

Introduction

1.1 Introduction

Coal is the world's most widely available, combustible, and extensively distributed energy fuel. It is a complex, compact, black or dark brown carbonaceous organic-clastic sedimentary rock formed by the compaction of layered, decomposed vegetation that occurs in stratified sedimentary formations. Coal, according to the UN (ECE), is a combustible sedimentary rock that has more organics (> 50) weight percent than inorganics. It is present in the rock strata in different layers, or veins called coal beds or seams. It is formed by undergoing geological temperature and pressure applied to plants and debris that remain beneath the earth for millions of years. Coal is an essential energy fuel; a resource primarily used for power generation, and currently meets 41% of global electricity needs. Fossil fuels are one of the most demanding energy sources, and their consumption has gradually increased with energy demand. A large amount of waste is produced during the extraction and processing of coal. Coal consumption has a negative environmental impact, mainly because burning fossil fuels in various industries has released vast amounts of CO₂ into the environment in the last few centuries. Scientists have identified that between 1970 and 2001, global CO₂ emissions increased by up to 70 percent (Alhorr et al., 2014). Since then, there have been great concerns over the ever-increasing concentration of CO₂ in the environment and its harsh effects on the environment (Singer et al., 2014). Permian Gondwana coal has received increased attention because this coal is a potential energy resource in developing countries like India. Northern Coal Fields Limited (NCL), a subsidiary of CIL, carried out the mining

work in the Singrauli coalfields, one of the world's largest open-cast coal mining complexes. Some of the substantial reserves of power grade coal facilitated thermal power generation units and power industries in the area. This large-scale industrialization will likely endanger the ecosystem and environment as it has already begun to pollute.

Although the Indian government promotes green and renewable energy resources, the high demand for energy for industrial growth and social well-being extends the life of non-renewable energy sources while minimizing environmental impact. Safe storage, transportation, and estimation of coal quality provide efficient and better utilization (Bridge et al., 2018; Tang et al., 2018).

1.2 Coal Origin and Properties

There are two main processes during the formation of coal, peatification and coalification. Bacterial disintegration of plant parts takes place during peatification while increasing temperature and pressure play important role during coalification (Phillips and DiMichele, 1990; Smyth, 1989). The depositional environment in which peat accumulates and its subsequent transformation into coal, control its physical and chemical characteristics during the combustion and utilization (Finkelman et al., 2002; Little, 2015). Depositional environment, where peat is formed, represents distinctive, waterlogged, low-lying, or elevated setting in wetlands where accumulation is controlled by biological, botanical, and chemical, activities (Dai et al., 2012b; Shen et al., 2018). The combined effect of geomorphological, hydrological, and physical processes and their interactions with biological, botanical, chemical, and geographical ecosystems produce different peatland types (Dai et al., 2020). Coal maceral analysis is an important method for knowing peat biomass characteristics (Hower et al., 2022a), and it is helpful to understand the coal sequences

on the macroscopic and mesoscopic scales (Dindarloo et al., 2015; Hower and Wagner, 2012; Smyth and Buckley, 1993). The prime drivers of peat environments are the availability of water (surface and groundwater), climate conditions (temperature, precipitation, and evapo-transpiration), nutrient supply from surroundings, and nature of external environments (riverine, lacustrine, and marine influences) (Dai et al., 2020; Page et al., 2010). Anaerobic bacteria decompose the plant to derive peat material. During the continued burial, increasing pressure and temperature begin the formation of low-rank coal (lignite), which subsequently undergoes further transformation into sub-bituminous coal, bituminous coal, and finally into anthracite coal. The amount of water and other organics in the coal decreases, and the coal becomes more dense and compact with higher carbon content. The development of peat and coal is not static; it involves a variety of decompositional pathways and diagenetic changes. O'Keefe et al. (2013) noted the chemical transformation in the organic composition of macerals during the coal metamorphism.

The mineral association in coal (Finkelman et al., 2019b; Ward, 2002b) better depicts the regional geological setting (Dai and Chou, 2007), and depositional environment of peat accumulation (Hower et al., 1991). Gondwana coal contains the first extensive non-tropical peats. Based on stratigraphic and sedimentological evidences studied worldwide by researchers (Glasspool, 2003; Phillips et al., 1985), two opposing schools of opinion regarding the origin of coal have been proposed. The hypothesis that homologizes the coal bed with an existing peat deposit is known as the autochthonous or in situ theory (Zodrow et al., 1996). In autochthonous coal deposits, plants grew and decayed in the same region where coal accumulated. Numerous fossil tree trunks and fossil roots in the coal seams favor the autochthonous theory

(Korasidis et al., 2019). Another opinion regarding coal deposits representing an accumulation of peat by transportation and sedimentation in the bottom of open lakes or lagoons is known as the allochthonous hypothesis or Drift theory (Babu and Ducher, 1966). The coal geologists of India suggested allochthonous deposition of the Indian Gondwana coal beds because they could not find any record of the occurrence of erect stems with attached roots suggestive of the position of growth or roots in the floors of the coal seams (Banerjee, 2005). According to this theory, the vegetable detritus got carried away by flowing water bodies into different basins. Fossil tree stems in the coal seams without attached roots are in favor of allochthonous origin (Cúneo, 1996).

There is selective distribution of coal both geologically as well as geographically (Lahiri-Dutt and India, 2014). The distribution of Indian coal belongs to two main geologic periods: Lower Gondwana coal of the Permian age, and Cenozoic coal of the Eocene to Miocene age (Singh and Singh, 1996b; Walker, 2000). The Permian period has a significant proportion of coal in India. Coals are primarily composed of carbon, which provides energy value and varying amounts of VM, moisture, and ash. As we know, the physicochemical properties of coal differ considerably. Coal-based thermal power plants are designed to consider available coal's specific properties and reduce the emission of impurities such as sulfur, mercury, and other dioxins (Hower et al., 2005a; Umrao et al., 2017).

1.3 Coal Reserves in India and World

Coal as a non-renewable energy source was produced by China (3846 Mt), India (756 Mt), and the USA (639 Mt) in year 2019, and they are also the top three consumers based on the BP World Energy Statistical Yearbook 2020 (Dale, 2021). Therefore, the coal production and consumption of these three countries

significantly impact research and environmental concerns around the world (Tong et al., 2022). The efficient utilization of coal in these countries and providing a practical policy guideline based on research have greater significance in developing cleaner and greener energy generation.

Of the total coal produced in India, 93.31% was extracted from open-cast coal mines. Coal quality is a significant concern in India because most coal seams are allocthonous and comprise high mineral content. Coal is produced in many countries and used in various industries, including the power and metallurgical steel industry. Based on Geological Survey India (GSI) reports (Acharyya, 2000), India's coal reserves are around 308802 Mt, up to a depth of 1,200 meters. Many other industries, such as metallurgical coke, cement, limestone, alumina smelting, and copper ore smelting, are based on coal-based energy. It is also used in different chemical-related industries. Coal in India has wide variations in its GCV due to different geological factors and mineral content. It has also been observed that GCV fluctuates within coal mines and coal seams (Patel et al., 2007).

Table 1.1. Total Coal Production and Consumption by Country in 2021 (IEA)			
Production (Mt)		Consumption (Mt)	
China	3925	China	4130
India	793	India	1056
Australia	470	USA	508
Indonesia	576	European union	435
USA	528	Russia	227
European countries (total)	329	Japan	184

Until 2011, coal pricing in India was done by useful (functional) heat value (UHV). UHV is an expression derived from ash and moisture contents for non-coking coals and calculated by the formula: $UHV \text{ (kcal/kg)} = (8900 - 138) \times (\text{percentage of ash content} + \text{percentage of moisture content})$. Later in 2012, the pricing was changed to GCV. It is based on the new system where 17 grades of coal were graded, and coal prices were fixed according to their grade.

Grades of Non-coking Coal		Grades of Coking Coal	
GCV Band (kcal/Kg)	Grade	Grade	Ash Content
> 7000	G-1	Steel Grade - I	< 15%
7000-6700	G-2	Steel Grade -II	18-15%
6700- 6400	G-3	Washery Grade -I	21-18%
6400-6100	G-4	Washery Grade -II	24-21%
6100-5800	G-5	Washery Grade -III	28-24%
5800-5500	G-6	Washery Grade -IV	35-28%
5500-5200	G-7	Washery Grade – V	42-35%
5200-4900	G-8	Washery Grade -VI	49-42%
4900-4600	G-9	Grades of Semi-coking and Weakly Coking Coal	
4600-4300	G-10	Grade	Ash+Moisture
4300- 4000	G-11	Semi Coking Grade -I	< 19%
4000-3700	G-12	Semi Coking Grade -II	24%-19%
3700-3400	G-13		
3400-3100	G-14		
3100-2800	G-15		
2800-2500	G-16		
2500-2200	G-17		

As a result, the new grading system has a range of 300 kcal/kg for each grade (Table 1.2), whereas in the earlier grading system, there were only seven grades whose range of grading was between 600 and 1000 kcal/kg. The design of boilers in thermal power plants must take into account the coal grade and quality performance,

which is an essential factor in determining coal prices. Atmospheric temperature and humidity may also affect the change in the grade, and the simplest way to calculate the GCV of coal samples is by proximate analysis (Patel et al., 2007).

India's top five states which have significant coal reserves are below:

- i. Jharkhand:** Located in northeast India, the state of Jharkhand tops the list of India's coal reserves with more than 26%. The state's main coal-mining centers are Jharia, Bokaro, Aurangabad, Hazaribagh, Giridh, Dhanbad, Ramgarh, Karanpur, and Hutar. Most of these coalfields are located in a narrow belt that runs east to west. The Jharia coalfield, which is located south of Dhanbad, is India's oldest and richest coalfield, with the significant coal reserves.
- ii. Odisha:** This state is located on India's east coast and ranks second in coal production, accounting for 24% of the country's coal resources and contributing 15% of the total output. The major coal mining areas are Dhenkanal, Sambalpur, and Sundargarh districts. Odisha's most extensive coalfield, Talchar mines, covers an area of about 500 km².
- iii. Chhatisgarh:** This state, located in the central portion of India, has a total of 17% of the country's reserves. The coal reserves envelop an area of about 1878 km² in the dense forest in the Mahakoshal region. Chirmiri, Johilla, Jhimli and Hasdeo-Aranya coal valleys are some of the largest mines.
- iv. West Bengal:** West Bengal ranks fourth with an 11% contribution of total reserves, with good quality coal found in Bankura, Puruliya, Vardhman, Jalpaiguri, Bankura, and Darjeeling districts. The coal reserve has an area of 185 km², and the Raniganj coalfields is the biggest and oldest coalfield with the highest carbon percentage of 50–60%.
- v. Madhya Pradesh:** It is situated in the central portion of the Indian peninsula, is

the fifth-largest coal producer, and supplies about 8% of the total coal reserves. The principal mines are located at Singrauli, Pench-Kanhan, Satpura, Muhpani, Sohagpur, and Sangli districts. Singrauli, being a significant producer, is the state's energy capital and a major consumer of this coal.

State	Coal reserves (BT)
Jharkhand	83.15
Odisha	79.30
Chhattisgarh	57.00
West Bengal	31.67
Madhya Pradesh	27.99

China, India, the USA, Australia, and Indonesia are the world's top five coal producing countries. These countries have 80% of the global coal production, with 43% from the Republic of China. About 7.0% of the global total coal reserves are in India. For the last 230 years, India has mined for coal resources (Höök et al., 2010). China, India, the United States, Germany, and Russia are the five sizeable coal consumers. The Indian Permian coal has low sulfur content and a high ash yield. The energy sector is India's biggest consumer of coal, followed by the metallurgical and cement-based industries.

States	Measured (Proved)	Indicated	Inferred (Exploration)	Inferred (Mapping)	Total
Jharkhand	45563.36	31438.52	6149.80	0.00	83151.68
West Bengal	14155.57	12868.81	4642.86	0.00	31667.24
Chhattisgarh	20427.71	34576.26	2201.90	0.00	57205.87
Madhya Pradesh	11958.28	12153.95	3874.67	0.00	27986.90

Odisha	37391.10	34164.54	7739.16	0.00	79294.80
Uttar Pradesh (UP)	884.04	177.76	0.00	0.00	1061.80
Maharashtra	7177.55	3073.55	2048.14	0.00	12299.24
Telangana	10474.9	8576.13	2650.92	0.00	21701.95
Andhra Pradesh	0	1149.05	431.65	0.00	1580.70
Bihar	161.11	813.49	392.15	0.00	1366.75
Sikkim	0.00	58.25	42.98	0	101.23
Assam	464.78	57.21	0.50	2.52	525.01
Arunachal Pradesh	31.23	40.11	12.89	6.00	90.23
Meghalya	89.04	16.51	27.58	443.35	576.48
Nagaland	8.76	0.00	103.64	298.05	410.45
Grand (Total)	148787.43	139164.14	30318.84	749.92	319020.33

1.4 Categorization of Coal

Coal categorization is the fundamental aspect of coal system science. Most of the classifications are based on the rank, type, grade, and other technical properties of coals.

Rank: Coal rank reflects the degree of metamorphism (or coalification) to which the original mass of plant debris (peat) has been subjected to during its burial history (Hower et al., 2022a). This depends in turn on the maximum temperature to which it has been exposed and the time it has been held at that temperature and for most coals, this reflects the depth of burial and geothermal gradient prevailing at the time of coalification in the basin concerned. However, heat flow from neighboring igneous intrusions may also play significant effects (Ward and Suárez-Ruiz, 2008b). Thus the

rank of coal refers to the changes in geochemical properties and consequent changes in reflectance, indicating the maturity of coal (O'Keefe et al., 2013b).

Based on rank, coal can be categorized from lignite to sub-bituminous, bituminous, and anthracite. The important drivers of lignite formation are the processes of compaction, dehydration, and biogeochemical gelification (Levine, 1993). Loss of moisture from peat and expulsion of water change the lignite's chemistry (Mukhopadhyay and Hatcher, 1993). Sub-bituminous coals is a low rank coal between lignite and bituminous coal; sub bituminous coal is further classified into subdivisions (A, B, C) based on calorific value . Bituminous coal, a medium-rank coal is black, shiny, and generally hard with volatile matter (ASTM D388 – 05, 2012). Low-volatile bituminous coal (14-22% volatiles on a dry, ash-free basis), medium-volatile bituminous coal (22-31% volatiles on a dry, ash-free basis), and high-volatile bituminous coal (>31% volatiles on a dry, ash-free basis) constitute the three types. High-volatile bituminous coals (high volatile B and C) are classified using gross calorific (heating) value based on VR reflectance and GCV (Standard, 2012). Anthracitic coal is a high-rank coal with a shiny luster and conchoidal fracture. Anthracitic coal is divided into semi-anthracite, anthracite, and meta-anthracite. Most coals do not achieve anthracitic rank. Based on VM, anthracitic coals have volatile matter (< 14%) and, fixed carbon (>86%) on a dry mineral matter-free basis (Standard, 2012). Therefore, anthracite, which comprises a small proportion of the world's coal, contains maximum carbon and the minimum moisture. The moisture decreases with an increase in coal rank. The coal rank increases with the rise in carbon. As the calorific value increases, the volatile matter decreases (Hower et al., 2019).

Type: The coal type reflects the nature of the plant debris from which the original peat was derived, including the mixture of plant components (wood, leaves, algae, etc.) involved and the degree of degradation to which they were exposed before burial (O'Keefe et al., 2013b). The individual plant components occurring in coal, and in some cases fragments or other materials derived from them, are referred to as macerals (Hower et al., 2022a); these form the fundamental starting point for many different coal petrological studies . The Carboniferous period was the most prolific period for coal deposition in geological history. Subsequently, large coal deposits were discovered in India, which belong to the Permian period (Feulner, 2017).

Grade: The grade of coal reflects the extent to which the accumulation of plant debris has been kept free of contamination by inorganic material (mineral matter), including the periods before burial (i.e., during peat accumulation), after burial, and during rank advancement. A high-grade coal is therefore a coal, regardless of its rank or type, with a low overall proportion of mineral matter, and hence a high organic matter content (Hower et al., 2022a; Ward and Suárez-Ruiz, 2008b).Coal grade specifications are established by its commercial or technological value for specific uses. Different grades of coal (steam and metallurgical grades) have been used for particular applications. The greater part of Indian Permian coal is thermal grade. In various coal markets, different quality classes are used for grade (Meshram et al., 2015; Mishra, 2009).

1.5 Composition of Coal

Evaluating coal's mineralogical and geochemical properties can provide helpful insight into the geological conditions and evolution of a coal-forming basin and helps in identifying different geological factors that controls the distribution of minerals and elements in coal. Coal has the following important properties.

- i. Volatiles:** Volatile matter is the component of coal which is driven off when the coal is rapidly heated out of contact with air. The gases released are usually a mixture of different hydrocarbons and sulfur (Osborne, 2013). Volatile matter is the percentage loss in mass, adjusted for moisture when coal is heated out of contact with air under standard conditions using the ASTM method (E872-82, 2013).
- ii. Ashes:** It is the inorganic mineral residues left after coal combustion (Standard, 2011a). High ash coal increases power generation costs and post-processing ash management environmental problems (Hower et al., 1996b).
- iii. Calorific Value:** It is the measurement of the energy generated by coal during combustion. It is a crucial for determining the grade, price, and coal marketing potential (ASTM D5865).
- iv. Chemical Reactivity:** During the combustion process of coal, it goes through three different phases. In the first phase, moisture loss occurs (usually, it terminates at >120 °C). During the second phase, the pyrolysis and oxidation of volatile (aliphatic and aromatic components) and carbon occur. Here we can see the pyrolysis of organic functional groups and oxidation reactions. The combustion characteristics of coal depend on the boiler types, the coal particles' residence period, the boiler's temperature condition, and the coal macromolecules' chemical features. In the last stage, ash is formed, primarily non-combustible by product (Saikia, 2015).

The mineralogical and geochemical properties of Permian coal samples and fly ash collected from the Singrauli coalfield have been evaluated. A multifaceted analytical approach has been used to obtain a better understanding and value in

assessing and monitoring environmental degradation in coal complexes. The relevant information using the general characteristics and some advanced techniques opens an avenue that may be helpful in environmental and coal quality management.

1.6 Indian Scenario of Coal Utilization

Coal is the essential resource for industries like power, steel, fertilizer, and cement in India. Coal consumption provides around 55% of the basic energy needs in India. In India, coal-based thermal power plants produce around 70% of the total energy. In India, coal mining started in 1774 by M/s Sumner and Heatly of the East India Company at Raniganj, West Bangal (Singh and Kumar, 2012). For a developing country like India, with significant coal reserves, economic progress depends greatly on the effective functioning of the coal industries. India's economy primarily depends upon the coal mining sector for its industrial growth, especially in the less developed regions like Orissa, Jharkhand, and Chhattisgarh, which have large coalfields. Coal India Limited controls around 85% of the total coal production, and is a leader in coal management (Tongia and Gross, 2019). Coal utilization for energy generation has many technical constraints due to combustion. Increasing its efficiency and related environmental problems are prime concerns. Many issues are related to coal's transportation, storage, and spontaneous combustion (self-heating) (Sahu, 1991).

However, coal mining has an immeasurable negative influence on the environment. The operations in the coal complexes affect the natural environment and influence the social structure in which they operate. Some of the significant issues relating to the environment in coal mining include dust generation (PM10 and PM2.5), emissions of harmful air pollutants, climate change, hazardous chemical waste generation and chemical residues, health and safety, public health, and urban

settlement issues around mines (Yadav, 2021). The simple reason is that coal is a very cheap and ready energy source. Naturally, coal is the backbone of the energy sector. In the last 20 years, India's coal production has tripled (Tongia and Gross, 2019). Aside from increased CO₂ emissions, coal combustion produces significant waste products such as fly ash, bottom ash, and flue gas and sludge, some of which contain toxic heavy metals (Cr, Ni, Hg, Fe, U, Th, As) (Clarke and Sloss, 1992; Dai et al., 2004). Coal generates fly ash and bottom ash which contaminate the ecosystem (Hower et al., 2017a). As a result, good ecological management is required in the current situation. Coal is a critical energy fuel for many developing countries, and it is converted into heat and electricity. Therefore the determination of coal quality is essential to knowing coal's physical and chemical makeup. The present research work is based on the chemical characteristics of coal properties. The quantity of heat produced (GCV) determines its grade and economic value. This research may help to address future concerns regarding coal trading and utilization (Sahu et al., 2009).

The proper management of pollutants is essential and must be taken seriously to restore the ecosystem and environment for future generations. A clean environment keeps people and animals healthy and aids in scientific production. As a result, this study of coal quality and its relation to environmental pollution. Large-scale combustion of coal generates a new set of problems with the environment, particularly acid rain and greenhouse gas emissions, especially carbon dioxide. The challenges of the future include the development of technology that could mitigate global warming and climate change (Finkelman et al., 2021a). Keeping in mind the threat posed by coal burning, a detailed coal quality study has been carried out in the Singrauli coalfields. Based on chemical investigations, a chemical approach has been suggested to benefit the environmental quality of coal. Improving coal quality for

cleaner utilization, beneficiation is essential, and coal conversion to another usable product facilitates the establishment of a clean and green coal sector.

1.7 Statement of the Problem

Energy is critical to a country's industrial development; as such, coal is one of the most important power sources, particularly in a growing country like India. Global coal production has increased, and India is now the world's second-largest coal producer. More than 75% of India's energy requirements are fulfilled by the country's huge coal reserves (Srikanth, 2018). Coal will continue to be a viable energy source for several decades because other alternative energy sources (nuclear, hydroelectricity, and geothermal) will take a long time to become economically feasible. Coal-burning power plants in India generate a wide range of combustion byproducts including airborne pollutants, which contributes to environmental deterioration (Yadav, 2021). Climate change and worldwide environmental problems are both caused by these pollutants. The main objective of this study is to investigate the chemical attributes of Indian Permian coal from the Singrauli coalfields and to benefit, thereby providing improved combustion characteristics to the fuel produced.

1.8 Approach to the problem

In developing countries such as India, reliance on low-quality, high-ash coal generates huge quantities of waste in the form of solids, liquids, and gases. High-volatile coals are prone to spontaneous combustion, posing a risk in storage and transportation (Misra and Singh, 1994). Furthermore, the environmental problems produced by coal combustion release poisonous gaseous into the atmosphere. The issue becomes more severe when coal contains volatile heavy metals like lead, zinc, cadmium, and mercury (Nzihou and Stanmore, 2013). This will pose a severe

environmental problem, depending on the composition of the coal. As evident from the above, large-scale coal burning causes degradation of the air quality in surrounding areas. The most crucial problem with Indian Permian coal is the wide variation in grades and ranks (Sarkar et al., 2021). There is, therefore, a need to have reliable and relevant appropriate coal quality control, and the development of beneficiation measures for successful and effective coal quality management on a large and small scale. Keeping in mind the above background, Singrauli Coalfield of Northern Coalfield Limited was selected to carry out the study with the below-mentioned objectives.

1.9 Objectives of Present Study

The objective of the present research encompasses the chemical characterization, and potential utilization of Permian Gondwana coal from the Singrauli coalfield, India, and its chemical beneficiation using green solvent prepared from choline chloride and urea. Five coalfields in the Moher sub-basin were selected for the investigation. About a hundred coals were collected using the pillar sampling method from the working faces of different mines. Based on collected information, an effort was made to classify the coal in terms of nature, type, chemistry, and mineralogy. These deductions have been made using proximate and ultimate analysis as the tool, and GCV was calculated to determine its grade. Coal's chemical quality is studied to be used effectively in thermal power generation. Finally, the present study aims to classify the coal according to available Indian and international classification schemes and focuses on the potential utilization of these coals. Optimization of energy consumption is required, and fuel characterization is essential to search for ways and means to optimize the energy production requirements. The following work has been carried out to achieve the above objectives. The broad objectives of the present

research work are as follows:

- (1) Chemical characterization of coal involving TGA, XRD, SEM, FTIR, XPS, and Raman spectroscopy to know the thermal behavior and the intrinsic properties of coal.
- (2) To investigate the nature and mode of occurrence of minerals and elements in coal, as well as the relationships between coal mineralogy and fly ash chemistry.
- (3) Environmental concerns related to coal utilization.
- (4) Beneficiation study of coal using deep eutectic solvent prepared with choline chloride and urea.