

ABSTRACT

Coal is the most abundant, instantly combustible, widely distributed fossil fuel globally. It is a compact black or dark brown carbonaceous stratified sedimentary deposit. The objective of the present research work focuses on the chemical characterization and beneficiation of Indian Permian coal from the Singrauli coalfield, India. The problem was taken on because of its growing importance and contribution to the energy sector. Coal is the most damaging fossil fuel for environmental concerns and carbon emissions. Climate change concerns limit the use of coal, yet coal is predicted to be a significant contributor to primary energy requirements in China and India.

This study summarizes the results of the chemical and mineralogical analysis performed to determine the geological control on coal quality. The utilization potential of coal chiefly depends on its carbon-containing organic constituents. However, the inorganic components, i.e. mineral matter present in the coal, can decide its end uses. Therefore, studying mineral matter in coal is inevitable, and this study in India is very scanty. In this research, we present the chemical characteristics of coal. Various physicochemical parameters have been considered for the qualitative and quantitative profiling of coal. These parameters include proximate analysis, ultimate analysis, and GCV (gross calorific value) determination. In proximate analysis, ash, moisture, volatile matter, and fixed carbon have been determined. The ultimate analysis determines carbon, oxygen, nitrogen, hydrogen, and sulfur.

Among these elements, nitrogen and sulfur are crucial from an environmental point of view because these two elements are potential pollutants. According to the ASTM classification, the volatile matter yield values of the coal indicate a medium

volatile bituminous coal. However, the hydrogen content in coal has little change, sulfur is moderate in all coal compared to Cenozoic Indian coal, and other world coal, and the oxygen content in most rank coals will be affected by oxidation and weathering. The high ash yield in coal may be due to the relatively high accommodation space or high level of groundwater of the peat mire favoring the accumulation of minerals in coal during their formation. In India, the grading of non-coking (thermal grade) is based on its Gross Calorific Value (GCV), and the grading of coking coal (metallurgical grade) is based on ash percentage. For semi-coking or weakly coking coal, the coal is categorized based on ash and moisture percentage as per notification of the Bureau of Indian Standards (IS 1350: Part 2: 2022). A comparative study was conducted to assess the marketing potential of this coal. Coal prices are fixed for industrial utilization based on heat liberated during combustion.

Six Permian coal samples, have been studied for combustion characteristics, pyrolysis behavior, and kinetics parameters through TGA and DTG analysis. The present study helps to understand the ignition and combustion performance of high-ash and low-ash coal considering the physicochemical constraints. The kinetic parameters were determined using the Arrhenius equation, and activation energies were calculated by using the Coats-Redfern method. Further detailed study of different combustion parameters reveals that the activation energy varies from 63–169 kJ/mol for different coal samples, and, values of activation energies for low-rank coal were found to be high (169.5 kJ/mol). It has been observed that the conversion degree obtained lies in the range of 0.34-0.54, and the mean correlation coefficient (R^2) value lies in the range of 0.965-0.999. This study can be beneficial to understanding the combustion performance of coal and help us use low-rank coal to upgrade environmental and energy constraints efficiently

The analyzed XRD diffractogram of coal reveals a significant phase of minerals (quartz, kaolinite, gypsum, muscovite, orthoclase, sulfur, hematite, siderite, pyrite, jarosite, and chlorite). It is revealed that coals contain silica and alumina-based quartz, feldspathoid, and clay-rich minerals.

In SEM photomicrographs of coal of two different varieties (high-ash coal and low-ash coal), the morphological and mineralogical information about coal and their associations have been revealed by SEM/EDS. It is very helpful in identifying clay minerals like kaolinite and quartz. Minerals, mainly quartz, are attached to the surface of coal macerals because of the drift origin. Sometimes, minerals are present as discrete units, especially quartz. Clay minerals present in coal are seen as lamellar, plate-like, and sandwiched between the macerals. Clay is present extensively and non-uniformly in coal, and kaolinite is the most abundant clay, along with illite and montmorillonite. These adhere to or are incorporated onto the surface of coal particles.

FTIR (Fourier transform infrared spectroscopy) has been carried out to decipher the presence of organic (aliphatic and aromatic) and inorganic (silicate, carbonate, and hydroxyl) components in sample. The FTIR analysis shows the occurrences of aliphatic ($-\text{CH}$, $-\text{CH}_2$, and $-\text{CH}_3$) groups. Aliphatic $\text{C}-\text{O}-\text{C}$ stretching is also present, along with $-\text{OH}$ and $-\text{NH}$ stretching vibrational peaks. Coal is composed of numerous groups of aliphatic and aromatic compounds.

The XPS survey spectrums confirm the presence of different elements of the coal; these are C 1s (286.0 eV), O 1s (534.5 eV), N 1s (399.9 eV), and S 2p (158.2 eV). The SiO_2 and Al_2O_3 correspond to Si 2p (102.7 eV) and Al 2p (75.6 eV) respectively. XPS spectra of C 1s confirm the presence of a considerable amount of aliphatic and aromatic hydrocarbons in the coal. The constituent estimation of N 1s

spectra also gives four peaks. The constituent estimation of N 1s spectra also gives four peaks. These peaks correspond to different nitrogen groups: Pyridine nitrogen, pyrrolic nitrogen, quaternary, and oxidized nitrogen with the binding energy of 398.2eV, 399.4 eV, 400.4 eV, and 401.8 eV, respectively. XPS also provides a comprehensive understanding of the heavy metals like Fe, Mn, Cr, Al, As, and Hg present in coal. Heavy metals are severe environmental pollutants because of their ability to bioaccumulate and be highly persistent in biotic environments.

Raman spectral methods are powerful tools for the non-destructive qualitative and semi-quantitative analysis of coal. Raman spectra in 1000 to 2000 cm^{-1} range were obtained, revealing two prominent peaks known as the D and G bands, which are located near 1370 cm^{-1} and 1590 cm^{-1} , respectively. Further deconvolution gives five different peaks: Lorentz peaks (D1, D2, D4, and G) located near 1137 cm^{-1} , 1610 cm^{-1} , 1240 cm^{-1} , and 1585 cm^{-1} , respectively, and one Gaussian peak (D3) near 1500 cm^{-1} .

G-D1 value for coal 1 was 230, indicating less distorted graphitic structures in coal 1. The ratio of A_{D1}/A_G represents the degree of growth of aromatic rings in coal, indicating that coal 1 has a less distorted structure than the others (coal 2, 3 and 4). The value of A_{D2}/A_{All} was smaller (0.157) for coal 1 than for the others (coal 2, 3 and 4); hence coal 4 has a more ordered structure and is less amorphous. The A_{D1}/A_G ratio of 0.388 indicates a higher order structure. In coal 4, the A_{D1}/A_G ratio of 0.963 or less indicates that the structure is ordered. The samples' G-D1 and I_{D1}/I_G range from 208 to 230 cm^{-1} and 0.388 to 0.963, respectively. For coal 4, the ratio of I_{D1}/I_G is highest (0.963), which indicates the degree of graphitization is lowest. Coal 1 has a lower ratio value of I_{D1}/I_G (0.388), which signifies a well-graphitized coal structure. The I_D/I_G ratio decrease indicates that graphitization has increased in coal. A decrease in the ratio of A_{D2}/A_{All} indicates a reduction in the amorphous nature of coal and an increase in the

order of coal molecular structure. The value of A_{D2}/A_{All} is smaller (0.157) for coal 1 than (0.347) for coal 2. Hence, coal 4 has a more ordered structure and is less amorphous.

Fly ash is a fine powdery residue produced by coal combustion. Coal combustion generates a huge amount of fly ash, and its management has a huge problem. General geochemical and mineralogical characterization of fly ash has been carried out to assess its chemical nature and behavior using SEM and XRF. Fly ash morphology and surface or internal crystals on a cenosphere depend on the exposure time to combustion and temperature. The elements present in the fly ash exist in their oxidized states. The major oxides in fly ash samples were SiO_2 , Al_2O_3 , CaO , MgO , MnO , Na_2O , K_2O , and Fe_2O_3 . Alumina benefits concrete and fly ash/lime-based mortars by providing strength-gaining mechanism. The highest SiO_2/Al_2O_3 ratio of (2.03%) was found in PFA 4. The molecular and structural properties of inorganic content in coal reveal inorganic mineral phases, including quartz, glass, and clay-derived minerals, which are constituents of the fly ash assemblage. The nature of fly ash samples was found to be primarily alkaline.

The wet beneficiation study was conducted to learn about coal samples' interaction and dissolution properties with deep eutectic solvents (DES), choline chloride, and urea. DES was synthesized using choline chloride as a hydrogen bond donor (HBD) and urea as a hydrogen bond acceptor (HBA) in an equimolar amount. The swelling of DES-treated coal is obtained over the raw coal samples in the 1.12 to 1.43 range. An FTIR study of raw and treated coal samples has been carried out, confirming the reduction of oxygen-containing and phenolic functional groups. The ultimate and proximate analysis of raw and DES-treated coal samples was determined, showing a decrease in ash yield and an increase in its gross calorific value. The DES is a green

solvent that is easy to synthesize, low cost, and useful for the increasing efficiency of coal.