COMPARING PHYSICAL AND THERMAL CHARACTERISTICS OF HANGU-ORAKZAI AND MAKHARWAL COAL AND CHAR IN AN INERT ATMOSPHERE

By

Khalid Munir

(NUST201261036MSCEE65112F)

A thesis submitted in partial fulfilment of requirements for the degree of

Master of Science (MS)

In

Environmental Engineering

Institute of Environmental Sciences and Engineering (IESE)
School of Civil and Environmental Engineering (SCEE)
National University of Sciences and Technology (NUST)
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It is certified that the contents and forms of the thesis entitled

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Has been found satisfactory for the requirements of the degree of Master of Science in Environmental Engineering

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DEDICATION

I would like to dedicate my efforts to

my venerable

Sweetest Mother, Brothers, Sisters,

and Professors & to my friends whose

love, prayer enabled me to complete

this Task.

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This dissertation would have not been possible without the guidance and the help of several individuals who, in one way or another, contributed in the preparation of my thesis and completion of my research work.

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Khalid Munir

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

XRD:	X-ray Diffraction
SEM:	Scanning Electron Microscopy
TGA:	Thermogravimetric Analyzer
XRF:	X-ray Fluorescence
H/O:	Hangu-Orakzai
Mak:	Makharwal
%:	Percentage
wt:	Weight
NaOH:	Sodium hydroxide
<:	Less then
mm:	Millimeter
GCV:	Gross Calorific value
^{0}C:	Centigrade
Eq:	Equation
rpm:	Rotation per minute
VM:	Volatile matter
Cu:	Cuppor
FeS:	pyrite
E:	Activation energy
A:	Pre-exponential factor
PEPA:	Pakistan Environmental Protection Agency
SO_x:	Oxides of sulfur
NO_x:	Oxides of nitrogen
CO_2:	Carbon dioxide
Kcal/kg:	kilo calories per kilogram
Min:	Minute
K:	Kelvin
L:	Litre
Fig:	Figure

ABSTRACT

Physical, structural and thermal characteristics of Hangu-Orakzai and Makharwal coal samples of Pakistan are investigated in this research by ultimate and proximate analysis, X-ray fluorescence (XRF), X-ray diffraction (XRD), Scanning electron microscopy (SEM) and by Thermogravimetric analysis (TGA). Coal sample were desulfurized by sodium hydroxide solutions of different molarity. 1.5 molar sodium hydroxide solutions desulfurized 87 % of the sulfur from Hangu-Orakzai coal while 60 % from Makharwal coal, more than at any other tested molarities. Thermogravimetric analyses of both raw coal samples were performed in an inert (nitrogen) and air (oxidizing) atmospheres at a heating rate of 10 ^{0}C/min and atmospheric pressure of 10 L/min. Based on better desulfurization and atmospheric comparison in TGA, and easy availability of air oxidizing atmosphere in the industry rest of the thermogravimetric study was continued with Hangu-Orakzai coal sample at different heating rates (10, 25, 40 ^{0}C/min) and air flow rates for combustion (3.5, 7 and 10 L/min). The research also computes activation energy determination from the raw and sodium hydroxide treated coal. The kinetic parameters for the coal combustion were investigated by the Arrhenius equation using 1st order kinetics. Hangu-Orakzai raw and treated coal sample have amorphous structure while Makharwal sample has crystalline structure. SEM analysis of raw Hangu-Orakzai coal sample shows that surfaces are generally covered with collotelinite, parallel laminated and debris micrinite. Desulfurized coal sample have rod and spongy like structure while Makharwal raw coal sample showed plate or rounded, collotelinite non-porous structure. Thermogravimetric results showed that higher activation energy was required for combustion at low heating rate and higher air flow rate. Coal desulfurization is not only essential for clean emissions to protect the environment, but also aids coal degradation at lower activation energy.

Chapter No. 1

INTRODUCTION

1.1 Background: Fuel from fossils is currently the world's primary energy source. Coal is the most abundant low-cost fossil fuel in the world. Traditionally coal combustion emits large amount of pollutants including carbon, nitrogen, sulfur oxides, and many other metallic oxides into the earth's atmosphere (Yingzhong *et* al., 2010). The organic content of the coal also known as coal macerals is the major energy provider while the inorganic constituents called mineral matters are the unwanted components in the coal that dilute quality and contribute towards pollution (Li S *et al*., 2009).

The major pollutants of the coal combustion are carbon dioxide, sulfur dioxide, nitrogen oxide, hydrocarbons, carbon monoxide, ash, arsenic, and trace elements of uranium. In coal combustion, the pollutant gases released accumulate in the environment. This brought adverse effects to the environment and human health e.g. global warming, acid rain, smog, lung damage, birth defects, brain damage. In Pakistan, the Ministry of Environment was established in 1975. During 1977 to 1988 very few environmental laws were published with no individual law established for coal mining.

In Pakistan, major coal sites are Thar in Sindh, Sor-Range in Quetta, Shahrig mines in Sibi where millions tons of coal reserves are reported. Keeping in view the coal deposits in Makharwal and Hangu-Orakzai areas of Punjab and Khyber Pakhtunkhwa provinces of Pakistan respectively. Their future use in power generation and other industrial purposes and the possible threats to the environment need to be studied.

The physical structure of coal represents the spatial layout of the complex molecules and effects on its chemical reactivity in pyrolysis and combustion processes. Coal structural characterization is very difficult due to complex and heterogeneous nature of coal. XRD, XRF and SEM analysis needs to be done to understand structure of coal. Thermochemical conversion is the approach to extract usable form of energy from coal. Combustion is the thermal conversion of fuel into energy with excess amount of oxidant which is affected by heating rate, operating temperature and characteristics of fuel, etc.

When coal is burn C, N, and S oxides are formed and if not removed from the combustion products are released to the atmosphere. In coal, mainly three forms of sulfur are present namely: organic sulfur, pyritic and sulfate. Due to the presence of sulfur in the coal, an increase takes place in the activation energy of the coal. Hence, the purpose of study is to focus upon the effect of desulphurization over the entire morphology of the two sources of coal: Makharwal and Hangu-Orakzai. Its impact will be studied before and after the phase of desulfurization over combustion characteristics.

Thermogravimetric analysis (TGA) can be used to determine the thermal conversion including sample degradation (with increasing temperature) the amount of mass change under a controlled atmosphere of air or inert material like nitrogen. TGA is a method which is used for the thermal degradation and order of kinetics study, in order to calculate the activation energy of coal. The apparent activation energies and pre-exponential factors from kinetic mechanism at different heating rate and atmospheric pressures are calculated by Arrhenius method and analyzed.

1.2 Statement of Problem: Coal combustion reserves in Pakistan is about 4.89 million tons. Pakistani coal is used in different types of industries like brick kilns, cement and coal briquette's and for different purposes like combustion, pyrolysis and gasification to produce energy. Coal has significant adverse environmental impacts in its production and use, but since Pakistan's electricity demand is increasing each day, so need to reduce environmental impacts from air pollutants including Sulfur oxides, Nitrogen oxides, and particulates from coal combustion plants. The problem arise here is whether coal combustion affects environment and how this impact can be reduced. The challenge in the future is to enhance both the efficiency and environmental acceptability of coal use by adopting cleaner coal technologies. The increased efficiency of clean coal technologies results in reduced emissions of environmental pollutants such as NOx, SOx and particulate matter.

1.3 Research Hypothesis: Oxidative desulfurization with sodium hydroxide at low temperature can remove organic sulphur from coal and can lower the required activation energy for effective degradation of coal without effecting calorific value.

1.4 Aim and Objectives: Keeping in mind the importance of Hangu-Orakzai and Makharwal coalfield sample and its future use in boilers for power generation purposes in cement or other industries, it is aimed:

- To determine proximate, carbon and sulfur percentage, analysis of Hangu-Orakzai and Makharwal raw coal samples.
- To treat Hangu-Orakzai and Makharwal coal sample for sulfur removal by using different molar solutions of sodium hydroxide for the specific purpose of environmental impact assessment.
- To determine structural and morphological analysis of raw and treated Hangu-Orakzai coal sample and Makharwal raw coalfield sample.
- To investigate and compare the thermal characteristics of Hangu-Orakzai and Makharwal coal in Air and Nitrogen.
- To determine the thermogravimetric analysis of the Hangu-Orakzai raw coal at different heating and flow rates in air.
- To check desulfurization effect on thermal degradation of Hangu-Orakzai coal sample in air at optimum condition.

1.5 Scope of the Study: It is hoped that the results will provide new data to develop a technical base for Pakistan environmental protection agency (PEPA) to propose industries of Pakistan a possible method for reduction in sulfur oxide emissions on coal combustion. There exists a great potential to develop alternative renewable energy resources for developing countries like Pakistan. Grand total reserves of coal in Pakistan are about 186,282.41 million tons. New project are assigned for coal gasification. Attention need to know the importance of these coalfields sites for coal combustion, pyrolysis and gasification.

LITERATURE REVIEW

2.1 Coal: Coal is considered as one of the world's most important fossil fuel reserves. However due to its large-scale use, release of toxic gases and particulate matter can take place which can pose serious environmental concerns. Coal deposits are widely distributed across the earth, in comparison with crude oil and natural gas reserves. Total coal reserves on earth was estimated at 948×10^9 tons in which Pakistan have 185.175 billion tons.

Numerous ranks of coal are formed due to in-situ compaction of sedimentary strata in the earth's crust. Organic carbonaceous matter, fluids and inorganic minerals are the substances of the formation of coal. Mainly three types of coal namely lignite, bituminous and anthracite, are present which can be classified on percentage of moisture content, volatile matter, fixed carbon and ash.

2.1.1 Hangu-Orakzai Coalfields: Hangu-Orakzai coalfields are located in Khyber Pakhtunkhwa province of Pakistan**.** The approximate coal reserves reported in Hangu-Orakzai coalfields are eighty one million tons with one million tons measured, four million tons indicated and seventy six million tons inferred. The coal seam thickness commonly ranges from 0.6 to 1 meter and can vary from 30 centimeters to 3 meters.

These coalfields are found in the Kohat and Hangu districts as well as in tribal Orakzai agency. Some coal mines are present in settled areas or districts while most of the mines are in tribal agency. Geologic formation of Hangu-Orakzai coalfields consist of coal, cross-bedded and interbedded with bluish grey shale, bioturbated sandstone, limestone and carbonaceous clay. In Darwazai and Dauli areas, the coal is nearly more than one million tons (highest) and clay present is nearly eight to ten million tons. Coal is also found in Torawai area, has high ash and high sulphur contents (Malkani M S., 2012).

2.1.2 Makharwal Coalfields: The Makharwal coalfields are located in Punjab province of Pakistan (Mohammad Qasim Jan Bangash., 1961). In his research thesis titled as "Geological report of Makharwal", states that Makharwal area is in south-west of Kalabagh. The top of these mountains is confined between the District of Kohat and Mianwali. The formation at Makharwal has been an important source of coal in the western part of Indo-Pak subcontinent for the last sixty years. The coal stocks of Makharwal have been estimated as high as 21.7 million tons in which 5 million tons are measured reserves, 7.5 million tons are indicated reserves and 9.2 million tons are inferred reserves from altitude of 300 meter to 600 meter above sea level.

Makharwal coalfields were mined as early as in 1903.The first organized and systemized coal production from Makharwal coalfields was started in 1911. A production of 500 tons' coal per day from Makharwal coalfield is reported. Ninety three mines of grid in Makharwal coalfield have been developed, in which productive mines are 67 and non-productive are 26. One of the major causes of non-productive mines is reaction of sulfide coal associated with water which forms acidic water that hinders safe mining activity. It is reported by geological survey of Pakistan that Makharwal coal is high in sulfur and low in ash. Makharwal and Gula Khel areas have the main coal exposures. The main coal seam varies from 0.5 to 3.5 meters, averaging about 1 meter (Malkani MS., 2012).

2.2 Environmental issues: Coal also contains C, H, O, and S molecules in both the organic and inorganic forms so whenever and wherever it is burned, oxides of carbon and sulfur as carbon dioxide, carbon monoxide and similarly sulfur oxides are produced. As said earlier, the industry is in the process of shifting its energy fuel to coal and with the current economic conditions and lack of the use of best available technologies in industries it will become an environmental hazard to deal with coal usage in the future. Therefore cleaning of coal without affecting its heating value is important before combustion otherwise sulfur oxides will cause acid rain. In mines, this also causes problems of acid mine drainage.

Carbon, sulfur, hydrogen, oxygen, nitrogen and other minerals are the constituents of coal. When coal is burnt, sulfur, carbon and hydrogen react with atmospheric oxygen to form oxides of sulfur and carbon as well as water. The oxides of sulfur form sulfur dioxide which can react with atmospheric oxygen to form sulfur trioxide. The sulfur trioxide dissolves in the atmosphere in water droplets to form an aerosol of sulfuric acid which causes acid rain. Regional environment and human health impacts caused by coal use mainly depend on toxic elements, minerals type and their abundance (Die *et al*., 2004).

2.3 Coal desulfurization: Binoy K. Saikia *et al*. (2014), desulfurized low grade medium to high sulfur coals by low energy ultrasonication. The method used atmospheric pressure and room temperature for three hours on 20 gram coal sample mixed with 100 ml of H_2O_2 exposed to an ultrasound treatment of 20 kHz and then washed until pH becomes neutral. He concluded that the maximum of 31%, 48%, 51% and 32% of total sulfur, organic sulfur, pyritic, sulfate sulfur and ash respectively were removed from the Indian coal sample under study.

Yingzhong *et al*. (2010), desulfurized high sulfur coal from PUAN country and used zinc chloride aqueous solution floatation liquid media in the test with different density levels for the float and sink test and reported that sulfur and ash increase as the floatation media density level gets higher. He concluded that desulfurization in the floatation media density below 1.4 g/cm^3 is almost complete and when flotation media density is greater than 1.8g/cm^3, the sulfur and ash content reaches the highest level respectively.

Salvatore Vaccaro (2010) desulfurized four sub-bituminous coal with hydrofluoric acid (HF) solution, sodium hydroxide (NaOH), potassium hydroxide (KOH) weight percentage aqueous solution at 60 ^{0}C for 24 hours. This was mixed with nitric acid (HNO_3). The combined acid and base aqueous solution demonstrated that treatment with HF solutions had negligible effects on the removal of sulfur while NaOH and KOH treatment of coal showed increase of ash percentage. Thus, the combined acid base treatment showed satisfactory results for sulfur removal followed by the treatment with the weak base.

2.4 Carbon and Sulfur determination: Yueqin *et al*. (2011), analyzed Luxing coal for carbon and sulfur percentage by using PerkinElmer 2400 Series II CHNS Elemental Analyzer. He proclaimed that the sample has average sulfur content of 3 percent, indicating that this is the coal fraction with the highest sulfur content and carbon content with an average value of 70 percent. Likewise, he concluded that the bigger lump coal has higher pyrite content due to higher inorganic sulfur fraction, although coal powder has higher organic sulfur content. Yingzhong *et al*. (2010), interpreted carbon and sulfur contents of Guizhou coal reserves by using ultimate analysis method and reported that percentage of carbon in coal sample was 92 % while sulfur was 2.95%. He further suggested that the raw coal is mature coal, with high coalification rank.

Binoy k. Saikia *et al*. (2009), evaluated Makhum coalfield sample for carbon by using elemental analyzer Perkin Elmer (model 2400), while total sulfur was determined by Eschka method and results showed that the sample have highest total sulfur content of 5.30 percent while carbon content was 75.4 percent. This also report the presence of maceral contents in these coals with high vitrinite (collotelinite). Sonibare *et al*. (2010), reviewed six Nigerian coal samples and interpreted carbon sulfur content on Vario El Cube elemental Analyzer equipment. Results showed that average carbon content was 74 percent while sulfur content was 0.38 percent.

2.5 Proximate Analysis: Yan *et al*. (2014), determined proximate analysis of lignite coal sample using Chinese testing standards, GB/T211, GB/T212. Determined moisture content was 9.41 weight percentage, volatile matter 40.19

wt %, fixed carbon 47.15 wt %, and Ash 12.67 wt %. Kang *et al*. (2014), persistent proximate analysis of Indonesian and Inner Mongolian coal sample was reported as having a low rank coal with high moisture and volatile matter content but low ash content. He concluded that if you need high quality rank coal from low rank, a drying process is needed. Results found by applying standard methods have shown that Indonesian coal has moisture content of 12.88 wt %, volatile matter 41.11 wt %, fixed carbon 40.56 wt % and ash 5.45 wt%.

Sonibare *et al*. (2010), grind samples into powder (72mesh) and determined proximate analysis according to ASTM (D-3172) standard and USGS method developed by Walthall and Fleming. Outcome shows that the average moisture content in six Nigerian coals noted was 5 wt %, Ash is 25 wt % and volatile matter is 38 wt %.

2.6 Scanning Electron Microscopy (SEM) analysis of coal: SEM analysis of coal is performed to analyze surface morphology of coal sample. Binoy K. Saikia. 2009, prepared SEM samples by sprinkling powder coal samples onto a carbon coated metallic holder followed by gold coating and analyze coal sample on JEOL scanning electron microscope, model JSM-5200. Results showed that Assam coal was rich in vitrinte with well-defined shape and they were useful for liquefaction and coal of different petrographic formation could tremendously affect the washability petrographics.

Binoy K. Saikia *et al*. (2014), inspected low grade medium to high sulfur coals after sulfur removal treatments by low energy ultra-sonication. The coal samples for SEM analysis were prepared by sprinkling powdered samples onto a carbon coated metallic holder followed by gold coating. The SEM analyses of coal samples were obtained at different magnifications. The morphology of the ultra-sonicated coal samples indicated the pitting of surfaces, crack formation, widened cracks and breakages of coal particles. These different types of changes in morphology of the coal structure are may be due to the cavitation occurring during ultra-sonication. It may be further due to the leaching effects of acidic H_2O_2.

2.7 X-ray Diffractive (XRD) analysis of coal: XRD analysis of coal was performed to analyze structural characterization of coal. Cheng *et al*. (2010), analyzed coal samples for XRD pattern, in the range of 2 Θ=30-30^0 and found that SiO_2 in two coal-bearing strata kaolinite is 45 % more than general kaolinite in the Xiaoxian kaolinite rock. Yueqin *et al*. (2011), accumulated data of Luxing coal by using "diffractometer Philips X' Pert Pro Alpha 1" over 2 θ values from 20-80^0. Identified that Luxing coal have crystalline phase and pyrite is mainly found in all coal samples. Coal of bigger particles is mainly composed of pyrite as compare to small size which has higher dolomite content.

Sonibare *et al*. (2010), tested six Nigerian coal structural parameters by X-ray diffraction. Samples were scanned in 2 θ from 3 to 85 ^{0} and found that all the samples exhibit high background intensity, indicating the presence of amorphous carbon in the coal in addition crystalline carbon too present in coal having graphite-like structure. It suggests that coal having intermediate structure in between crystallite and amorphous state, can be considered to be the so called turbostratic structure. Θ and 2 θ in xrd study is the angle of analyzer in which minerals detected.

Cutruneo *et al*. (2014), indicated in his research that interstrafied, ilite, smectite, kaolinite, calcite, melanterite, rutile, jarosite and quartz are major minerals in the sample on XRD analysis. Ankerite and calcite are also present in fine sample but do not have feldspar. In the other sample, XRD also indicated a trace amount of sphalerite while Gypsum was present in all cases as a minor but significant component.

Binoy K. Saikia *et al*. (2014), using low ultrasonic energy (20 kHz) to clean coal sample of low rank having medium to high sulfur in the presence of H_2O_2 solutions. He analyzed the coal sample in X-ray diffractometer with an angle set

5-100^0, at the scanning rate of 4^0/min and concluded that treated and raw samples show presence of calcite, kaolinite, quartz, hematite, pyrite, illite, albite and muscovite, and further observed that some peaks in treated coal sample during the ultrasonification process were disappeared or their intensity was reduced. Observed that during ultrasonification, some coal sample display less removal of mineral matter.

Song Dangyu *et al*. (2011), used XRD to analyze the organic crystalline unit on Henan and Shanxi province coal sample. The method was adopted with an angular range 2-90^0 (2 θ). He used Scherer's equation to find the crystallite unit and concluded that crystallite structure depends on coal rank, and that the average diameter of coal crystallite unit increases as the coal rank increases and inter-layer spacing decreases slightly. He further determined a structure with an inter-layer spacing from 1.9-2.8 nm exits in coal sample crystallites. He concluded that the presence of organic sulfur in coal produces noise signals on XRD while pyritic and sulfate presence give sharp peaks.

2.8 Isothermal and Non isothermal Thermogravimetric analysis of coal:

In Non isothermal thermogravimetric analysis, the flow of temperature is not constant. Conversely isothermal analysis has constant internal energy and temperature. Tae-Jin Kang *et al*. (2013), worked on Indonesian and Inner Mongolian coal with different heating rate kinetics for catalytic gasification and found that the non-isothermal drying conversion is less affected by heating rate, than by moisture. The suitable method for Indonesian and Mongolian low rank coal for the kinetic analysis was the Coats and Redfern model.

Cheng *et al*. (2010), used kaolinite claystone of volcanic origin found as partings in coal and the methodology adopted was to analyze sample on thermo gravimetric analyzer with heating rate of 5 ^{0}C/min, from temperature 25 to 1000 ^{0}C. Found that decarbonization is necessary before calcinations of coal-bearing strata kaolinite for environment protection. Pintana and Tippayawong. (2013), investigated Thai lignite with SO_3 free CaO contents under oxygen rich environments with heating rate of 10, 30 and 50 ^{0}C/min from room temperature upto 1300 ^{0}C, and found that activation energy vary with the conversion factor. Higher activation energy was observed in high CaO lignite coal than the low CaO coal.

Jayaraman *et al*. (2013), investigated coal samples of India and Turkey with the help of thermal analyzer coupled to a mass spectrometer system with different atmospheric environments of oxygen, argon and steam with heating rates of 35 and 45 K/min. Found that at temperature 350-700 ^{0}C, the maximum weight loss from coal devolatilization occurs because of release of O_2, CO_2, CO, H_2 and CH_4 in argon ambience and CO_2, CO and H_2 gases produce above 800 ^{0}C when coal particles react with decomposed steam. At about 950 ^{0}C, the exothermic reactions are completed.

Zhigang Li *et al*. (2013), investigated combustion, pyrolysis and gasification properties of pulverized char and coal in CO_2-rich gas flow by using TG DTA with changing temperature gradients, flow rates and O_2 % and indicated that at temperature lower than 1100 ^{0}C, Oxygen % has an considerable effect on carbon oxidation and concluded that coal mass decreases linearly with increasing coal matrix temperature at numerous O_2 concentrations.

Binoy K. Saikia *et al*. (2014), worked on two coal samples from India and using TG DTA under air atmosphere and temperature upto 800 ^{0}C, and concluded that 20-27 % weight loss occurs after combustion and DTA results indicated that at 80-110 ^{0}C, chemical reactivity of the coal sample occurs due to removal of moisture content and at 420 and 530 ^{0}C, other reactions occurs due to primary and secondary volatilization.

Wang *et al*. (2009), investigated Chinese coal, which are considered rich in barkinite, by thermo gravimetric analysis with heating rates of 10, 15 and 25 ^{0}C/min in a nitrogen atmosphere and reported maximum mass loss occurred at temperatures of 330 to 550 ^{0}C which possessed H/C atomic ratios over 0.8.

Chapter No. 3

METHODOLOGY

3.1 Materials: Hangu-Orakzai and Makharwal coalfield sample for study was donated by the Mines & Minerals Department of Khyber Pakhtunkhwa Province, Pakistan. Hangu-Orakzai coal sample provided was dark black in appearance in all large and small particle lumps while Makharwal coal sample was shading brown colour. On arrival sample was air dried at ambient conditions, pulverized and sieved up to < 2mm, 2mm and 3.5 mm size with the help of lab scale mortar and pestle. Sodium Hydroxide pellets, 99% pure, were purchased from local chemical supplier of Sigma (Sigma-Aldrich Co.) in Pakistan.

3.2 Methods:

3.2.1 Carbon and Sulfur determination: Carbon and sulfur percentage in Hangu-Orakzai and Makharwal coalfield sample were determined by tube furnace IR based, Leco (SC-144DR), in accordance with the help of ASTM D 2016-08. Sulfur carbon analyzer is a controlled infrared software instrument which measure carbon and sulfur contents in a wide variety of inorganic and organic materials. Determination method required that weighed 0.250 gram of sample placed insight the instrument.

The Hangu-Orakzai and Makharwal coalfield sample combust in instrument in pure oxygen environment at regulated temperature of 1350 ^{0}C at controlled oxygen flow. The sulfur gets oxidized to form sulfur dioxide and carbon forms carbondioxide. The gases produced from combustion flow through two anhydrone tubes to remove the moisture and then through a flow controller that set the flow of the sample gases to 3.5 L/min. These combustion gases then pass through the infrared (IR) detection cell. The carbon IR cell measures the concentration of carbon dioxide and sulfur dioxide gas. Software of the equipment converts these values to percent carbon and percent sulfur by taking into account the weight of sample taken.

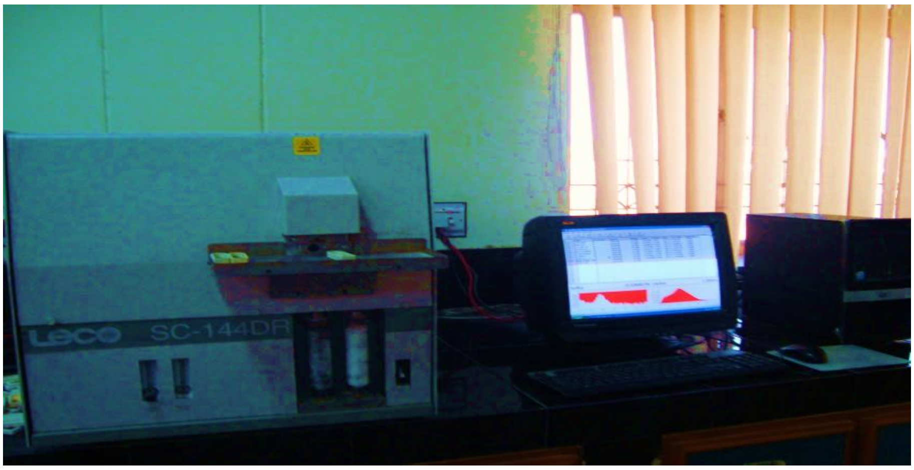

Figure 3.1: Carbon-Sulfur Analyzer Leco (SC-144DR) in Research lab of Centre for Coal Technology Punjab University Lahore

3.2.2 Gross Calorific Value of Coal field sample: Gross calorific value (GCV) of Hangu-Orakzai and Makharwal coalfield samples were determined by using Automatic bomb calorimeter according to ASTM D-5865-07a. Which is a software controlled instrument, the sample was placed in a combustion vessel in which oxygen environment is in high pressure (25 atmosphere). The combustion vessel is surrounded by a noticeable quantity of water and increases in its temperature is noted by the instrument after the sample is ignited. Heat absorbed by combustion vessel, calorimetric vessel and other parts of the calorimeter is driven as water equivalent of the calorimeter by making use of a noted weight pellet of benzoic acid. Gross calorific value of fuel is computed by the software controlled instrument knowing water equivalent of the calorimeter, water placed inside the calorimeter and increase in its temperature after ignition of the fuel.

Figure 3.2: Digital Calorimeter (LECO AC-500) in Research lab of Centre for Coal Technology Punjab University Lahore

3.2.3 Proximate analysis: Proximate analysis of Hangu-Orakzai and Makharwal coal field sample was done with the help of muffle furnace made from mild steel with powder coating finish. **Temperature range of muffle furnace** was up to 1200 °C. Temperature was controlled by digital display temperature controller cum Indicator. A commonly used analysis for reporting fuel properties include: volatile matter, fixed carbon, moisture, ash, and heating value (higher heating value).

Figure 3.3: Muffle furnace in research lab of waste water, IESE NUST

3.2.3.1 Moisture content: 1 gram of Makharwal and Hangu-Orakzai coal field sample of mesh size less than 2 mm, 2mm and 3.5mm was heated in an oven at a temperature of 100-110 ^{0}C for an hour. After one hour, crucible are then removed from the oven and cooled in desiccator and measurement of the remaining sample in crucible is done by weight balance and calculated as follows:

$$\% \text{ Moisture content} = \frac{(\text{ wet weight} - \text{dry weight})}{\text{Dry weight}} \times 100$$

3.2.3.2 Volatile matter: 1 gram of Makharwal and Hangu-Orakzai coal field sample of mesh size < 2 mm, 2mm and 3.5mm in a standard volatile matter crucible was heated in a muffle furnace to about 7-8 minute at about 500 ^{0}C. Crucible was then removed from the muffle furnace and cooled in desiccator and then weighed with the help of weight balance. The % volatile matter are calculated with the help of formula stated below:

$$\% \text{ Volatile matter} = (\text{weight loss } \times 100) - \% \text{ moisture}$$

3.2.3.3 Ash: 1 gram of Makharwal and Hangu-Orakzai coal field sample of mesh size <2 mm, 2mm and 3.5mm in a crucible was heated in a muffle furnace for 2 hour at about 750 ^{0}C. The crucible is then cooled in the desiccator and weight of residue remained in the crucible was done with the help of weight balance. The % Ash is calculated with the formula stated below.

$$\% \text{ Ash} = \frac{\text{Weight of residue}}{\text{Weight of sample}} \times 100$$

3.2.3.4 Fixed carbon: Percent fixed carbon is that carbon content which is determined when moisture content, volatile matter and ash percentage are subtracted from the organic or inorganic matter. Fixed carbon was calculated with the help of formula which described as under:

$$\% \text{ fixed carbon} = 100 - (\text{ V.M } (\%) + \text{Ash } (\%) + \text{Total moisture } (\%)$$

3.2.4 Desulfurization: Coal desulfurization is a process by which sulfur is removed from coal to upgrade its value. Coal desulfurization processes are categorized as either physical cleaning or chemical desulfurization. Sodium hydroxide aqueous solutions with variable strengths (0.5, 1.0, 1.5, 3.0, 4.0 and 5.0 molarity) were used to desulfurize the coal samples according to the following procedure: A 10 gram coal sample was mixed at 120 rpm with sodium hydroxide solution for 3 hours at room temperature. After mixing, the coal sample was filtered, dried in oven at 105-110 ^{0}C for 2 hours for removing moisture, and then analyzed for the sulfur treatment.

3.2.4.1 Coal treated with 5 M NaOH: Solution was prepared by dissolving 12.5 gram of NaOH in distilled water of 62.5mL in a volumetric flask and then 10 gram coal samples of Hangu-Orakzai and Makharwal were placed in it respectively, and mixed with the help of magnetic stirrer for 3 hours and at ambient temperature. The sample was filtered, dried in an oven at temperatures 105-110 ^{0}C for 2 hours and the dried sample was then analyzed with the help XRF for sulfur %. Observed analyses results are discussed below. Similarly experiments were performed at different molar solutions of NaOH prepared as follow.

Table 3.1: Coal treated with different molarity

NaOH molarity	NaOH weight (gm)	Volume of distilled water (mL)
3	15	125
1.5	7.5	125
1	5	125
0.5	2.5	125

3.2.5 Physical characteristics of coal field samples:

3.2.5.1 X-Ray Fluorescence (XRF): The raw and treated grind coal samples were analyzed using Jeol JSK-320M element analyzer Japan. The X-ray tube current was set at 1000 µA and voltage 30 kV. Characteristic X-rays from the sample were measured by Silicon Drift Detector with the counting time set 120 s. The XRF device was calibrated with JSK standard multicomponent glass JSK 3200. The samples were homogenized during the crushing. All the samples were analyzed in pellet form. Pellets were prepared using hydraulic press at pressure of 40 Mpa.

3.2.5.2 XRD Analysis of Coal: Crystal structures of raw (untreated) and best desulfurized (treated) coal samples were analyzed by X-ray diffraction. For analysis (diffraction patterns) X-Ray diffractometer (Theta/ 2Theta STOE Jeol Germany) was used. Radiation source Cu-Kα was used to capture the X-Ray patterns at 2θ (20^0 to 80^0). X-Ray generator was supplied electric potential of 40 kV and an electric charge of 40 mA.

3.2.5.3 Scanning Electron Microscope (SEM): Scanning electron microscopy of the raw and the best desulfurized coal sample were performed to find surface morphology of the coal. Jeol JSM-6490A, Japan analytical scanning electron microscope was used following the equipment protocols. Both coal samples were first coated with gold and then magnified (100, 500, 1000, 5000, 10000, 20000) having length size (1.0, 5.0, 10.0, 30.0, 100, and 500 µm with 15–20 kV) accordingly. SEM images were captured from the detector as result of strike of a high energy electron beam to the surface of the coal and returned generated scattered x-rays.

3.2.6 Thermal characterization of coal field samples:

3.2.6.1 Thermogravimetric Analyses (TGA) of coal sample: Thermogravimetric analysis of raw and treated coal was conducted using high resolution instrument Leco TGA 701 (MI, USA). Inert (nitrogen) and air (oxygen) atmospheric conditions were applied at various heating rate (10, 25, and 40 ^{0}C/min) and atmospheric flow rate (10, 7, and 3.5 L/min). Leco TGA was operated up to 1000 ^{0}C for every sample analyzed. The instrument consists of multiple sample furnace and computer.

Figure 3.4: TGA 701 leco available in research lab of Centre for coal technology Punjab university

3.2.7 Mathematical Analysis of kinetic reaction model:

3.2.7.1 Arrhenius type kinetic model assuming a first order reaction:

First order reaction kinetic model was used to determine the activation energy. Arrhenius rate constants and the de-volatilization rate were considered proportional to the amount of remaining volatile matter as described in the following equation.

$$\frac{dm}{dt} = km^n \qquad \text{Eq. (1)}$$

where:

$$k = A(exp)^{\frac{-E}{RT}} \qquad \text{Eq. (2)}$$

n = 1, for first order kinetics

E = activation energy, kJ/mol

R = universal gas constant, J/^{0}K-mol

m = mass of the substance, gm

T = temperature, ^{0}K

Substituting Eq. 2 in Eq. 1 and taking the logarithm on both sides of the resulting equation yields:

$$ln\left(\frac{dm/_{dt}}{m}\right) = ln(A) - \left(\frac{E}{R}\right) \times \frac{1}{T} \qquad \text{Eq. (3)}$$

A plot of the left hand side of equation 3 and (1/T) should yield a straight line with a slope of (E/R) which will be used to determine the activation energy. Activation energy require for all the raw and treated samples were determined accordingly.

RESULTS AND DISCUSSION

4.1 Carbon and Sulfur determination: Coal’s carbon and sulphur content determination is important to understand its combustion process and environmental impacts. It is to understand the qualitative formation of coal sample. The results obtained in percentage form of sulphur and carbon in Makharwal and Hangu-Orakzai raw coal from carbon and sulphur determination are described in table 4.1. The analysis result showed that Makharwal coal field sample have 34 percent more sulphur content than Hangu-Orakzai coal field sample. Also, Makharwal coal field sample has 24 percent more carbon content than Hangu-Orakzai coal field sample which shows that Hangu-Orakzai coal will have more ash content, hydrogen and oxygen as compared to Makharwal coalfield samples.

4.2 Gross Calorific Value: The gross calorific value (GCV) depends mostly on carbon content. If we have more carbon content values, we have more GCV. Combustion of organic carbon takes place quickly as compared to inorganic carbon. If the coal sample has less organic carbon, it will have less GCV and vice versa**.** The obtained results of gross calorific value from Auto bomb calorimeter of Makharwal and Hangu-Orakzai raw coal in Kcal/Kg are described in table 4.1.Results of Auto bomb calorimeter show that Makharwal coal field sample has 16 percent more GCV than Hangu-Orakzai coal field sample (because of more carbon content in coal sample). The GCV of Makharwal coal sample shows that it is an excellent coal sample that can be used for combustion purpose as compared to Hangu-Orakzai coal sample.

4.3 Proximate Analysis: Proximate analysis described the thermal composition of coal sample. The degradation of coal after heating at fixed temperature gave results of its four constituents. The percentage of average fixed carbon, moisture content, volatile matter, and ash of Hangu-Orakzai as well as Makharwal coal samples are described in table 4.2 and 4.3 respectively.

In our results, Hangu-Orakzai coal samples have 20% more fixed carbon than Makharwal coal. As discussed earlier, the justification for difference between fixed carbon and qualitative carbon is that the fixed carbon is the remaining composition of coal sample, when ash, moisture and volatile matter has been removed. Fixed carbon contains both organic and inorganic carbon. Also, inorganic carbon does not combust in low temperature, as it needs high temperature. Hangu-Orakzai coal sample has 100% less moisture content as compared to Makharwal coalfield sample, and the ash content in Hangu-Orakzai coalfield sample is 4% less than Makharwal coal sample.

The volatile matter in Hangu-Orakzai coal field is 83 % less than Makharwal coal field sample. In comparative study about proximate analysis, results describe that Hangu-Orakzai coal field sample is more favorable for combustion, because of high fixed carbon and less ash content, moisture content and volatile matter.

Table 4.1: Comparison of carbon sulfur content and gross calorific value of Hangu-Orakzai and Makharwal coalfield sample.

Coalfield Sample	Carbon (%)	Sulfur (%)	Gross Calorific Value (Kcal/kg)
Hangu-Orakzai	65.7	3.7	5634.00
Makharwal	85.7	5.6	6713

Table 4.2: Proximate analysis of Makharwal coalfield sample

Makharwal coalfield sample								
Sample	**%Moisture content**	**Ave**	**%Volatile Matter**	**Ave**	**%Ash**	**Ave**	**% Fixed Carbon**	**Ave**
>2 mm	1.52		26.77		4.9		66.8	
2 mm	1.11	1.04	19.77	22.87	8.4	8.83	70.71	67.2
3.5mm	0.50		22.07		13.2		64.22	

Table 4.3: Proximate analysis of Hangu-Orakzai coalfield sample

Hangu-Orakzai coalfield sample								
Sample Size	**%Moisture content**	**Ave**	**%Volatile Matter**	**Ave**	**%Ash**	**Ave**	**%Fixed Carbon**	**Ave**
< 2 mm	0		5.5		5.7		88.8	
2 mm	0	0	4.4	3.93	9.7	8.46	85.9	87.6
3.5 mm	0		1.9		10		88.1	

4.4 Desulfurization of coal with different NaOH molarity: Both Hangu-Orakzai and Makharwal raw coal analysed found to have above 3% sulphur content. Sulphur oxide emissions on combustion have an adverse impact on environment causes acid rain. For achieving low sulphur coal desulfurization with 1.5 molar sodium hydroxide solution showed a maximum of 87% removal from Hangu-Orakzai coal while a maximum of 60% from Makharwal raw coal. This shows that Hangu-Orakzai coal has more organic sulphur in marcels as organic sulphur is easily desulfurized with alkaline solutions due to C-S cleavage (M.Senkan *et al*., 1979) and inorganic sulphur (pyrite and sulphate) are removed at acidic pHs.

A decrease in % present removal above 1.5 molar solutions is due to metal oxide formation in the coal samples. However it is believed below 1.5 molar solution the sulphur removed from coal is mainly inorganic sulphur as pH of the system decreases. The treated samples were analyzed on X-Ray fluorescence (XRF), which gave the quantitative analysis of coal samples. The sulphur percentage in raw and treated coal samples are represented in table 4.4 and in appendixes A B and C. The analysis of results shows that 1.5M NaOH aqueous solution treated sulphur content in raw coal is more than other tested molar NaOH solution.

Table 4.4: Sulfur percentage in raw and treated coal samples of Hangu-Orakzai and Makharwal

Molarity NaOH	**Sulfur % in Hangu-Orakzai coal sample at room temperature**	**Sulfur % in Makharwal coal sample at room temperature**	**50^oC Hangu-Orakzai coal sample**	**50^0C Makharwal coal sample**
Raw coal	46.09	24.45	46.09	24.45
0.5	13.55	24.24		
1	17.49	9.22	13	9.63
1.5	6.11	9.56		
3	18.66	7.91	10.95	11.09
4	18.62	8.39		
5	28.56	11	21.49	12.2

4.5 Scanning Electron Microscopy (SEM) Analysis: SEM analysis was performed to find the morphological differences between the raw and best treated coal samples. SEM results are presented in Fig. 4.1. SEM analysis indicated that the raw Hangu-Orakzai coalfield sample has a smooth and homogeneous surface at 1 mm observation. However at magnification of 50, 1000, and 10,000 having length of 1, 5, 10, and 500 micrometer respectively, show different shapes and surfaces. At 1 micrometer, particle size observation indicates the mineralogy as collotelinite with no pore structure. On the other hand, 5 and 10 micrometer length have higher magnification, shapes shows parallel lamination. At 500 micrometer, surfaces are generally covered with debri's of micrinite.

The Hangu-Orakzai coal sample for sulfur treated with sodium hydroxide solution shows structure of rod like cylinders at lower magnifications and of spongy like structure at high magnifications as shown represented in Fig 4.3. Based on these results, it can be concluded that treatment has changed the internal morphology of the coal samples and turned the coal into spongy structure. This change in surface morphology of the coal is due to the dissolution of minerals from the coal in to the sodium hydroxide solution and this is owing to the treatment in the presence of oxygen at the surface and breakup of the surface carbon sulfur bonds (M.Senkan *et al*., 1979).

However, SEM analysis of Makharwal coal sample having 1 mm length on EDS report shows a collotelinite non-porous structure. At higher magnification it shows different morphological structure. In 500 micrometer length at 10 50 SEI, the surface covered with debri's of micrinite have plate or rounded like shape while at 10, 5 and 1 micrometer at 10 50 SEI and 10 40 SEI well-ordered system of rod-like cylinder same as vessels of xylem plant are represented in figure 4.2. The concluded result is that the porous condition in Hangu-Orakzai treated coal sample is wide because of morphological spongy like structure.

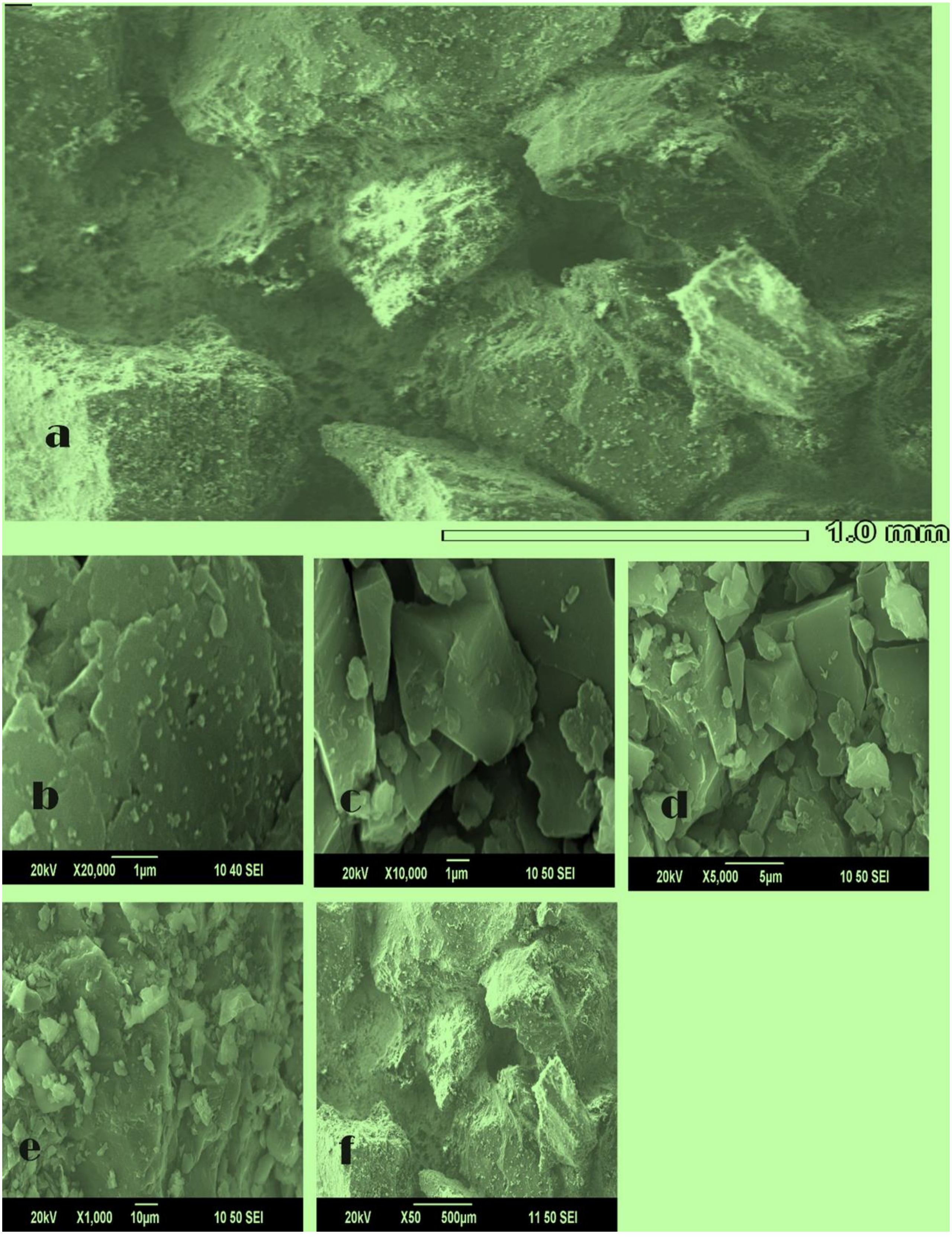

Figure 4.1: Scanning Electron Microscope images of Hangu-Orakzai coalfield sample

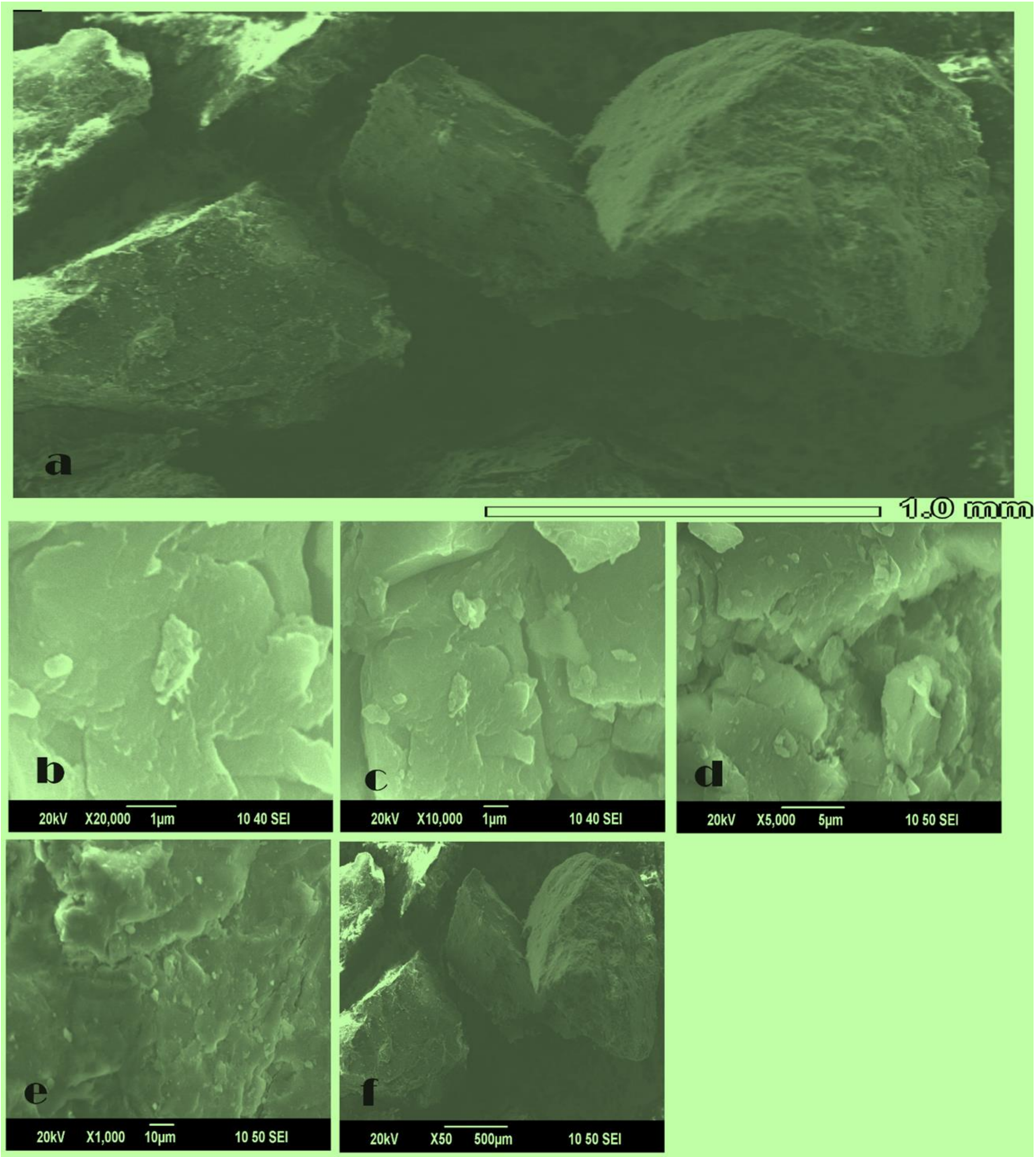

Figure 4.2: Scanning Electron Microscope images of Makharwal coalfield sample

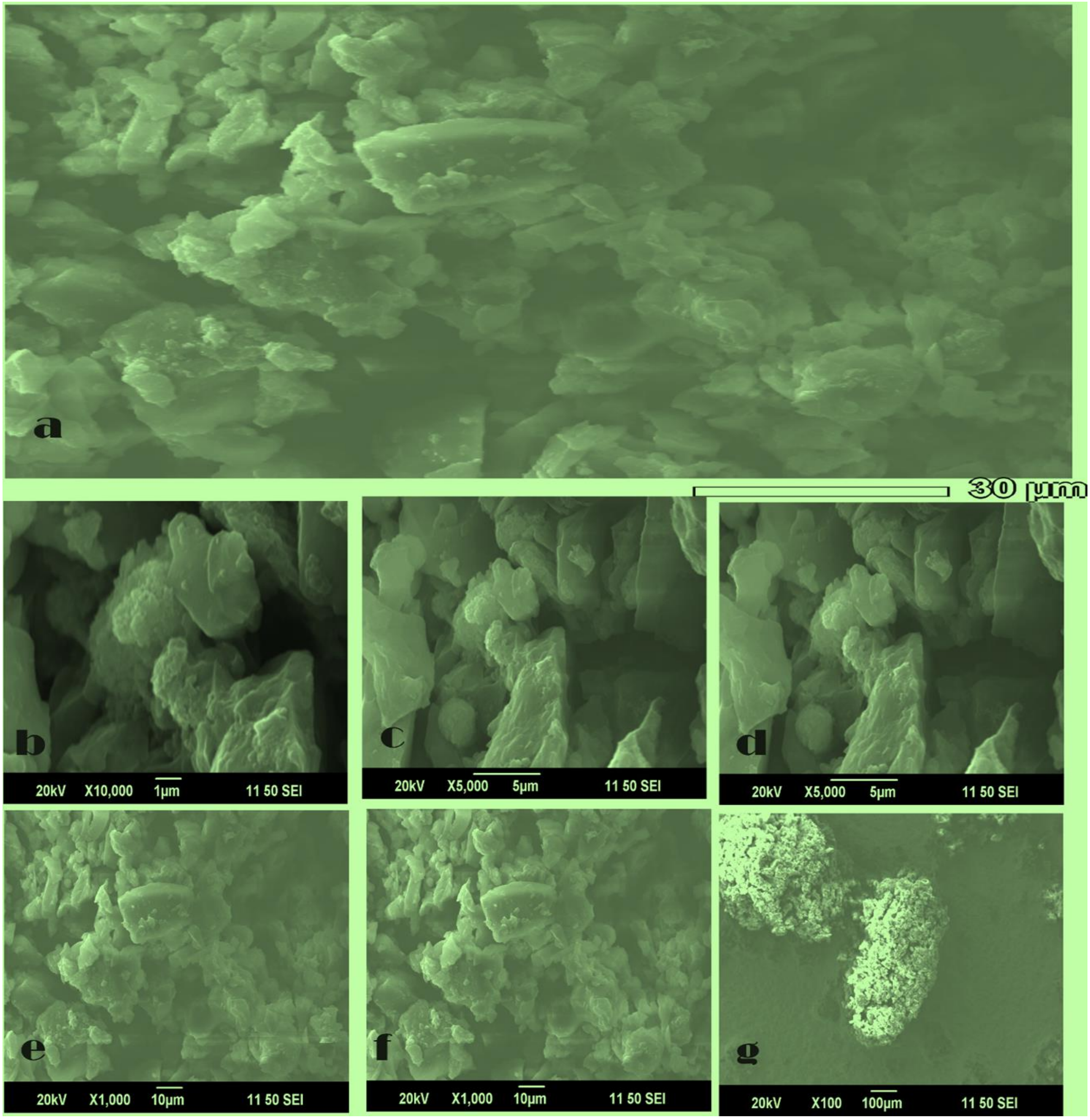

Figure 4.3: Scanning Electron Microscope images of Hangu-Orakzai treated coal for sulfur with 1.5 molar solution of NaOH

4.6 X-Ray Diffractive (XRD) Analysis: XRD results show that Makharwal raw coal sample have three peaks. First peak shows the representative of Silica (SiO_2) which is the dioxide form of silicon and the most generous element in the

Earth's crust. Second peak is the representative of Silicon Sulfide (SiS_2) in which dioxide of sulfur shows enormous extent of sulphur in coal sample, which was formed from the fine powder of silicon covered with sulphur at low temperature that is less than 800 ^{0}C in vacuums surface of coal. The third peak describes the Iron Sulfide (FeS), which shows different crystalline structure. XRD analysis of Makharwal coal samples are represented in figure 4.4. While XRD pattern of the Hangu-Orakzai raw coal samples show that it is amorphous in nature having no apparent or real crystalline form. Amorphous form of Hangu-Orakzai coal samples are represented in figure 4.5. After treatment, XRD result shows no effect on Hangu-Orakzai coal sample structure. It has same amorphous structure while Makharwal coal sample loss its one peak of FeS and also degraded the peak of $SiS_{2.}$ Results are described in figure 4.6 and 4.7

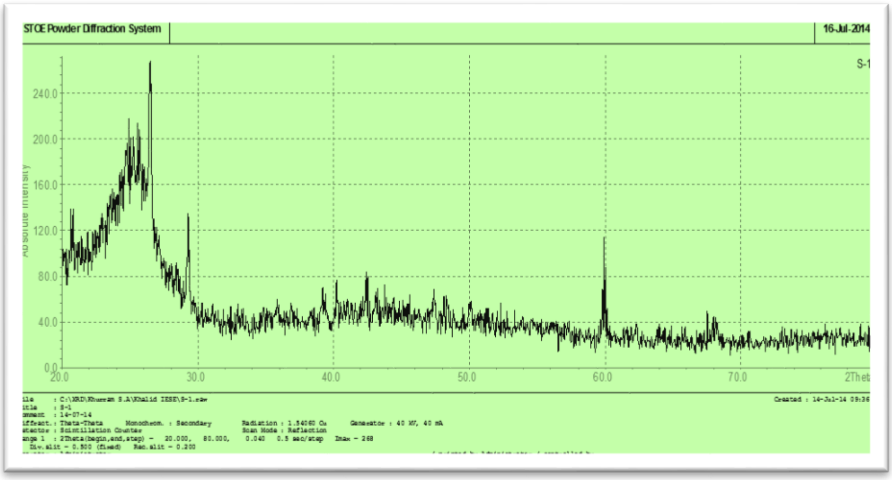

Figure 4.4: XRD pattern of Makharwal coal field sample

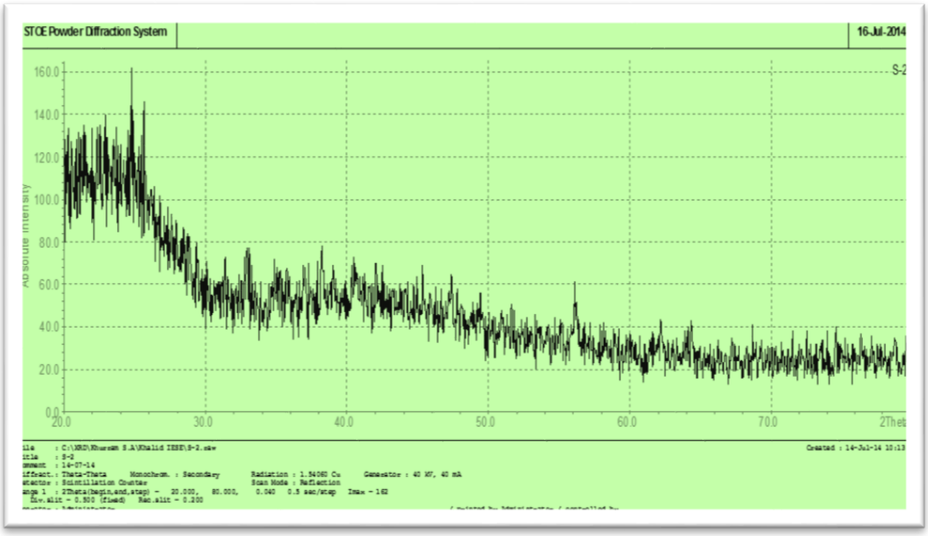

Figure 4.5: XRD pattern of the Hangu- Orakzai coalfield sample

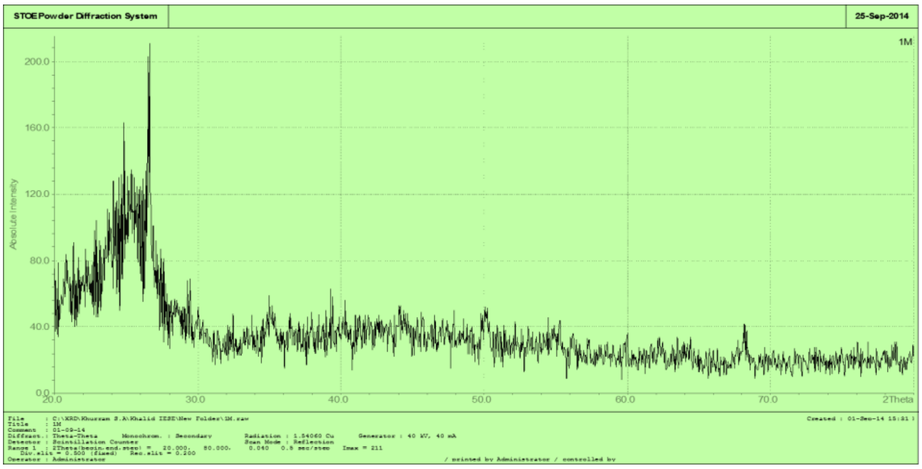

Figure 4.6: XRD pattern of treated Makharwal coalfield sample

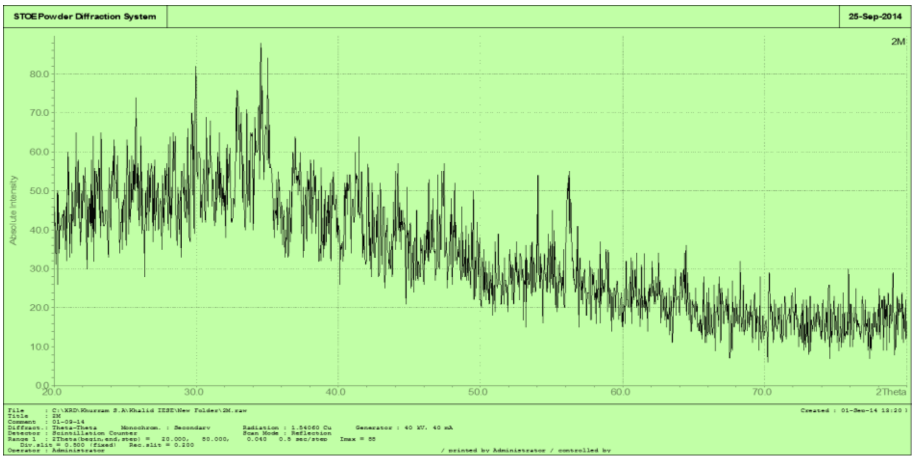

Figure 4.7: XRD pattern of the treated Hangu-Orakzai coalfield

4.7 Thermogravimetric Analysis (TGA) of Hangu-Orakzai Coalfield sample: To compare the effect of nitrogen and air atmosphere on the thermal degradation of coal by combustion, its activation energy calculation was studied. In Nitrogen Atmosphere at heating rate of 10 ^{0}C/min and flow rate of 10 L/min, coal samples started losing their weight after 50 minute and lost 22 percent weight, and kinetic parameters were measured from temperature 600-1000 Kelvin (K). The TGA and regression figure is shown as figure 4.8 and 4.9 and in appendix D1.

While in air atmosphere, same coal starts losing its weight after 85 minutes for the same 22 percent weight loss, when the kinetic parameters were measured from temperature 600-1000 K. The slope and activation energy calculated from TGA and regression graph, are presented in fig 4.10 and 4.11 and in appendix E1.The concluded result from experiments is that, the oxidizing atmosphere (Air) affects thermal degradation as compared to nitrogen, which is according to the findings of Mortari et al. This was due to the fact in the absence of oxygen endothermic reaction occurs first and thermal degradation process start earlier than oxygen atmosphere where endothermic reaction proceed after exothermic reaction.

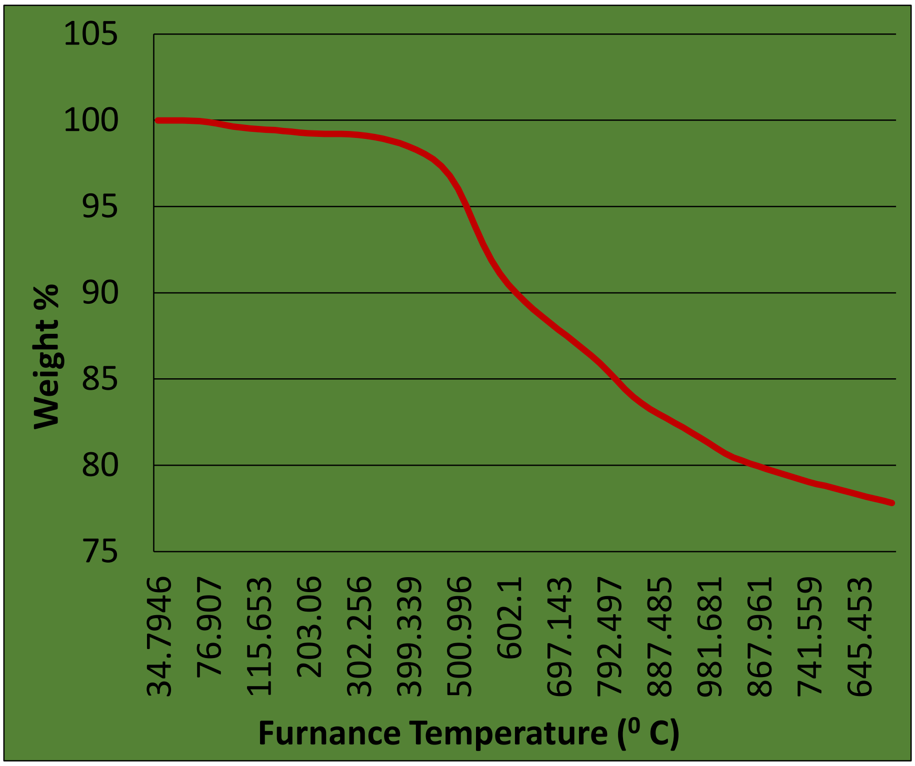

Figure 4.8: TGA Of H/O coal field sample in nitrogen atmosphere

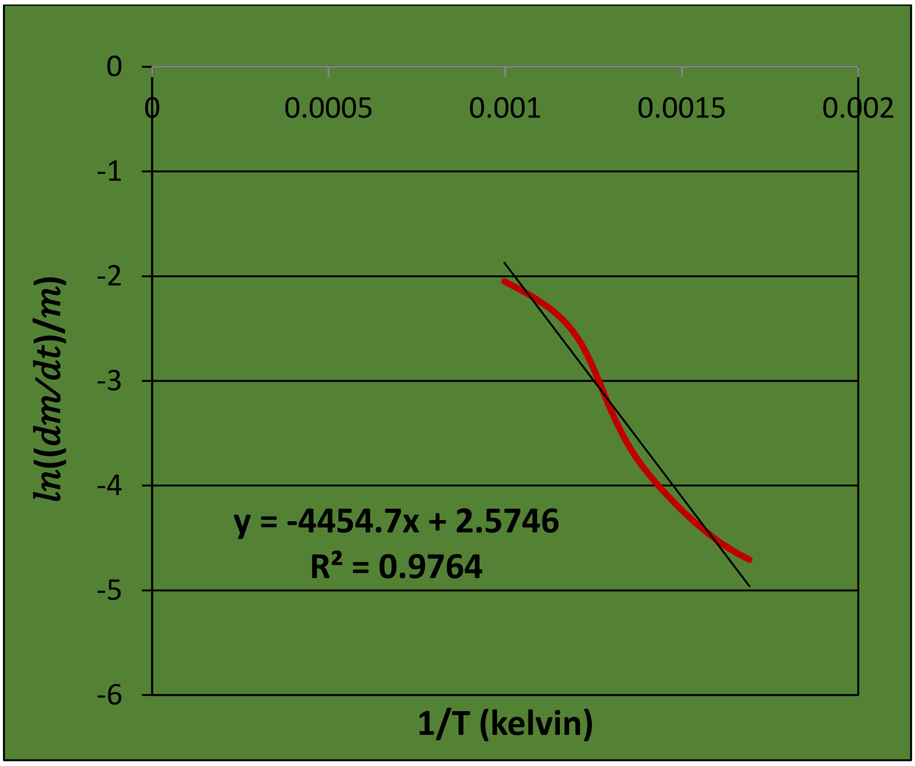

Figure 4.9: Regression figure of Hangu-Orakzai coal in nitrogen

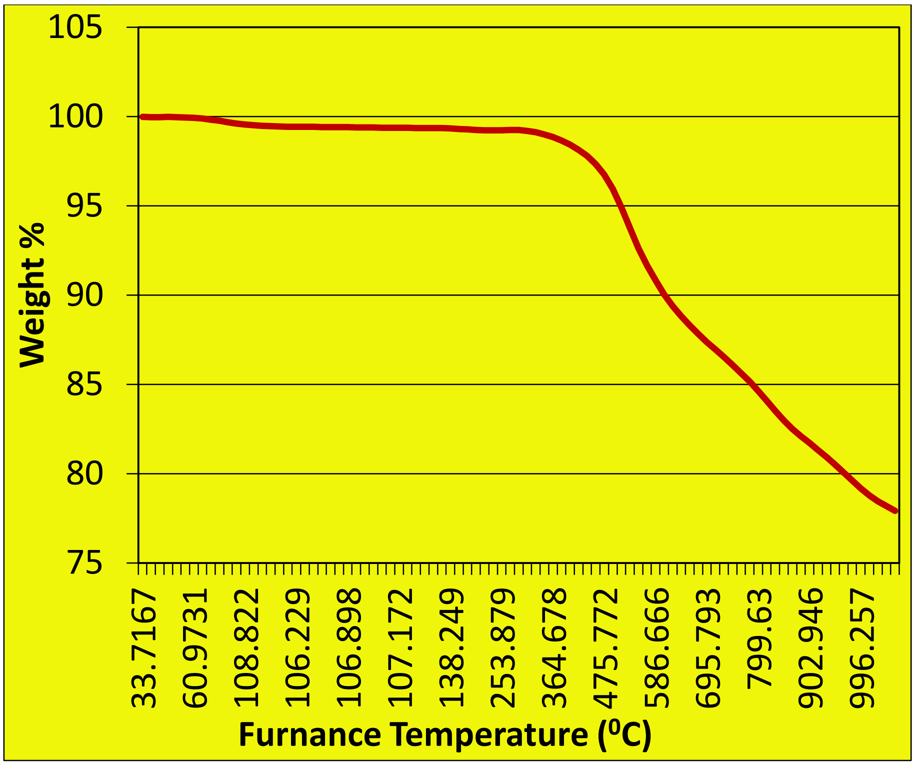

Figure 4.10: TGA Of Hangu-Orakzai coalfield sample in Air atmosphere

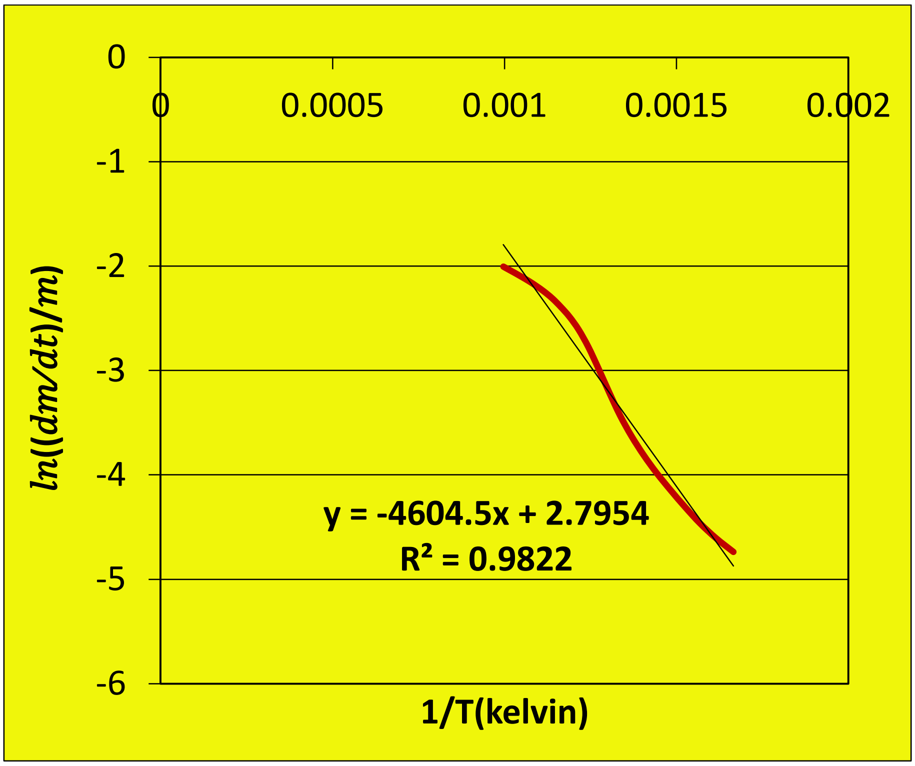

Figure 4.11: Regression of H/O coal in Air atmosphere

4.8 Thermogravimetric Analysis (TGA) of Makharwal coalfield sample:

To know how different coal sample behave when used for thermal degradation in TGA at same heating rate and atmospheric environment. Makharwal coal sample was used, which is different from Hangu-Orakzai coal field in moisture content, ash, fixed carbon and in %volatile matter. In nitrogen atmosphere, with heating rate of 10^0C/min and flow rate of 10 L/min, raw coal sample started losing its weight just after 16 minutes and 45 % weight loss was noted. The TGA and regression figures are illustrated in figure 4.12 and 4.13 and in appendix D2.

So in comparison with Hangu-Orakzai coalfield sample which takes a time of 50 minutes in nitrogen atmosphere, this sample started losing its weight in one third of the time span. The concluded result is that coal having more moisture content goes through thermal degradation quickly, because its loses moisture when temperature reaches 100-350 ^{0}C and difference between weight loss in Hangu-Orakzai and Makharwal coal field sample is due to presence of more organic carbon. The coal sample which have more organic carbon display more weight loss when undergo primary and secondary devolitalization compares to other samples when heated up to 1000 ^{0}C.

While in Air atmosphere, samples start losing its weight after 24 minutes and lost about 45 percent weight after heating at 1000 ^{0}C, and parameters of kinetic is measured from temperature 600-1000 K. The slope and activation energy is calculated from TGA and regression graph, which is presented in fig 4.14 and 4.15 and in appendix E2. The concluded result from experiment is that, the different atmosphere does affect weight loss and activation energy depending up on the rank of the coal.

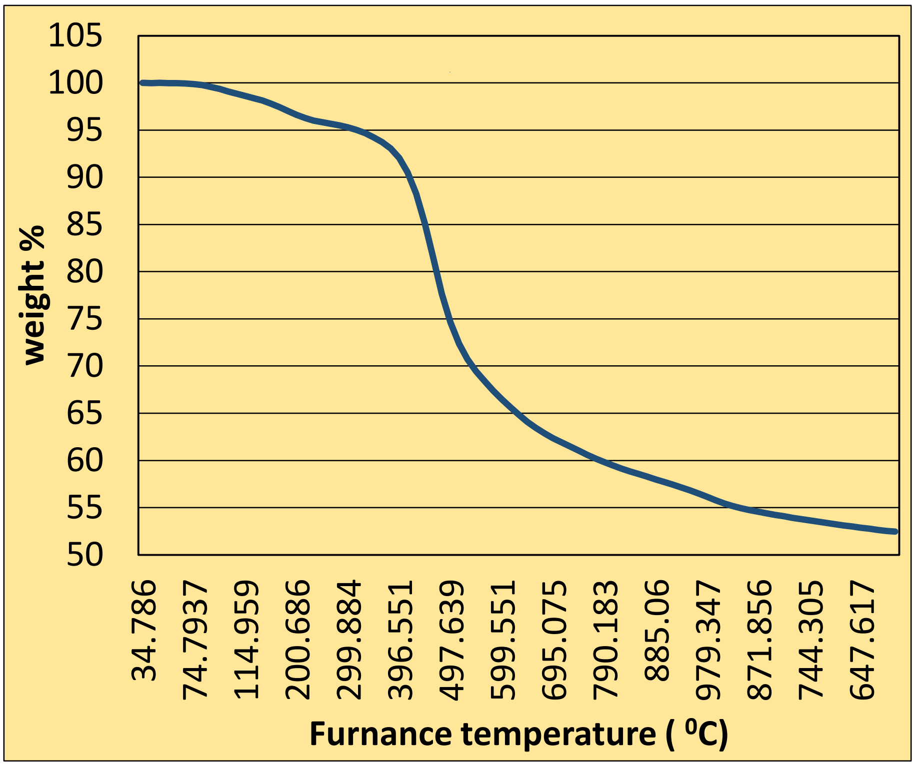

Figure 4.12: TGA of Makharwal coal field sample in Nitrogen atmosphere

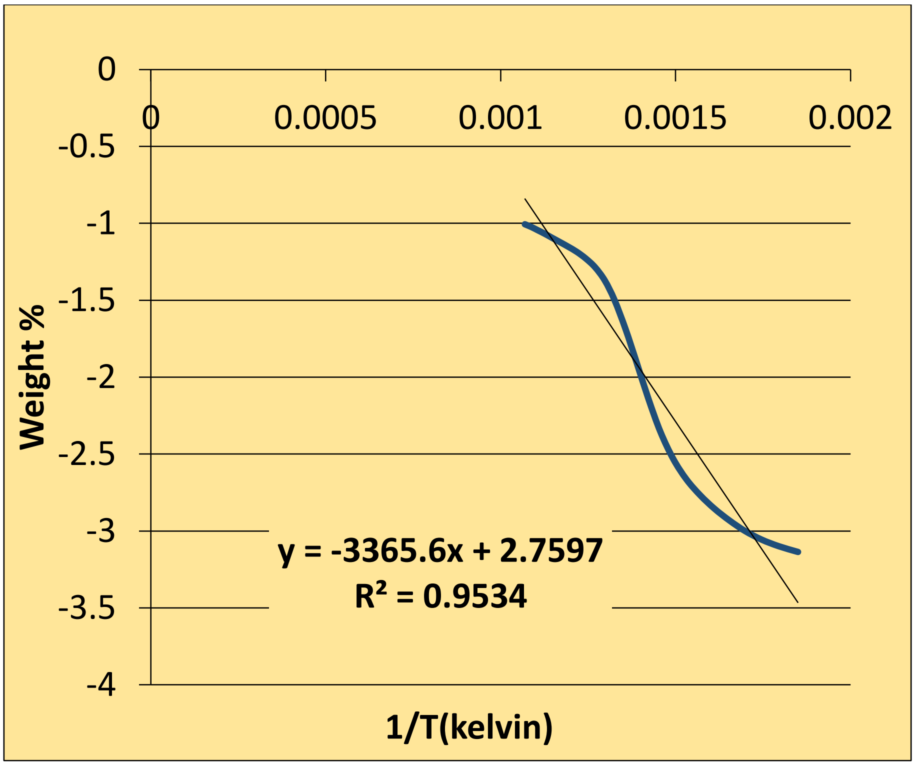

Figure 4.13: Regression of Makharwal coal in Nitrogen atmosphere

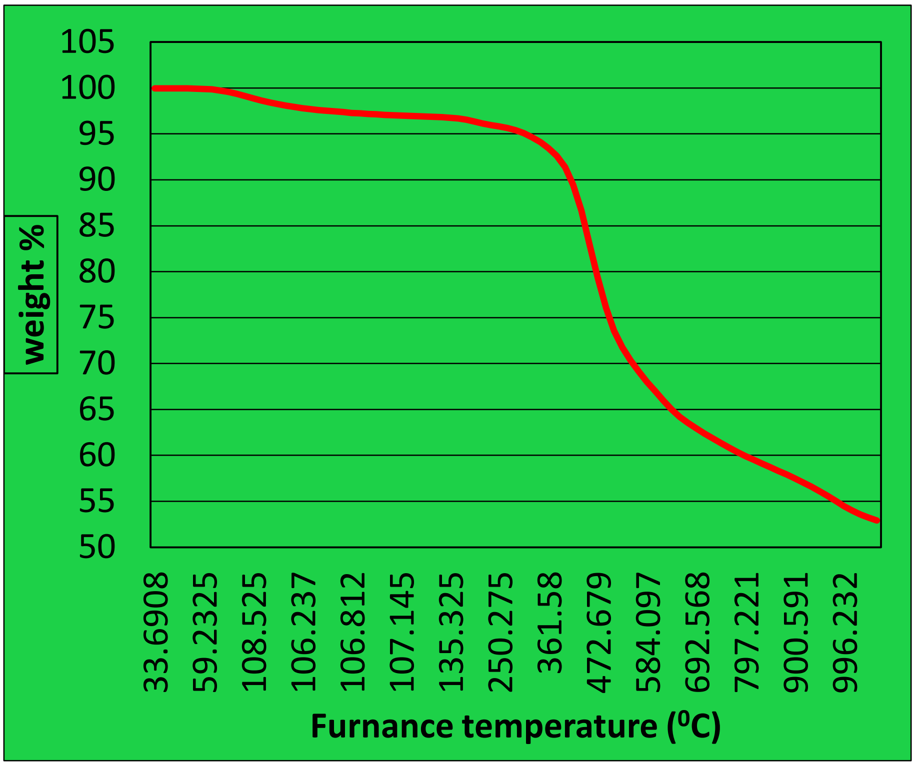

Figure 4.14: TGA of Makharwal coal field sample in Air atmosphere

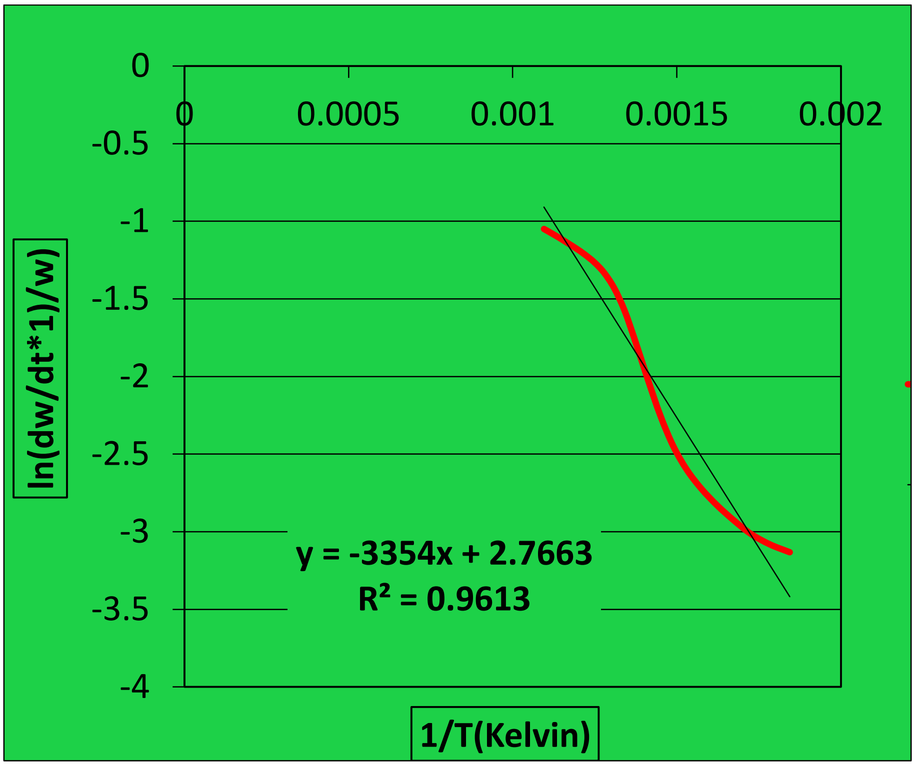

Figure 4.15: Regression figure of Makharwal coal in Air atmosphere

In Appendix H, values of furnace temperature in Kelvin, and inverse of furnace temperature, and ln ((dw/dt*1)/w) data are shown. The activation energy found from these values is described in table 4.5.

Table 4.5: Activation energy of two coal field sample with inert and oxidizing atmosphere

Makharwal (nitrogen)	Hangu/Orakzai (Nitrogen)	Makharwal (Air)	Hangu/Orakzai (Air)
E=2.303×8.34×3365	E=2.303×8.34×4454	E=2.303×8.34×3354	E=2.303×8.314×4604
E=64430 J/mol	E=85281 J/mol	E=64219 J/mol	E=88153J/ mol
E=65 kJ/mol	E=85 kJ/mol	E=64 kJ/mol	E=88 kJ/mol

4.9 Comparative study of Hangu-Orakzai coalfield sample with different heating rate: To know which heating rate is best for combustion and thermal degradation of coal and can reduce the activation energy of the coal in air atmosphere when air flow rate is kept constant at 10 L/min, the Hangu-Orakzai coal sample is combusted in TGA at heating rates of 10, 25, 40 ^{0}C/min. The concluded result is that at low heating rate, thermal decomposition starts later but has best activation energy as compared medium and high heating rates.

We know from proximate analysis that Hangu-Orakzai coal sample have approximately zero moisture content. The thermal degradation starts when temperature reached up to 300 ^{0}C. At heating of 10^{0}C/minute, the coal sample took more time to achieve the thermal degradation whereas heating at 40 ^{0}C/min showed a fast thermal degradation. The heating rate provided in 10 ^{0}C/min upto 300 ^{0}C achieved late as compared to 25 and 40 ^{0}C/min as represented in figure 4.16 and in appendix F1 and F2.

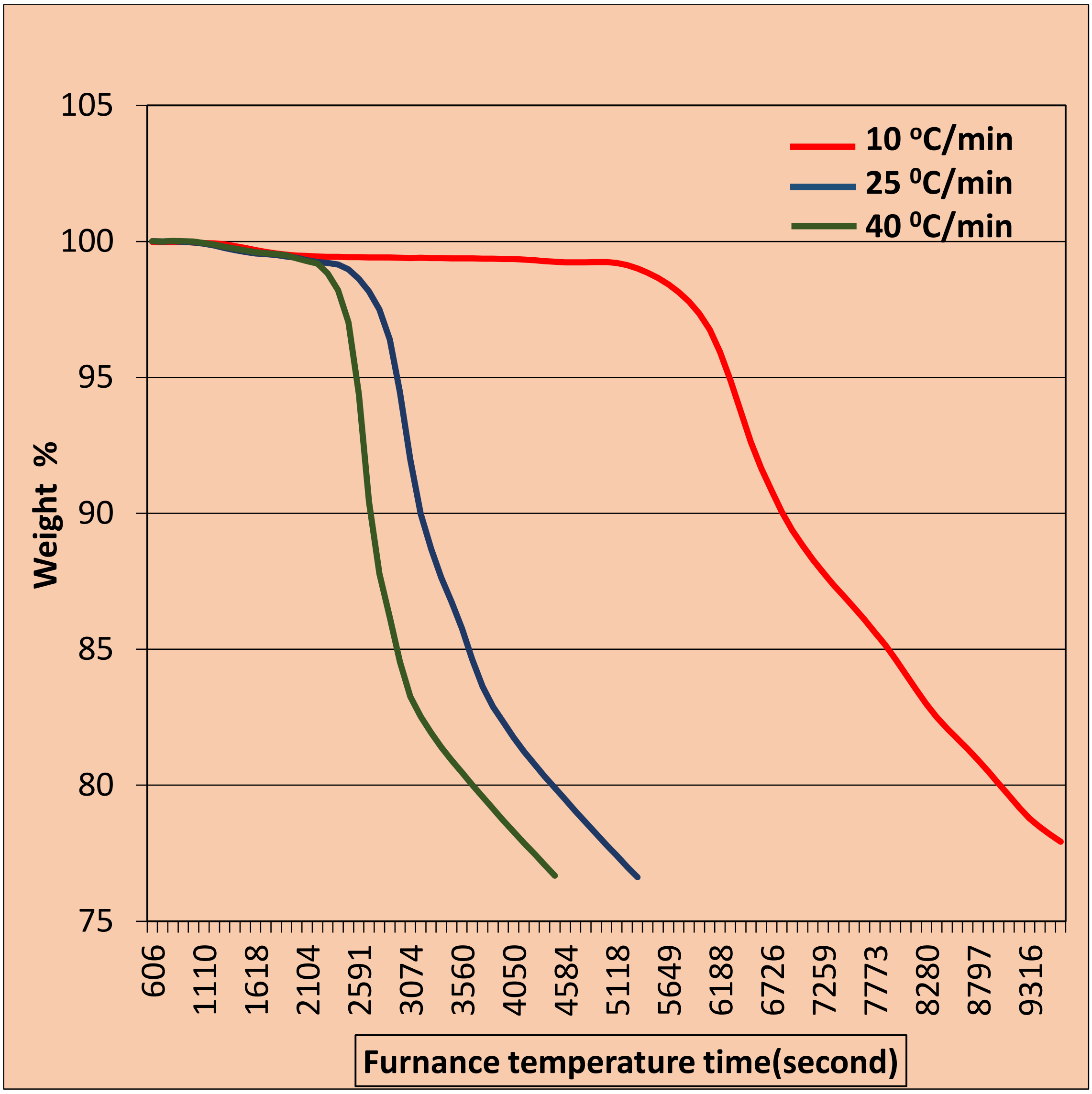

Figure 4.16: Comparison of H/O coalfield sample with different heating rate

4.10 Comparative study of Hangu-Orakzai coalfield sample with different flow rate of Air at heating rate of 25 ^{0}C/min: To study the impact of gas flow rate when heating is kept contact at 25^{0}C/min, the Hangu-Orakzai coalfield sample was combusted in TGA at atmospheric air pressure of 10, 7 and 3.5 L/min. The results indicate that a slight increase in the weight loss was observed at higher air flow rate. This is matching the numerical values of the activation energy shown in Table 4.6 and in appendix G1 and G2 which showed higher activation energy at higher flow rate.

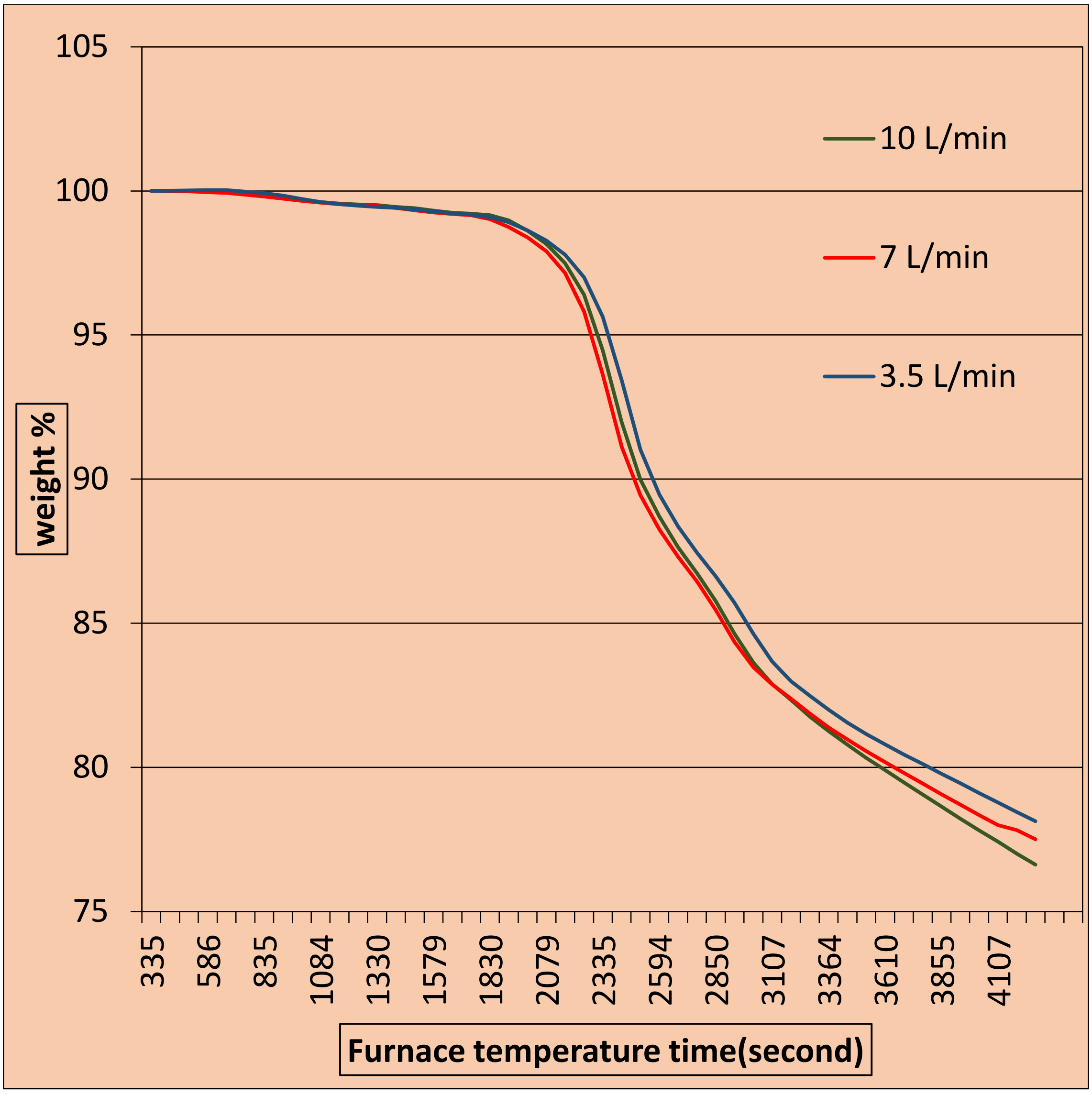

Figure 4.17: Comparison of H-O coalfield sample with different flow rate of oxidizing atmosphere

4.11 Comparison of Raw and best treated Hangu-Orakzai coal field sample with best optimized condition: TGA analysis of best desulphurized Hangu-Orakzai coalfield sample shows a change in the thermal characteristics of the coal due to the chemical modification in the structure. In particular, the treated coal samples resulted in higher thermal degradation and hence reported, lower activation energy.

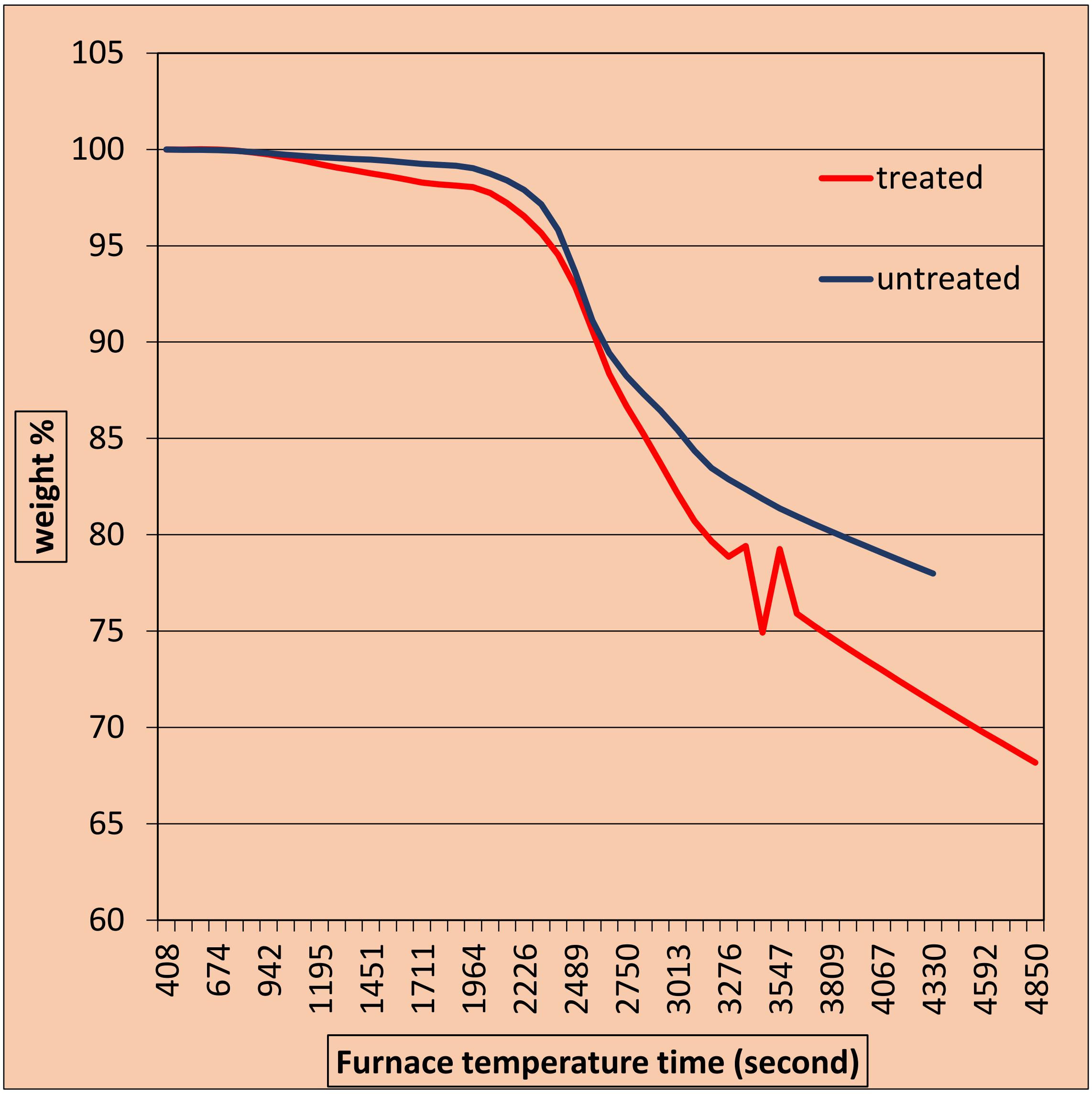

Figure 4.18. TGA of Hangu-Orakzai coalfield raw and treated sample with same flow rate 7 L/min and heating rate 25 ^{0}C/min in oxidizing air atmosphere

Table 4.6: Calculated activation energy of all Thermogravimetric analyses

Sample	Gas flow rate (L/min)	Heating rate (^{0}C/min)	Temp (K)	R^2	Slope	E(kJ/mol)
Makharwal	Nitrogen(10)	10	600-1000	0.95	3365	65
Makharwal	Air (10)	10	600-1000	0.96	3354	64
Hangu/Orakzai	Nitrogen(10)	10	600-1000	0.976	4454	85
Hangu/Orakzai	Air (10)	10	600-1000	0.982	4604	88
Hangu/Orakzai	Air (10)	25	600-1000	0.940	4077	78
Hangu/Orakzai	Air (10)	40	600-1000	0.885	3499	67
Hangu/Orakzai	Air (7)	25	600-1000	0.976	3846	73
Hangu/Orakzai	Air (3.5)	25	600-1000	0.977	3628	69
Treated Hangu/Orakzai	Air (7)	25	600-1000	0.977	3301	63

Chapter No. 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions:

Hangu-Orakzai and Makharwal coalfield samples have higher sulfur and ash content.

Sodium hydroxide having 1.5M solution desulfurize Hangu-Orakzai coalfield sample more as compared to other tested molar solutions and samples.

Structurally Hangu-Orakzai coal has amorphous nature while Makharwal coal has crystalline nature due to the presence of SiO_2, SiS_2 and FeS observed on X-ray diffractive analyzer.

SEM confirms its morphology as irregular shaped. Hangu-Orakzai have collotelinite, parallel lamination, surface covered debris micrinite and Makharwal have plate, rounded and rod-like cylinder shapes. Sulfur treated Hangu-Orakzai coal sample have spongi like structure same as vessels of xylem plant. The porous condition in Hangu-Orakzai and treated coal sample is wide because of morphological spongy like structure while Makharwal coal sample have non porous structure of collotelinite.

Nitrogen atmosphere for thermal combustion is better than Air atmosphere because oxygen starts molecular reactions along with combustion.

Coal TGA has showed that both heating rates and atmospheric flow rates have an impact on the degradation of coal. Low heating rates degrade coal sample in more time and vice versa. Different flow rates have different activation energies.

For protection of environment, desulfurization of coal not only cleans the combustion emissions but also help in its degradation at less required activation energy. Some irrelevant result at high temperature is due to the presence of sodium in desulfurized coal sample which have boiling point of 860 ^{0}C.

5.2 Recommendations:

I like to say at NUST or IESE study should be done on following topics as Pakistani Industry wants to adopt coal as future fuel source. Like but not least

1. Coal blending with various biomasses to find the impact on energy required for thermal degradation of coal blends.

2. Analysis of gases produced from coal combustion and gasification.

3. Coal combustion performance in various type of reactors.

4. Development of Liquid fuels from Hangu-Orakzai and Makharwal coalfield sample and their environmental analysis on burning.

APPENDIXES

Appendix A: XRF Analysis of Hangu-Orakzai coal sample treated for sulfur removal with Sodium Hydroxide (NaOH) at ambient temperature:

Table A1: XRF analysis of Hangu-Orakzai coal sample treated with 0.5 M NaOH

Quantitative result

Element	ms%	mol%	Sigma
16 S	24.2416	33.8749	0.8976
20 Ca	16.6408	18.6030	0.1381
22 Ti	6.8660	6.4225	0.0614
23 V	0.0432	0.0380	0.0501
26 Fe	49.4050	39.6374	0.0415
38 Sr	2.3424	1.1978	0.0644
40 Zr	0.4610	0.2264	0.0775

Table A2: XRF analysis of Hangu-Orakzai coal sample treated with 1 M NaOH

Quantitative result

Element	ms%	mol%	Sigma
16 S	13.0944	19.6141	0.9425
20 Ca	16.6760	19.9831	0.1233
22 Ti	6.1792	6.1958	0.0561
26 Fe	61.3609	52.7705	0.0418
38 Sr	1.7366	0.9519	0.0725
40 Zr	0.6195	0.3262	0.0872
44 Ru	0.3334	0.1584	0.2969

Table A3: XRF analysis of Hangu-Orakzai coal sample treated with 3 M NaOH

Quantitative result

Element	ms%	mol%	Sigma
16 S	18.6640	26.8478	0.8195
19 K	1.4555	1.7169	0.2321
20 Ca	17.2410	19.8407	0.1224
22 Ti	6.2739	6.0412	0.0546
26 Fe	52.8668	43.6621	0.0378
30 Zn	0.5699	0.4021	0.0508
38 Sr	1.8716	0.9852	0.0607
40 Zr	0.4368	0.2209	0.0730
44 Ru	0.6206	0.2832	0.2499

Table A4: XRF analysis of Hangu-Orakzai coal sample treated with 5 M NaOH

Quantitative result

Element	ms%	mol%	Sigma
16 S	28.5656	38.8350	1.0704
20 Ca	16.9641	18.4501	0.1768
22 Ti	6.1778	5.6221	0.0781
23 V	0.5979	0.5116	0.0637
25 Mn	0.5489	0.4356	0.0532
26 Fe	44.8364	34.9968	0.0511
38 Sr	2.3093	1.1489	0.0756

Appendix B: **XRF Analysis of Makharwal coal sample treated for sulfur removal with Sodium Hydroxide (NaOH) at ambient temperature:**

Table B1: XRF analysis of Makharwal coal sample treated with 0.5 M NaOH

Quantitative result

Element	ms%	mol%	Sigma
16 S	13.5512	21.3170	1.1917
20 Ca	1.5351	1.9319	0.1371
22 Ti	0.6699	0.7054	0.0454
26 Fe	83.9419	75.8128	0.0429
30 Zn	0.3019	0.2329	0.0853

Table B2: XRF analysis of Makharwal coal sample treated with 1 M NaOH

Quantitative result

Element	ms%	mol%	Sigma
16 S	9.2246	14.9642	1.3795
20 Ca	1.3575	1.7617	0.1471
22 Ti	0.6445	0.6999	0.0491
23 V	0.0610	0.0623	0.0403
26 Fe	88.3774	82.3130	0.0485
38 Sr	0.3350	0.1988	0.1179

Table B3: XRF analysis of Makharwal coal sample treated with 3 M NaOH

Quantitative result

Element	ms%	mol%	Sigma
16 S	7.9171	12.9260	1.4149
20 Ca	1.7796	2.3244	0.1481
22 Ti	0.6496	0.7100	0.0496
26 Fe	89.6536	84.0396	0.0500

Table B4: XRF analysis of Makharwal coal sample treated with 5 M NaOH

Quantitative result

Element	ms%	mol%	Sigma
16 S	11.0056	17.6482	1.6567
20 Ca	1.1517	1.4774	0.1815
26 Fe	87.8428	80.8744	0.0583

Appendix C: XRF Analysis of Hangu-Orakzai and Makharwal coal sample treated for sulfur removal with Sodium Hydroxide (NaOH) at 50 ^{0}C temperature:

Table C1: XRF analysis of Hangu-Orakzai coal sample treated with 5 M NaOH at 50 ^{0}C

Quantitative result

Element	ms%	mol%	Sigma
16 S	21.4941	30.2528	0.9716
19 K	1.6145	1.8633	0.2848
20 Ca	17.3072	19.4878	0.1505
22 Ti	6.7531	6.3626	0.0670
26 Fe	50.6049	40.8937	0.0458
38 Sr	1.8861	0.9714	0.0713
40 Zr	0.3402	0.1683	0.0857

Table C2: XRF analysis of Hangu-Orakzai coal sample treated with 3 M NaOH at 50 ^{0}C

Quantitative result

Element	ms%	mol%	Sigma
16 S	10.9594	17.6361	1.5117
20 Ca	1.3020	1.6762	0.1699
26 Fe	86.8295	80.2236	0.0536
44 Ru	0.9091	0.4641	0.5076

Table C3: XRF analysis of Makharwal coal sample treated with 5 M NaOH at 50 ^{0}C

Quantitative result

Element	ms%	mol%	Sigma
16 S	9.6382	15.5909	1.6014
20 Ca	1.5974	2.0672	0.1722
22 Ti	0.5931	0.6422	0.0573
26 Fe	87.2849	81.0648	0.0562
29 Cu	0.4916	0.4013	0.1203
38 Sr	0.3947	0.2336	0.1364

Table C4: XRF analysis of Makharwal coal sample treated with 1 M NaOH

Quantitative result

Element	ms%	mol%	Sigma
16 S	12.2006	19.4264	1.5281
20 Ca	1.7254	2.1978	0.1751
22 Ti	0.7739	0.8249	0.0583
26 Fe	84.1637	76.9401	0.0548
38 Sr	0.4739	0.2761	0.1276
44 Ru	0.6625	0.3346	0.5073

Appendix D: Thermogravimetric analysis of Hangu-Orakzai and Makharwal coal sample at 10 ^{0}C/min in nitrogen atmosphere of 10 L/min.

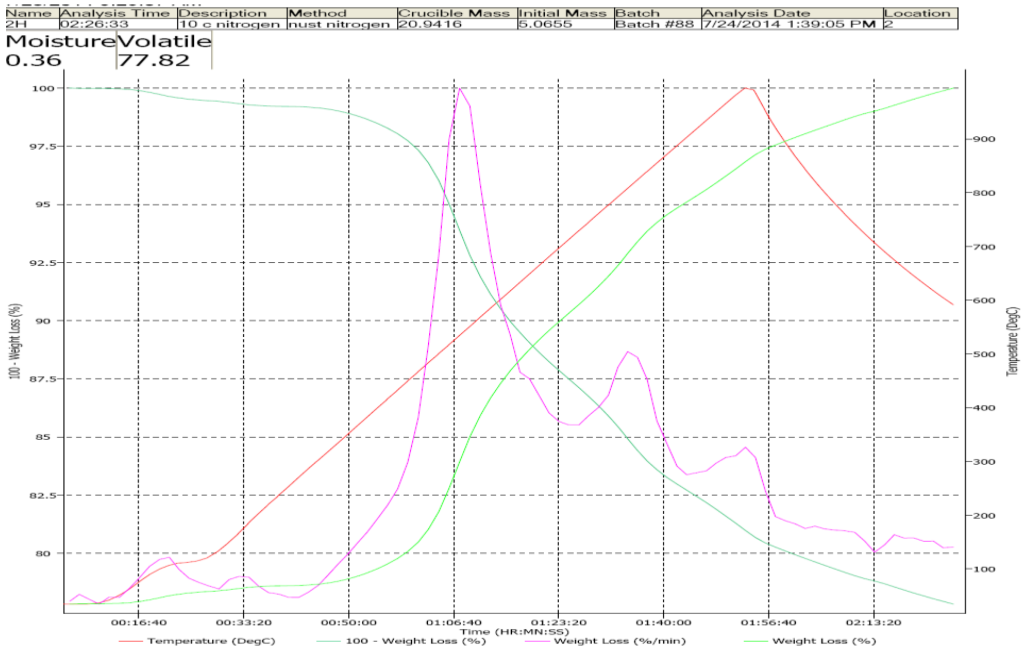

Figure D1: TGA of Hangu-Orakzai at nitrogen atmosphere of 10 l/min at 10 ^{0}C/min

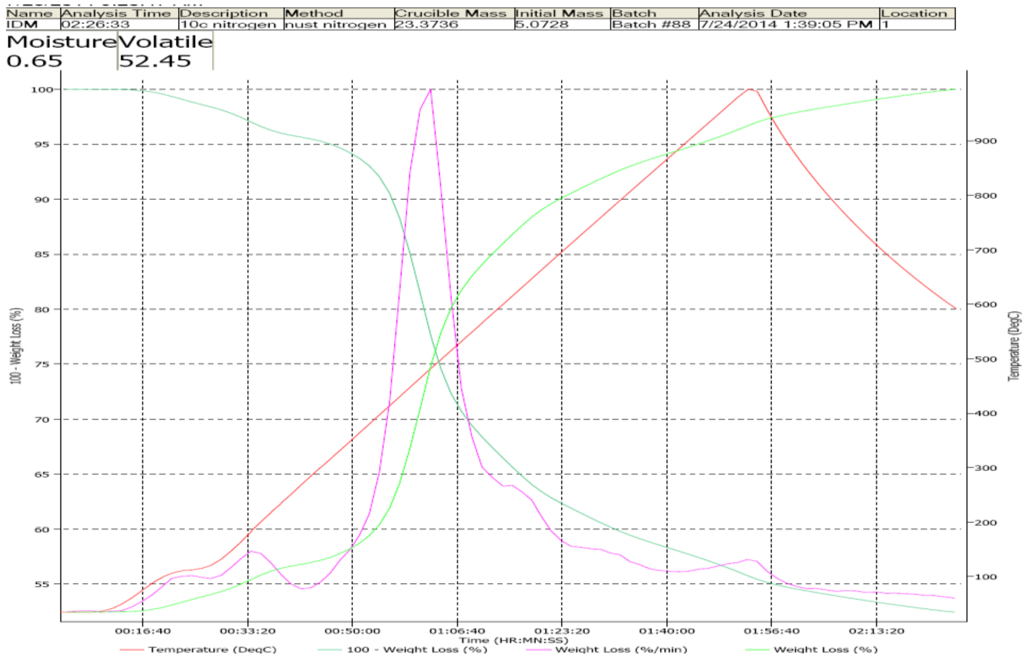

Figure D2: TGA of Makharwal coal sample at nitrogen atmosphere of 10 l/min at 10 ^{0}C/min

Appendix E: Thermogravimetric analysis of Hangu-Orakzai and Makharwal coal sample at 10 ^{0}C/min in Air atmosphere of 10 L/min.

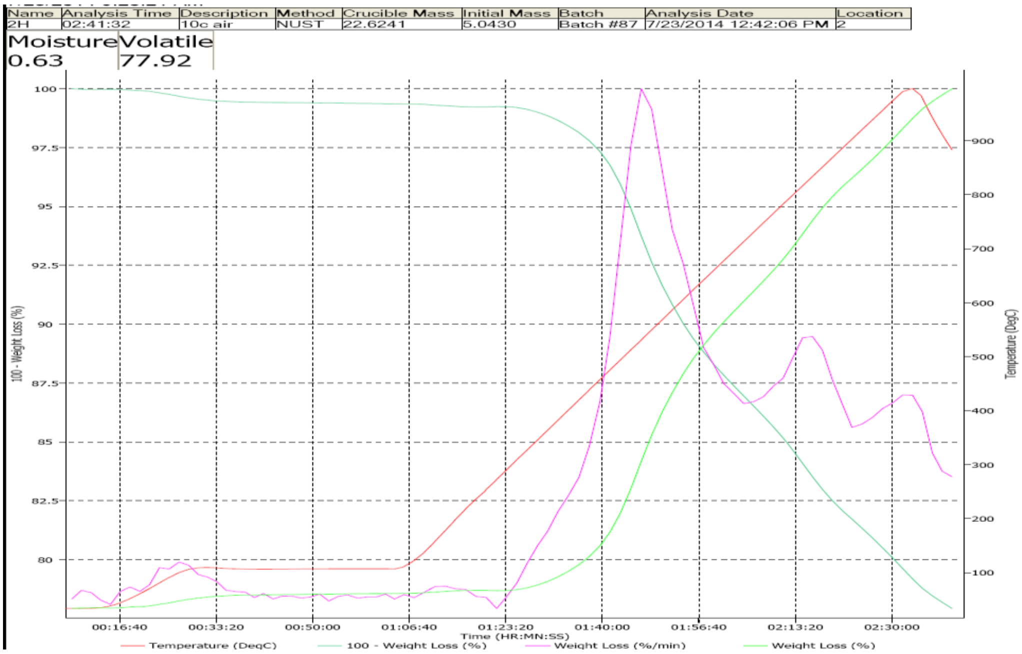

Figure E1: TGA of Hangu-Orakzai coal sample in air atmosphere of 10 l/min at 10 ^{0}C/min

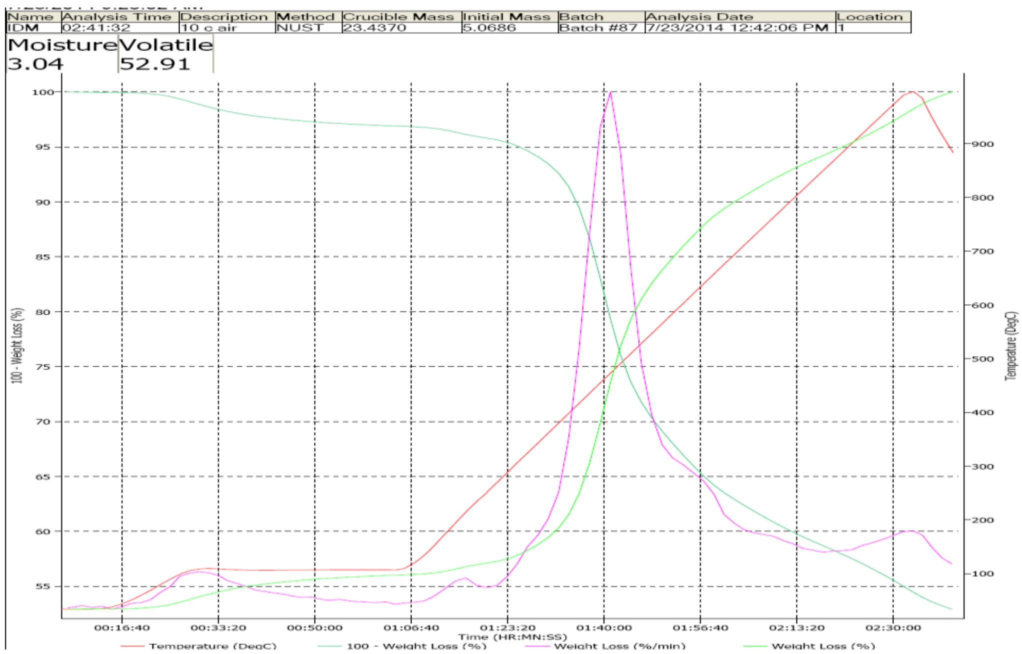

Figure E2: TGA of Makharwal coal sample in air atmosphere of 10 l/min at 10 ^{0}C/min

Appendix F: Thermogravimetric analysis of Hangu-Orakzai coal sample at 25 and 40 ^{0}C/min in Air atmosphere of 10 L/min.

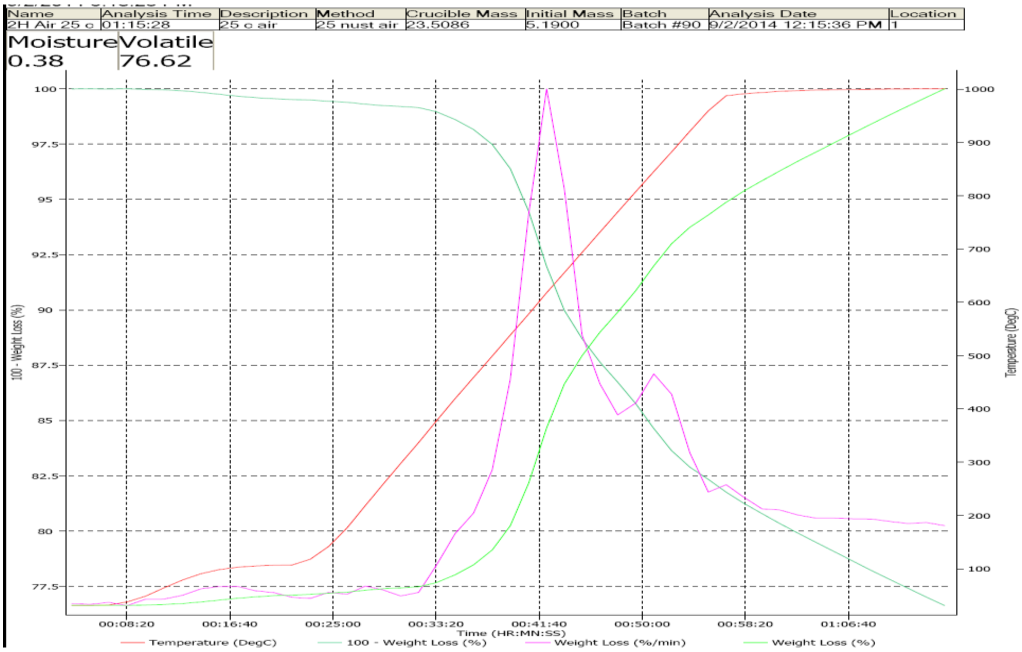

Figure F1: TGA of Hangu-Orakzai coal sample in air atmosphere of 10 l/min with heating rate of 25 ^{0}C/min

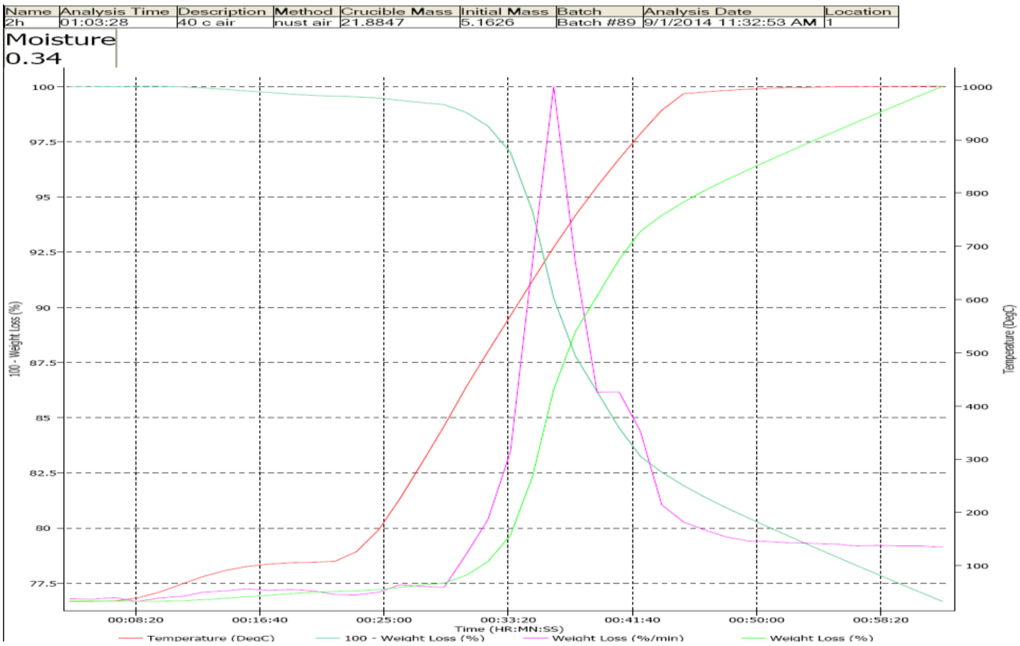

Figure F2: TGA of Hangu-Orakzai coal sample in air atmosphere of 10 l/min with heating rate of 40 ^{0}C/min

Appendix G: Thermogravimetric analysis of Hangu-Orakzai coal sample at 25^0C/min in Air atmosphere of 3.5 and 7 L/min.

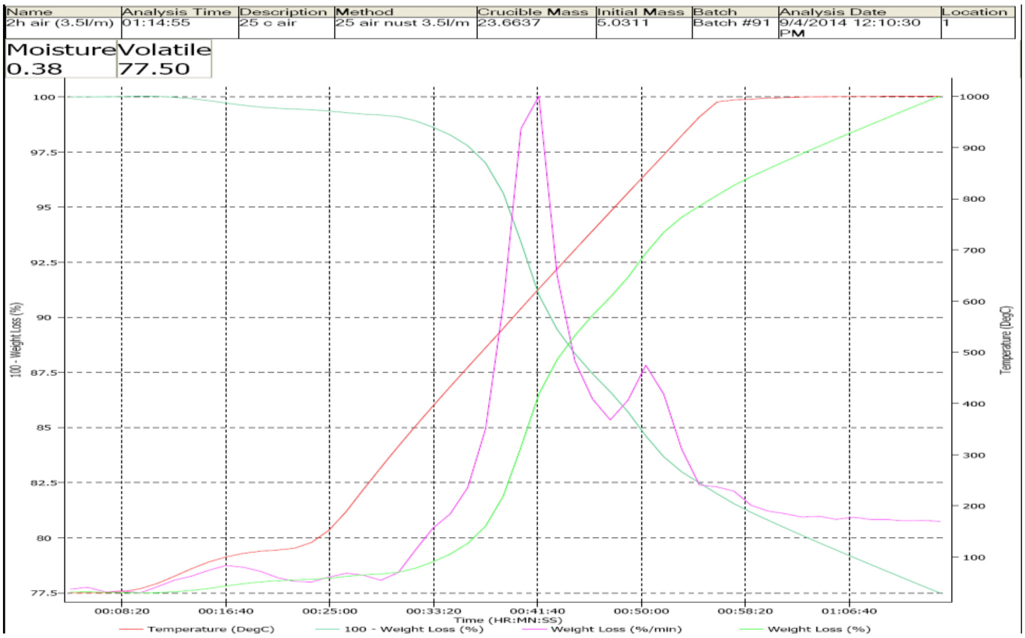

Figure G1: TGA of Hangu-Orakzai coal sample in air atmosphere of 3.5 L/min with heating rate of 25 ^{0}C/min

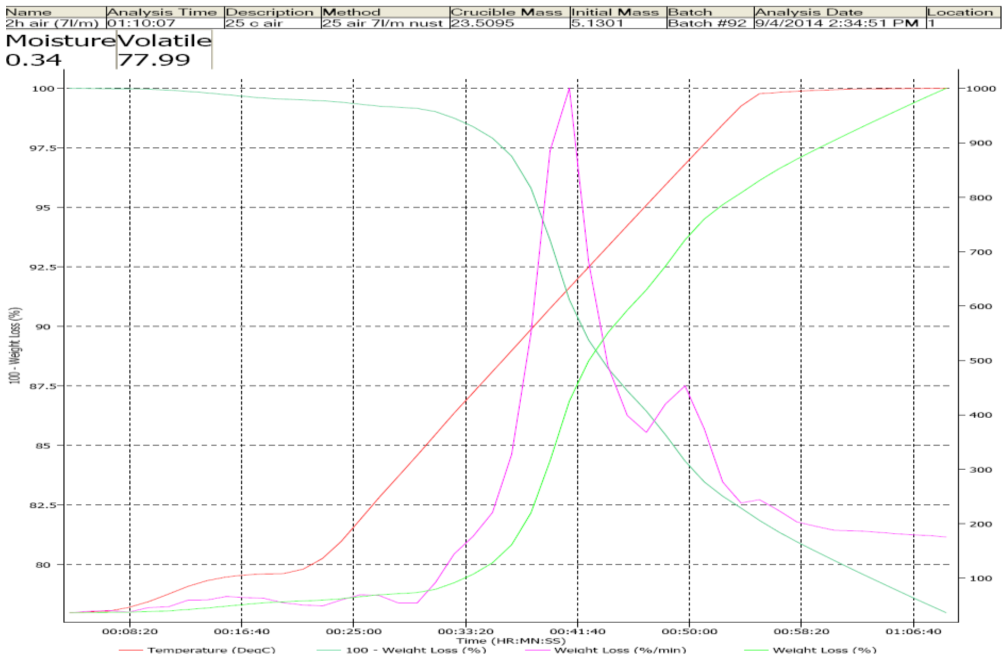

Figure G2: TGA of Hangu-Orakzai coal sample in air atmosphere of 7.0 L/min with heating rate of 25 ^{0}C/min

Appendix H: Values to find activation energy.

Table H1: Calculation for finding activation energy

Hangu (Air Atmosphere)		Hangu (Nitrogen Atm)		Makharwal (Air)		Makharwal (Nitrogen)	
1/T(K)	**ln(dw/dt*1)/w)**	**1/T(k)**	**ln(dw/dt*1)/w)**	**1/T(K)**	**ln (dw/dt*1)/w)**	**1/T(K)**	**ln (dw/dt*1)/w)**
0.001665	-4.73757079	0.00169	-4.707126503	0.00184	-3.132397715	0.0018499	-3.136181252
0.001615	-4.605919467	0.00165	-4.626424466	0.00178	-3.082000654	0.0017951	-3.098943988
0.001568	-4.463523065	0.0016	-4.53142728	0.00173	-3.013531749	0.0017456	-3.055518372
0.001525	-4.307602141	0.00156	-4.427224858	0.00167	-2.924902956	0.0016982	-2.999527466
0.001484	-4.149259142	0.00153	-4.315018665	0.00162	-2.830907904	0.0016539	-2.931633224
0.001443	-3.98450768	0.00149	-4.192305853	0.00158	-2.725543317	0.0016106	-2.854284796
0.001405	-3.812598574	0.00145	-4.063386739	0.00153	-2.603769919	0.0015705	-2.767964232
0.001369	-3.625735655	0.00142	-3.931970643	0.00149	-2.450695386	0.0015313	-2.665441963
0.001336	-3.42786071	0.00138	-3.79018155	0.00145	-2.252082111	0.0014935	-2.532725566
0.001304	-3.205897904	0.00135	-3.624452189	0.00141	-2.013848577	0.0014565	-2.355326804
0.001273	-2.976765289	0.00132	-3.438727924	0.00137	-1.773988316	0.0014221	-2.139522811
0.001243	-2.772902371	0.00129	-3.223931081	0.00134	-1.576394896	0.0013883	-1.903057578
0.001215	-2.607133947	0.00126	-2.999162149	0.00131	-1.42953177	0.0013568	-1.687275137
0.001189	-2.48383003	0.00124	-2.79554133	0.00128	-1.330329993	0.0013252	-1.498200698
0.001163	-2.38941285	0.00121	-2.631935351	0.00125	-1.264228952	0.0012976	-1.371827512
0.001139	-2.308307434	0.00119	-2.512455869	0.00122	-1.214966346	0.0012696	-1.285110556
0.001115	-2.242497086	0.00116	-2.422507791	0.00119	-1.1751489	0.001243	-1.228402118
0.001093	-2.190453553	0.00114	-2.354022608	0.00117	-1.139562416	0.0012177	-1.185576394
0.001072	-2.145128455	0.00112	-2.299619495	0.00114	-1.107881112	0.0011928	-1.151617574
0.001052	-2.105908728	0.0011	-2.253642559	0.00112	-1.077813099	0.0011687	-1.121127873
0.001032	-2.069190266	0.00108	-2.211848995	0.0011	-1.049973565	0.0011461	-1.093096528
0.001014	-2.036734605	0.00107	-2.174323813	0.00107	-1.026956965	0.0011264	-1.068384778
0.000997	-2.004705196	0.00105	-2.140763907	0.00105	-1.008724054	0.0011064	-1.045244048
0.00098	-1.972892932	0.00103	-2.108779728	0.00104	-0.99272911	0.0010875	-1.023672734
0.000963	-1.93984657	0.00101	-2.079601554	0.00102	-0.977666261	0.0010691	-1.005972034
0.000947	-1.90760139	0.001	-2.049750709	0.001	-0.963812201	0.0010509	-0.990884976
0.000932	-1.873514141	0.00098	-2.020184443	0.00098	-0.950579427	0.001033	-0.977275575
0.000918	-1.837876709	0.00097	-1.990522652	0.00097	-0.937366269	0.0010166	-0.965533498

Table H2: Calculated data of H/O coal field sample at 10, 25 and 40 ^{0}C/min

Hangu-Orakzai coal field sample at heating rate 10 ^{0}C, 25 ^{0}C and 40 ^{0}C at temperature 600-1000 ^{0}C.					
10 ^{0}C		25 ^{0}C		40 ^{0}C	
1/T	ln(dw/dt*1)/w	1/T	ln(dw/dt*1)/w	1/T	ln(dw/dt*1)w
0.001716	-4.832973326	0.001753	-4.840783665	0.001765	-4.929640732
0.001665	-4.73757079	0.00164	-4.774103763	0.001574	-4.811718454
0.001615	-4.605919467	0.001538	-4.577807969	0.001409	-4.444165903
0.001568	-4.463523065	0.001445	-4.281320132	0.001289	-4.021090383
0.001525	-4.307602141	0.001366	-3.99717248	0.001187	-3.513481812
0.001484	-4.149259142	0.001295	-3.686218996	0.001101	-2.878438246
0.001443	-3.98450768	0.001232	-3.32260434	0.00103	-2.346368761
0.001405	-3.812598574	0.001175	-2.893664975		
0.001369	-3.625735655	0.001122	-2.521899734		
0.001336	-3.42786071	0.001077	-2.300906503		
0.001304	-3.205897904	0.001035	-2.180217029		
0.001273	-2.976765289				
0.001243	-2.772902371				
0.001215	-2.607133947				
0.001189	-2.48383003				
0.001163	-2.38941285				
0.001139	-2.308307434				
0.001115	-2.242497086				
0.001093	-2.190453553				
0.001072	-2.145128455				
0.001052	-2.105908728				

Table H3: Calculated data of H/O coal field sample at 25 ^{0}C/min of Air flow 3.5 and 7 L/min

Hangu coal sample in Air atmosphere 10 L/min		**Hangu coal sample in Air atmosphere 7 L/min**		**Hangu sample in Air atmosphere 3.5 L/min**	
1/T(K)	**ln(dw/dt*1)/w**	**1/T(K)**	**ln(dw/dt*1)/w**	**1/T(K)**	**ln(dw/dt*1)/w**
0.001833	-4.887736035	0.001671	-4.776421247	0.001698	-4.707371254
0.001774	-4.880731348	0.00157	-4.625559645	0.00159	-4.521325484
0.001716	-4.832973326	0.001478	-4.378783898	0.001497	-4.288106511
0.001665	-4.73757079	0.0014	-4.125364752	0.001417	-4.059450503
0.001615	-4.605919467	0.001328	-3.865602313	0.001344	-3.810035171
0.001568	-4.463523065	0.001264	-3.556876229	0.001279	-3.508105761
0.001525	-4.307602141	0.001205	-3.172677111	0.00122	-3.130869526
0.001484	-4.149259142	0.001151	-2.753084179	0.001165	-2.720693289
0.001443	-3.98450768	0.001103	-2.421150184	0.001115	-2.409935365
0.001405	-3.812598574	0.001059	-2.247907532	0.001069	-2.249584756
0.001369	-3.625735655	0.001017	-2.140882997	0.001028	-2.150593886
0.001336	-3.42786071	0.00098	-2.063662685	0.00099	-2.074955618
0.001304	-3.205897904	0.000945	-1.998709841	0.000954	-2.011453975
0.001273	-2.976765289	0.000913	-1.927627303	0.000922	-1.945743163
0.001243	-2.772902371	0.000882	-1.854897372	0.000892	-1.872264784
0.001215	-2.607133947	0.000854	-1.800235288	0.000863	-1.812429633
0.001189	-2.48383003	0.000829	-1.764776798	0.000836	-1.771163039
0.001163	-2.38941285	0.000806	-1.735982342	0.000811	-1.742141077
0.001139	-2.308307434	0.000792	-1.707149974	0.000792	-1.714492919
0.001115	-2.242497086	0.00079	-1.680552676	0.00079	-1.68987278
0.001093	-2.190453553	0.000789	-1.658570385	0.000789	-1.668784601
0.001072	-2.145128455	0.000788	-1.63806375	0.000788	-1.649786061
0.001052	-2.105908728	0.000787	-1.618458476	0.000787	-1.631949405
0.001032	-2.069190266	0.000786	-1.599764848	0.000786	-1.615028511
0.001014	-2.036734605	0.000786	-1.581647663	0.000786	-1.598191392
0.000997	-2.004705196	0.000786	-1.563762117	0.000786	-1.582309245
0.00098	-1.972892932	0.000786	-1.546693187	0.000786	-1.56562679
0.000963	-1.93984657	0.000785	-1.529504441	0.000785	-1.549783173
0.000947	-1.90760139	0.000785	-1.513491571	0.000785	-1.534738687

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