Chapter- 4

Materials and Methods

4.1 Materials

4.1.1 Introduction: The research started with a field survey in the study area. First, the field information was collected from five coal mines in the Singrauli Coalfield of India. Further, the macroscopic study was carried out for the collected coal samples and used for the characterization to study and understand their properties.

4.1.2 Collection of Coal Samples

The samples were collected directly from the mining faces of five different collieries (Bina, Kakri, Krishnshila, Dudhichua, and Jayant). The sampling method used for the collection was the blocks or pillar method, numbered from bottom to top. The seam's complete profile of the working face could be analyzed in the laboratory for characterization. Samples were sealed and put in plastic bags immediately to prevent moisture loss and contamination so that the entire coal property could be preserved in the laboratory investigation. The collected coal samples were taken for a detailed laboratory investigation. More than a hundred blocks of samples were collected from these mines after the monsoon season, so moisture content was primarily present in nature, in November 2018.

The coal was collected from the opencast mines belonging to NCL, a subsidiary of CIL, in the Singrauli coalfield region, situated in the northeastern part of the Gondwana basin in India. These coal samples were collected from the horizon known as the Purewa top, Purewa bottom, and Turra coal seams. These samples were collected and labeled as PC (Permian coal) with suffixes A, B, C, D, and M. These samples were coded as following codes.

i. PCA 5, PCA 4, PCA 3, PCA 2, and PCA 1 belong to Bina mines from top to bottom, collected from the Turra seam.

ii. PCB 5, PCB 4, PCB 3, PCB 2, and PCB 1 belong to Kakri mines from top to bottom, collected from the Turra seam.

iii. PCC 5, PCC 4, PCC 3, PCC 2, and PCC 1 are all Krishnshila mines collected from the Turra seam.

iv. PCD 9 and PCD 8 from the Purewa top seam; PCD 7 and PCD 6 from the Purewa bottom; and PCD 5, PCD 4, PCC 3, PCD 2, and PCD 1 from the Turra seam all belong to the Dudhichua mines.

v. PCD 8 and PCD 7 from the Purewa top seam;PCD 6 and PCD 5 from the Purewabottom;and PCD 4, PCD 3, PCC 2, and PCD 1 from the Turra seam belong to the Jayant mines.

vi. Figure 3.6 shows the specifications of coal seams and followed a standard procedure for sample collection (Mahapatra, 2016).

4.1.3 Preparation of Coal Samples

The collected pillar coal samples were numbered according to their position in the coal seam sections. Coal samples were taken from the exposed seams of active mines in the Singrauli coalfield. Following sample collection; they were crushed and homogenized in a jaw crusher/ball mill. One kg of representative samples was made by the homogenization, coning, and quartering methods for the studies under the current research and sieved with a filter of <75 μm (-212 mesh size) for further investigations. Different sub-samples were also prepared, and various analytical methodologies were used to determine the nature of coal composition (Bullock et al., 2002).

4.2 Experimental Methods and Procedure

The details of various analytical techniques applied in the present investigation are as follows:

4.2.1 Proximate and Ultimate Analysis of Coal Samples

The proximate and ultimate analysis of the samples has been carried out to know the percent of moisture, FC, VM, and ash present in coal on a dry basis. It overviews coal quality parameters, which helps know thermal properties. The parameters of ultimate analysis include carbon, nitrogen, hydrogen, oxygen, and sulfur. To calculate the different proximate analysis parameters in this study, 1 gram of sample was taken. The Standard Practice and Procedure for Proximate Analysis of Coal and Coke by the American Society for Testing and Materials (ASTM D 3172) were followed (Standard, 2002).

i. **Moisture:** The moisture is the water (H_2O) present in the coal at the mine site, specific time, and conditions under which the coal was sampled. It analyzed the quantity of moisture in samples by measuring the loss in mass between a collected sample and a sample that has been heated under controlled conditions to leave off the water that is not contained within the chemical structures of the sample. The samples were kept at 105 °C for 1 h, and the difference between the initial and final weight of the sample was measured and calculated after heat treatment (Standard, 2011b).

ii. **Volatile matter (VM):** Except for water, all the components have been included in the VM of coal, which is released at a high temperature in the condition of being devoid of oxygen. Furthermore, the furnace temperature was set to 925 °C for 7 minutes to measure the volatile matter. In all the experiments, the weight of coal samples before and after heat treatment was taken down. The volatiles released are detected by luminous flames seen from the outside. Then the decrease in weight was calculated before and after heating. Results have been expressed in the form of a weight percentage of the sample. VM is a significant health and safety concern, as coal has a high VM and is prone to spontaneous combustion (E872-82, 2013).

iii. **Ash:** Ash is generated by the complete pyrolysis of inorganic mineral matter in the sample. In a porcelain dish, one gram of air-dried, sieved by 212 microns filtered sample, was placed for ash estimation. Firstly, the temperature was raised to 500 °C for 30 minutes and then again to 815 °10°C for 30 to 60 minutes. This temperature was maintained for another 60 minutes. After that, the dish was taken out of the muffle furnace(Standard, 2011a).

To measure percent ash yield, a muffle furnace manufactured by ISO-TECH (Varanasi-India) has been used. After cooling, the weight of residue was taken. Then the difference in the weight was calculated and expressed as the percentage of ash present in the coal. For the determination of the ash yield of the coal sample, the following calculation method has been applied:

$$\text{Ash yield weight \%} = \frac{c-a}{b-a} \times 100$$

Where, a = Weight of the Crucible,

b = Weight of the crucible and sample,

c = Weight of the crucible and sample after heating.

iv. **Fixed Carbon (FC):**The FC weight percentage in coal was determined by deducting the percentages of moisture, VM, and ash yield from the sample's initial weight.

v. **Ultimate Analysis:** This analysis gives more inclusive results than the proximate analyses. The ultimate analysis estimates the elemental composition of the coal, which includes carbon, hydrogen, nitrogen, sulfur, and oxygen (by difference). We calculate each element through chemical analysis and express it as a percentage of the total mass of the original coal. The Euro EA-3000 elemental analyzer was used for ultimate analysis and was conducted according to ASTM D 3173–3187 standards (Standard, 2009).

4.2.2 Gross Calorific Value (GCV)

The GCV of coal is the heat produced when the coal undergoes complete combustion in the presence of oxygen. The sample burns in a bomb calorimeter and measures the total heat liberated to get an accurate result. For the GCV estimation, we used an oxygen bomb calorimeter made by the Parr 6100 Series. The bomb calorimeter has been used to measure the heat of combustion in a set condition. The bomb was prepared with Ni-Cr fuse wire for GCV estimation. For this analysis, 1 g of coal was taken and followed the standard (ASTM D5865) method (Testing and Material, 1998). The results of proximate, ultimate and GCV analysis have been tabulated in Table 5.1.

4.2.3 Thermo-gravimetric Analysis (TGA)

TGA was carried out for six different samples (coal 1, coal 2, coal 3, coal 4, coal 5, and coal 6). Coal 1, coal 2, coal 3, and coal 4 were relatively low ash coals, and 5 and 6 had high ash yields. The coal samples were crushed with a jaw crusher, then pulverized and sieved with a 212-micron filter to collect the samples using standard sieves. Using the TGA-50 (M/s Shimadzu (Asia Pacific Ltd.) instrumentation technique, pyrolysis experiments were performed on samples with a particle size of less than 75 μm. All experiments were carried out at the Central Instrument Facility (CIF), IIT BHU, Varanasi, Uttar Pradesh, India, with a heating rate of 10 ^{o}Cmin^{-1}, and data from TGA was analyzed to determine kinetic and thermodynamic parameters in an air atmosphere.

4.2.4 Scanning Electron Microscope (SEM)

The representative coal samples were selected and examined by scanning electron microscopy (EVO-Scanning Electron Microscope MA15/18 by CARL ZEISS MICROSCOPY LTD, EDS: 51N1000 – EDS System) equipped with EDS at CIF, IIT (BHU) Varanasi. The agglomerates were mounted on carbon tape and directly scanned using the SEM. The morphological features, structure, and composition of the coal and FA samples were investigated, and mineral identification was based on morphology and grain composition using both secondary and backscattered electron modes.

4.2.5 X-ray diffraction (XRD)

An X-ray diffraction study of the coal samples from the Singrauli coal mine has been acquired for the study. The XRD was performed at room temperature (27 °C) using the Rigaku-Miniflex 600 X-Ray Diffraction System (Central Instruments Facility (CIF), IIT BHU). Powder coal samples were used for XRD measurements, which were well crushed and sieved with a 212-micron -mesh sieve (<75 μm) shaker. For the recording of the XRD pattern, coal samples were put in the sample holder and scanned using CuKα (λ=1.54Å) radiation, using XPERT PRO software for the 2θ range of 5°-70°and a step size of 0.02°. The minerals present were identified by reference to the International Center for Diffraction Data for (ICDD) Powder Diffraction File. Mineral phase recognition using the XRD technique depends on the diffraction peaks at different values relating to the mineral's d spacing value. The X-ray plot of a diffraction angle (2θ) versus the radiation intensity reveals the inter-planar spacing and, in turn, the type of mineral present in the sample.

4.2.6 Fourier Transform Infrared Spectroscopy (FTIR)

The representative coal samples were firstly dried for 36 hours at 40°C. In order to minimize the effect of minerals contained in these samples, they were washed with dilute HCL (0.1 M) for 3 hours. The HCL-treated samples were washed till we got a neutral pH. Then, by drying for 36 hours at 80 °C in a vacuum oven, the analysis was done by the Nicolet iS5 FTIR by THERMO Electron Scientific Instruments LLC. The pellets of coal samples were prepared in K-Br media and pressed by the hydraulic pressure machine. Infrared rays of the analyzer pass through the sample, and then graphs are plotted between the transmittance and wave numbers of those coal samples plotted with the help of Origin Pro software. The spectrum range of IR 4000-500 cm^{-1} was recorded for each coal sample. FTIR is employed as a powerful tool to understand the structure and composition of minerals in a sample. This technique can be used to characterize a coal sample's inorganic and organic matter, especially to recognize organic compounds in the coal (Medunić et al., 2020b).

4.2.7 X-ray Fluorescence Spectroscopy (XPS)

An XPS survey has been carried out to decipher the surface structure, composition, and elements present in the coal samples through their binding energies. The XPS analysis has been executed by K-Alpha (Thermos Fisher Scientific) on the

CIF IIT (BHU), Varanasi. The data processing peaks were recorded with the XPS Peak fitting software. The XPS measurements have been performed, and the data was recorded by passing energy of 93.3 eV with a step size of 0.5 eV at room temperature (27°C) in vacuum conditions. The binding energy has been calibrated based on graphite C1 hydrocarbon, and the peak was recorded at 284.6 eV.

4.2.8 Raman Spectroscopy

The four bituminous coal samples (coal1, coal 2, coal 3, and coal 4) were analyzed by Raman spectroscopy microscopy (Witec Model Alpha 300 RAS) at Central Discovery Centre, Banaras Hindu University, and Varanasi. A Raman spectrometer with an Nd-YAG laser light (512 nm) at 10x and 50x objectives, with laser power is 50 mW was used to focus on the coal surface, and the spot was about 2 μm. The point-wise Raman mapping was performed on an automated platform with a step size of 4 and an integration period of 5 s. Raman spectra with a resolution of 1 cm^{-1} in the range of 100 to 4000 cm^{-1} with a 50 m entrance slit were used to generate the Raman spectra. The acquisition time for each spectrum was 30 s. Different 2-D planes of samples were taken for study.

Further data, peak separation, and semi-quantitative calculations were carried out to get more precise information using the curve-fitting program in Origin software. For each Raman spectrum, the chosen regions were baseline–linearized, and the area was normalized before the curve fittings. To have a good initial estimate of the frequency and intensity of peaks, it is essential to calculate the number of peaks in a specified region. Various researchers have reported the detailed process for curve fitting. Raman spectroscopy is also carried out to learn about minerals; several authors have reported the procedure of Raman spectroscopy (Das and Hendry, 2011).

4.3 Collection and Characterization of Fly Ash Sample

4.3.1 Collection of fly ash sample: This investigation collected fly ash from Singrauli Super Thermal Power Station (SSTP), using coal from Jayant mines. The fly ash was collected from the electrostatic precipitators in the dry state. The sample collection followed ASTM C 618-19 guidelines (Kaladharan et al., 2019).The collected fly ash derived through the combustion in SSTP was coded as PFA 1, PFA 2, PFA 3, and PFA 4 for analysis. These FA samples were air-dried for 24 hours in a drying oven made by ISO-TECH (Varanasi-India) and mixed by coning and quartering to acquire a representative sample for analysis (Karfakis et al., 1996)

4.3.2 X-ray Fluorescence Spectroscopy(XRF)Analysis

XRF determined the significant oxides. It is a non-destructive chemical analysis of the fly ash and was performed using a Philips PW 2400 spectrometer and Super Q software, and the values were expressed as percentages of the elemental oxides in each sample. XRF was used to identify mineral elements present in FA. A scanning wavelength dispersive X-ray fluorescence spectrometer was used to determine significant oxides (i.e., SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, MnO, Na_2O, and K_2O) in fly ash.