum and magnesium. Coal is an excellent economic source for countries with abundant coal mines, such as China, India, the United States, and Russia.

Finkelman et al.(2021a) also studied the future related environmental and health concerns from burning coal. They reported that the USA and many European countries have declining coal consumption and the closure of many power plants. There was a significant rise in quality of life, in addition to a reduction in health-related disorders including silicosis and coal pneumoconiosis. However, coal consumption is increasing in many developing countries, including China, India, Russia, and many other Asian countries. In many cases, the old power plants adversely affect the environment by releasing contaminants such as arsenic, mercury, selenium, and fluorine from combustion.

Oreščanin et al.(2012) analyzed fly and bottom ash and reported S, Se, Sr, Hg Cd, Cr, Pb V, U, Cd, Sr, Pb, Cu, Cr, Pb, Cu, and Zn levels in the coal, fly ash, bottom ash, and sediment sample from the river Dretulja. Their levels were compared with

published information from different world localities of major Croatian coal mining regions. He said heavy metals are harmful to the environment, even in low concentrations.

Chen et al.(2021)studied the environmental risk associated with emissions of volatile elements in the local coal-based thermal power plants. Using the simple mass balance method, they assessed the level of heavy metals Fe, As, Se, Cd, Hg, and uranium, with the results showing that the atmospheric emissions were 578 t, 2.01 t, 15.3 t, 0.57 t, 2.80 t, 23.7 t, and 0.099 tons, respectively.

Zhang et al.(2015) studied a coal sample using TGA and DTG and correlated the occurrence of functional groups in coal with FTIR results. They found changes in aliphatic (CH₃) and hydroxyl-containing groups in aromatic structures while increasing carbonyl-containing groups of carbonyl species in coal. For lignite, both -CH₂- and -CH₃- containing groups decreased, and carbonyls increased initially and later decreased, corresponding to forming many ether-containing compounds and substituent aromatic compounds increasing slightly in the case of lignite.

Aich et al.(2020) reported the study of the pyrolysis characteristics of high-ash coal (28%–40%) collected from the Singrauli coalfield, India. Proximate, ultimate, and GCV analyses were performed on the coal samples. The pyrolysis activity of the coals was characterized using TGA to observe the burning profile of coals. Different kinetic parameters like ignition temperature, burnout temperature, ignition index, peak temperature, burnout index, combustion performance index, intensity index rate, activation energy, and pyrolysis process were analyzed to more fully understandthe combustion behavior of coal. Furthermore, these parameters were compared with each coal's VM, ash, FC, and fuel ratio. Their study indicates that with the increase in ash

yield, the combustion process initially increases and later decreases. Further, coal with VM ($25\pm 1.75\%$), ash (20%–35%), and an FR of (1.4–1.5) was ideal for coal combustion.

Hassid et al.(2022) studied lignite and bituminous coal of Late Pliocene and Early Pleistocene age from Hambach Coal Mine, Germany, supplied to the power plant in Israel. The most important aspect of coal that determines its value is its GCV. However, VM, ash yield, and moisture content are essential properties that need the quality control of the coal used to maintain maximum combustion efficiency in a furnace. They studied using TGA and DSC analytical techniques to analyze the reactivity patterns of the aliphatic and aromatic organic constituents present in the samples, which were correlated to the VM of coals. The findings indicate that the combined TGA/DSC technique can give a good knowledge of the chemical reaction pattern of coals during their pyrolysis and combustion processes.

India and China are developing nations with rapid industrial and economic growth and an increased demand for clean energy sources. Coal is mostly used for electricity and metallurgical purposes in the iron and smelting industries. Based on the data of the Integrated Energy Policy Committee, coal will be India's most critical energy fuel till 2050 (Indian Minerals Year Book, 2018). Indian coal has been of inferior quality because of the high ash content of thermal grade coals. Those coals require beneficiation to meet the application-based qualitative value of coal. Due to the decline in coal quality and scarcity of coking coal in India, a low grade of coking coals with high ash content and non-coking coal, both present in abundance, can be used in the iron and smelting industries, thermal-based power plants, the cement industry, and many different industries after preparation, beneficiation, and treatment. Beneficiated coals have the considerable prospect of being utilized as a blendable mix

for metallurgical applications (Halдар, 2010; Misra and Mohanty, 2005; Reddy and Biswal, 2006; Sahu et al., 2011). Moreover, the blending techniques of CCT optimize the blend of non-coking coal with other coking coal to serve the metallurgical industries' requirements and reduce dependency on coke import. They described the physical beneficiation of high ash content non-coking coals from Talcher coalfields, Odisha, India, having an ash yield of 34%, to reduce the ash content to 25%, to procure low-ash coal, which can be utilized as a blendable mix for industrial application purposes (Misra and Mohanty, 2005).

The utilization techniques of coal are a significant concern because of serious environmental pollution and energy-related issues. To propose clean, green, and effective coal utilization is a prime concern. The physicochemical quality of coal is an essential requirement for its utilization. For example, GCV, which defines coal's heating efficiency, is the primary requirement for designing boiler systems and evaluating other pollution compliance measures in industries (Channiwala and Parikh, 2002). The ultimate coal analysis is important for evaluating the full chemical transformation process, and identifying the flow rate of noxious gases and air quality in coal combustion activity (Nhuchhen, 2016).

2.4 Fly ash

Fly ash is generated by coal pyrolysis in thermal power plants along with various other residues like bottom ash, desulfurization sludge, fuel gas, and coal gasification ash. The physicochemical and mineralogical properties of FA depend on the nature and type of coal utilized in boilers (Hower et al., 2005b). FA is an amorphous mixture of ferro aluminum silicate minerals derived from clay mineral combustion and glass particles derived from pulverized coal combustion at temperatures ranging from 800

to 1600 °C. The leaching of potentially harmful and toxic trace elements from coal-derived fly ash makes them bio-available to plants and animals, whereas micron and nano-sized ash particle emissions degrade atmospheric quality parameters and human health (Kumar et al., 2015a; Saikia et al., 2015).

Rao, (1992) studied the properties of coal and coke and found that the high ash content in coke produces a good amount of slag. The increase in slag volume is also because of the high flux rate for the desulfurization process in the blast furnace. These cause high fuel rates, a decline in productivity, and an adverse impact on the cost of the Indian iron and steel smelting processes.

Saikia et al.(2021a) studied the mechanisms and properties of coal and derived FA, which affects human health and is responsible for global climate change by CO₂, NO₂, and CO emissions. Their study concluded that fly ash shows a good amount of rare-earth elements, and significant oxide minerals like quartz, silica, kaolinite, illite, anatase, hematite, pyrite, and calcite are present in coal, as confirmed by XRD diffractograms. Fly ash rich in rare earth elements indicate the presence of Nd, Ce, and Pr with different hazardous elements connected with glass, pyrite, haematite, anatase, and clay minerals like kaolinite.

Khan and Umar, (2019) investigated the effects of FA on groundwater quality. FA is a waste product derived from thermal energy generation, having various heavy metals like Cr, Ni, Pb, and many other toxic heavy elements such as Cd and Hg, in different concentrations and values. It is commonly disposed of in fly ash ponds, resulting in the groundwater in industrial regions being affected by these elements. To estimate the potential impacts of these FA on groundwater quality, water samples from along the ponds will be analyzed to determine the potential implications in detail.

Poon et al.(2003) found that FA is a burnt powdery residue of various chemical constituents and minerals derived from alumina, silica, iron, titanium, calcium, magnesium, and sulfates in associated and complex forms. Its utilization as pozzolanic material in manufacturing FA blended cement has been examined in great detail in different parts of the world (Bouzoubaa et al., 1999). Different investigations, patents, and reports have been conducted to establish processes and recommend using FA as a pozzolanic material in cement. The particle nature, chemical properties, calcium content, residual carbon, and crystallinity of fly ash all play essential roles in its use as a pozzolanic material for cement and cement-based products.

Coal-derived fly ash from Indian high-ash coals has minimum lime reactivity and requires better chemical activation. Further, investigations have been required to improve fly ash's physical and chemical properties by using different activation processes for blending material into cement mortars. Coal-derived FA has been activated using various mechanical, physical, chemical, and thermal techniques to remove unburned residual carbon, improve its pozzolanic mechanism, and maintain uniform quality for use in cement-based mortar. The improved pozzolanic properties indicate an effective response in blended cement as strength gaining and other properties (Krishnaraj and Ravichandran, 2019).

2.5 Chemical and Biological Beneficiation of Coal

Coal is the most abundant available natural fossil energy fuel in the world, especially in India, to meet the energy requirements of a developing nation through the continued exploitation of coal as an alternate energy source. Non-coking coal in India also attracts the benefit of concern over energy demand and sustainability, with concerns about climate change and greenhouse gas emissions from coal-based thermal

plants. Coal beneficiation is a process in which the inorganic constituents are separated from coal by providing high-value coal and combustion characteristics to the fuel produced. The separation techniques are based on the physical parameters between the coal's organic maceral and inorganic mineral groups (Park et al., 2021). This process must be separated into easy-cheap, cost-effective, and efficient steps to be utilized in the industry. The most commonly used procedures for beneficiation are jigging, froth flotation, density separation, and sizing. Typical configurations divide the ROM coal into different sizes and utilize various separation techniques for each size fraction (Xia et al., 2015).

Singh et al.(2012) studied the biochemical beneficiation of coal and lignite using microbes developed by research from the Institute of Sciences (BHU), Varanasi, Uttar Pradesh, India. Their approach was to transform or degrade the contaminants present in coal, and make them suitable for the environment. They used mixed microbial combinations to find the possibilities of different toxic elements present in coal. The removal efficiency was 80% for Cd, Cu, Zn, Ni, and Cr, and 45% for Pb, which are environmentally toxic heavy metals.

Saikia et al.(2014a) conducted a study in which they utilized ionic liquids for de-ashing and de-sulfurizing high-sulfur coals. Different ionic based liquids, like 1-n-butyl-3-methyl-imidazolium tetra-fluoro-borate, and 1-n-butyl-3-methylimidazolium chloride, were used in HCOOH/H₂O₂, and V₂O₅ medium. The optimum removal efficiencies obtained were 50.2%, 48.0%, and 70.3 wt% for total sulfur, organic sulfur, and ash yield, respectively. Their study indicated the excellent efficiency of removing significant amounts of inorganic and organic sulfur content from the high-sulfur Cenozoic coal.

Hammond et al.(2016) studied the deep eutectic solvent's synthesis, properties, and applications. Green solvents have good availability, biodegradability, recyclability, flammability, non-toxicity, and low cost. They describe a new type of ionic solvent known as Deep Eutectic Solvents (DES). DES are fluid consisting of two or three environmentally safe and cheap chemical components that can be self-associate by adding hydrogen bonding to form a eutectic solvent, have a melting point lower than that of each component compound, and are basically liquid below 100 °C. DES show identical physicochemical properties to traditional ionic liquids while being much cheaper and more eco-friendly. Because of these valuable advantages, DESs are now being studied in various fields.

Fatma and Banerjee, (2022) studied the morphological and FTIR characteristics to analyze the interaction of Deep Eutectic Solvents (DESs) with low-grade coal. The beneficiation experiments observed that DESs could help disperse and disrupt the coal molecular structures through intermolecular interactions. They concluded that choline chloride and urea combination could disrupt the coal molecules to the maximum extent, followed by choline chloride, ethylene glycol, and choline chloride and glycerol combinations. Choline chloride and urea have a more significant charge density than other DES. DES exhibited similar swelling index characteristics to other ionic liquids and can be used as a suitable substitute for more expensive green solvents.

2.6 Environmental Concerns

Different workers have studied acid mine drainage problems globally. Coal mining activities in India are done by opencast and underground techniques, affecting the environment's quality directly or indirectly. AMD generation is still one of the

most severe environmental concerns in coal mining. AMD creates an ecological disturbance in different Gondwana and Cenozoic coalfields of north-eastern India. The high percentage of sulfide minerals in the coal of the Barakar Formation of India and the Cenozoic systems in the northeast region, including Jammu and Kashmir, is the reason for the severe AMD generation (Jamal et al., 1991).

From the above literature, it has been concluded that little work has been done on the coal of the Singrauli coalfield, which is part of the Gondwana basin in India. Physical, chemical, biological, and biochemical tools for coal beneficiation are available. In the case of the Singrauli coalfield, there is a dearth of literature available on such tools because the characterization and beneficiation of Singrauli coal have not been carried out systematically. Therefore, the present investigation has been conducted for the assessment of coal quality parameters (proximate and ultimate) to know the utilization potential, mineral matter, and functional group composition to know coal chemistry and enhance the combustion attribute (GCV) of Permian coal from Singrauli coalfields by the process of chemical beneficiation.