GEOCHEMICAL AND ORGANIC PETROGRAPHIC CHARACTERISTICS OF COAL FROM HANGU FORMATION, DARA ADAM KHEL, NW PAKISTAN

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A thesis submitted to Bahria University, Islamabad in partial fulfilment of the requirement for the degree of M.S in Geology

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Certificate

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DEDICATIONS

I dedicate this thesis to my loving family, specially to my father and eldest brother whose unwavering support and encouragement have been instrumental in my academic journey.

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All glorification and reverence belong to Allah S.W.T and it is of utmost significance to bow my head before Allah almighty, who is the solitary provider of all erudition. The greatest of all, who refined my heart with enhanced perceptions and blessed me robustness to complete my research. I am appreciative of my dear parents' well wishes, prayers and unwavering love for helping to accomplish the objective. I owe a great deal of gratitude to my supervisor Dr. Mumtaz Ali Khan, Senior Assistant Professor, Department of Earth and Environmental Sciences, Bahria University, Islamabad, and co-supervisor Mr. Adeeb Ahmad, Lecturer, Department of Earth and Environmental Sciences, Bahria University, Islamabad.

ABSTRACT

The present study focuses on ultimate, proximate and, organic geochemical analyses of Hangu Formation, Dara Adam Khel, Khyber Pakhtoonkhwa, Pakistan. Organic geochemical analyses include TOC, Rock-Eval pyrolysis, organic petrography, and vitrinite reflectance study. The proximate analysis shows moisture content ranging from 0.3 to 1.1%, ash from 6.3-22.3%, volatile matter from 7.9 to 12%, fixed carbon from 64.6 to 84.9%, with mean values of 0.68, 12.45, 10.1, and 76.77 %. The total carbon ranges from 62.0 to 81.9 % and the total sulfur ranges from 2.6 to 12 %, having an average values of 61.16, and 6.9 %. It is evident from the proximate study that the analyzed coal has a low percent of moisture content, volatile matter, and a medium percentage of Fixed carbon, which place the studied coal in a low volatile bituminous rank. The sulphur percent from the ultimate analysis is high and may have adverse effects, causing corrosion to machinery and makes the environment polluted. The TOC value of the coals, shales and coaly shales are 3.5 to 83.3 wt.% indicating very good-excellent source rock for hydrocarbon generation. According to organic geochemical analysis, the kerogens are of type III and IV which belong to terrestrial sources. The petrographic study showed different maceral such as vitrinite (collinite and gelocollinite), followed by inertinite (inertodetrinite). The dominance of vitrinite macerals contributes to gas prone-type III kerogen. On the base of HI vs TOC plot, the analyzed samples have gas generation potential. This is supported by the thermal maturity, which lies in the mature stage, as indicated by vitrinite reflectance values of 0.71-0.91%.

References

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVATION

HCL	Hydrochloric acid
HDIP	Hydrocarbon development institute of Pakistan
MMT	Main mantle thrust
MBT	Main boundary thrust
OM	Organic matter
RO/Vr	Vitrinite reflectance
TOC	Total organic carbon
RE	Rock Eval
VM	Volatile matter
FC	Fixed carbon
GCV	Gross calorific value
MC	Moisture content
Tmax	Temperature of maximum
GP	Generation potential
VS	Verses
PI	Potential index
HI	Hydrogen index
OI	Oxygen index
CHNS	Carbon, hydrogen, nitrogen, sulphur analyzer

CHAPTER 01

INTRODUCTION

1.1 General Description

Coal is the primary fossil fuel, mostly use in the world for the chemical production, cement/concrete making, electricity, and gas generation etc. (Guan, 2017). The rapid growth of technology and population in the last decades has made the need of increasing demand for energy sources (liquid and gaseous hydrocarbons) in most countries of the world (Hartnady, 2010).

Coal are largely deposited in all provinces of Pakistan: Punjab, Sindh, Sarhad, Baluchistan and also in Azad Kashmir. Coal in different area of Pakistan generally falls in category of lignite to bituminous which containing high volatile matter. These coals can break into fragments easily, and contain relatively high content of ash and sulphur. The total reserves of coal in Pakistan are improved upto 186,282.43 million tones (mt) due to some enlargement of many new coalfields of Balochistan and previous coalfields (Malakani, 2012). Out of 186.28241 billion tons of coal in Pakistan, 122.99 million tons (mt) are discovered in Hangu-Orakzai, Dara Adam Khel, Cherat, Gulakhel/Kurd-Sho, and Shirani areas of Khyber Pakhtunkhwa and FATA (Malkani, 2012). In Khyber Pakhtoonkhwa, coal is trapped in the Formation of Hangu. The age of Hangu Formation is CretaceousTertiary/K-T boundary to Early Paleocene, whereas the coal of Shirani area has been deposited in Early Eocene period (Malakani, 2013).

In the present time, the energy needs of the world are mostly provided from fuels formed from fossils like fuel-oil, natural gas, and coal. Among these fuels, the great important energy sources is the coal which is used by many country. The coal can be converted by different technology to heat and for electricity generation. Therefore, determining coal rank is an important task and depends on determining its physical and chemical composition. In order to find out the chemical composition of coals, proximate and ultimate analyses are usually used. In the result of proximate analysis, the moisture content, ash, volatile matter, and fixed carbon are find out as weight percent, whereas the ultimate analysis focus on the determination of the elements of carbon, hydrogen, nitrogen, oxygen and sulphur (Patel, 2007).

The sedimentary rock contains organic matter from which coal and other hydrocarbons are formed. The TOC, kerogen types, and thermal maturity of organic matter control the source rock potential to generate hydrocarbon (Tissot and Welte, 1978). In present study, laboratory analyses were conducted to find if a sedimentary rock may have any petroleum potential. For this purpose, the proximate, ultimate, TOC, Rock Eval pyrolysis, and organic petrology for Hangu Formation, Dara Adam Khel were carried out to determine the coal rank and quality, quantity, maturity, macerals, and hydrocarbon generation potential of source rock (shale).

1.2 Previous work

On reconnaissance visit to Dara Adam Khel coalfield, Malakani and Mehmood, (2017) for first time reported the Dara Adam Khel deposit of coal. It is a newly developed coalfield. Malik (2020) investigated the possibility of microbial transformations of Dara Adam Khel coal to gas (bio gasification) as a replacement of conventional coal mining because this goal has the importance to be low cost, cleaner, and provide greater approach to deeper coal resources.

Ahmad et al. (2022) performed the process of removing of sulphur and ash on Darra Adam Khel Coal (Pakistan) by adding oxygen using Hydrogen peroxide (H_2O_2) and formic acid (HCOOH) oxidation system. Wazir et al. (2022) prepared activated carbon from coal of Dara Adam Khel by using a chemical-activating agent such as potassium hydroxide.

Umair et al. (2022) studied the Padhrar and Darra Adam Khel coal's geochemical and mineralogical properties, to explore the kerogen in coal, element enrichment procedure, sedimentary medium conditions and elements which are valuable potentially for coal uses.

1.3 Location and accessibility of the study area

The researched area lies in the Kohat sub basin between latitude and longitude of 36′69″45ºN 71′49″59ºE. In the North of the Kohat Sub-basin there are Parachinar Ranges, in the South Bannu Depression, Kurram Fault in the West and Indus River lies in the East (Kazmi and Rana, 1982). There is the Ghorzandi fault in the South-East and in the South, lies the Samana Range. The coal is reported in the Hangu Formation of Paleocene age.

The present objective area is located in the Dara Adam Khel, Khyber Pakhtoonkhwa, 46 km away from Peshawar city and 25 km from Kohat Kacheri (Fig. 1.1).

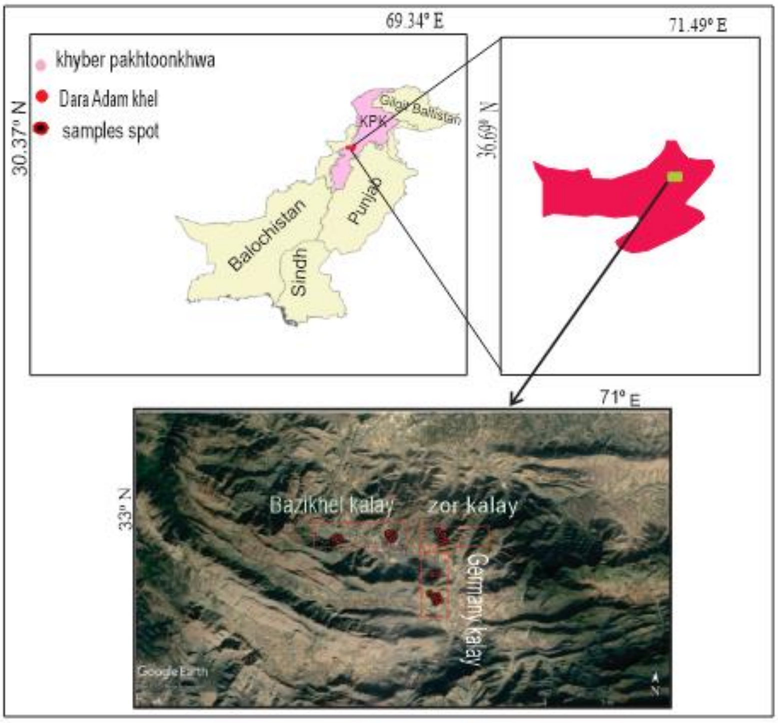

Figure 1.1: Map of Pakistan, showing study area (prepared by Google Earth).

1.4 Significance of the study

Coal is the primary fossil fuel, used worldwide for energy production. Pakistan has huge amount of coal reserves some of which is being exploring currently. In Pakistan, coal mining and exploration activity are in progress in various parts of the country including Dara Adam Khel which is new coal field of Khyber Pakhtoonkhwa (Malakani, 2013).

Coal contains different matters i.e. the content of moisture, ash content, volatile matter, and fixed carbon. Also have many elements such as carbon, hydrogen, nitrogen, and sulphur etc. These matters and elements controls that where this coal is fit to be used. Therefore, present study will help determining coal rank. The present study also approaches the organic geochemical as well as organic petrography to determine quantity, quality, maturity, maceral composition, and capacity of hydrocarbon of coal and source rock of Hangu Formation in Dara Adam Khel, Khyber Pakhtunkhwa, Pakistan.

1.5 Problem Statement

In Dara Adam Khel new coalfield is reported and analyzed by many researcher, but the detailed work on geochemical, and organic petrography have not been carried out yet. Therefore, an attempt has been made to perform the proximate, ultimate, organic geochemical, and petrographic analysis of Paleocene coal and shale of Hangu Formation, Dara Adam Khel.

1.6 Objective of the study area

The main goals of the research work are

1) To determine the rank of coal of Hangu Formation
2) To determine organic matter quantity, quality and maturity of Hangu Formation
3) To evaluate the hydrocarbon potential of Hangu Formation

1.7 Data acquired

Eleven samples of shale and coal were collected from 10 mines located in different area of Dara Adam Khel. Complete proximate, ultimate analysis, TOC, Rock Eval pyrolysis, and organic petrology analyses were conducted at Hydrocarbon Development Institute of Pakistan (HDIP).

CHAPTER 02

GEOLOGY AND TECTONICS

2.1 Regional Tectonic

The largest orogeny, the Himalayan, resulted from the collision of the India-Asia plates which is an important geologic episode that occurred in the Cenozoic age. The largest and youngest collisional orogeny of the world is represented by the Himalayas, and there is not only compression and thickening related with mountain-building but also rifting and thinning (Zhang et al., 2012). The supercontinent, Pangaea, started splitting in the early Jurassic (200 – 300 million years ago) which resulted in the formation of Tethys, and marked the boundary between the northern-lying Eurasian plate and the southern Gondwanian plate (Veer, 2004). Europe and Asia are part of Eurasia while African, Arabian, Australian, and Antarctica plates are part of Gondwana. Between Eurasia and Gondwana, there are many other small plates of the Precambrian and Paleozoic ages that divided the Tethys Ocean into two parts. The Northern part of Tethys is called Paleo-Tethys and the southern part is called Neo-Tethys (Veers, 2004).

Chaman left lateral transform fault marks the western boundary of the Indian plate. The fault extends about 100 to 200 kilometers from Kharan to Kabul. The Chaman transform fault connects the southern Makran convergence zone with the Himalayan convergence zone in the north. In Pakistan, the Himalayas can be divided into five sub-tectono stratigraphic blocks and regional fault boundaries (Powell, 1979).

Karakorum block is located in the Northern most part of Pakistan, and comprises of highly stressed sedimentary, meta-sedimentary, and igneous rocks. In the Permian age, the northern Karakorum separated (rifted) away from Gondwana and became micro-plate, and reached a deep marine condition in the age of the Early Triassic and marginally recorded compressive movement in the Liassic (Searle, 2011). A latter orogenic event points to a rearrangement of the southern Asian margin possibly around the middle Cretaceous age. Eventually, in the Cenozoic episode, the strong fold-thrust deformation and low to very low-grade metamorphism affected the northern Karakorum, related to the collision of the India and Asia plates (Gaetani, 1990).

2.1.1 Kohistan Island Arc

The Kohistan is located within the Northern area of Pakistan, contains an island arc of intra-oceanic of Cretaceous age (Petterson, 2010). KIA marks the boundary between the Indian plate to the south and the Karakoram (Asian) plate to the north within the Indus suture zone of northern Pakistan (Searle, 1990). KIA consists of different types of rock including intrusive and extrusive igneous rocks and metasedimentary rocks. KIA is an oriented arc and subdivided into Kohistan and Ladakh arcs, Nanga Parbat Haramosh massif (N-S trending), and underlain by the Indian Plate (Seeber, 1979).

There are two thrust faults extend in the north and south of KIA:the Main Karakorum Thrust and the Main Mantle Thrust. MMT laterally joins in India and Tibet which makes the suture zone in Afghanistan, which is called the Indus Tsangpo Suture Zone (ITSZ). Towards the western side of KIA, the MMT and MKT meet with the Kunar Fault. The Kohistan arc has been stressed, uplifted, tilted to the north, and eroded, providing information about the depth of the arc crust (Tahirkheli and Jan, 1979).

2.1.2 Attock Cherat Ranges

The southern boundary of the Peshawar basin is formed by the Attock-Cherat Ranges. These ranges comprise transition of rocks between metasediments of the Lesser Himalaya and foreland-basin strata to the south (Yeats and Hussain, 1987). In northwestern Pakistan the Main Boundary Thrust is a basement thrust along which a thrust system incorporating Precambrian and Phanerozoic age rocks of the Kala Chitta and Attock-Cherat Ranges was thrust over the Cenozoic strata of the northern Kohat and Potwar Plateaus (McDougall et al., 1993). In Peshawar: Nowshera and Attock districts, ACR covered 567 km^2 and 80 km^2 areas respectively. The height of ACR is less in the east of the Indus River but gradually increases and reaches 1000 m near Cherat (Yeats and Hussain, 1987).

2.1.3 Hill Ranges

Hill Ranges is used as the collective name for Samana, Kohat, Margalla Hill, Attock-Cherat, and Kalachitta ranges. The primary lineament deformation (folds and faults), has deformed the Hill ranges shown near MBT. Most of the faults are directed toward the north while some are toward the south (Burbank, 1982). The MBT separates the Kohat-Potwar plateau and the Hill ranges (McDougall et al., 1993).

2.1.4 Main Boundary Thrust

The Main Boundary Thrust which run in the northwestern Pakistan act as a basement thrust along which a thrust system incorporating Precambrian and Phanerozoic rocks of the Kala Chitta and Attock-Cherat Ranges was positioned over Cenozoic strata of the northern Kohat and Potwar Plateaus (McDougall 1993).

From the front of the main Himalayan Range, around the Hazara-Kashmir syntaxial bend, the Main Boundary Thrust (MBT) runs and extend to the west, and placed (thrust) the hill ranges above the northern foreland fold-thrust belt in northern Pakistan. The process of MBT Spreading (thrusting) into the north of the Kohat and Potwar plateaus has been taken placed from 2.1- 1.9 million year ago (Burbank and Raynolds, 1988). In the Kohat-basin, the MBT carries the Mesozoic and younger strata over the eroded mountain sediments of the Siwalik Group (Khan et al., 1986). Deformation within the fold of the Kala Chitta and thrust belt pre-dates placement of the Kala Chitta Range over the Kohat and Potwar plateaus (Yeats and Hussain, 1987).

2.1.5 Southern deformed Fold and thrust Belt

stressed Fold and Thrust Belt in the Southern extends from the Kashmir Basin in the east toward the Kurram region in the west, close to the border of Afghan (Ahmad et al., 2003). Located south to the MMT, the Deformed Fold and Thrust Belt of the Northern composed of volcanic, sedimentary rocks, and meta-sedimentary that are organized in a festoon pattern. The Nanga Perbat-Haramosh massif was formed when the MMT, which serves as its northern border, had a notable shift in direction 10 towards the northeast (Ahmad et al., 2003). The massif is composed of Proterozoic Gneisses and Schists with a thickness exceeding 15 kilometers (Madin, 1986).

2.1.6 Kohat Plateau

The Plateau of Kohat lies between latitude of 32ºN and 34ºN and longitude of 70ºE and 74ºE. East-west striking anticlines (tight anticline) are cored by reverse faults of angle greater than 45º (steep reverse fault) with broad synclinal valleys dividing them (Sercombe, et al., 1998). The United States Geological Survey (USGS) published the geological map of the Kohat Plateau (Meissner 1974).

The Kohat Plateau lies to the north of the MBT, where the intense deformed Mesozoic rock of Kohat Range is run (thrust) over its Eocene-Miocene deposits (Lillie et al., 1987). The Kurram Fault, which runs along the western side of the plateau, divides the heavily stressed rocks of Mesozoic age found in the Darsamand, Samana Thai, and North Waziristan Agencies from the Eocene to Miocene age sediments of the Kohat Plateau (Ahmed, 2006).

2.1.7 Potwar plateau

The most complex tectonic area of northern Pakistan is the Kohat Basin area of the Kohat-Potwar Plateau. The Kohat area in northern Pakistan is a complex tilted plateau and also sometimes similar to a “Cuesta” region with its difficult geological attributes, e.g. moderate-steeper dips and asymmetrical structures that may have been developed by a large number of reverse/normal faults. Sedimentary rocks of Paleocene age to Pleistocene crop exposed on the Plateau of Kohat, no rocks are visible in the Kohat plateau which are younger than Eocene age (Meissner, 1974).

2.1.8 Salt Range thrust

The Salt Range and Potwar-plateau of the Kohat are the southern limit of the Himalayan collision zone of Pakistan. It is an active foreland and fold-thrust. The strongly outcropped central salt range is located between a weakly outcropped thrust front at the Surghar Range and a buried thrust front at the easternmost Salt Range (Terminology of Morley, 1986). The Salt Range and Potwar Plateaus were moved southward and emplaced over the Jhelum plain as a massive block as a result of the effective separation of the Salt Range Thrust's sediments from base salt layer rock (Lillie, 1987).

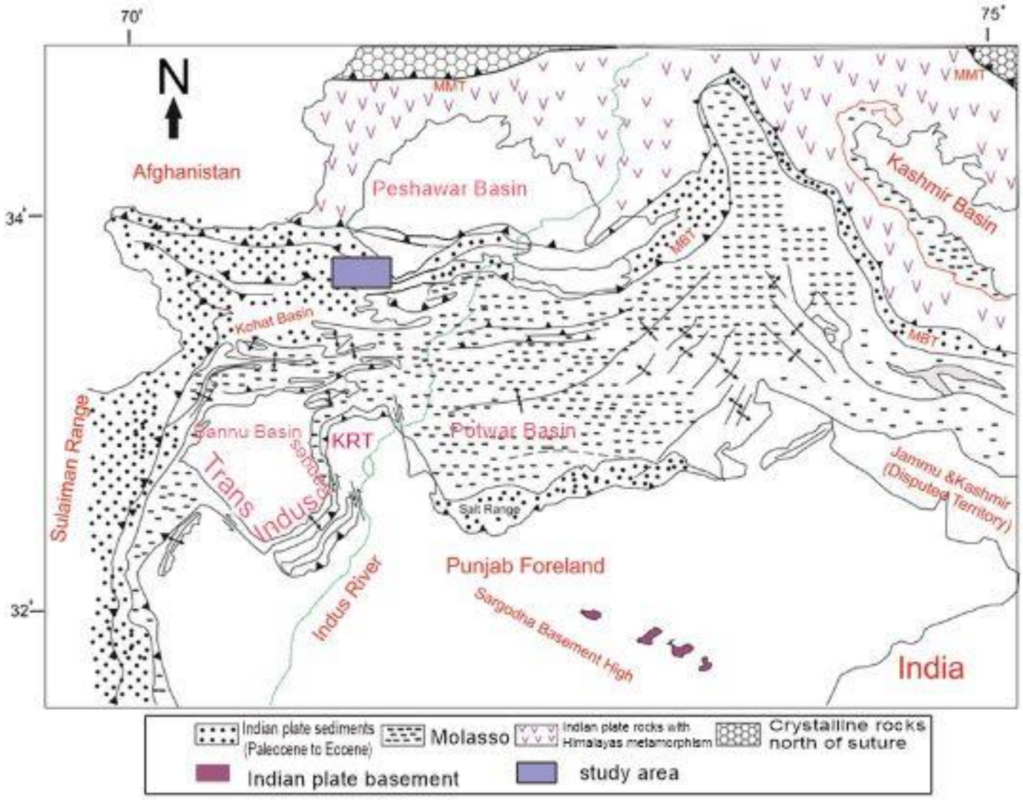

Figure 2.1: Tectonic map of Pakistan showing study area (modified after Kazmi and Rana, 1982).

2.2 Stratigraphy of the study area

The study area contains different Formations (figure 2.2). These are discussed below in detail.

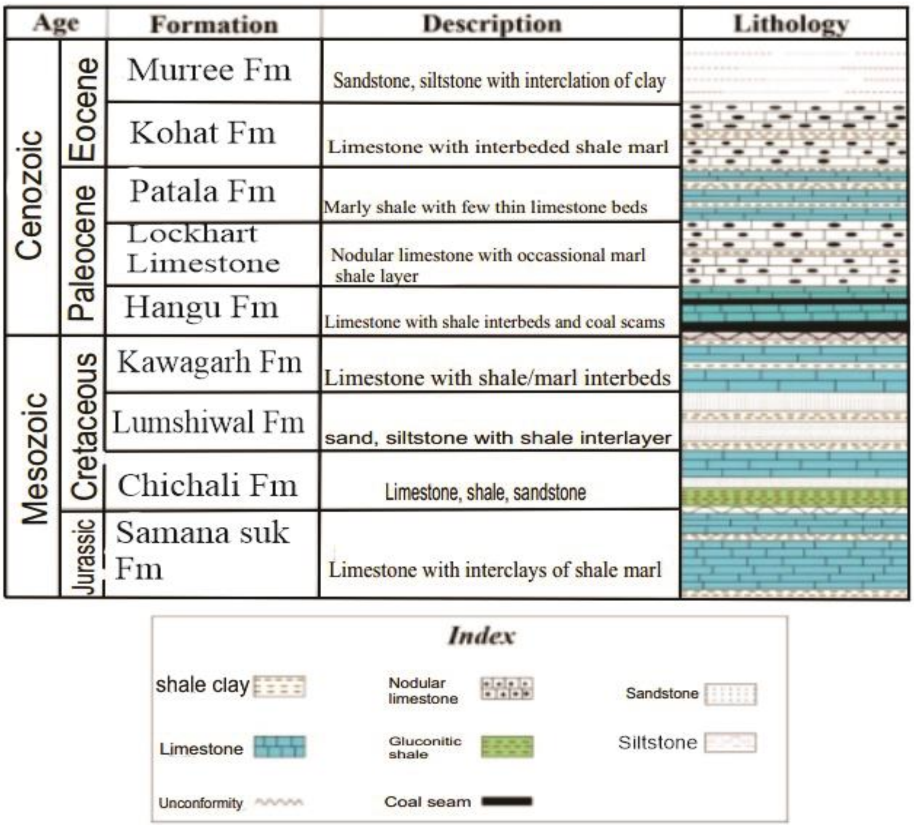

Figure 2.2: Stratigraphic Column of the study area (modified after Latif et al., 2002).

2.2.1 Samana Suk Formation

In the study area, the Samansuk Formation is prominently exposed, and characterized by a different lithology. It consists of calcareous shale, sandy limestone, and oolitic limestone, exhibiting variable thickness in its bedded structure (Shah, 1977).

The upper contact of the Samansuk Formation is disconformable with the Chichali Formation, indicating a hiatus in deposition, while the lower contact is not visibly recognized. Chronologically, the Samansuk Formation is situated within the Jurassic period (Shah, 1977).

2.2.2 Chichali Formation

The Formation is predominantly composed of a variety of lithology: silty shales with different colors, including gray, black, and greenish grey. These shales include iron nodules as well as bands of sandstone, limestone, and marl (Shah, 1977). The interface between the formation and the underlying Samana Suk Formation is deformable, indicating a period of non-deposition or erosion. On the other hand, the top contact with the Lumshiwal Formation is conformable, implying continuous sedimentary deposition (Shah, 1977).

2.2.3 Lumshiwal Formation

The Formation was originally termed Lumshiwal Sandstone (Gee, 1945), but the Stratigraphic Committee of Pakistan later changed it to Lumshiwal Formation (Shah, 1977). The Formation of Lumshiwal in the Surghar Range, Northern Pakistan, mainly display deposition of clasts with an overall upward-coarsening sequence that contains shale at the bottom, the middle contained fine-grained sandstone, and medium to coarse-grained sandstone deposited at the upper part (Waseem, 2024). The Formation of Lumshiwal has been deposited in a fluvial-dominated deltaic environment (Memon and Tietze, 1997).

2.2.4 Kawagarh Formation

The name Kawagarh Formation (Fatmi, 1973) was given by the Stratigraphic Committee of Pakistan given the name for the Kawagarh Shale of Cotter (1933) from its area of location, Kawagarh Hills, northern Kala Chitta Range and run for comparable exposures in the Samana Range, Hazara Mountains, and the Kohat Plateau. The Kawagarh Formation is analyzed by Fatmi (1977) from its type locality and in the vicinity of western and eastern Kohat (Mazari Tang and Wuch Khwar sections), Nizampur, and northern Kala Chitta Range.

There is disconformable contacts of Kawagarh Formation with both the Early Cretaceous Lumshiwal Formation which are lying below and the overlying Hangu Formation of Paleocene age (Shah, 2009).

2.2.5 Hangu Formation

In 1930, Davies referred to the Hangu Formation, the “Hangu sandstone” and “Hangu shale”. These terms were later referred to as Hangu Formation by the Stratigraphy Committee of Pakistan (1973). The age of the formation is Early Paleocene (Shah, 1977).

The Hangu Formation is visible in the Kohat-Potwar and Hazara areas and has a typical locality at Fort Lockhart. In the Kohat area, sandstone is the main constituent in the upper part of the Formation, with sandstone, with grey shale intermixed. The sandstone is conglomeratic in some areas, fine to coarse-grained, and can range in hue from light grey to reddish-brown. Furthermore, the bedding size is medium-thick (Shah, 1977). The formation's lower contact in the Kala Chitta, Hazara, and Kohat areas, with the Kawagarh Formation is disconformable, despite its upper boundary with the Lockhart Limestone being conformable.

In the researched area, the Hangu Formation dominantly consists of Limestone with shale interbedded coal seams are present.

Figure 2.3: Mines located in Germany kalay (A). Lockhart limestone in upper part of outcrop (b). Coal mine in Bazikhel kalay (c).

2.2.6 Lockhart Limestone

The lower boundary of the Lockhart Limestone has discontinuous contact with the Kawagarh Formation, whereas the upper boundary shows conformity with the Patala Formation. The limestone has medium to thick bedding, occurring in massive sections, and displays a color spectrum ranging from light to dark gray in its fresh state, while weathered portions reflect hues of yellowish-brown to dirty gray.

2.2.7 Patala Formation

The name Patala Formation has been arisen from Patala shale. The name Patala shales applied by Davies and Pinfold (1937) to the rocks in the Patala Nala in the Surghar Range (Meissner 1974). The Lockhart limestone lies under the Patala Formation with a transitional contact relationship. The Patala Formation is overlain by a transitional contact based on the increase of limestone inter-beds of the Eocene Nammal Formation contains both limestone and shale (Shah et al., 1977). In the Kohat-Potwar Plateau the estimated measured thickness of Patala Formation ranges from 25 meters to 140 meters. However, in the Hazara area a maximum thickness of approximately 182 meters has been reported (Khan et al., 2018).

2.2.8 Kohat Formation

The Formation of the Eocene age is basically characterized by different layers of limestone and subordinate shale. It contains distinct members. The lower boundary of the Kohat Formation is conformable with the Patala Formation, while its upper boundary makes an unconformity with the Murree Formation (Shah, 1977).

2.3 Petroleum Rocks of the study area

The sedimentary sequence of the Kohat sub-basin was built on the northwestern boundary of the Indian plate, ranging in age from Jurassic to Quaternary (Wandrey, 2004).

The Datta and Samana Suk Formations of Lumshiwal, Jurassic and Kawagarh Formations of Cretaceous, and Patala and Lockhart Formations of Paleocene period are the main reservoirs of hydrocarbon in the researched area (Zeb et al., 2020). The shales of Datta, limestone of Chichali Formation, Hangu, Lockhart and Patala formations act as the rocks of source for hydrocarbons (Zeb et al., 2020). The Hangu Formation of the present study has the property of very good-excellent source rock for gas hydrocarbon.

CHAPTER 03

METHODOLOGY

3.1 Background

For the purpose of objective achievement, the field work was conducted to the studied area. 19 samples were collected from 10 mines in different area. Collected samples were stored in Zipper bag and brought to the lab of Hydrocarbon development institute of Pakistan (HDIP), Islamabad for lab analysis.

3.2 Field work

For suggested goal achievements, field trips were conducted to the studied area, Dara Adam Khel, Khyber Pakhtunkhwa. A total of 19 samples were collected from different coal mines. The samples were named as S1ZkM1, S4ZkM2, S6GkM3, S7GkM3, S8GkM4, S10GkM5, S11GkM6, S15BkkM7, S13BkkM7, S17BkkM9 and S19BkkM10. The samples names were used according to the name of area where the samples were picked from, such as Zk was used for Zor kalay, Gk for Germany kalay, Bk for Bazikhel kalay and M for Mine. GPS was used in field work to note location coordination of samples. The location coordination of samples S1ZkM1 and S2ZkM2 from Zor kalay are 33º40′8″N 71º31′58″E, and 33º40′42″N 71º31′23″E respectively. The samples from 5-12th were collected from Germany kalay and their coordination noted are 33º40′46″N 71º31′59.4″E. The samples 13, 14, 17, and 18th were collected from Bazikhel Kalay with coordination of 33º41′16.9″N 71º29′9.3″E. The coal samples were taken in polythene bag for lab analysis. The bags's open were made tight to avoid any contamination. Out of 20 samples, 11 were selected for lab analysis.

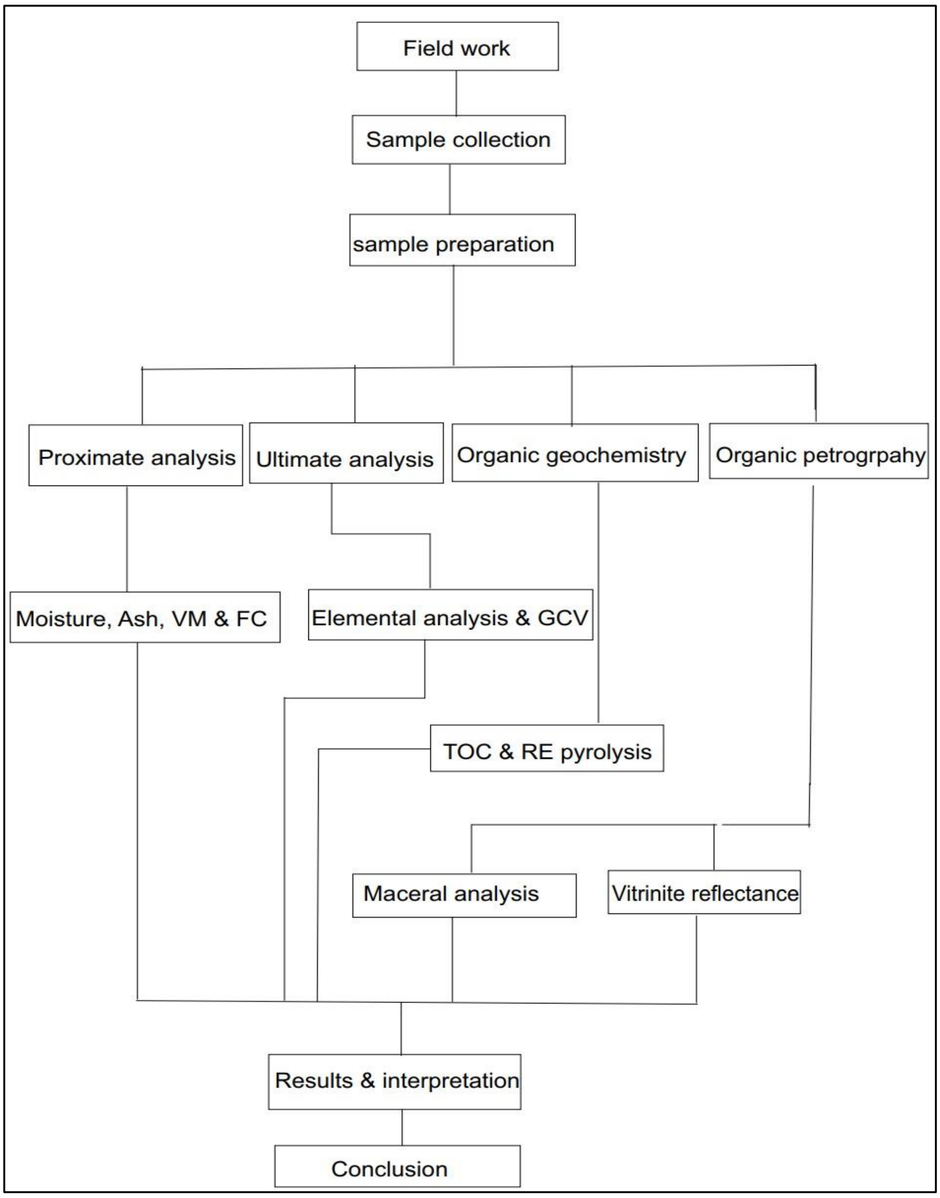

Figure 3.1: Methodology workflow adopted for coal and shale characterization.

Figure 3.2: Observing coal sample containing pyrite (A). photograph shows out crop located in Germany kalay (b).

Figure 3.3: Sample bag containing coal and shale (A). Photograph shows Coal samples (B).

3.3 Lab Work

The collected samples were brought to the lab of Hydrocarbon Development institute of Pakistan, Islamabad (HDIP). The purpose of lab analysis is to assess the geochemical and organic petrographic characteristic of coal from studied area. Lab analysis includes:

a) Sample preparation
b) Geochemical analysis
C) Organic geochemical analysis
d) Organic Petrography

3.3.1 Sample Preparation

The preparation of sample needs several steps to make sure the reliability and accuracy in laboratory examination. These steps of sample preparation are: washing of sample to remove any outside contamination, pulverization by methods such as crushing and grinding to assess an accurate particle size, polishing to get a sample of smooth surface, elimination of any potential source of contamination and drying of sample is conducted for any moisture impurity to eliminate.

The study samples were washed with water and then placed in oven at 40^{o}c for drying. They are then crushed and grinded by ceramic pestle and metal mortar. Before crushing and grinding, the tools (pestle and mortar) were washed with solution including hot water, methanol or dichloromethane (DCM).

Figure 3.4: Machine used for grinding of sample to suitable size.

3.3.2 Proximate Analysis

Proximate analysis of 4 samples was conducted by heating the coal samples in China Dish. These samples are S4ZkM2, S11GkM6, S13BkkM7, and S19BkkM10. In this method four parameters were analyzed: (1) moisture content, (2) ash content, (3) volatile matter, and (4) fixed carbon.

The determination of moisture content is accomplished by loss in weight when subjected the sample to heat about 105ºC. The loss in weight occurred due to release of different contents from coal. This process of heating, cooling, and weighing was repeated until the weight of sample become constant. Actually, the loss in weight noted is the percentage of moisture content.

The moisture contents were calculated by the following formula:

$$MC = \frac{\text{weight of samples before heat} - sample\ weight\ after\ heat}{\text{sample weight initially taken}} * 100\%$$

In the above formula, MC represents moisture content.

For Volatile matter determination, the samples of coal approximately 1 gram were taken in pre-weight silica crucible. The crucible open was covered with lid to avoid contamination, like oxidation of solid carbon when subject to air. The coal samples in crucible were heated up to 950ºC for 7 minutes. After heating, the samples were cooled in desiccator and weighted again. The volatile matter (VM) is calculated from the percentage loss in weight after hating the samples. The following formula helps to find out VM.

VM = % of weight loss – moisture contents (ASTM method D3175-11).

To find out ash content, 1 gram pulverized of each sample were taken in pre-weight silica crucible (without lid) and placed in muffle furnace and heated up to 750ºC for 3 hours. After 3 hours of heating, the residue which left in crucible is the ash contents. Ash contents can be calculated by the formula:

$$Ash\ contents = \frac{W2-W1}{sample\ weight\ initially\ taken} * 100\%$$ (ST. John, 1939)

The Fixed Carbon for the studied samples was determined by indirect way by subtracting the percentage of moisture content, volatile matter, and ash of coal samples from 100.

FC = 100 – (MC+VM+A).

3.3.3 Ultimate analysis

The ultimate analysis for the 4 samples S4ZkM2, S11GkM6, S13BkkM7, and S19BkkM10 was conducted. The ultimate analysis includes Total Carbon concentration, sulphur, and calorific value analysis.

3.3.3.1 Analysis of Total Carbon concentration

For carbon analysis, the samples were crushed to a uniform size. Then dry the sample in Oven at a temperature of 100 ºC-150 ºC to remove moisture. The prepared crushed samples then were put in CHNS analyzer.

3.3.3.2 Sulphur

The content of sulphur have been determined by combining a 1gm sample of coal of 0.2mm particle size with mixture of Eschka and heated up until all the sulphur has been converted to sulphate. The solution of sulphate was formed in result. The solution was then extracted and determined gravimetrically by precipitation with barium chloride. Eschka mixture is formed by mixing either K_2CO_3 or Na_2CO_3 and magnesia. But Na_2CO_3 (sodium carbonate) was used in present study. A coal of 5gm was boiled with dilute hydrochloric acid to bring the sulphur of sulphate and iron which contained no pyrite into solution and filtered. The filtrate was then made alkaline to settle down the iron (non-pyritic iron) which was then removed by filtration. In the result of filtration, the barium sulphate was obtained and determined gravimetrically. The barium sulphate is sulphate sulfur that was precipitated from filtrate. The contrast between the total sulphur and sum of the sulphate sulphur and pyritic sulfur was calculated as the organic sulphur.

Figure 3.5: Display of Carbon/sulfur analyzer CS-580A.

3.3.3.3 Gross calorific value

The calorific value of coal was determined using bomb calorimeter, in the lab of HDIP, Islamabad. The water equivalent value is used in formula to find out calorific value (CV) of coal. To find out water equivalent value, 1 gram of benzoic acid (of known calorific value) was used previous to coal sample.

After determination of water equivalent value, 1-gram sample of coal with a particle size of 60-mesh compressed by pelleting press and placed in a crucible inside the bomb calorimeter, along with a pellet of high purity-oxygen. The crucible is then fastened and the bomb was filled with oxygen with a pressure of 26 kg/cm_2. The bomb calorimeter was then submerged in a known mass of water and electric spark was used to ignite the coal sample inside the bomb. In the result of combustion of sample, the heat released from the coal is transferred to surrounding water, and by using thermometer, the later increase in temperature was measured. The maximum temperature was noted and placed in formula.

Formula for the calorific value:
CVs = [T*W – (CV thread + CV wire)]/M.
Formula for Water Equivalent:
W = [M* CVB + (CV thread + CV wire)]/T.
Where,
M is the mass of sample.
T represents final temperature.
CV_S is the calorific value of sample.
CV_b = benzoic acid's calorific value.
W is the water equivalent in calories per degree^o.
CV_W is calorific value of ignition wire.
= 2.33/cm (when using wire 4 cm, CVw = 2.33x 4 = 9.32 cal).
CVt = Thread's Calorific Value of.
= 2.1/cm (when using thread 10 cm, CVt = 2.1x 10 = 21 cal).

3.3.4 Organic Geochemical analysis

Organic Geochemical analyses of11 samples were conducted. These samples are S4ZkM2, S8GkM4, S11GkM6, S13BkkM7, and S19BkkM10. This analysis includes Screening analysis (TOC analysis, Rock Eval pyrolysis.

For source rock evaluation, the screening analysis was carried out to find out TOC, and Rock Eval-pyrolysis' parameters such as S_1, S_2, S_3, and temperature of maximum.

3.3.4.1 TOC analysis

For TOC determination, 100-150 mg of sample was taken in crucible and the inorganic carbon was eliminated by treatment with 5% HCl. The carbon was removed before subjecting the sample to TOC measurements. The HCl was added to drop by drop until effervescence stops. This process also helps in removing moisture contents from sample that adversely effects the measurements (Schafer, 1980). The sample was placed on hot plate at temperature of 40ºC for drying. Then it was subjected to LECO CS-300 for TOC evaluation (fig 4.3). To make better the accuracy of analysis, LECO standard was used for calibration. TOC measurements are done by oxidizing the organic material into CO2. The carbon contents are detected by infra-Red ray (IR) detector in TOC analyzer.

Figure 3.6: Leco CS-300 used for TOC assessment.

3.3.4.2. Rock Eval pyrolysis

Petroleum explorer use Rock Eval pyrolysis technique to analyze the TOC, quality and thermal maturity of organic matter in source rock (Peters and Cassa, 1994).

The rock-Eval Pyrolysis of 11 samples was conducted. These samples include S1ZkM1, S4ZkM2, S6GkM3, S7GkM3, S8GkM4, S10GM5, S11GkM6, S13BkkM7, S15BkkM8, S17BkkM9, and S19BkkM10. In this method a sample with a mass of between 4-150 mg depending on its nature was placed in the pyrolysis oven. The sample is decomposed thermally when exposed to program temperature increase. The continuous measurement of carbon produced by a sample is performed. The increasing in temperature causes the hydrocarbon to release from sample. The carrier gas carries the hydrocarbons which is released from rock as a result of heating. The Flame Ionization Detector helps detecting the hydrocarbon. At the same time, CO and CO_2 gases released and carried by the carrier gas are analyzed and using an Infrared Detector. The temperature at which S_2 reaches its peak is the T_{max} which depends on the behaviour and thermal maturity of the kerogen. The CO_2 is produced from kerogen cracking at temperature between 300-390˚C and trapped. The CO_2 which has been trapped is heated, and as a result, the CO_2 is released and detected on a Thermal Conductivity Detector (TCD) during the cooling of the Pyrolysis oven (S_3 peak). The HI was measured as the yield of reduced products of pyrolysis (S_2) relative to the TOC (mg HC/g TOC) and OI is the yield of the oxygen and bound organic carbon (S_3).

Figure 3.7: Instrument used for source rock evaluation (Rock-Eval 6).

3.3.5 Organic Petrography

Polished blocks were prepared for petrographic analysis. The microscope Carl Zeiss Axio Imager Z1M with point counter and photometer attached at Hydrocarbon Development Institute of Pakistan (HDIP) laboratories was used for the analysis. In this observation, oil immersion in plane polarized reflected white light is used to carried out the analysis. Out of the total eleven samples that were used for geochemical analysis, three samples were choose for petrology analysis and vitrinite reflectance (VR). Random vitrinite reflectance (% Ro) measurements in oil immersion are made in reflected white light. The reflected white light (using oil) is used for measurement of random vitrinite reflectance. These samples named as S8GkM4, S13BkkM7, and S17BkkM9. Approximately, 21-25 measurements were made for each sample to identify the macerals.

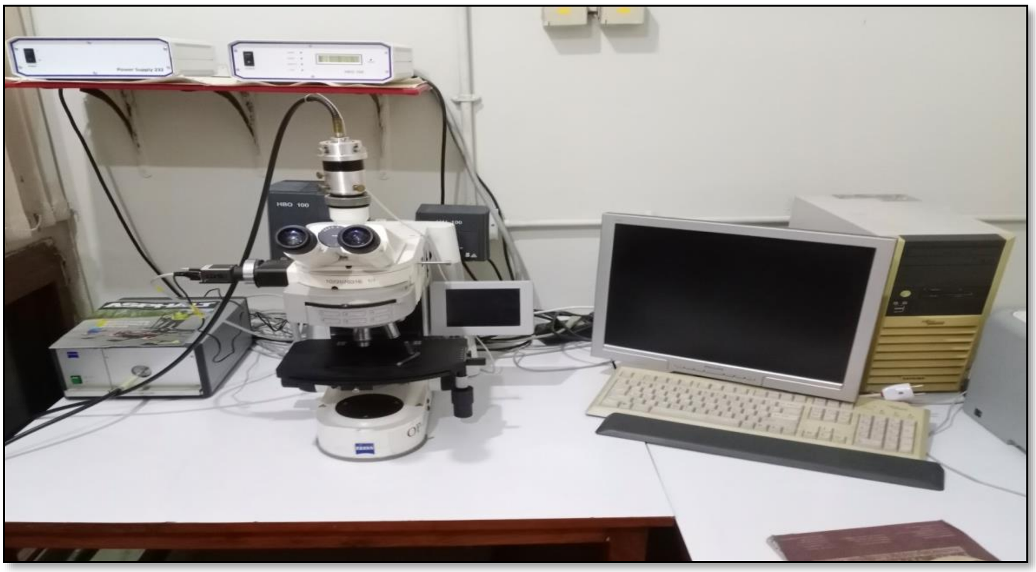

Figure 3.8: Zeiss microscope used for organic petrography.

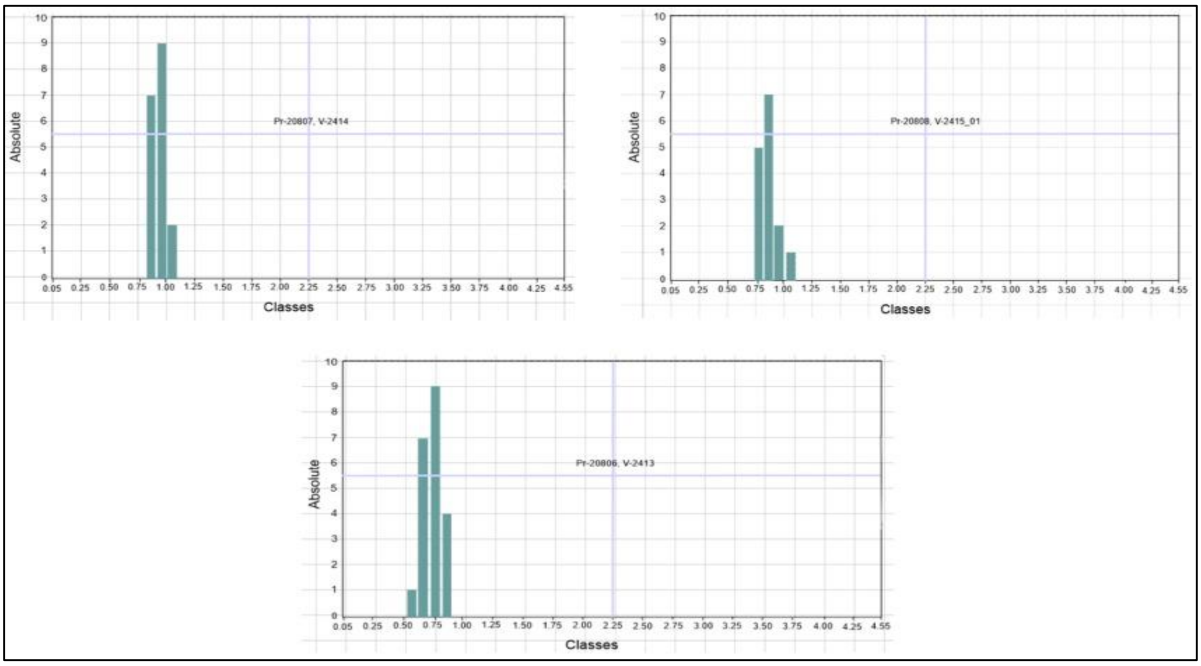

Figure 3.9: shows Histograms of vitrinite reflectance of studied samples of Hangu Formation.

CHAPTER 04

RESULTS AND DISCUSSION

4.1 Proximate analysis

A proximate analysis was conducted to find out the ranks of coal. A single parameter is not enough to find the coal rank, but using many physical and chemical parameters: moisture content, ash, VM, fixed carbon, and GCV. The detailed Results of the proximate analysis of 4 coal samples from the Hangu Formation, Dara Adam Khel are described below.

4.1.1 Moisture content

The percentage of moisture content helps determine the calorific value of coal. The moisture content is inversely related to the maturity and ranking of coal (Stach, 1982). Coal with high moisture content is not preferred because it consumes some of the heat (calories) during burning and add up extra weight when transported from one to other place (Thomas, 2002).

The percentage of moisture content in the studied area ranges from 0.3 % to 1.1 % with an average of 0.68 %. According to ASTM D3302, the moisture content below 10 % is considered low. The studied coal contains low moisture content (0.3-1.1 %) and will not affect the calorific value during coal combustion.

4.1.2 Ash content

The ash content of coal refers to the residue which are non-combustible, that remain at the end of the burning of coal. It represents the bulk mineral matter after carbon, oxygen, sulphur and water are ejaculated during combustion. The ash content suggests the quality of the coal (Onifade et al., 2023). Some characteristics of coal combustion are affected by the presence of ash content in coal. The extent of the effect depends on the composition as well as on the quantity of ash (Jayanti et al., 2007).

The studied coal samples have ash content ranging from 6.3 % to 22.3 % with an average value of 12.45 % (Table 4.1), suggests that these coal falls in low ash category of coal, as clarify by Thomas (2022) that the suitable concentration of ash for the purpose of general usages would be around 20 %. This decides that the calorific value of the study coal would not be affected by ash content. The present study also suggests that the studied coal can be typically used for power generation.

4.1.3 Volatile matter

Volatile matter is the gaseous constituents of coal that is released when the coal is heated without the contact of air at high temperature (Farhaduzzaman et al., 2015). The high-ranking coals contain low volatile matter while the ranked coal contains high VM (Stach et al., 1982). The studied coal contains VM ranging from 7.9 % to 12.0 % with an average value of 10.1 % (Table 4.1), indicating that this coal has low VM (e.g., Farhaduzzaman et al., 2015).

Low-volatile coal takes a longer time for complete combustion because of low vm and low transport rate of gases (CO2/O2) (Aich, 2020). Therefore, the vm in the study area is in medium range and will not affect the combustion rate.

4.1.4 Fixed carbon

The fixed carbon is the primary factor that classifies the coal ranks. The fixed carbon content of the coal is the carbon found in coal which is left at the end of volatile materials elimination. It has a direct relation with coal ranks. The studied coals have

FC ranging from 64.6 % to 84.9 % with an average value of 76.77 % (Table 4.1). According to the guidelines of Speight, (2015) the studied coal is placed in low-volatile Bituminous.

An increase in the percentage of fixed carbon in coal will be followed by an increase in calorific value (Imran et al., 2020). Fixed carbon has the opposite relation with volatile matter because increasing the elimination of volatile matter from coal will increase the relative quantity of carbon (Stach and others, 1982). The study coal has low volatile matter (VM) and medium Fixed carbon as shown in table 4.1.

Table 4.1: The result of proximate analysis. Coal rank is adopted according to ASTM.

Sr. No	**Sample ID**	**Rank**	**Moisture (%)**	**Ash** (%)	**VM (%)**	**Fixed C** (%)
1	S4 ZK M2	Low volatile bituminous	1.1	22.3	12.0	64.6
2	S11 GK M6	Low volatile bituminous	0.9	6.3	7.9	84.9
3	S13BKKM7	Low volatile bituminous	0.4	9.6	10.9	79.1
4	S19BKK M10	Low volatile bituminous	0.3	11.6	9.6	78.5

4.2 Ultimate analysis

The ultimate analysis of the studied samples includes:

a) Gross calorific value

b) Carbon Concentration

c) Sulphur content

Table 4.2: Shows the ultimate analysis results of the studied samples.

Sr.no	Sample ID	GCV (kcal/k)	Carbon %	Sulphur %
1	S4 ZK M2	3220	62.0	2.6
2	S11 GK M6	7863	81.9	3.3
3	S13BKKM7	7750	76.1	9.2
4	S19BKK M10	7550	73.3	12.0

4.2.1 Gross calorific value

The gross calorific helps to find out the heat energy driven in the result of the combustion of coal. It is a parameter of coal ranks. The gross calorific value (GCV) is an important property determining the energy content and output heat of fossil fuels, i.e. coal. The gross calorific value of coal can be estimated by correlating the coal samples on the basis of their proximate and/or ultimate analyses (Patel et al., 2007)
The present studied samples have GCV ranging from 3220 kcal/k to 7863 % with a mean value of 5878 % (Table 4.2). The ash, moisture contents and the types of coal affects the intensity of gross calorific value of coal (Patel et al., 2007). As shown in tables 4.1 and 4.2, coal 1 has more ash content (22.3 %) than the other three coal which is 6.3, 9.6, and 11.6 % respectively. Hence, coal 1 has the lowest GCV (3220 kcal/k) than coal 2, 3, and 4 which have GCV of 7863, 7750, and 7750 kcal/k respectively.

According to ASTM D388, coal that has a calorific value of less than 20.3 MJ/kg (8700 BTU/lb) is considered low GC coal, which cannot be used for power generation and industrial applications. The study coal has a suitable moisture content, ash content, and volatile matter but has a low calorific value as discussed above. The low GCV is because of clay minerals in coal.

4.2.2 Carbon concentration

The high concentration of carbon has a relationship with vitrinite macerals (Berkowitz, 2012). It is also known that C contents are directly related to coal ranks:

High C contents are characteristics of high-rank coal and vice versa (Ward and Gorba, 2010). Instead of some limitations, C concentration is the most important parameter among the other chemical parameters for coal rank determination (Scott, 1999, Tailor, 1998).

The Carbon concentration in the study area ranges from 62.0 % to 81.9 % with a mean value of 61.16 %. The highest value of C concentration is in sample S11GkM6 (81.9 %), while the lowest value is present in sample S4zkM2 (62.0 %). The result indicates that the study coal lies in the bituminous rank of coal.

4.2.3 Sulphur content

The total sulphur is the percentage of sulphur in coal. There are two sources from which sulphur originates in coal: (a) either an organic sulphur source such as a peat-forming process or (b) an inorganic sulphur source such as elemental sulphur (Casagrande, and Ng, 1979).

The average concentration of sulphur in the studied area ranges from 2.6 % to 12.0 % with a mean value of 6.9 % (Fig 4.2), indicating that the studied coal is higher in sulphur (super high organic sulphur) than the coal of Attock-Cherat Range which has sulphur concentration range from 0.97-1.26 % with a mean value of 1.0% (e.g. Khalid Latif et al., 2021). High sulphur indicates a marginal marine environment of deposition (Chou, 2012).

The higher sulphur concentration causes corrosion to machinery and is also unsuitable for the environment and to human health. The sulphur-containing coal releases sulphur into the atmosphere when it is burned (Winarno et al., 2018). The sulphur combines with oxygen and forms sulphur dioxide which may adversely affect animals, the environment, and humans: causing respiratory problems, acid rain, etc. Sulphur also affects marine life indirectly through acid rain (Kalenga, 2011).

4.3 Results of organic geochemical Analysis

Results of organic geochemistry include TOC and Rock-Eval pyrolysis parameters such as S1, S2, S3, Tmax, PI, GP, HI, and OI. These results are presented in table 4.3. Coal and source rock are analyzed based on organic matter quantity, quality, and thermal maturity (Peter and Cassa, 1994). The detail is described below.

Table 4.3: Rock Eval pyrolysis result of source rock.

SR No	Sample ID	lithology	TOC (wt.%)	S_1 (mg/g)	S_2 (mg/g)	S_3 (mg/g)	T_{max} (^{o}C)	GP (mg/g)	PI (mg/g)	HI (mg/g)	OI (mg/g)
1	S1ZkM1	Shale	7.2	-	0.1	0.1	540	0.01	-	1	1
2	S6Gk M3	Shale	5.1	0.01	0.2	-	553	0.21	0.05	4	-
3	S7Gk M3	Shale	3.5	-	0.4	0.4	581	0.4	-	11	11
4	S8Gk M4	Shale	12.5	0.5	6.1	-	474	6.6	0.07	49	-
5	S4Zk M2	Coal	62.0	0.1	1.9	1.5	608	2.0	0.05	3	2
6	S10GM5	Coal	74.0	0.2	10.7	-	522	10.9	0.02	14	-
7	S11Gk M6	Coal	81.9	0.1	8.4	0.1	592	8.5	0.01	10	0.1
8	S13Bkk M7	Coal	76.1	0.5	25.23	-	523	25.8	0.02	33	-
9	S15BkkM8	Coal	74.0	0.1	7.7	0.1	590	7.8	0.01	10	0.1
10	S17BkkM9	coal	83.3	0.5	43.4	-	529	43.9	0.01	52	-
11	S19Bkk M10	coal	72.3	0.7	16.5	-	523	17.2	0.04	23	

4.3.1 Organic matter quantity

The total organic carbon analysis helps to measure the organic richness of rock (Jarvie, 1991). Bacon et al., (2000) classified the source rock on the basis of TOC wt. %. The rock with a TOC value less than 0.5 wt. %, 0.5-1wt. %, 1-2 wt. %, and greater than 2 wt. % falls in the poor, fair, good, and very good source rock categories respectively.

The TOC value of the studied source rock ranges from 3.5-83.3wt%, (Table 4.3) indicating that this rock is very good source rock for hydrocarbon generation. Among these samples, the sample S17BkkM9 has the highest TOC value, while sample S7GkM3 is the lowest Wt.% TOC.

Only the TOC value does not reveal the perfect organic matter, because with the thermal maturity increasing and with the passage of time, the organic matter transforms to hydrocarbon. Source rock generation potential is also carried out through GP vs TOC plot (fig 4.1).

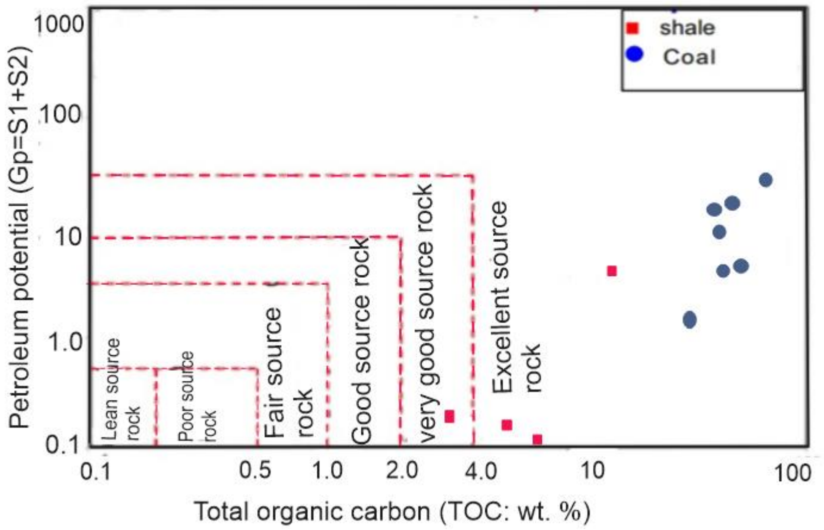

Figure 4.1: Show Quantity of source rock of the study area.

4.3.2 Organic matter quality

After quantity, the next important parameter of coal and source rock evaluation is determining the kerogen types. These are determined through HI vs OI plot etc. or maceral types (Peters et al., 2007).

4.3.2.1 Kerogen types based on Macerals study

Macerals are microscopic organic matter derived from lacustrine, terrestrial, and plant remains in marine and their presence helps to give information of parent material, of initial stage decomposition and before and during the peat stages, and also reflect the magnitude of changes undergone**.** There are three group of macerals: liptinite, inertinite, and huminite/vitrinite (Isabel, 2012).

In the study area, macerals have been identified as per the classification system by ICCP 1994, and Taylor et al., 1998. Two groups of macerals were found, these are vitrinite and inertinite in the study area (figure 4.2). The samples from mine 4 named S8GkM4, contain little organic matter and are coarse in size, where vitrinite is the dominants maceral in the form of collinite. Inertinite is the second major maceral present in the form of inertodetrinite. The sample from Mine 7, named S13BkkM7 contains very common and coarse grain organic matter. Vitrinite is the major maceral (collinite and gelocollinite). Inertinite is the second major macerals (inertodetrinite). The sample from Mine 9, named S17BkkM9 also contains very common and coarse grain organic matter. Vitrinite is the major maceral (collinite) that is oxidized in nature. Inertinite is the second major maceral (inertodetrinite) present in the studied coal. The dominant vitrinite macerals indicate that the study coal contains type III kerogens that has the capacity of generating gas (e.g., Peters and Cassa, 1994).

The composition of different groups of vitrinite macerals gave a better indication of coal ranks (Stach et al., 1982). The macerals are transformed from one type to another: with increasing rank concerning higher temperature and time effect, the macerals vitrinite and liptinite transform into inertinite (Stach et al., 1982). Inertinite maceral also indicate in figure 4.2.

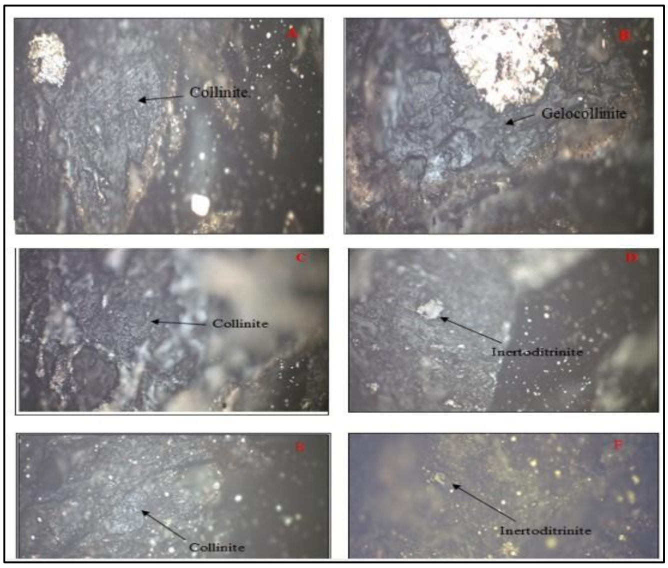

figure 4.2: Photomicrographs for the studied coal samples of Hangu Formation, Dara Adam Khel showing vitrinite (a, b, c, and e), and inertinite (d and f).

4.3.2.2 Kerogen types based on HI

In the study area, the HI and OI values were very low, therefore Van Krevelen diagram (Van Krevelen, 1961) doesn't give a clear identification of kerogen types (figure 4.3). Based on this diagram samples fall in type III and type IV kerogen region. Whereas type III kerogen was also confirmed by maceral study as discussed previously. So, considering the maceral study as reliable it can be concluded that the analyzed samples have dominantly kerogen type III.

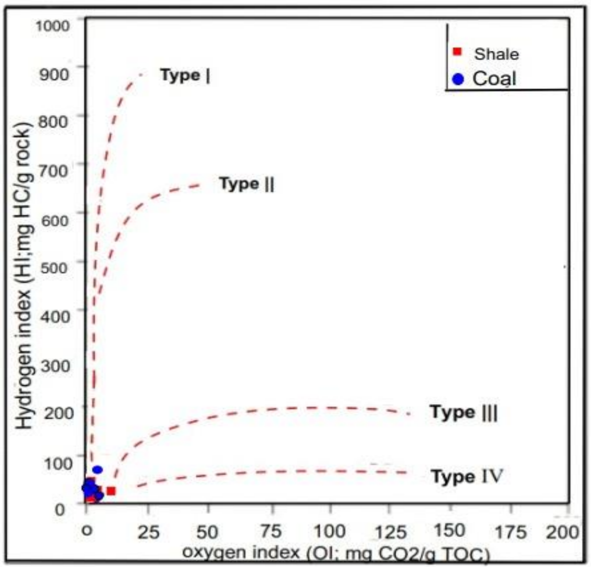

Figure 4.3: Plot of HI vs OI (modified van Krevelen diagram) showing kerogen type of studied samples.

4.3.3 Organic matter maturity

Thermal maturity of hydrocarbon can be determined by Rock-Eval pyrolysis as well as vitrinite reflectance value. The coal of high-rank category has a high VR value and vice versa. The source rock generation potential as well as the types of hydrocarbon gas or oil) varies significantly, depends on the thermal maturity of the source rock. Several maturity indicators determine the source rock generation potential. These indicators include Tmax values, production index (PI), and vitrinite reflectance (Panwar et al., 2017).

Tmax is associated with the chemical nature of kerogen, as the Tmax value will be different for different kerogen types (Hartmann & Beaumont, 1999).). According to Bacon et al., (2000), the organic matter types such as type I, II, and III, refer to different maturity levels for the oil window across a range of vitrinite reflectance and Tmax values.

The thermal maturity values of the study area are much higher, which ranges from 474 to 608 ^{o}C (Table 4.3). There are many causes of high Tmax value: high value of Tmax can be the result of clay minerals, which decrease S2 value and increase Tmax. Sample size also affects the S2 value and Tmax. E.g. increasing the amount of sample size leads to a decrease in S2 value and an increase in Tmax (Yang, and Horsfield, 2020). According to Shah (2001), the maturity level of Cherat, Hangu area (Khyber Pakhtunkhwa), and Balochistan province is believed to have enhanced because of high tectonics activity as compared to other coal fields of Pakistan. The high Tmax value of the study area is because of clay minerals and high sulfur content (Yang and Horsfield, 2020).

The maturation level can be determined by plotting HI versus Tmax. On the base of the HI versus Tmax plot, the study area source rock is placed in post mature stage and capable of generating dry gas. The Tmax values of the study area were very high, therefore, the VRo study was encountered. The vitrinite reflectance (VRo) measurements are provided in figure 4.5. Minimum values of VRo for individual samples were recorded as 0.58, 0.72, 0.84%, while maximum VRo are 0.83, 1.00, 1.07%. The Statistical details of VR measurements in the selected samples are given in Table 4.5 and Fig. 3.9. The study source rock has a mean VRo value ranging from 0.71-0.91 %, which falls them in the mature stage, and in the gas generation zone (e.g., Hakimi et al., 2021).

Table 4.4: Guideline for maturity and generation potential of different hydrocarbons.

Phase	Maturity (%)
Immature	<0.5
Oil	0.5-1.1
Wet gas	1.1-1.4
Dry gas	1.4-4.0
Post mature	<4

Table 4.5: Random Vitrinite reflectance and statistics of selected samples from study area.

Sr.no	**Sample ID**	**R_o (%)**	**Min R_o**	**Max R_o**	**St.d**
1	S8 GK M4	0.71	0.58	0.83	0.07
2	S13 BKK M7	0.84	0.84	1.00	0.05
3	S17 BKK M9	0.91	0.72	1.07	0.08

4.3.4 Hydrocarbon generation potential

The ability of kerogen to generate hydrocarbon is controlled by kerogen types, hydrogen value, organic matter quantity (TOC), and thermal maturity. The organic matter is composed of C, H, and oxygen; therefore, the HI is used to identify kerogen type in coal (Salman et al., 2024).

TOC is a semi-quantitative scale; it expresses the quantity but not the quality of organic matter. As discussed above, the analyzed coal and shale have “Good to excellent” source rock properties, therefore, these samples underwent additional tests to assess organic matter quality and maturity. The kerogen has been divided into different types on the base of the source of organic matter, which largely controls the chances of generating hydrocarbons: Type I and II derive from algae and are considered oil-prone, while higher plant remains form the type III kerogen and is considered the source of gas generation (Moldoveanu,2021). On the basis of the HI vs TOC plot, the study samples are in the gas generation zone (Fig 4.4).

The vitrinite and inertinite groups have derived from terrigenous higher plants origin (Isabel, 2012). As determined by the HI vs TOC plot, it is confirmed too from vitrinite reflectance and maceral study that the analyzed samples are thermally mature, and have dominant vitrinite macerals followed by inertinite, which shows the stage of gas generation zone.

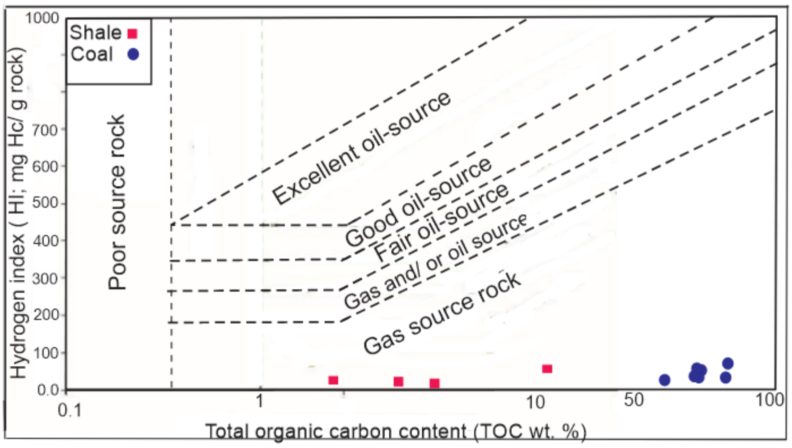

Figure 4.4 Plot of HI vs TOC of Hangu Formation (Jackson and Bennet, 1985).

Conclusions

a) The proximate and analysis shows that the amount of moisture content, ash, volatile matter fixed carbon, ranges from 0.3-1.1, 6.3-22.3, 7-12.0%, 64-84.9%, with mean value of 0.68, 12.45, 10.1, 76.77 %. Based on volatile matter (7.9 % to 12.0 %) and fixed carbon (64.6-84.9 %), the study coal is placed in low volatile bituminous rank. Results of the ultimate analysis indicate that the percent of carbon and sulphur ranges from 62.0 to 81.9, 2.6 to 12.0 % with an average value of 61.16, and 6.9 % respectively. The ultimate results also point out that the sulphur percentage is high in the study area.

b) The organic geochemical study revealed that the coal of Hangu Formation is placed in very good to excellent source rock intervals in terms of organic-richness. The organic-rich shale has the quantity of very good-excellent source rock, whereas the coal intervals hold the excellent source rock property.

c) The hydrogen index and temperature of maximum of Rock Eval pyrolysis determined that the study samples are in post mature stage. Actually, the T_{max} values were very high, ranges from 522-608 ^{o}C, therefore, for thermal maturity, the vitrinite reflectance value were encountered. On the base of R_o, the samples are placed in mature stages with values ranging from 0.71 to 0.91 %.

d) The organic petrography suggests that the study samples are vitrinite (collinite and gelocollinite) dominants which are related to type III kerogen and have the potential to generate gas hydrocarbon.

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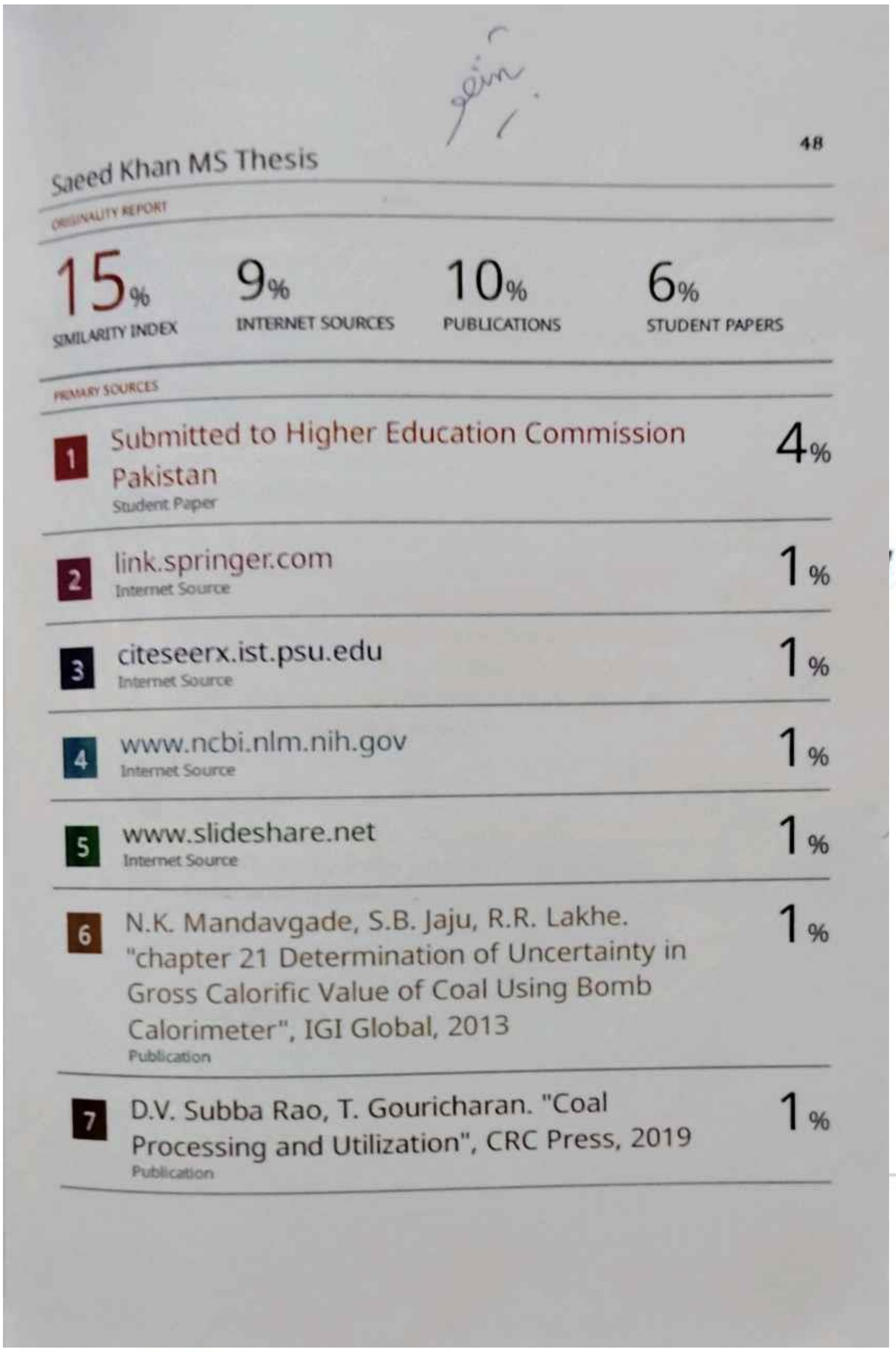

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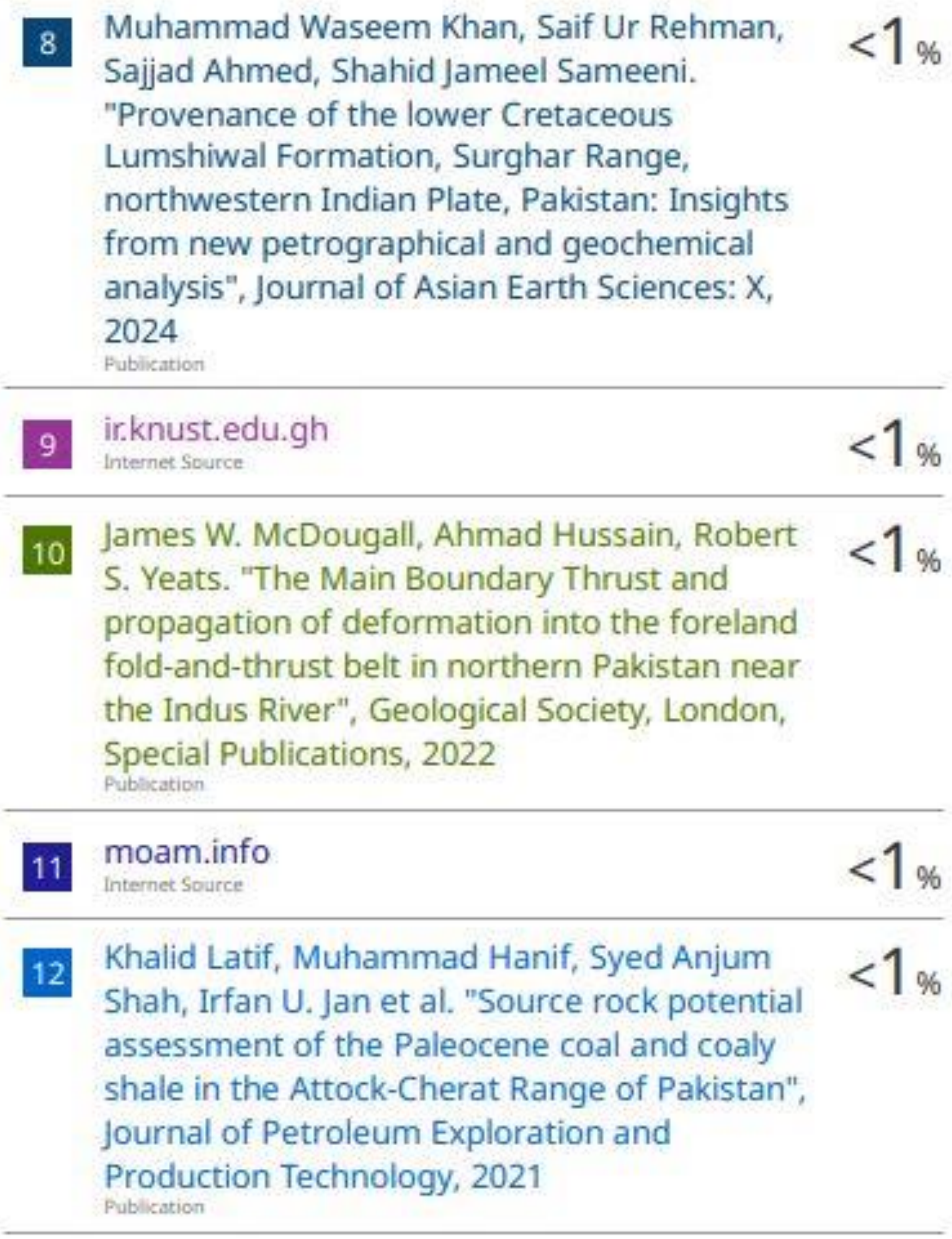

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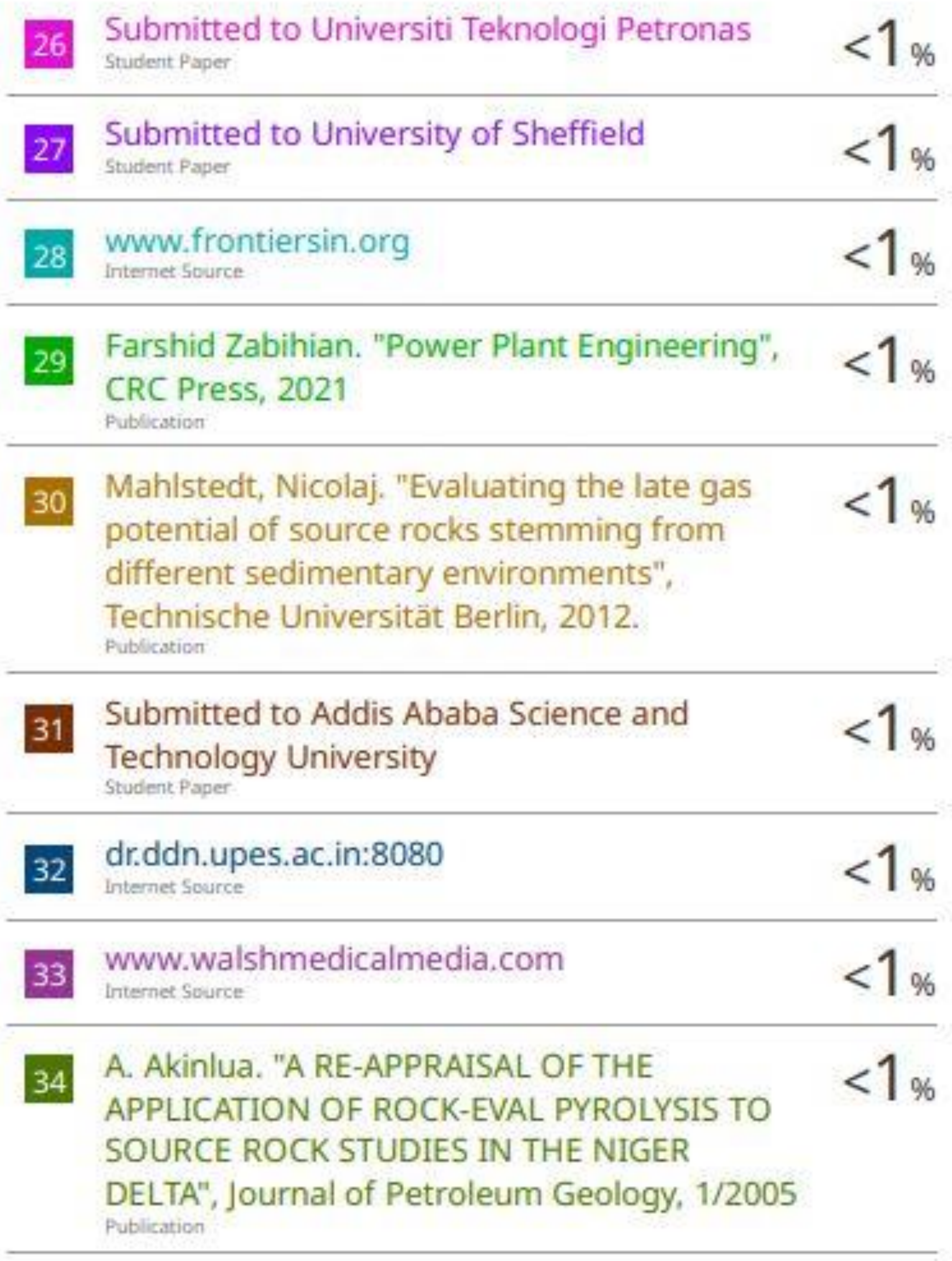

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