An Investigation into the Thermal Behavior of Tharparker Coal

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Summary: Four coal samples from the Islam Kot, (Tharparkar) were characterized by Thermogravimetric (TG) analysis. Thermal decompositions were carried out in inert (pyrolysis) and air (combustion) atmosphere at temperature range 25-1000 ^{0}C. Characteristic temperatures were determined from the burning profiles. Burning profile could provide a valuable rapid laboratory method of ranking coal in terms of burn out performances. Burning profile data were compared with volatile results. A comparison of the total H/C release from raw and de-mineralized coal were made. The effect of sample amount, pyrolysis atmosphere, Nitrogen and Helium, particle size, heating rate and gas flow rate were studied. Peak temperature and burn out temperature were slightly decreased as the particle size decreased.

Introduction

Coal is an alternative form of energy, and the uses of coal are mainly for power generation by thermal power plants, household heating and the other industrial branches. The physical and chemical properties of coal and material derived from coal are of considerable importance in industrial coal utilization. For example in combustion gasification and steel making processes [1]. The characterization of coal is vital for the efficient operation of a power plant for electricity generation. Various methods are used for this purpose e.g. proximate analysis, determining petrographic constituents, reflectance and thermal analysis. Thermogravimetry (TG) and differential thermogravimetry (DTG) are the methods widely used in characterization of fossil fuels undergoing combustion or pyrolysis [2].

Thermogravimetry (TG) is widely used to investigate rate processes. This method involve the continuous measurements of the change in mass or rate of mass loss, DTG, of a sample with temperature or time. Such Date has been used to determine kinetic parameters such as activation energy and order of reaction. Thermogravimetric analysis (TGA) studies are useful tools for determination of combustion characteristics (e.g. peak temperature burnt out temperature and activation energy) of coals and chars and other combustible materials [3-7]. The producer is strongly affected by particle size, ash content, sample amount, heating rate and gas flow rate [8-9]. The intrinsic reactivity of a coal char may conveniently be measured at low temperature where mass transfer limitation is not an issue. Many combustion (or oxidation) kinetic measurements of chars have been obtained using Thermogravimetric analysis (TGA). Which is a common way of measuring intrinsic reactivity because of low temperature range for this process typically < 1000 ^{0}C. In TGA the weight of a char sample is determine as a function of time and temperature as it is subjected to controlled temperature. TGA experiment are usually carried out in two ways

Isothermal where the sample is heated at a constant temperature [10-17] and linear heating where the sample is heated at a constant rate [18-23]

Cumming *et al.*, [24] has developed a method for describing the reactivity or combustibility of solid fuel such as lignite, bituminous coals and petroleum coke in terms of weighted mean apparent activation energy derived from TGA / SDTA reading on 20 mg sample heated at constant rate in a flowing air atmosphere. He proposed that mean activation energy is the established method, which involves recording overall temperature on the burning profile.

The main objective of this study is to compare the thermal analysis (burning profile and volatile profile) data of Tharparker coal. The present steady also cover the effect of particle size, sample amount, on the thermal properties of the Coals.

Results and Discussions

Burning profile

Thermogravimetric analysis is the method which is extensively used for characterizing fossil

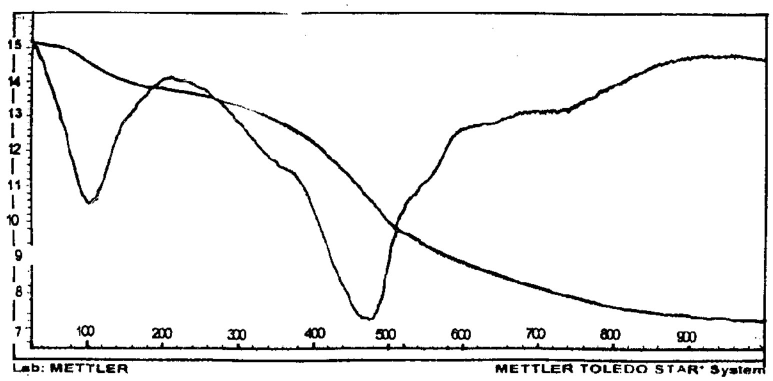

Fig. 1: TG/DTG curve of Islam Kot coal (pyrolysis)

fuel undergoing combustion (burning) and (pyrolysis) volatile. Combustion of coal is obtained when coal is heated in an oxidizing atmosphere. The TG/ DTG curve of representative coal is reported in Fig. 1. The TG/ DTG curve of the entire coal sample in oxidizing atmosphere show two peaks. The first peak in the temperature region below 120 °C is due to loss of moisture content of the coal. The moisture contents were calculated ranged, from 4.1 % to 5 % as shown in Table-1. The amount of water evolved from the coal illustrates the coal rank. Coal having great porosity will have higher amount of moisture content indicating the rank of coal. The second peak illustrated the de-volatilization of organic matter of the coal which appearing in the temperature region 300 –720 °C. The main characteristics point of the DTG curve is the peak temperature (PT) and burnt temperature (BT). The peak temperature is the temperature at which the rate of weight loss is maximum. This variable is mainly used for analyzing the combustibility. Burnt out temperature represents the temperature where sample oxidation is complete. The characteristics temperature of the coal sample derived from the combustion profile are reported in Table-1. The low value of peak temperature classified the coal as belongs to low rank class.

Volatile profile

Volatile profile plays an important role in gasification and coking studies processes. It is widely used for identifying and comparing the coal samples. A volatile profile is that when coal is heated in inert atmosphere. The derivative weight changes illustrate the progressive thermal break down of organic matter present in the coal and evolution of gaseous processes. The coal studied in inert atmosphere shows

Table-1: Thermogravimetric Characteristics of Therparkar Coal

Pyrolysis	Peak Temp.	Burn out Temp.	Moisture (wt %)	Volatile (wt %)
TopSeam1	485	780	4.8	47
Middle Seam 1	465	775	5	47
TopSeam1	472	800	4.7	49
Middle Seam 1	460	765	4.5	50
Combustion:				
TopSeam1	520	720	4.5	76
Middle Seam 1	522	665	4.1	75
TopSeam1	525	675	4.3	76
Middle Seam 1	522	683	4.4	77

similar trend in behavior. The TG/ DTG curves of representative coal are given in Fig. 2. Two peaks were observed in thermogram. The first temperature range 25-120 °C represents the region where elimination of water occurs. Loss of volatile materials due to primary and secondary devolatiliza-tion occurs within the range of 300-780 °C.

The amount of volatile matter = weight of moisture – weight of residue

The estimated amount of volatile content ranged form 47 % to 50 % are presented in Table-1

Effect of Minerals

Under identical condition as used for raw coal pyrolysis and combustion of de-mineralized coal were carried out. The volatile materials from each coal were computed. The results are given in Table-2. The comparison of the results clearly indicates that the removal of inherent mineral from each coal increases the volatile material. The observed increase in the volatile material was attributed to the enhance volatilization of condensable organic component due

Table-2: Effect of Demineralization on Thermo gravimetric Properties of Coals.

Combustion	Peak Temp 1	Peak Temp.2	Burnout Temp1	Burn out Temp2	Moisture (wt %)	Volatile (wt %)
TopSeam 1	340	575	460	740	0.8 %	75
Middle Seam 1	360	570	465	730	1 %	72
TopSeam 1	350	575	455	750	1.5 %	73
Middle Seam 1	345	573	450	720	1.2 %	76
Pyrolysis						
TopSeam 1	350	580	440	575	1.2	54
Middle Seam 1	350	560	430	570	0.8	55
TopSeam 1	360	550	440	575	1.6	53
Middle Seam 1	340	575	460	573	0.9	56

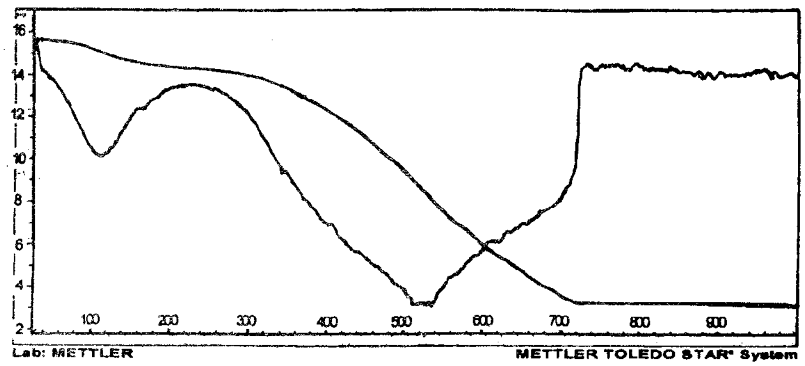

Fig. 2: TG/DTG curve of Islam Kot coal (combustion).

Table-3: Concentration of Metals in Coal Samples

Name of Matel		Cu	Mn	Cr	Zn	Fe	Na	K
Top Seam 1	Concentration in(ppm)	1.01	10.98	2.43	4.86	2801.0	338.16	338.28
Middle Seam1		0.93	10.73	2.36	4.28	2546.1	317.59	313.33
Top Seam 2		0.993	10.567	2.250	4.108	2719.3	324.87	297.29
Middle Seam 2		1.12	11.05	2.36	4.27	2926.0	329.58	315.78

to the removal of cations from the coal. The concentration of Fe, Na, K, were found significantly high than other metal in the coal samples .The results are reported in Table-3. Thermograms of the burning profile of the demineralized coal show three peaks. The thermogram of the representative coals are shown in Fig. 3. The first small peak occurs at temperature below 120 °C is due to elimination of water. The second peak is appearing at temperature range 240 –450 °C is due to release of lower hydrocarbon . The third temperature range 460 – 740 °C is due to loss of higher molecular weight hydrocarbon.

Effect of Particle Size

In order to observe the effect of sample size on burning profile. The burning of coal samples were carried out over the temperature range 25 - 1000 °C using 100 - 250 mesh sample size. The results are reported in Table-4. The thermogram of all the size ranges show slight difference in peak and burnout temperatures and residue amount depending on the mineral materials and fixed carbon content. Peak temperature decreases slightly as the particle size is decreased. Lower peak temperature indicates more easily burn out sample. The increased surface area of the samples due to decrease in size allowed more rapid start ignition. The burnt out temperature decreases slightly as the particle size decrease. Ozbas *et al.*, [25] in their study of thermal decomposition of coal observed similar results.

Effect of Pyrolysis Atmosphere

To Study the effect of pyrolysis atmosphere on nature of volatile material produced. The pyrolysis of coal was carried out in nitrogen atmosphere and

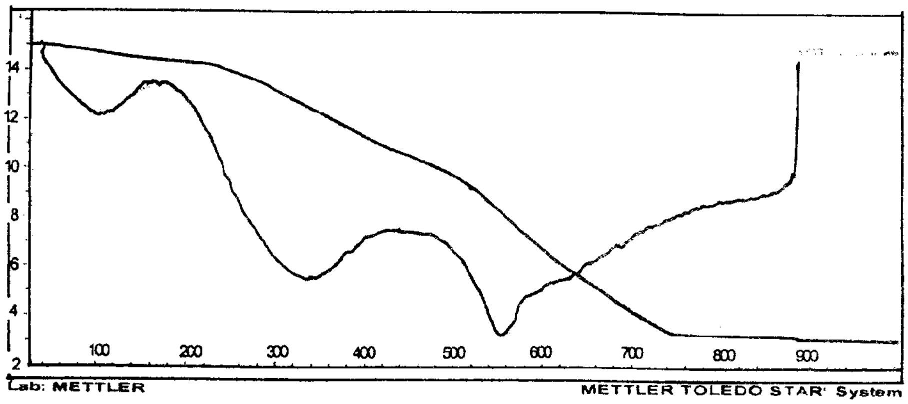

Fig. 3: TG /DTG curve of Islam Kot Demineralization coal (combustion).

Table-4: Effect of Sample Size on Thermal Properties of coal

S. #	Sample size	Peak Temp.	Burn out Temp.	Residue %
Top Seam 1	Feed	485	780	48
	0.150mm	482	776	48
	0.106mm	479	777	48
	0.075mm	471	770	45
Middle Seam 1	Feed	465	765	48
	0.150mm	469	775	48
	0.106mm	464	770	48
	0.075mm	462	767	47
Top Seam 2	Feed	472	766	43
	0.150mm	473	795	43.8
	0.106mm	472	790	43
	0.075mm	467	782	41
Middle Seam 2	Feed	460	765	42.9
	0.150mm	461	762	42
	0.106mm	555	760	40
	0.075mm	450	757	41

helium atmosphere. The results are given in Table-5. From the results it is clear that no significant changes in burning profile of volatile profile were observed. When the atmosphere was change from nitrogen to helium. This is consistent with the work reported by

Ozbas *et al.*, [25] in similar work reported that the pyrolysis atmosphere has no effect on the volatile material from the decomposition of coal.

Effect of Sample Amount

A coal sample of 10 – 15 mg was pyrolyzed over the temperature range 25 - 1000 °C. The purpose was to study the effect of sample amount on volatile materials of coal. The results are presented in Table-6. In examination of these results illustrated that a slight increase in volatile material was

Table-5: Effect of Pyrolysis Atmosphere on Thermo gravimetric Characteristics of Coal.

Pyrolysis	Peak Temp.	Burn out Temp.	Moisture (wt %)	Volatile (wt %)
Nitrogen				
Top Seam1	485	781	3.7	48
Middle Seam 1	465	764	4.0	47
Top Seam 2	472	798	4.1	50
Middle Seam 2	460	765	3.6	49
Helium:				
Top Seam 1	482	779	3.1	50
Middle Seam 1	467	765	3.7	49
Top Seam 2	475	795	4.0	51
Middle Seam 2	460	770	3.8	48

Table-6. Effect of sample amount on Thermo gravimetric Properties of Coal

Top Seam 1 Weight (mg)	Peak Temp.	Burn out Temp.	Moisture (wt %)	Volatile (wt %)
10	360	595	4.0	72
11	350	495	4.7	71
12	550	710	3.1	85
13	550	730	3.7	77
14	580	750	4.1	79
15	580	800	4.0	76

observed with an increase in the sample amount. Peak temperatures and burn out temperatures were slightly affected by changing the sample amount. As the sample amount increased peak temperatures and burn out temperatures were linearly increased.

Effect of Heating Rate

In order to investigate the effect of heating rate on the burn out and peak temperatures of volatile matter. The heating rate study was carried out in the range of 10-18 °C/ min of coal over the temperature range 25-1000 °C. The results are reported in Table-7. It can be seen from the results that no significant

Table-7: Effect of Heating rate on Thermo gravimetric of Coal.

Heating rate C°/ min	Peak Temp.	Burn out Temp.	Moisture (wt %)	Volatile (wt %)
Top Seam2				
10	540	750	2.1	51
12	560	760	3.7	50
14	550	775	4.1	52
16	540	760	3.2	54
18	545	780	1.3	52

Table-8: Effect of Flow rate on Thermo gravimetric Characteristics of coal

Flow rate ml/ min	Peak Temp.	Burn out Temp.	Moisture (wt %)	Volatile (wt %)
Top Seam 1				
40	460	750	3.1	48
50	485	780	4.0	47
60	497	785	3.8	47
70	520	790	4.0	48
80	540	790	2.3	47

changes were observed in the peak and weight percentage of volatile matter, some linear increase was observed in the burnout temperature, when the heating rate was increased from 10 °C/min to 18 °C/ min. This increased may be due to rapid ignition of fired carbon content and mineral matter

Effect of Flow Rate

To study the effect of temperature the flow rate on the volatile material, the pyrolysis of coal were carried out over the range 25-1000 °C. The flow rate of the nitrogen gas was change from 40 - 80 ml / min. The results are shown in Table-8. From the results it is observed that peak temperature and burn out temperature decreased slightly as the flow rate is increased from 40-80 ml / min.

Experimental

The coal samples used in this study were collected from four different locations in IslamKot (Thurparkar). The samples were crushed by using jaw crusher under closed control and four different fractions (100, 150, 200, 250 mesh) of the samples were obtained. The TGA/ DTG and DTA measurements were carried out in Mettler Toledo TGA/ SDTA 851e thermal analyzer. 10 mg of the coal sample were placed in a platinum crucible and heated at a linear heating rate of 10 °C/min over a temperature range 25-1000 °C. The experiment were performed separately in air and nitrogen at a flow rate of 50 ml/ min. Prior to the experiment TGA/ SDTA unit was calibrated for temperature reading using indium as melting standard. Hitachi Z-5000 polarized Zeeman atomic absorption spectrophotometer with automatic background correction was used for the determination of metal. The analysis were carried out using respective hallow cathode lamps under standard operational condition as given by manufacturer. All the chemicals used were of analytical reagent of the highest purity, and were purchased from BDH limted peol.

Demineralization

2 gm of each coal sample were treated with 25 ml of a mixtuer of perchloric acid and nitric acid (1: 2 ratio) in a Teflon beaker and were shake for 1 hour. The samples were allowed to stand for one week at room temperature. This time was observed to be sufficient for extraction of all type of native mineral content from the coal samples. The coal samples were then washed several times with distilled water to remove last traces of acid mixer from the treated coal. The coal samples were then filter, washed again with distilled water and dried in an oven at 100 °C. These samples were transfer to labeled bottles for further study. The filtrate was treated for different matel.

Conclusions

As the rank of coal increased, peak temperature and burnout temperature of the sample increased. The burning profiles provide a valuable and rapid method of ranking coals in terms of their burnout performance. Peak and burnout temperatures of the sample studied were slightly affected by the change in the particle size; as the particle size decreased peak temperatures and burnout temperature of the sample decreased slightly. TG/ DTG thermograms of all sample showed two reaction regions at two different temperature ranges. First region which is in the range of 250 - 600 °C was found to be due to the combustion of carbon part of the samples and the second peak which is between 630 -740 °C indicated the decomposition of the mineral matter in the sample took place. Comparison of the results of raw and demineralized coal indicates that an increase in the volatile material was observed when inherent minerals from these coal were removed.

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