

THERMAL CHARACTERIZATION AND GASIFICATION KINETICS OF
THRACE-SARAY REGION COAL

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

BETÜL YILDIRIM

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE MASTER OF SCIENCE
IN
PETROLEUM AND NATURAL GAS ENGINEERING

JULY 2015

Approval of the thesis:

**THERMAL CHARACTERIZATION AND GASIFICATION KINETICS OF
THRACE-SARAY REGION COAL**

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ABSTRACT

THERMAL CHARACTERIZATION AND GASIFICATION KINETICS OF THRACE-SARAY REGION COAL

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August 2015, 125 pages

In this thesis being up as-received and washed and dried, two different coal samples from Saray-Edirkoy field were experimented in order to determine effects of different variables as coal type, heating rate, gas flow rate, isothermal duration, gasifying medium, and final gasification temperature, on isothermal gasification profiles of the coal samples.

In the scope of this study, heating rate was changed in the range of 20-50°C/min as 20, 30, 40 and 50°C/min whereas two different gas flow rate values as 60 ml/min and 100 ml/min were used throughout the experiments. Isothermal period was increased from 60 minutes to 120 minutes to determine increased waiting period effect on process at designated temperature of the reaction. Carbon dioxide (CO₂) and dry air were used as gasifying agents whereas nitrogen (N₂) gas was selected as the inert gas. To be in the range of 750-950°C, totally five different final temperature values were tested (750, 825, 850, 900 and 950°C) for calculation of activation energies of the coal samples.

In the study, important parameters for thermal characterization of the samples as reaction intervals for different stages of the gasification process, weight changes occurred in these reaction intervals, peak temperatures where maximum mass losses of the specified

intervals occur, and the ignition temperatures were determined from thermogravimetry/differential thermogravimetry (TG/DTG) curves by TA Universal Analysis software program. As a result, for carbon dioxide gasification experiments, three reaction regions were identified which were matched with moisture loss, volatile matter release and gasification steps. On the other hand, for some of the dry air gasification experiments, four reaction intervals were observed which were correlated with free moisture loss, devolatilization, combustion of light volatile matter and some part of the char, and gasification steps respectively.

In kinetic analysis session, first order Arrhenius kinetic model was used as a result of which activation energies (E_a) of the samples were calculated under both carbon dioxide and dry air atmospheres as two different gasification environments. In both environments, washed and dried coal sample was found to be more reactive than as received coal. Moreover, activation energies of both samples were found to be lower under dry air atmosphere than those determined under carbon dioxide gas.

Additionally, scanning electron microscope (SEM) and X ray diffraction analysis were conducted in the Middle East Technical University Central Laboratory for determination of the compositional and physical morphologies of the samples at pre- and post- pyrolysis and gasification conditions. With evaluation of SEM results, sequence increment and decrement of porosity was identified with consecutive pyrolysis and gasification reactions especially for carbon dioxide gasification experiments. Moreover, by qualitative SEM and XRD analysis, general information was obtained about mineral matter of the samples.

Keywords: thermogravimetry, isothermal coal gasification, scanning electron microscope, kinetic analysis, x ray diffraction

ÖZ

TRAKYA SARAY BÖLGESİ KÖMÜRLERİNİN TERMAL KARAKTERİZASYONU VE GAZLAŞTIRMA KİNETİĞİ

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Yüksek Lisans, Petrol ve Doğal Gaz Mühendisliği Bölümü

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Ağustos 2015, 125 sayfa

Bu çalışmada, kömür çeşidi, ısıtma hızı, gaz akış hızı, izotermal bekleme süresi, gazlaştırma aracı olarak tercih edilen gaz ve gazlaştırma sıcaklığının numunelerin izotermal gazlaştırma profilleri üzerindeki etkilerini belirlemek adına, tüvenan ve yıkanmış kurutulmuş olmak üzere, Saray-Edirköy Bölgesi'nden alınmış olan iki farklı kömür numunesi test edilmiştir.

Çalışma kapsamında, ısıtma hızı değerleri 20-50°C/min aralığında sırasıyla 20, 30, 40 ve 50 °C/dak.; gaz akış hızı ise 60 ml/dak ve 100 ml/dak olarak belirlenmiştir. 60 dakikadan 120 dakikaya çıkarılan final gazlaştırma sıcaklığında uygulanan izotermal bekleme periyodunun gazlaştırma prosesine etkisi gözlemlenmiştir. Etkisiz gaz olarak azot (N₂) tercih edilirken, karbon dioksit ve kuru hava, gazlaştırma aracı gazlar olarak tercih edilmişlerdir. 750-950°C sıcaklık aralığında olmak üzere, kömür numunelerinin aktivasyon enerjilerinin hesaplanabilmeleri için 5 farklı gazlaştırma sıcaklığı kullanılmıştır (750, 825, 850, 900 ve 950°C).

Çalışmada, reaksiyon aralıkları, bu reaksiyon aralıklarında meydana gelen kütle kayıpları, belli reaksiyon bölgelerindeki maksimum kütle kayıp hızının gerçekleştiği en yüksek sıcaklıklar ve reaksiyonların başladığı sıcaklıklar gibi numunelerin termal karakterizasyonunda önemli olan parametreler, TA Universal Analysis programı ile analiz

edilmiş olan termogravimetri/diferansiyel termogravimetri (TG/DTG) eğrilerinden elde edilmiştir. Sonuç olarak, karbon dioksit ile yapılan gazlaştırma deneylerinde nem kaybı, uçucu madde kaybı ve gazlaştırma evreleriyle eşleştirilmiş olan üç farklı reaksiyon bölgesi belirlenmiştir. Diğer bir taraftan, kuru hava ile yapılmış olan bazı deneylerde, sırasıyla serbest nem kaybı, uçucu madde kaybı, hafif uçucu maddelerin ve kömürün (char) bir kısmının yandığı yanma evresi ve gazlaştırma evreleri olmak üzere dört farklı reaksiyon bölgesi gözlemlenmiştir.

Kinetik analiz kısmında, Arrhenius modeli kullanılarak kömür numunelerinin hem karbon dioksit hem de kuru hava ortamları altında aktivasyon enerjileri (E_a) hesap edilmiştir. Her iki atmosferde de, yıkanmış kurutulmuş kömürün daha düşük aktivasyon enerji değerine sahip olduğu bulunurken, her iki numunesinin de kuru hava altında düşük aktivasyon enerjisine sahip olduğu gözlemlenmiştir.

Ek olarak numunelerin orjinal, piroliz ve gazlaştırma öncesi ve sonrası koşullarında bileşimsel ve yüzey morfolojileri hakkında bilgi alabilmek adına, Orta Doğu Teknik Üniversitesi Merkezi Laboratuvarı'nda taramalı electron mikroskobu (SEM) ve X ışını kırınımı (XRD) analizleri gerçekleştirilmiştir. SEM sonuçlarının analiziyle, özellikle karbon dioksit ile yapılmış olan gazlaştırma deneylerinde numunelerin gözenekliliğinde birbirini takip eden artış ve azalış trendi gözlemlenmiştir. Ek olarak, kalitatif SEM ve XRD analizleri ile numunelerin mineral madde kompozisyonu hakkında genel bilgi edinmek mümkün olmuştur.

Anahtar kelimeler: thermogravimetri, izotermal gazlaştırma, kömür, taramalı elektron mikroskobu, kinetic analiz, x ışını kırınımı

To my unique family

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor Prof. Dr. Mustafa Verşan K  k for his guidance, criticism, advice, encouragements and support from initial to the final level of my study which enabled me to gain more detailed insight about my thesis subject.

Besides my advisor, I would like to thank the rest of my thesis committee: Prof. Dr. Mahmut Parlaktuna, Prof. Dr.   mit Atalay, Assoc.Professor Emre Altun, and Prof. Dr.   zcan Yıldırım G  lsoy for their comments and contributions to my study.

I would like to present great thanks to ever the best workmate, Ő  kr   Merey, who always supported me from both technical and psychological point of views all through my study. Next thanking is for all of my other workmates who have not refrained to support me from beginning of my study up to this point. I also want to thank Research Assistant Kıymet Gizem G  l who helped me in learning instrument procedure at the beginning of my study and Research Assistant Deniz Talan from Mining Engineering Department for her assistance in sieve analyses of the tested samples.

Most importantly, my heartfelt gratitude goes to my mother, father, and sister, Hatice, Faik, and Nazan, for their unflagging love and support throughout my life; not only this study but also being at this level would be simply impossible for me without them. They are the biggest and endless wealth of me. Lastly, I also appreciate my great warmhearted educator uncle, Vasfi Yıldırım, who has been an angel during the writing up process of this thesis. I will always remember him and his advices in my heart.

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CHAPTER 1

INTRODUCTION

Energy is inevitable part of the modern life. Most of the basic needs of living as electricity, transportation, and heating are related with the energy market and the world's energy need is mainly supplied from nonrenewable; i.e. fossil fuels and nuclear, and partially met by renewable sources as solar, wind, water, biomass and geothermal energy. One of the nonrenewable sources of energy is coal, which has many usages worldwide. Its main usage area is known as electricity production but it is also used for metallurgical processes as steel production, or it may be used in production of a liquid fuel, gaseous fuel, chemical product or a fertilizer.

Coal is the most widespread fossil fuel around the world, and more than 75 countries have coal deposits. Based on BP Statistical Review of World Energy, worldwide proven coal reserves have been estimated to be 891 billion tons in 2014 which can supply world's need for approximately 110 year lifetime. In addition to be a long-term resource, since coal has a wide distribution in each part of the world, it has lower cost when compared with its counterparts; i.e. oil and gas. Thus, even it has many environmental drawbacks, coal remains a crucial contributor to energy supply in many countries whose share in world primary energy generation was stated to be 30 % whereas its about 40% in electricity generation in 2014 (BP Statistical Review of World Energy, 2015).

Thus, especially for developing countries, coal has always been an appealing source of energy. However, mainly due to greenhouse gas emissions and climate change, world awareness about clean energy technologies has gained more importance in recent years.

Oxy-fuel combustion, carbon capture and storage (CCS) activities in coal-fired power plants, and coal gasification technologies can be specified as precautions taken in accordance with the purpose of decreasing gas emissions. Coal combustion in oxy-fuel environment or coal gasification instead of coal-firing are preferred in order to minimize carbon dioxide gas emission which is accepted as one of the major responsible of the climate change.

Coal gasification cannot be specified as a new issue in the world. It dates back even in the early 1800s when it was being used as town gas in Europe and in United States for mainly lighting and heating purposes. Gasification process has been exposed to many technological advancements in recent years. Two main reasons for recent popularity of the gasification, are specified in the literature as high price of natural gas and highway transportation fuel and as increased awareness of environmental impacts of direct coal combustion.

It is obvious that gasification process is one of the most effective measures taken in the scope of clean coal consumption. Since it is both environmentally friendly and an efficient system, gasification technology is stated as a highly promising process. Environmentally, it significantly decreases the amount of detrimental products of coal as NO_x , SO_x , some particulates, mercury (Hg) and carbon dioxide (CO_2) to lower levels. Also, with integrated gasification combined cycle (IGCC) system which is comprised of dual source of electric power with combination of gas turbine and steam turbine, efficiency of the system can be increased when compared with traditional coal combustion.

When comes to its technical side, even it has a complex chemistry, gasification process is basically defined as a process in which carbonaceous materials like coal are exposed to limited scale oxygen, air, air-steam mixture or oxygen enriched air leading formation of flammable gases (CO , H_2 , CH_4 etc.). Coal undergoes firstly moisture loss and then devolatilization step that generally begins above 400°C .

At the end of the devolatilization step, coal produces coal char, and coal volatiles which consist of tars, condensable liquids, and light gases. On the other hand, gasification step

is generally expected to begin at about 800 °C after devolatilization stage. Based on the used gasification reagent, reaction progression as well as the products of the reaction change.

Gasification process is affected from original coal properties as well as from ‘char’ properties formed under different pyrolysis conditions. Parent coal properties as carbon amount, hydrogen amount and oxygen amount are directly related with the coal rank and so with the char reactivity. To illustrate, lower carbon content and higher oxygen amount of coals are classified as lower rank coals which create more reactive coal chars.

In addition to parent coal properties, as mentioned before, char formation conditions as final pyrolysis temperature and heating rate may have significant effects on char gasification rate. For example, previous studies mostly show that higher char preparation temperatures lead decrease in surface area of char and so decrease in char reactivity. Thus, it is important to determine both original coal samples’ properties and the optimum conditions for both pyrolysis and gasification reactions which is possible by changing some parameters as heating rate, final reaction temperature, gas flow rate and isothermal duration.

In pyrolysis, combustion and gasification kinetics of coal, thermogravimetric analysis plays a part by determining parameters that are important in thermal characterization of the sample. It measures the mass change of a sample when it is exposed to a selected temperature program in a defined atmosphere which is either inert or reactive gas based on the planned reaction type. Reaction intervals for any type of reaction, weight changes occurred in those intervals, burn-out temperatures, and peak temperatures can be identified by TG/DTG curves. Data gathered from TG/DTG curves can be used in reactivity evaluation and kinetic calculation of the coal sample under different experimental conditions which leads to determination of optimum conditions for any conversion process.

In this study, it was aimed to analyze gasification profiles of Saray-Edirkoy lignite samples under different conditions by thermogravimetry (TG/DTG) analysis. At the end,

optimum gasification conditions for both as received and washed-dried samples as well as char reactivity's were tried to be determined. In this context, on the brink of being conducted under carbon dioxide and dry air atmospheres, seven isothermal gasification experiment procedures with different subgroups were performed. In addition to thermogravimetry experiments, in order to observe morphological properties and qualitative elemental analysis of samples, scanning electron microscope (SEM) and x ray diffraction (XRD) analysis were performed by Middle East Technical University Central Laboratory.

CHAPTER 2

GASIFICATION BACKGROUND

2.1 Gasification Chemistry

Gasification is defined as a conversion technology of any carbon-containing material as coal, biomass and waste into synthesis gas which is mainly composed of carbon monoxide (CO), hydrogen (H₂) and some byproducts as hydrogen sulphide (H₂S), carbon dioxide (CO₂) and some minerals (slag) in the case of gasification of coal with steam (Breault, 2010).

Crushed and dried coal samples are fed into the gasifier to let gasification reaction between coal particles with steam and either air or oxygen. Gasification reaction is expected to occur at high pressure (up to 10 MPa) and at higher temperatures, generally between 800°C and 1900°C. Gasifying medium highly affects the product of the reaction. If limited air without steam is used, then the produced gas is stated to be a low-heating gas which can be used as a fuel gas after purification. On the other hand, limited oxygen rather than limited air causes medium-heat content gas which can be used as synthetic gas. Based on requirements of different synthetic gases for producing liquid fuels, SNG, ammonia or methanol, further hydrogen (H₂) can be produced by shift reaction between carbon monoxide (CO) and steam (H₂O) (Sha, 2005).

Differently from combustion process, coal gasification is the incomplete combustion of coal with limited amount of oxygen. It mainly aims to convert non-ash part of coal into gas whose heat value is desired to be as much as possible with the original feedstock. Coal

gasification process is said to be mainly composed of *dehydration*, *pyrolysis*, *combustion* and *gasification* stages. If carbon dioxide capture and storage is aimed in the gasification process, water-gas shift and methanation reactions are also included in addition to mentioned steps. Complex chemistry of coal gasification reactions with their enthalpies are given in the following table (Table 2-1).

Table 2-1: Chemical reactions occurring throughout coal gasification process (Higman& van der Burgt, 2008, Phillips, 2006, & National Energy Technology Laboratory website)

Process	Chemical Reaction	Heat of Reaction (ΔH)(kJ/mol)
Gasification with oxygen	$C + 1/2O_2 \longrightarrow CO$	-111.4
Combustion with oxygen	$C + O_2 \longrightarrow CO_2$	-393.4
Gasification with carbon dioxide	$C + CO_2 \longrightarrow 2CO$	170.7
Gasification with steam	$C + H_2O \longrightarrow CO + H_2$	130.5
Gasification with hydrogen	$C + 2H_2 \longrightarrow CH_4$	-74.7
Water-gas shift reaction	$CO + H_2O \longrightarrow H_2 + CO_2$	-40.2
Methanation	$CO + 3H_2 \longrightarrow CH_4 + H_2O$	-210

When coal is exposed to heat, it firstly undergoes moisture loss process which is mainly turning of liquid water into its gaseous phase and which is named as *dehydration*. As a second step pyrolysis occurs when coal begins to decompose its components as *coke* and *volatiles*. Chemical bonds rupture between atoms that leads release of the volatile matter is generally stated to begin after 320°C and continues up to 900°C. Both moisture loss and pyrolysis processes are endothermic; i.e. heat is adsorbed from surrounding during both reactions. Depending on mainly the coal type, pyrolysis process yield of a coal sample differs.

If the gas (in the case of oxygen or air is used as a reactant gas) entry and coal feed entry are closely spaced in the gasifier, released volatile matter may be exposed to the exothermic combustion reaction as a result of which heat is released. Combustion and partial combustion of volatile matter is composed of carbon monoxide (CO), carbon dioxide (CO₂), water (H₂O), hydrogen (H₂), hydrogen sulphide (H₂S) and sulphur dioxide (SO₂).

In addition to the combustion of these gaseous species, reaction of char (C) with oxygen/air is also expected as a result of which carbon monoxide and carbon dioxide gases are the main products of char/oxygen exothermic reaction. This reaction is mainly the combustion reaction of coal char which is followed by endothermic gasification reaction of the char in the gasifier. These gasification reactions are actualized by either *steam* (H₂O) or *carbon dioxide* (CO₂) gases.

As a result of gasification process, heating value of the *syngas* is desired to be high which is possible by increasing the endothermic gas forming reactions as much as possible. Exothermic combustion reactions create the required heat to drive endothermic gasification reactions. Typical feeds of coal gasifier are coal, oxygen/air and water. Water can be in the form of coal moisture, coal slurry water or steam. Oxygen and water feed amounts should be enough for complete and effective gasification. If oxygen ratio is used higher, for example in O₂/H₂O feed, combustion of coal occurs rather than gasification as a result of which lower heating value gases are produced (Bell et.al, 2011).

Selection of oxygen or air as an oxidative gas also affects the gasification process substantially. If air is used, heat value of the *syngas* is expected to be between 150-200 Btu/ft³ whereas it is stated to be as 300-400 Btu/ft³ in the case of oxygen. Moreover, as gasifying agent rather than steam, carbon dioxide gas can also be preferred for coal gasification process; however, it is stated in the literature that coal gasification rate is slower than that is under steam. In carbon dioxide gasification, pyrolysis stage is followed by gasification by different oxygen/carbon dioxide mixtures at high temperature.

It is also cited that carrying out the pyrolysis and gasification reactions with the same gas (CO_2) is an appealing technique since it preserves the fresh char for one reaction (Higman & van der Burgt, 2008).

Also as cited in the study of Cakal and his friends, even carbon dioxide is not used industrially as much as steam in the gasification process, it is the preferred agent used at laboratory level and the carbon- CO_2 reaction is of great importance. The slower reaction rate at temperatures around 1000 K allows a better control of the gasification process and the analysis of the different variables, which may be modified (Cakal et.al, 2007).

2.2 Gasifier Types

Mainly three types of gasification systems are discussed in the literature which are *entrained flow gasifiers* as the mostly used ones of the available gasification plants, *fluidized bed gasifiers*, and *moving bed* (fixed bed) gasifiers.

2.2.1 Entrained Flow Gasifier

Entrained flow gasifier systems work under high temperature (1200-1600°C) and high pressure (2-8 MPa with average 2.5 MPa) with smaller size sample as pulverized coal (< 1mm). Oxidant gas requirement is higher in entrained flow gasifiers when compared with other types. As an advantage, entrained flow gasifier is stated to be able to gasify all type of coals regardless of rank, caking characteristics or amount of fines (Lieuwen et.al, 2010, Higman and van der Burgt, 2008 & Phillips, 2006).

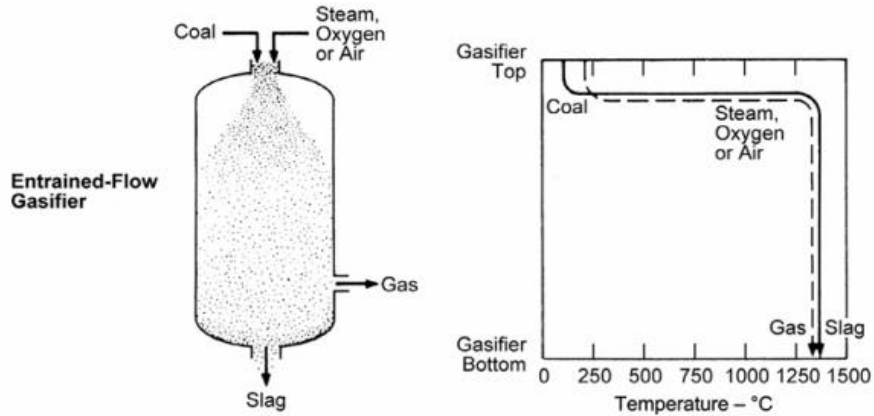


Figure 2-1: Diagram for entrained-flow gasifier (Phillips, 2006).

As can be seen from the diagram, co-current flow of coal and gas is provided in the entrained flow gasifier. Because of this orientation of the gasifier, reaction between coal and oxygen/air occurs rapidly which, in turn, leads to lower residence time (seconds or tens of seconds). Higher temperatures, generally above slagging temperature, are required for sufficiently high carbon conversion since the residence time is short (Lieuwen et.al, 2010, Higman and van der Burgt, 2008 & Phillips, 2006).

2.2.2 Fluidized Bed Gasifier

On the other hand, fluidized bed gasifiers work under lower temperatures which are generally lower than ash fusion temperature of the used fuel (900-1050°C) with solid crushed samples that have usually larger size (0.5-5mm) than those used in entrained flow gasifiers. Requirements of oxidant and steam gases are moderate when compared with entrained flow gasifier. Also, temperature distribution throughout the bed is uniform and moderate. Achievement of the extensive recycling of the larger particles that are captured by the cyclone generally being set below gasifier, is stated as an advantage of this system (Lieuwen et.al, 2010, Higman and van der Burgt, 2008 & Phillips, 2006).

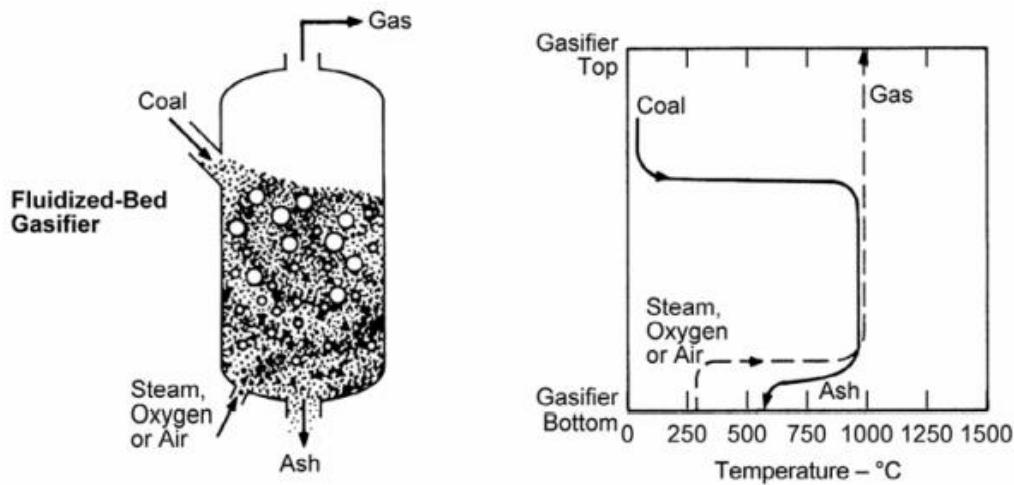


Figure 2-2: Diagram for fluidized-bed gasifier (Phillips, 2006)

2.2.3 Moving Bed (Fixed Bed) Gasifier

Finally, moving bed gasifiers' ability to handle with fine particles and caking coal are stated to be lower than that potential of entrained flow gasifier systems. Coal size, as another issue, is stated to be in between 5-80 mm in moving bed gasifiers and the average pressure is stated to be 3 MPa whereas it can be up to 10 MPa. As can be seen from the diagram of moving bed gasifier (Figure 2-3), countercurrent flow of coal feed and oxidant and steam gases are provided as a result of which the heat of reaction from the gasification reactions serves to pre-heat the coal before it enters the gasification reaction zone. Thus, the temperature of the syngas exiting the gasifier is significantly lower than the temperature needed for complete conversion of the coal. Moreover, residence time, when compared with previously mentioned types of gasifiers, is much higher which can be up to on the order of hours; thus, oxidant requirement of a moving bed gasifier is lower (Higman and van der Burgt, 2008 & Phillips, 2006).

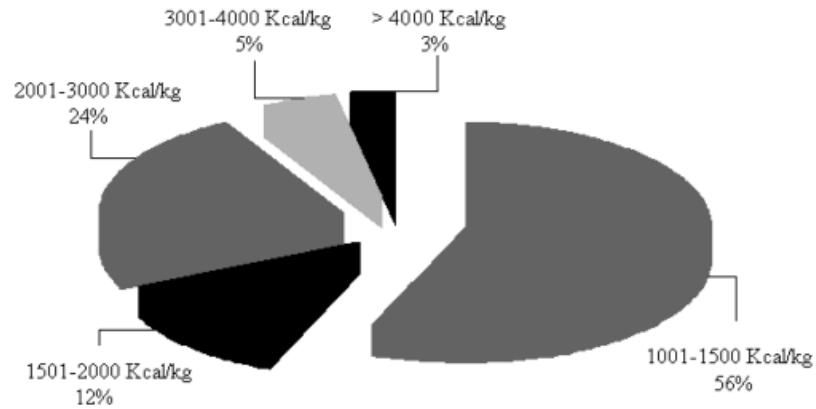


Figure 2-6: Pie chart showing heating value distribution of Turkish lignites (Balat, 2008)

2.4.1.2 Thrace Region Coal

Thrace Region is accepted as one of the significant basins in terms of its high potential in hydrocarbon resources. Availability of a variety of mineral deposits directed researchers to conduct several geological studies in the region.

In the Thrace Basin, exploration studies for coal basins have been conducted by General Directorate of Mineral Research and Exploration (MTA). Based on General Directorate of Energy conducted study in 2011 ‘Update of Coal Reserves’, total reserve amount in Thrace Region was specified to be above one billion ton as 1.137.660.000 tons whereas Saray field total coal reserve amount was specifically mentioned as 136.7 million tons.

Lignite formations in the north part of the basin generally occur in Istranca edging strip skirts. These fields are known as Saray (Edirkoy, Kucuk Yoncali, and Safaalan), Kırklareli (Vize, Pınarhisar), and Edirne (Demirhanlı). On the other hand, coal formations are referred as Kesan, Malkara, Uzunkopru and Meric fields in the southern part of the basin.

Lignite outcrops in the southern and northern parts of the basin whereas it deepens in the central part gradually such that lignite can be found exceeding 600 meter depth in 10,000 meter sedimentary stacking.

Lignite occurrence is stated to be in Danisman Formation whose age was finally updated to Lower Miocene (Senguler, 2012). Generalized stratigraphic section for tertiary sequence of Thrace region is shown by Figure 2-7.

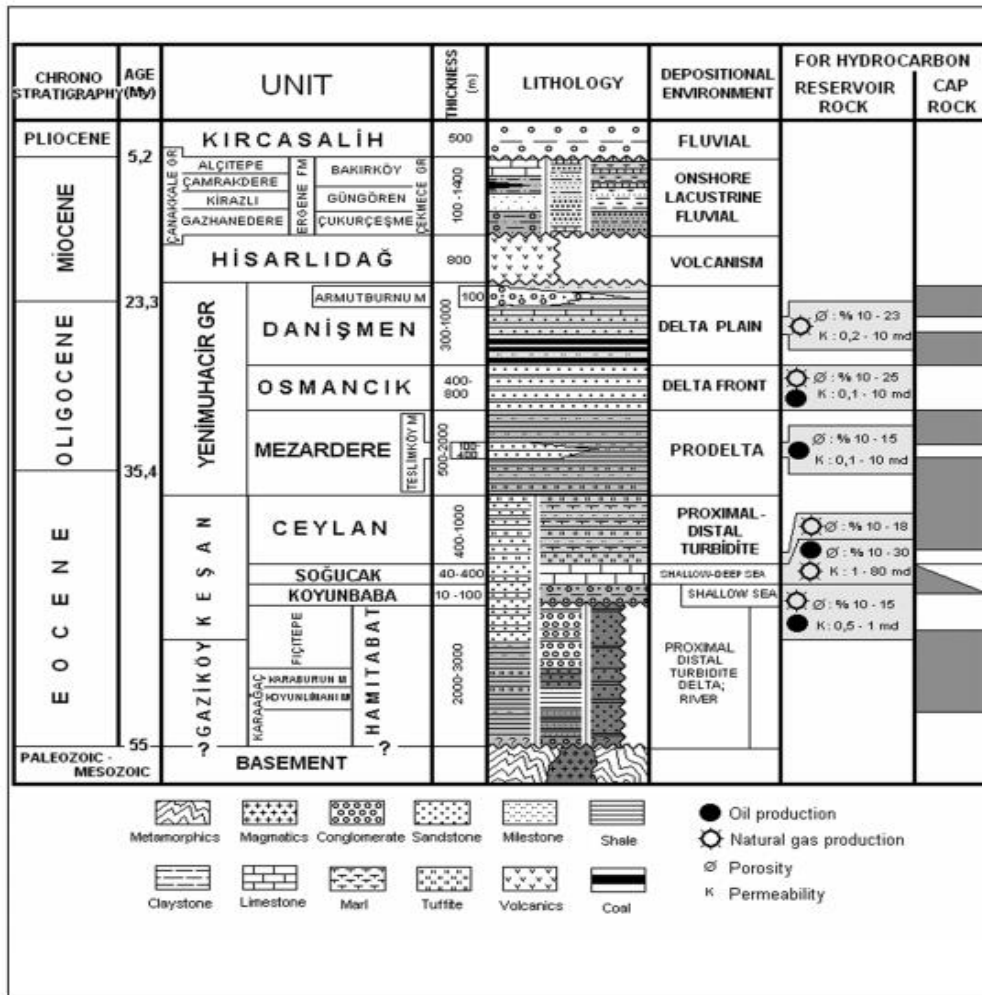


Figure 2-7: Generalized stratigraphic section for tertiary sequence of Thrace region (Siyako, 2006)

As in the case of most of the Turkish lignites' properties, Thrace region coal is also classified as low rank coal being composed of high ash, high volatile and matter high

moisture. Thus, gasification process can be mentioned as an attractive option of Thrace Region coal reserves for environmentally friendly and effective energy production. Table 2-2 shows reserve amounts, heating values, densities, intended usages and average moisture and sulphur values of Thrace region lignites. For this study, Saray region coal properties have greater importance.

Table 2-2: Thrace region lignite inventory (Data taken from TR 21 Thrace region energy report-2012)

Region	Place	Reserve (million ton)	Lower Heating Value (kcal/kg)	Density (ton/m ³)	Intended Use	Average Chemical Values (%)		
						moisture	ash	sulphur
Demirhanli-Geckinli	Edirne	10.3	2100	1.5	Heating	40	11.65	1.63
Meric-Kucukdoganca		1.8	2500	1.5		38	20	2
Meric-Karayusuflu		1	2005	-		32.6	30.45	-
Uzunkopru-Harmanli		13.6	3500	1.1		19.2	23.29	0.71
Enez-Cavuskoy		1.5	2600	1.5		29	25	3.98
Vize-Topcukoy	Kirklareli	34.2	2300	1.4	Heating Industry	32.5	22.5	1.5
Saray-Kucukyoncali	Tekirdag	73.6	2000	1.39	Heating Thermal Power Plant	41	22	1.8
Saray-Safaalan		50.1	1677			42.2	21	1.4
Saray-Edirkoy		14.3	1716			42	24	2.4
Malkara-Ahmetpasa		6.9	2200	1.3	Heating	22.1	37.4	1.6
Malkara-Evrenbey-Karamurat		14.4	2359	1.3		33.3	27.3	1.41
Malkara-Haskoy-Ibrice		8.5	2277	1.3		28.3	31.1	1.6
Cerkezkoy		495	2075	1.4	-	33	25	2

2.4.2 Gasification Activities in Turkey

First coal gasification pilot plant of Turkey has been opened in Kutahya Tuncbilek region. Turkish Coal Enterprise (TKI) has begun research and development studies for gasification in the year of 2008. Scientific and Technological Research Council of Turkey (TUBITAK) Marmara Research Center (MAM) also began to give support for the activation of this plant beginning from 2011 and plant was initiated in 2012. Aim of producing synthetic gas in that plant was stated to be as methanol production.

Next gasification project was concerning Manisa Soma region lignites which was planned to be founded in 2013. Produced syngas from Soma lignites was stated to be producing liquid fuel from coal/biomass mixtures.

Thrace region coal gasification process can be specified as a part of an OPTIMASH project which aims to gasify high ash Turkish and Indian lignites.

- Within the scope of research project financed by the Scientific and Technical Research Council of Turkey (TUBITAK), gasification technologies special to high moisture, high ash Tekirdag-Saray basin lignites were examined and accordingly the most suitable technology will be determined .
- Main aim of the study is to support power generation and cogeneration by coal gasification which can be an alternative source for increasing energy demand.
- At the end, gained data will be used in the basin plant which will be designed nearest to 10MWth capacity.

CHAPTER 3

LITERATURE REVIEW

Thermal characterization studies applied to coal samples mainly aim to search relationship between coal type and thermal properties of coal, to study different steps of combustion and gasification processes.

Back to date 1980, Ratcliffe and Pap analyzed different coal samples in their studies. In the research conducted, it was observed that reaction consists of two separate reactions. Faster reaction in the first region was controlled by back volatility speed whereas the second step limited rate of the reaction and controlled by coal surface characteristics.

Seragaldin and Pan [1984] found linear relationship between activation energy and reaction heat in thermogravimetry experiments that they have conducted. Alkaline metals effect on coal dissociation has been investigated under three different atmospheres (N_2 , CO_2 , and air). In this study, catalyzer utilization effects on coal conversion and CH_4 , CO_2 and CO gases evolution were correlated with changes occurred in activation energies.

Pitkanen et al. [1999] analyzed coal, peat, and chock samples with TG-FTIR spectrometry. By taking spectrum and thermal analysis curves into account, most of the gas emissions were found to be CO_2 and water, in addition to them release of a trace of carbon monoxide, methane, ethane, methanol, ethanol, formic acid, acetic acid, formaldehyde were deduced.

Cakal et al. [2007] analyzed pyrolysis and CO₂ gasification behavior of four different lignite samples by thermogravimetry method within the 750-1000°C temperature range. In this study, it was found that, for each lignite sample maximum pyrolysis ratio was related with final carbonization temperature. It was observed that, gasification reactivity of lignite samples gathered from four different regions under same experimental conditions were different and reactivity order of samples were related with the temperature. Activation energies of studied coal samples were found by Arrhenius plots and they were found to be in 29 - 124.8 kJ/mole range.

Tomaszewich et.al [2013] determined gasification reactivity of char samples that were obtained from different rank coal samples. Kinetic studies were conducted under 900, 950, and 1000°C by isothermal thermogravimetry method. Activation energies of char samples were observed to be changing in the range of 180 - 240 kJ/mol.

Micco et al. [2007] studied kinetics of fixed bed reactor char gasification under CO₂ atmosphere by gas chromatography. Analyses of two different char samples were conducted under 850 and 950 °C pyrolysis temperatures. In the study, activation energy values of both char samples were found to be close to each other.

Wu et.al [2008] analyzed CO₂ gasification of char sample by isothermal thermogravimetry method under 950-1400°C temperature range. In this study, effect of pyrolysis heating rate on char reactivity was analyzed. With decreasing gasification temperature, increase in char reactivity was observed. It was also concluded up that, chemically controlled gasification reactions under low temperature range (950-1150°C) turned into gas diffusion controlled processes under higher temperature range (1150-1400°C).

Hou et.al [2012] studied non-isothermal pyrolysis and gasification behavior of lignite samples under N₂-CO₂ atmosphere by thermogravimetry (TG), Fourier transform infrared spectroscopy (FTIR) and x ray diffraction (XRD) methodologies. In this study, thermogravimetry analyses showed that neither N₂-CO₂ atmosphere affected pyrolysis behavior of lignite sample nor gasification reaction was influenced by CO₂ atmosphere under 670°C.

It was found up that, gasification reactivity of coal sample decreased with increased pyrolysis temperature (800-1000°C).

Sawettaporn et.al [2009] performed CO₂ gasification analyses of lignite and coal samples under 900-1100°C temperature range. Research results were evaluated in the context of reactivity constant, reaction ratio and activation energy. Results showed that reactivity constant increased with gasification temperature.

Saha et.al [2013] conducted isothermal gasification analysis of lignite samples under three different final temperatures of 900, 950, 1000°C via inert (Ar) and gasification reagent (CO₂) gases. In this study, heating rate and isothermal duration were remained constant and effects of char formation temperature (pyrolysis final temperature), gasification temperature and char surface area alteration on coal reactivity were determined. It was observed that, increasing pyrolysis temperature decreased coal reactivity whereas increasing gasification temperature enhanced surface area, which increased reactivity of the coal.

In the study of Jayaraman et.al [2013] pyrolysis, combustion and gasification behaviors of Turkish and Indian coal samples were analyzed by TG-MS method. At the end of the isothermal gasification experiments conducted under water vapor, dry air and oxygen gases, optimum final temperature for high ash coal samples were found to be 950°C. Moreover, it was concluded up that gasification reactivity of high ash coal samples were mainly related with used gas concentrations and reaction temperature. Effect of coal particle size on coal/char samples reactivity's was found to be minimum under high temperature range.

In the other study of Jayaraman and Gokalp [2015], gasification behaviors of two different size high ash Turkish coal samples were analyzed by thermogravimetric analysis. Aim of the study was stated as the determination of pyrolysis heating rate, coal particle size, final gasification temperature, and reactant gas type on char gasification reactivity. Moreover three different kinetic models specifically as volumetric model (VM), grain model (GM), and random pore model (RPM) were used in the study for determination of kinetic

parameters as a result of which activation energy values (E_a) were found to be close enough to each other calculated by different models. Firstly, high rate (100 K/min, 500 K/min and 800 K/min) pyrolysis of coal the samples were performed under an inert, specifically under argon (Ar) atmosphere. Then prepared char samples were cooled to room temperature after which temperature was increased by 40 K/min up to the char gasification temperature range 850-950°C by argon gas firstly which was then turned into reactive gas; i.e. either steam or carbon dioxide, at the specified gasification temperature. At the end of the study, it was concluded up that, higher heating rate used for pyrolysis reaction and smaller coal size led more reactive char samples for gasification reaction by increasing surface area. Moreover, increased gasification temperature was found to be more advantageous for the gasification reactivity of both size samples which was determined based on decreased time for 50% conversion of the char.

Veca and Adrover [2014] determined effects of particle size and gasification temperature on gasification kinetics of two different coal samples by thermogravimetry analysis. Isothermal gasification experiments which were performed for four different gasification temperatures in the range of 800-1100°C were carried out in two steps as pyrolysis and gasification. When results were evaluated, it was found that conversion factors of subbituminous coal were found to be higher under high gasification temperature (1100°C) whereas lower particle size coal samples (0.125-0.15 mm) were found to be more reactive. For both of the samples, activation energy values calculated by three different kinetic models were found to be close each other.

Chen et.al [2007] studied pyrolysis and gasification behavior of four different coal samples by pressurized thermogravimetry. Isothermal gasification experiments were conducted as two gradual steps as pyrolysis phase under argon atmosphere (Ar) and isothermal gasification stage under carbon dioxide (CO₂) atmosphere. In this study, effects of pyrolysis pressure and coal rank on both pyrolysis and gasification reactivity of four different ranked coal samples were tried to be determined. It was observed that coal samples having higher volatile matter, i.e. samples of lower rank (brown and bituminous), had higher pyrolysis and gasification reactivity values.

It was also concluded up that pyrolysis and gasification reactivity of coal samples were inversely proportional with the pyrolysis pressure.

Wang et.al [2015] performed isothermal and non-isothermal coal gasification experiments under CO₂ atmosphere. Isothermal gasification experiments of coal char were conducted under three different gasification temperature values determined by non-isothermal experiments (900, 950, and 1000°C). In this study, effects of gas flow rate, heating rate and gasification temperature on char gasification reactivity were searched. Gas flow rate was changed between 20-80 ml/min, and an optimum value (60 ml/min) which was greater than or equal to 40 ml/min was selected in order to eliminate reagent gas limitation problems. On the other hand, gasification reactivity of coal sample was found to be proportional with gasification temperature whereas it was obtained to be inversely proportional with the heating rate.

Irfan [2012] searched for coal pyrolysis and gasification behavior by thermogravimetric analysis under different conditions. In addition to gas composition effect, effect of pyrolysis conditions as final temperature, isothermal duration and heating rate on coal gasification reactivity were analyzed in this study. It was concluded up that, pyrolysis of coal was faster under carbon dioxide (CO₂) atmosphere when compared with that under (N₂) most probably due to different bulk gas properties. On the other hand, lower pyrolysis temperature values (400-500°C) were found to be more advantageous for coal reactivity whereas any effect on gasification mechanism could be detected for isothermal duration introduced at final pyrolysis temperature which was changed between 0-90 minutes. Increased heating rate was stated to be effective only in reaching designated final temperature faster and it did not affect the overall reaction mechanism markedly. It was also noted that, increased oxygen concentration in CO₂/O₂ mixture affected reaction mechanism positively such that burnout temperatures shifted to lower values.

Another research of Irfan et.al [2011] touched upon previous studies that analyzed different parameters' as coal rank, final temperature, heating rate and particle size effects on coal gasification and combustion reactivity under carbon dioxide or oxy-fuel environment.

Even it was emphasized in the study that coal had a complex structure and it was really difficult to make exact conclusions for coal gasification mechanism, general inferences were made based on previous analyses' results supporting each other. It was concluded up that lower rank and smaller size coal had higher gasification reactivity. On the other hand while higher gasification temperature (up to ash fusion temperature) was found to be more advantageous for gasification process, it was found that increasing heating rate only shortens time to reach final temperature but it has a little effect on combustion mechanism.

Zu and Li [2008] studied coal particle size and mineral matter of coal effects on pyrolysis and char reactivity of two different coal samples (lignite and bituminous coal), that were milled and sieved to three different size fractions, by using x ray diffraction (XRD) and thermogravimetric (TGA) methods. At the end of the study, it was concluded up that increase in particle size affected char reactivity in a negative way whereas demineralization decreased the effect of particle size on char reactivity.

In the study of Mandapati et.al [2012], four coal samples' CO₂ gasification reactivity's were compared by thermogravimetric analyzer. Firstly, coal samples were undergone pyrolysis reaction under nitrogen atmosphere to allow coal samples to lose their moisture and volatile matter content. Cooled and milled char samples were heated with inert gas (nitrogen) up to designated temperature of 800-1050°C and then reactive CO₂ gas came into play for gasification process. At the end of the study, lowest ranked lignite sample throughout four different coal specimens was found to be the most reactive one. Moreover, catalytic effect of inherent ash minerals of coal samples were discussed by taking the calculated activation energy values into account.

In Master Thesis study of Sarilar [2011], on the brink of indigenous lignite, biomass, petroleum coke and these three fuel's blends with various proportions, pyrolysis and combustion profiles were analyzed under four different atmospheres (dry air, oxygen enriched air, oxy-fuel environment and oxygen enriched oxy-fuel environment) by TGA-FTIR methodology.

In the study, it was found up that at lower temperature values for pyrolysis reactions, CO₂ behaved as an inert gas and any difference could be detected in between N₂ and CO₂ pyrolysis behaviors of used samples. On the other hand for oxy-fuel combustion mechanisms of samples, it was concluded up that increasing oxygen concentration in the atmosphere led combustion reaction temperatures (peak, burnout) to shift lower values, and cause reaction to complete faster with higher amount of total mass loss. Moreover, replacing N₂ in air with CO₂ resulted in slight delay in peak and burn-out temperatures in combustion reactions.

In the study of Silbermann et.al [2013], CO₂ gasification kinetics of nine coal samples from both surface mines and unmineable coal seams were analyzed by TGA experiments. In this experimental study, three different gasification procedure was used in which one of the experiment was conducted only under the reactive gas (CO₂) whereas the other two were conducted sequentially by switching the gas from inert (N₂) to reactive one (CO₂) at the desired temperature. It was found up that, using same gas throughout the pyrolysis and gasification steps as in the case of first experiment type, was more effective in terms of gasification reactivity. Moreover, three different gasification temperatures (800, 850, 900°C) were used and being consisted with the previous studies, it was concluded up that higher gasification temperature led coal samples to have higher reactivities. On the other hand, from the point of coal properties, coal samples having higher ash contents were found to be more reactive most probably due to the ash mineral content, especially those formed from alkali metals. Conversion degree versus reactivity plots were mostly found to follow logarithmic function. Activation energies were calculated based on Arrhenius plots for different kinetic models as volumetric model (VM), integrated core model (ICM), shrinking core model (SCM), normal distribution model (NDM) and random pore model (RPM) as a result of which the best match was achieved by the integrated core and normal distribution models (117-233 kJ/mole).

Tancredi et.al [1996] conducted a study on isothermal kinetic analysis of eucalyptus wood chars' CO₂ gasification reactions. Experiments were conducted by thermogravimetric analyzer (TGA) and carbonized biomass samples with different final temperatures (400,

600, and 800°C.) under N₂ environment, i.e. biomass chars, were undergone gasification reactions for different final gasification temperatures. At the end of the experiments, it was found that char sample formed under lower pyrolysis temperature had higher CO₂ gasification reactivity. Moreover, it was concluded up that increasing char conversion led to increase of reactivity, which was tied to increase in pore volume of char with conversion. Calculated conversion and reactivity values for isothermal CO₂ experiments were then used in formation of Arrhenius plots. Calculated activation energies were in the range of 230-260 kJ/mol.

Struis et.al [2002] investigated coal char CO₂ gasification reactivity under different conditions by isothermal thermogravimetric analysis. Process was conducted under two separate steps as pre-pyrolysis and post-pyrolysis and gasification. Particle size, gas flow rate, initial charcoal amount and gasification temperature were the variables changed throughout gasification step in order to observe mass transport or pore diffusion limitations. At the end, it was concluded up that reactions were chemically controlled and neither mass transport nor pore diffusion limitations were faced. Average reactivity values were calculated for five different gasification temperatures (700, 750, 800, 850, 900°C) which were then used in Arrhenius plot construction. Arrhenius plots ($\ln(R_{ave})$ vs $1/T$ (K)) were linear and activation energy was calculated as 212 kJ/mole which was also consisted with previous studies.

In the study of Zuo et.al [2015], isothermal carbon dioxide gasification reactivities of coal char (CC), biomass char (BC) and their blends of different ratios (1:1, 1:3, 3:1) were determined under three different final temperatures (900, 950 and 1000°C) by thermogravimetric analyzer. Moreover, three different kinetic models as volumetric model (VM), grain model (GM), and random pore model (RPM) were used for the calculation of kinetic parameters. At the end of the study, it was concluded up that when the percent of biomass char increased in the blend, gasification reactivity of the sample increased as a result of two main reasons first of which was specified as the increased surface area of coal char (CC) with increased amount of biomass whereas the second was explained as the intrinsic chemical property of coal char; i.e. more uniform and crystalline

structure of the coal char than that of biomass char. For kinetic models, random pore model (RPM) was found to be the most reliable method than volumetric model (VM) and grain model (GM) for coal and biomass char samples as in the case of previous studies in the literature. Moreover, the minimum activation energy value was found to be belonged to the blend consisting of the highest ratio of biomass to coal char ratio (BC/CC).

In the study of Huo et.al [2014], CO₂ gasification kinetics of six different samples on the brink of three coal, two biomass and one petroleum coke were analyzed by TGA. Moreover, in order to characterize the crystalline structure of char samples, XRD analyses were conducted in the study. In the first step which was specifically stated as devolatilization process, samples were heated by 25 K/min up to 1123 K and they were kept for 30 minutes at this temperature. Then, for following gasification experiments, <46 µm and ~ 250 µm sized char samples were selected throughout sieved char samples. Then, via 25 K/min heating rate, char samples were heated up to four different gasification temperatures as 1123 K, 1173 K, 1223 K, and 1273 K under purge gas nitrogen gas (N₂) which was then turned into a reactive gas, carbon dioxide gas (CO₂) at the target temperature. Throughout the experiments, five different gas flow rate values (20, 40, 60, 80, 100 ml/min) were used. At the end of the study, it was concluded up that, relatively lower sized char particles (<46 µm) were more reactive. Moreover at higher temperatures (>1273 K), gasification rates were found to be decreased due to pore diffusion effects as in the case of large particle sizes. For gas flow rate effects, it was stated that for the elimination of the external diffusion effect of reactant gas, flow rate values higher than 60 ml/min were used and no significant effects of those values (>60 ml/min) on gasification reactivity of char samples were observed. Moreover by XRD analysis, crystalline structures of the samples could be determined as a result of which, coal and petroleum coke char samples were found to be having more uniform crystalline structures leading them to be less reactive than biomass chars.

In the study of Dong et.al [2015], pyrolysis conditions; specifically the temperature and pyrolysis time effects on Zhundong coal char properties were tried to be understood by different analyses as X-ray diffraction (XRD), Fourier transform infrared spectroscopy

(FTIR), and scanning electron microscope (SEM). In addition to them surface area and pore structure of char samples were determined mainly by carbon dioxide (CO_2) adsorption isotherms. In the study, Zhundong coal samples were firstly crushed and sieved as 0.18 mm and 0.355 mm which were then pyrolyzed in an electric heated horizontal tube furnace. Changing from 200 to 900°C, different pyrolysis temperatures and different isothermal durations (few seconds to 60 minutes) were used to determine effects of these parameters on char structure. At the end of the study, it was concluded up that, increased temperature and time of pyrolysis process had resulted in more developed pore structures as well as increased surface area of char samples. Moreover, FTIR results supported the evolution of H_2O , CO , $\text{CH}_4/\text{C}_2\text{H}_2$ gases during pyrolysis stage. As a conclusion, it was stated that structural properties of char samples were strongly dependent on pyrolysis temperature and time.

Rathnam et.al [2009] studied four different Australian coal samples' combustion reactivities under oxy-fuel (O_2/CO_2) and typical air (O_2/N_2) conditions. Oxygen gas percentages in both environments had been changed between 3-21% and 5-30% respectively. Firstly, coal samples were undergone devolatilization stage in drop tube furnace (DTF) under either nitrogen (N_2) or carbon dioxide (CO_2) gases at 1673 K temperature. Then, formed coal chars were combusted by thermogravimetric analyzer (TGA) under oxy-fuel and air atmospheres with changed amounts of oxygen at the temperature value being or less than 1473 K. When results of the DTF experiments were analyzed, it was seen that volatile yield measured in CO_2 environment was higher than that measured in N_2 which was stated to be due to the gasification reaction between char- CO_2 above 1030 K determined by TGA analysis. For comparison of char samples' structural properties, SEM analyses were performed. It was observed that, char samples formed under CO_2 gas showed reacted surfaces and also they had greater surface areas than others obtained under nitrogen (inert) gas environment all of which were attached to the reason that the char-carbon dioxide gasification reaction. On the other hand, when combustion experiments done by TGA were analyzed, it was concluded up that increased amount of O_2 in both environments had resulted in lower burn-out temperatures and higher peak reactivity of char samples.

Moreover, the volatile yield trends of four different coal samples were found to be directly proportional with burnouts (reactivity) of the samples. Thus, it was concluded as that not only the environment but also the coal properties effected the reactivity of the coal sample.

Dutta et.al [1977] worked on two raw coal samples and four char samples derived from these coals whose gasification reactivities under carbon dioxide (CO_2) environment were tried to be determined. For each thermogravimetry experiment, coal and char samples were experimented between the temperature range of 843-1093°C. Reactions were divided into two stages which were mainly specified as pyrolysis and char- CO_2 reaction; i.e. gasification. Pyrolysis stage was stated to be completed before reaching the temperature value 815°C. It was added that increased pyrolysis temperature led higher total conversion being originated from pyrolysis stage. Its kinetic model was defined by Arrhenius type of equation as a result of which activation energy of this stage was calculated as 2.5 Kcal/mole. In the following gasification reactions, where char samples were said to be composed of mainly carbon (C) and ash, reaction rate was stated to be comparatively slower than rate of the pyrolysis stage. In these experiments, it was aimed to determine effects of the sample size, particle size, and gas (CO_2) flow rate on char gasification. Gas flow rates were used in the range of 42-210 ml/min and it was found up that, no rate change occurred above 70 ml/min flow rate value and 150 ml/min was selected as the flow rate for all experiments. For particle size, it was come up with that -35+60 mesh sized particles led negligible interparticle diffusion up to 1000°C. In the kinetic analysis section of gasification part, differently from kinetic analysis of pyrolysis part, new parameter 'a' representing the change in available pore surface areas of the particles during reaction was defined in the rate equation in order to account for the rate-conversion curves as a result of which activation energy for the gasification process was found as 56 Kcal/mole. For pore structure properties of the samples, SEM analyses (with 6000 magnification) were performed for macro pore structure observation and BET N_2 adsorption method was used for micro pore pattern identification of the samples which yielded to compare changes occurred in pore structures of samples formed at different conversion degrees.

Bassano et.al [2009] studied isothermal carbon dioxide gasification of two different coal samples under three different final temperatures (900, 1000, 1100°C) by thermogravimetric analysis (TGA). Process was divided into two stages as pyrolysis being conducted under the inert environment, nitrogen (N_2), and then gasification under carbon dioxide (CO_2) gas. Goals of the study were stated to be as checking the validity of the n^{th} order kinetic Arrhenius type model, determination of effect of temperature on reaction rate and comparison of low rank and high rank coal samples' reactivities. At the end of the study, Arrhenius type kinetic model was found to be fitted well with the experimental data and based on the kinetic calculations, Arrhenius kinetic constants (E & A) were found. Moreover, reactivity index ($R_{0.5}$) values were calculated and T vs $R_{0.5}$ charts of both samples were formed for three different temperature values. As a result, by taking both activation energy (E_a) and reactivity index ($R_{0.5}$) values into account, low rank Sulcis coal that was richer in volatile matter was found to be more reactive than high rank South African coal.

CHAPTER 4

STATEMENT OF THE PROBLEM

This study aims to observe isothermal gasification profiles of Saray-Edirkoy coal samples. Effects of different parameters as final reaction temperature, heating rate, gas flow rate, gas medium type and isothermal duration on coal gasification mechanism were tried to be determined in order to find the optimum conditions for such a global and current gasification process.

For gasification reactions, two different Saray-Edirkoy coal on the brink of as received and washed and dried coal samples were analyzed by TGA experiments. Reaction regions were identified from TG/DTG curves by analysis of regions where mass losses occurred and peak temperatures were observed on DTG curves. Depending on different gasification atmospheres (CO_2 , N_2/CO_2 , $\text{N}_2/\text{Dry Air}$), heating rates ($20^\circ\text{C}/\text{min}$, $30^\circ\text{C}/\text{min}$, $40^\circ\text{C}/\text{min}$, $50^\circ\text{C}/\text{min}$), gas flow rates (60 ml/min, 100ml/min), gasification temperatures (750°C , 825°C , 850°C , 900°C , 950°C) and isothermal durations (60 min, 120 min), totally seven different experiment procedures with their sub-groups were executed as part of this study. For isothermal gasification experiments, Arrhenius plots were drawn in the scope of kinetic analysis in order to determine activation energies of coal samples under identified optimum conditions. In addition to all, scanning electron microscope (SEM), and x ray diffraction (XRD) analyses of coal samples were conducted in Middle East Technical University Central Laboratory in order to observe morphological changes occurred during experiments and to execute qualitative elemental analyses of different samples (original, post-pyrolysis and post-gasification).

CHAPTER 5

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Isothermal coal gasification experiments in the scope of the study were conducted by TGA Q500 equipment, technical properties of which are given in the following section.

5.1 Thermogravimetric Analyzer (TGA)

5.1.1 Technical Properties

Thermogravimetric Analyzer (TGA) monitors weight change and rate of weight change of sample as a function of temperature or time under a controlled atmosphere. This method can be used to detect sample composition, phase changes as decomposition, oxidation or gasification and behavior of the sample under such different processes; i.e. its stability.

TGA equipment is composed of six different units which can be listed as *furnace*, *balance*, *sample platform*, *cabinet*, *heat exchanger* and *mass flow controller*.

Furnace (standard) controls sample atmosphere as well as its temperature. Furnace assembly can be seen from Figure 5-1.

Balance provides weighing sample precisely.

Sample platform performs loading and unloading the sample to and from the balance.

Cabinet houses all system electronics and mechanics.

Heat exchanger spreads heat from the furnace.

Mass flow controllers manage purge gas to the both balance and furnace.

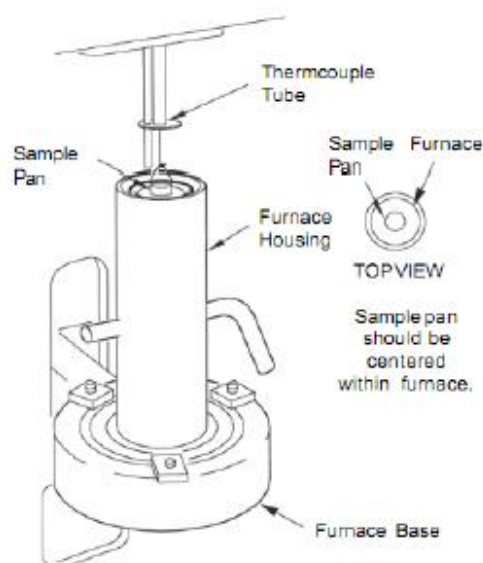


Figure 5-1: TGA furnace assemblage (Thermogravimetric Analyzer, 2006)

5.1.2 Experimental Procedure

All combustion and gasification experiments in this study were executed with respect to TA Instruments Manual. General experimental steps for TGA instrument can be summarized as *selection of pan type and material, taring of empty pan, placing sample in platinum pan, loading the pan, entering the experimental procedure through TA instrument software, starting the experiment, and finally unloading and cleaning pan at the end of the experiment.*

In this study, 10 mg of samples were used in all TGA experiments which were being heated under 20, 30, 40 and 50 ° C/min within the temperature range of 25-950 ° C. Nitrogen, carbon dioxide and dry air gases were used as inert and non-reactive pyrolysis and gasification agents. Inert gas (N₂) was used for the balance chamber as well as for the furnace chamber for pyrolysis reactions whereas dry air or carbon dioxide was used for

the furnace chamber for gasification reactions. Gas flow rates were used as 40 ml/min for balance whereas they were within the range of 60-100 ml/min for sample furnace.

For the purpose of observing different experimental conditions' effects on coal gasification process, variables as heating rate, final gasification temperature, isothermal gasification duration, gasification agent and gas flow rate were changed and experiments were divided into seven different analyses with their subgroups (Tables 5.1 –5.5).

Table 5-1: Experimental procedure of Analyses 1-2-3 and their subgroups

Analyze	Group	Gas	Sample Amount (mg)	Gas Flow Rate (ML/min.)	Heating Rate (°C/min)	Final Temperature (°C)	Isothermal Duration (min.)
1	1	CO ₂	10	60	20	750	60
	2					850	
	3					950	
2	1				20	950	60
	2				30		
	3				50		

Table 5-1: Experimental procedure of Analyses 1-2-3 and their subgroups (Continued)

Analyze	Group	Gas	Sample Amount (mg)	Gas Flow Rate (ML/min.)	Heating Rate (°C/min)	Final Temperature (°C)	Isothermal Duration (min.)
3	1	CO ₂	10	60	20	950	120
	2				30		
	3				50		

Table 5-2: Experimental procedure of Analyze 4

Analyze	Group	Gas	Sample Amount (mg)	Gas Flow Rate (ML/min.)	Heating Rate (°C/min)	Final Temperature (°C)	Isothermal Duration (min.)
4	1	N ₂	10	60	20	950	120 (Pyrolysis-N ₂)
	2	CO ₂					60 (Gasification-CO ₂)
							60 (Pyrolysis-N ₂)
							120 (Gasification-CO ₂)

Table 5-3: Experimental procedure of Analyze 5

Analyze	Group	Gas	Sample Amount (mg)	Gas Flow Rate (ml/min.)	Heating Rate (°C/min)	Final Temperature (°C)	Isothermal Duration (min.)	
5	1	N ₂	10	60	40	950	120 (Pyrolysis-N ₂)	
		CO ₂					60 (Gasification--CO ₂)	
	2	N ₂				CO ₂	750	60 (Pyrolysis-N ₂)
							825	
							850	
							900	120 (Gasification--CO ₂)
							950	

Table 5-4: Experimental procedure of Analyze 6

Analyze	Group	Gas	Sample Amount (mg)	Gas Flow Rate (ML/min.)	Heating Rate (°C/min)	Final Temperature (°C)	Isothermal Duration (min.)
6	1	N ₂	10	100	40	950	120 (Pyrolysis-N ₂)
							60 (Gasification--CO ₂)
	CO ₂	2					60 (Pyrolysis-N ₂)
							120 (Gasification--CO ₂)

Table 5-5: Experimental procedure of Analyze 7

Analyze	Group	Gas	Sample Amount (mg)	Gas Flow Rate (ML/min.)	Heating Rate (°C/min)	Final Temperature (°C)	Isothermal Duration (min.)
7	1	N ₂ Dry Air	10	60	40	750	60 (Pyrolysis-N ₂)
	2					825	120 (Gasification-Dry Air)
	3					850	
	4					900	
	5					950	

5.1.2.1 TGA Calibration

In order to obtain accurate results, weight and temperature calibrations of TGA Q500 equipment were repeated regularly throughout the experiments, and it was specifically performed when reactive gas was changed.

5.1.2.1.1 Temperature Calibration

TGA equipment temperature calibration is achieved by Curie point method. Ferromagnetic nickel as Curie standard sample is loaded and a magnet is placed under furnace as a result of which increase in sample weight is recorded due to magnetic force. With the increase of heat, at the Curie point, which is specified as 354 °C., ferromagnetic sample losses its ferromagnetic property and its weight begins to decrease. Temperature at the deflection point is recorded as observed temperature and temperature calibration is adopted based on this actual and observed temperature difference (Thermogravimetric Analyzer, 2006). Example of temperature calibration result is presented in Appendix B (Figure B-1).

5.1.2.1.2 Weight Calibration

Weight calibration procedure of the instrument calibrates both the 200 mg and 1 g weight ranges. In this study, weight calibration procedure was adopted by using 100 mg and 1 g standard weight samples. After taring the empty pan, standard weights are placed in turn and during weighing each, it is waited until weight deviations are eliminated. All steps are saved in the instrument internally (Thermogravimetric Analyzer, 2006).

5.2 Saray Edirkoy Coal Properties

5.2.1 Compositional Analyses

Smoot and Smith [1985] indicated that understandability of any coal conversion process requires physical data as thermal conductivity, specific heat, density and swelling index. Moreover, it was added parent coal's chemical properties as coal composition, which can be determined by proximate analysis or ultimate analysis, should also be known in modelling of any coal conversion process.

In this study, two coal samples from Saray-Edirkoy were used in all of the analysis. One of them was as-received (original) sample while the other one was washed and dried sample. Proximate and ultimate analysis of both samples are given in the following Table 5-6. Moreover chemical and mechanical properties of as received coal ash are shown by Table 5-7 and Table 5-8.

Table 5-6 : Proximate and ultimate analysis of coal samples

Sample	Moisture Cont. (%)	Volatile Matter (%)	Fixed Carbon (%)	Ash Content (%)	Heating Value* (Cal/g)
As received coal	42.01	23.30	13.39	21.31	2524
Washed and dried coal	24.95	35.54	26.48	13.03	4152

**HHV - upper heating value*

Sample	C (%)	H (%)	N (%)	S (%)	O (%)*
As received coal	42.90	3.38	0.96	4.15	27.30
Washed and dried coal	58.03	4.16	1.18	4.56	19.04

**by difference*

Table 5-7: Chemical Analysis of as received coal ash

Na ₂ O %	0,4
MgO %	4,1
Al ₂ O ₃ %	16,8
SiO ₂ %	49,3
P ₂ O ₅ %	0,1
K ₂ O %	1,8
CaO %	4,2
TiO ₂ %	0,7
MnO %	<0,1
Fe ₂ O ₃ %	11,2
SO ₃ %	5,9
As(ppm)	76
Ba(ppm)	370
Cr(ppm)	185
Cu(ppm)	59
Mo(ppm)	18
Pb(ppm)	49

CHAPTER 6

KINETIC ANALYSIS

For kinetic analysis of isothermal gasification experiments, Arrhenius method as one of the model fitting kinetic methods, was used which assumes that the total mass loss of the sample is dependent only on reaction rate constant, weight of the sample remaining and the temperature with reaction order of unity (Kok, 2011). General kinetic model is given as;

$$dw/ dt= k*w^n \quad \text{where } k=Ae^{(-E_a/RT)} \quad (6.1)$$

When first order kinetics is assumed ($n=1$); then equation becomes;

$$(1/w)*(dw/dt) = Ae^{(-E_a/RT)} \quad (6.2)$$

Char reactivity is defined based on initial char mass (w_o) and instantaneous mass loss rate (dw/dt) as;

$$k= (1/w_o) * (dw/dt) \quad (6.3)$$

By combining equation (6.2) and equation (6.3), following equality is obtained;

$$k =A \exp (-E_a. /RT) \quad (6.4)$$

Where k is defined as the coal reactivity, A is Arrhenius constant (pre-exponential factor), R is universal gas constant and E is the activation energy.

By *TA Universal 2000* software, all saved data could be analyzed as an excel report which enabled calculation of reactivity values at desired temperature intervals. Throughout all reactivity values, maximum value was picked up as the maximum reactivity (R_{max}).

In addition to calculation of activation energies based on R_{max} values, reactivity index values were also calculated. Reactivity index of a coal is defined as R_s (1/min) and;

$$R_s = 0.5/t_{0.5} \quad (6.5)$$

Where $t_{0.5}$ is defined as time required for 50% conversion of coal sample at isothermal conditions.

As a result, Arrhenius plots of coal samples under carbon dioxide (CO_2) and dry air mediums were formed based on both maximum reactivities (R_{max}) and reactivity index values (R_s) by the following linearized form of the equation (6.4):

$$\ln(k) = \ln A - (E/R)1/T \quad (6.6)$$

Where k values were used as either R_{max} or R_s rates under different temperatures.

CHAPTER 7

RESULTS AND DISCUSSION

Coal samples are difficult to be interpreted because of their heterogeneity. When they are heated, they undergo different subsequent chemical reactions as moisture loss, devolatilization, combustion and gasification depending on the used purge gas, final reaction temperature and other parameters. Thermogravimetric analysis (TGA) is an instrument with immense utility for analyzing numerous coal systems. Although TGA instrumentation technology limits the heating rate, TGA is very useful in making valid predictions of the chemical and physical properties of coal. TGA's foremost advantages are the precision, speed, and ease that samples can be analyzed. One person can analyze small samples on the order of grams that would demand a larger staff and much more money to analyze in a largescale system (Li et.al, 2005). In this study, as received and washed and dried coal samples were used in comparison of gasification reactivities under different experimental conditions by thermogravimetric analysis.

7.1 Carbon dioxide (CO₂) Gasification Results

7.1.1 Thermogravimetry Analysis Results

When experimental results in the scope of this study were analyzed, it was observed that all of the carbon dioxide gasification experiments were including three subsequent reaction regions which were correlated with moisture loss, devolatilization and gasification steps respectively.

Isothermal gasification regions were attached to third reaction region. Important parameters for TG/DTG curves such as reaction interval, maximum mass loss rate, total weight change or residue percent, and peak temperature were determined by using TA Universal 2000 software program.

An example for TG/DTG curve analysis of as received coal sample under CO₂ gasification process that was analyzed by software program is given in the following Figure 7-1. Explained analysis procedure was applied to whole experiment results.

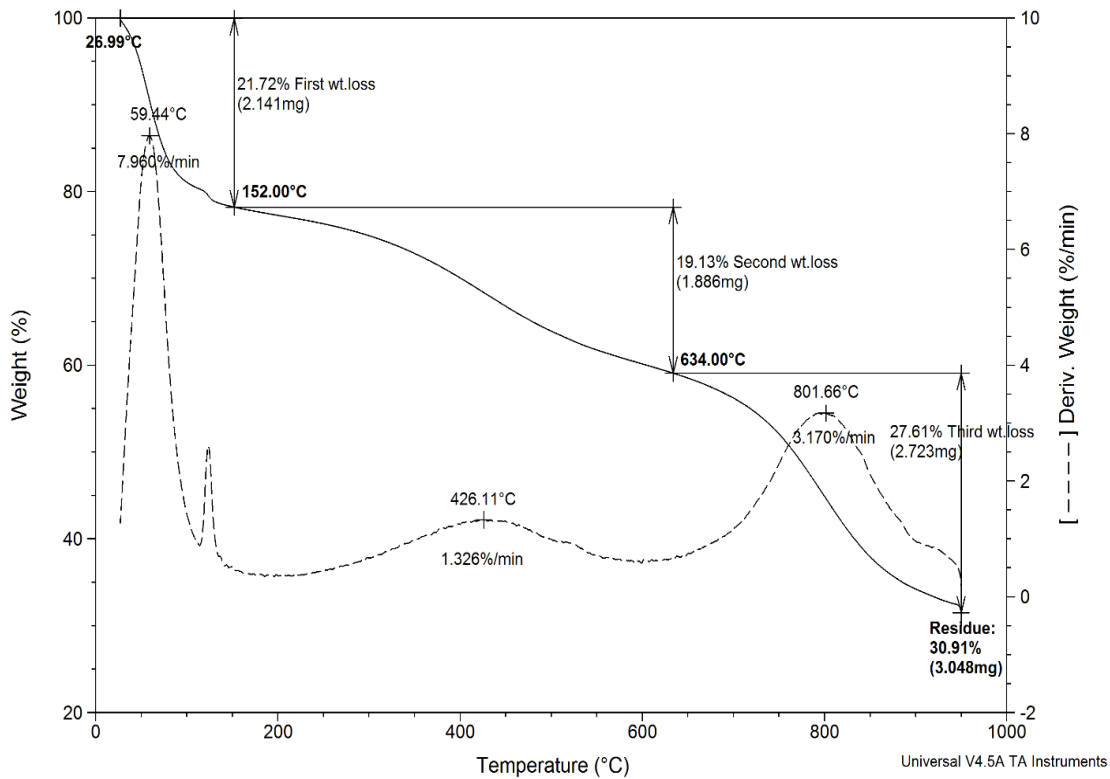


Figure 7-1: Analyze 1, Group-3 experiment result evaluation by software for as received coal sample

As shown by Figure 7-1, reaction intervals, mass losses occurred in specified range of different type of reactions, peak temperatures, maximum mass losses occurred in those intervals, and residue percentages were found by coupling TG/DTG curves. Reaction intervals were determined based on slope changes occurred in TG curve which were also supported by DTG curve peaks.

First mass loss which was found as 21.72% was correlated with moisture and some part of the volatile matter loss. Smaller peak taking place between the temperature interval of 114-152°C, which can be seen from Figure 7-1 as in the case of all results being tabulated under Appendix C and Appendix D sections, were correlated with beginning of devolatilization step. However, since its mass loss is really small and there is no time lag between these consecutive stages, following interval was also evaluated within the first region. Maximum mass loss (7.960 %/min) in this first reaction interval occurred at 59.44°C which was defined as the peak temperature of first reaction interval. For the second interval between 152-634°C, lighter volatile matter of the as received coal sample were said to be volatilized and maximum mass loss rate (1.326%/min) was seen to be decreased when compared with moisture loss rate occurred in the first interval. For the final reaction region starting from 634°C and continues up to final designated gasification temperature, 950°C, char gasification was expected to be occurred and as it can be easily recognized from Figure 7-1, main mass loss occurred in that interval. Results of Analyses 1, 2 and 3 are presented by Table E-1 in Appendix E.

Based on the results, three reaction intervals were detected for all Analyze 1 experiments. First stage, that generally occurred between 30-165°C, was correlated with the moisture loss and the release of easily volatilizable part of the volatile matter whereas following reaction interval generally occurred in the temperature range of 165-640°C and processes occurred in this stage were thought to be as the main devolatilization reactions. Finally, gasification reactions were assumed to be involved in the third reaction interval; i.e. 640-950°C.

When variables' effects (coal sample and final temperature) on Analyze 1 experiments, which were conducted under only carbon dioxide gas (CO₂), were examined, it was inferred that increased final gasification temperature positively affected coal samples' gasification reactivities by decreasing residue amounts; i.e. unreacted sample amount. Thus, higher gasification temperature; i.e. 950°C which is also lower than the ash fusion temperature of coal samples, that is stated to be 1237°C, was determined as the most advantageous temperature for gasification process. Lower peak temperatures being

occurred at lower final temperature values for both samples should not be evaluated in support of low temperature gasification, since it is expected to have lower peak temperatures for an early terminated reaction. On the other hand, maximum mass loss values indicated that the washed and dried coal samples had lower moisture amount and, mass loss rates occurred in first stage were found to be higher than those happened in the following secondary devolatilization and especially in rate determining tertiary gasification stages for both samples. Moreover, when washed and dried coal and as received samples' results were compared between each other, it was seen that overall mass losses of washed and dried coal were generally almost two times more than those of as received sample; which, in turn, indicates that washing coal is an advantageous pretreatment option for coal conversion process.

Rather than final temperature, for evaluation of the other parameters'; i.e. heating rate and isothermal gasification duration, effects on carbon dioxide gasification, highest reaction temperature 950°C was selected as the optimum gasification temperature for Analyze 2 and Analyze 3 experiments.

Results of Analyze 2 experiments indicated that increased heating rate caused a delay in start of the third reaction process. Moreover, it caused increase in peak temperature values and increase in maximum mass loss rates whereas any specific trend of residue percentages with respect to heating rate could be found except for observation of minimum residue percent at the lowest heating rate value (20 °C. /min) especially for washed and dried coal sample.

In addition to evaluation of final gasification temperature and heating rate effects on gasification process, isothermal duration effect was also examined by conducted Analysis 3 experiments. Isothermal waiting period was increased from 60 minutes (Analyze 1&2 experiments) to 120 minutes (Analyze 3 experiments) for that purpose. When results were compared, it was concluded up that increased isothermal duration led decrease in residue percentages most probably as a result of more allocated time for the char sample to react with the purge gas.

Also, delay in starting temperature of third reaction region was observed with increased heating rate for both of the coal samples. On the other hand, any exact trend for heating rate-residue percent relationship could be detected as in the case of Analyze 2 experiments. Residue percentages increased when heating rate increased from 20°C/min. to 30° C/min. whereas they decreased when heating rate increased from 30°C/min. to 50 ° C. /min. However, it was again observed that the lowest residue amount occurs at the lowest heating rate value (20°C/min.) for both coal samples.

For general inferences for the Analysis 1, Analysis 2 and Analysis 3 experiments, except for the higher peak temperature values, depending on the residue percentages, maximum mass losses and gasification ignition temperatures, it can be said that washed and dried coal sample shows higher reactivity for gasification process when compared with as received coal sample. This also supports the thesis that cleaning coal before any conversion process is an effective option from both environmental and technical point of views even coal cleaning economy should be evaluated before founding plant. All results of Analyses 1, 2 and 3 experiments are shown by Table E-1 in Appendix E part.

Since exact transitions between pyrolysis and gasification stages could not be identified exactly by just using a single carbon dioxide (CO₂) gas, gradual isothermal gasification experiments under both nitrogen (N₂) and carbon dioxide (CO₂) gases were conducted via Analyze 4, 5, and 6 experiments in addition to Analyze 1, 2 and 3 experiments. To remind their procedures once more, they can be summarized up as follows. Analyze 4 experiments were conducted under 20°C/min constant heating rate up to 950 °C final temperature with 60 ml/min gas flow rate of both gases nitrogen and carbon dioxide for sample furnace.

In order to see the effect of heating rate on gasification reaction, Analyze 5 experiments were conducted under constant heating rate of 40° C/min up to same designated temperature 950 °C. and same gas flow rate (60 ml/min) with Analyze 4 experiments was used.

Finally, for determination of gas flow rate effect on gasification process, Analyze 6 experiments were carried out under 40°C/min heating rate up to again the highest gasification temperature 950 °C but with higher flow rate of 100 ml/min.

When they were analyzed by the TA Universal Analysis software program, reaction regions were evaluated under three parts as heating from room temperature to designated temperature by nitrogen (N₂), an isothermal period under same atmosphere to let the pyrolysis reaction to be completed and the second isothermal part under carbon dioxide gas (CO₂) for gasification reaction. Those analyses were evaluated under two groups depending on different isothermal durations (60 or 120 minutes) for pyrolysis and gasification reactions. Concordantly, in Group 1 experiments isothermal pyrolysis duration was longstanding part (120 min) when compared with gasification duration (60 min) and the contrary condition (higher duration for gasification part) was implemented for Group 2 experiments. The following inferences were made for Analyze 4, 5, and 6 experiments results of which are tabulated by Table E-2 in Appendix E.

By evaluating results of Analyze 4 experiments, especially for washed and dried coal sample, residue percentages were found to be having lower values under Group 2 experiments where gasification duration was extended to 120 minutes. On the other hand, any significant difference could be observed between Group 1 and Group 2 experiments of as received coal sample. Again lower peak and ignition temperatures were detected for washed and dried coal sample when compared with those of as received coal.

When Analyze 5 experiment results were analyzed, lower residue amounts were observed with increased duration of isothermal gasification region. For Group 2 experiments, based on residue amount, any effect of heating rate could be observed for washed and dried coal sample when compared with those of Analyze 4 experiments. On the other hand, for as received coal samples, observable decrease in residue percentages were observed for Analyze 5 experiments. Moreover, it was seen that even residue amounts were found to be lower, higher peak and ignition temperatures were detected under higher heating rate (40°C/min).

Just by looking increased residue percentages, any positive impact of increased isothermal duration for gasification process (Group 2) could be deduced for Analyze 6 experiments.

Additively, based on general trend of residue percentages and peak temperatures, when Group 2 experiments of Analyze 4 and Analyze 5 experiments were compared with those of Analyze 6 results, 60 ml/min. flow rate of purge gas was found to be the most advantageous for gasification process of both as received and washed and dried coal samples (Table E-2).

7.1.2 Conversion Factor and Reactivity Results

There were several parameters as peak temperature, residue amount, and ignition temperature being used in comparison of different conditions' suitability for coal gasification process. Thus, just by comparing the results of TA Universal Analysis software, it was difficult to state that one condition was much more advantageous by taking all parameters into account in one step since they could give contrasting results. To illustrate, when one experimental procedure was found to lead favorable effects on one of those parameters being used as basis of comparison, opposite results or ineffectiveness of the same experimental procedure could be observed based on other parameters.

For that reason, to be able to do more realistic comparison of experimental conditions for coal gasification process, two quantitative parameters; specifically as 'conversion factor' and 'reactivity' of both coal samples under different experimental conditions were calculated. At the end of each experiment, all saved data could be analyzed by TA Universal Analysis software and they were exported to Microsoft Excel to be evaluated as spreadsheets. Accordingly, needed parameters for calculation of conversion factor and reactivity as W_o , W_t , W_{final} , and dw/dt were exported to MS Excel as spreadsheets.

Within this context, conversion factor versus reactivity curves for pyrolysis and gasification stages were formed (Figure 7.2-7.13).

'Conversion factor' and 'reactivity' parameters that are important in kinetic analysis were calculated by following formulas.

7.1.2.1 Conversion Factor

$$X = (W_o - W_{t.}) / (W_o - W_{final}) \quad (7.1)$$

Where;

X= coal conversion degree

W_o = coal weight (mg) for pyrolysis stage, char weight (mg) for gasification step

$W_{t.}$ = Instantaneous weight of the sample (mg)

W_{final} = Final weight of sample for either pyrolysis or gasification phases (mg)

7.1.2.2 Reactivity

$$R = (1/W_o) * (dw/dt) \quad (7-2)$$

Where;

R= Reactivity of coal (mg/mg-min)

dw/dt = instantaneous mass loss rate (mg/min)

When conversion factor and reactivity charts of coal samples under pyrolysis stages were analyzed (Figure 7-2-Figure 7-4) for all three different experimental conditions (Analyze 4, 5 and 6), it was seen that as received coal had higher pyrolysis reactivity than washed and dried coal sample which was tied to the fact that washed and dried coal sample had been purified from its moisture and from some impurities. On the other hand, when conversion factor-reactivity relationships of coal samples under gasification stage were analyzed, washed and dried coal sample's maximum reactivity distribution was observed under Analyze 5 Group 2 experiment whereas any regular trend could be detected for as received coal sample (Figure 7-5-Figure 7-13).

manganese (Mn), magnesium (Mg), lithium (Li), and iron (Fe) were found in XRD peaks of post pyrolysis samples. On the other hand, for post gasification samples, only calcium oxide (CaO) and calcium carbonate (CaCO₃) minerals could be identified. As mentioned previously, 2 theta-intensity curves of all samples are shown by Figure 7-24. Run of mine and washed and dried coal samples' XRD analyses show similarities, common peaks in XRD results of post-pyrolysis and post-gasification samples (Washed and dried sample: 1-2&As received sample:3-4) were also detected.

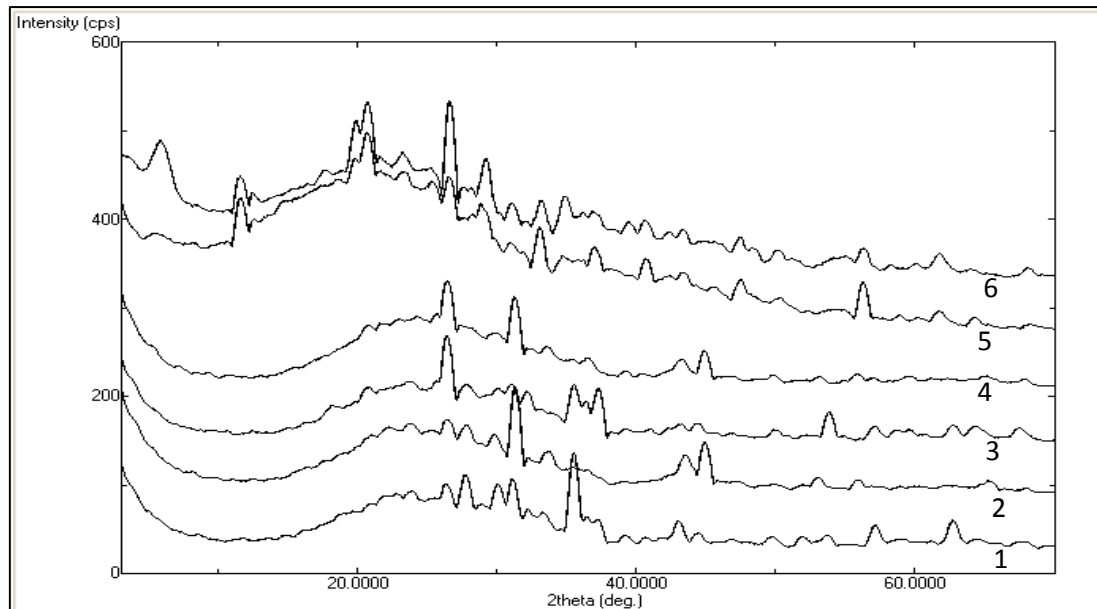


Figure 7-24: As received coal original (6), post-pyrolysis (4), post-gasification (3) and washed and dried coal original (5), post-pyrolysis (2), post-gasification (1) samples' XRD images

7.2 Dry Air Gasification Results

7.2.1 TGA Results

When dry air gasification experiments of as received coal sample were evaluated, differently from carbon dioxide gasification and except for the results being belonged to temperature values of 750°C and 850°C, four reaction regions were observed. Much the

same with gasification experiments performed via carbon dioxide (CO₂) gas, regions were matched with moisture loss, devolatilization, for some experiments combustion and gasification stages respectively. By evaluation of TG/DTG curves analyzed by TA Universal Analysis software program, some of the important parameters in thermal characterization as reaction interval, peak temperatures (Tp), residue percentages and maximum mass loss values (%) were determined and tabulated by Table E-3.

When results were compared for both of the coal samples, it was observed that with increased gasification final temperature, peak temperatures of gasification regions had mostly increased whereas residue percentages (%) were observed to be decreased with increased final temperature. Moreover, general trend of ignition temperature was found to be degressive with increasing final temperature. When compared with as received coal sample, washed and dried coal again showed higher tendency for dry air gasification process which was determined by general trends of ignition temperature, residue amount and peak temperature values. In addition to them, as in the case of carbon dioxide gasification, conversion factor vs reactivity graphs under five different reaction temperatures were formed for both as received and washed and dried coal samples (Figure 7-25-Figure 7-26).

7.2.2 Conversion Factor and Reactivity Results

Conversion factor and reactivity values were calculated by formulas given in section 7.1.2. When results were analyzed, consistency of conversion factor versus reactivity data, especially for as received coal sample, could not be found. As can be seen from Figure 7-25, considerably rare data distribution was tied to the reason of weight gain occurred in isothermal gasification region and its result of negative reactivity and conversion factor values. One possible reason for weight gain of as received coal sample could be explained by a reaction occurred between pyrite (FeS₂) available in coal sample ash and oxygen part of dry air.

Highest reactivity distribution trend was observed under 825°C final temperature for as received coal whereas 850°C and 900°C temperature values were found to give the

CHAPTER 8

CONCLUSION

In this study, to be on the point of being as received and washed and dried, two coal samples taken from Saray-Edirkoy field of Thrace region were experimentalised by seven different gasification analyses. Isothermal gasification profiles of both samples were analyzed under carbon dioxide (CO_2), nitrogen (N_2) /carbon dioxide (CO_2), and nitrogen/dry air atmospheres. To determine optimum gasification conditions for both of the coal samples, effects of some parameters as heating rate, final gasification temperature, isothermal duration and gas flow rate were analyzed. Correspondingly, in CO_2 gasification experiments six different analyses with different subgroups and the seventh experiment with its five subgroups under dry air atmosphere were conducted. Based on the experiments, below inferences were made.

When TG/DTG curves of Analyze 1-2-3 experiments, in which only carbon dioxide gas was used, were analyzed, it was concluded up that higher final temperature throughout three final temperature values (750, 850, 950°C) as well as the lower heating rate among three heating rate (20, 30, 50°C/min) and the longer isothermal duration (120 min. rather than 60 min.) were more advantageous for gasification process. In all gasification experiments, as observed in previously conducted combustion experiments, washed and dried coal showed much more favorable results than those shown by as received coal. These results also support the idea that the purification of coal from its impurities enables any thermal process to occur in much more effective way even coal cleaning process should be further studied especially from economical point of view.

Since transitions between reactional regions could not be identified exactly by using only one gas for both pyrolysis and gasification steps, Analyze 4-5-6 experiments were performed which were executed by dual gas system; i.e. nitrogen (N_2)/ carbon dioxide (CO_2) or nitrogen (N_2)/ dry air gases with different isothermal periods.

When TG/DTG curves of Analyze 4-5-6 experiments which were conducted gradually under nitrogen (N_2) and carbon dioxide (CO_2) gases, it was again concluded up that gasification reactivity of the washed and dried coal was much higher than that of as received coal. As in the case of previous experiments' results (Analyze 1-2-3), longer isothermal duration (120 min.) was found to be more advantageous for gasification process. On the other hand, effect of heating rate on gasification of two different coal samples was not same. Irregular trend of conversion factor versus reactivity distribution made interpretation and determination of optimum gasification conditions highly difficult for as received coal sample (Figure 7-8).

On the purpose of studying out the optimum gasification temperature and for determination of kinetic parameters, five different final temperature values (750-825-850-900-950°C) were experienced under Analyze 5 Group 2 experiments and it was observed that the most ordered conversion factor versus reactivity trend was belonged to 900°C data for as received coal (Figure 7-9). On the other hand, when all analysis results were compared, it was finalized as that Analyze 5 Group 2 experiment was the optimum gasification condition for washed and dried coal sample (Figure 7-12). Under the same conditions of other parameters as heating rate (40°C/min.), gas flow rate (60 ml/min.) and isothermal duration (120 min.), optimum temperature value for washed and dried coal gasification was found to be 950°C throughout five different temperature values (Figure 7-13).

As mentioned previously, Arrhenius plots of both coal samples were formed based on Analyze 5 Group 2 experimental conditions conducted under five different temperature values (750-825-850-900-950°C.) which can be seen on Figure 7-16 and Figure 7-17. When all data points were used, a perfect linear distribution could not be obtained for both of the samples. For that reason, points that being belonged to three final gasification

temperature giving the maximum linear correlation coefficient values were used. Finally, as received coal sample's activation energy was calculated as 127.11 kJ/mole based on R_{max} and 143.86 kJ/mole based on R_s values whereas it was found as 87.62 kJ/mole based on R_{max} and 102.62 kJ/mole based on R_s values of washed and dried coal sample. Thus, to be more realistic, results should be given as ranges rather than a specific value for activation energies of coal samples; i.e. E_a values found samples as a result of this study can be stated as to be between 127.11-143.86 kJ/mole for as received coal and 87.62-102.62 kJ/mole for washed and dried coal.

In addition to the thermogravimetry experiments (TG/DTG) used in order to identify optimum gasification conditions, scanning electron microscope (SEM) analyses were conducted for the purpose of observing the changes that occurred in surface morphologies of coal samples after pyrolysis and gasification processes.

On the other hand, even the amorphous structure of coal samples led noise rather than distinct peaks, x ray diffraction (XRD) analyses were also carried out for gaining a general idea about the qualitative designation of different fractions of coal at the end of which it was found up that both of the coal samples were mainly composed of pyrite (FeS_2), quartz (SiO_2) and gypsum ($CaSO_4$) minerals. Presence of the pyrite and quartz minerals were supported by SEM analyses results as well. SEM/ETD images of both of the post gasification samples gave clue about the possible reason of sintering images (Figure 7-20-Figure 7-23). Based on the data in hand, this result could be explained as the probable reaction of the calcium oxide available in coal ash (CaO) with the gasification agent carbon dioxide (CO_2) and which in turn formed calcium carbonate ($CaCO_3$) mineral that caused blockage of the pore space.

When x ray diffraction analyses come into question, it can be said that sample amount in short supply and the irregular crystalline structure of the coal made evaluation of low intense XRD peaks difficult. Results that were designated by the software program, PDXL, which uses a huge database in electronic environment, and that were correlated with SEM analysis could be summarized as follows:

- i. Mainly gypsum (CaSO_4), pyrite (FeS_2), and quartz (SiO_2) minerals in original coal samples,
- ii. Oxidized compounds of calcium (Ca), sodium (Na), iron (Fe) magnesium (Mg), lithium (Li), and manganese (Mn) elements, and quartz (SiO_2) mineral in post-pyrolysis samples,
- iii. Only calcium oxide (CaO) and calcite (CaCO_3) minerals in post-gasification samples could be detected.

On the other hand, for Analyze 7 experiments which were conducted under combination of nitrogen and dry air gases, five different temperature values that were same with carbon dioxide gasification experiments were used. When those results were evaluated, it was seen that residue amounts (residue %) decreased with increased final temperature. Moreover, when as received and washed and dried coal samples were compared between each other, gasification reactivity of washed and dried coal was found to be higher than that of as received coal based on its lower peak temperature (T_p) and lower residue percentage (residue %) values. While the irregular trend of the as received coal's reactivity-conversion factor distribution complicated the determination of optimum gasification temperature process, the most ideal trend was observed at 825°C temperature (Figure 7-25). Washed and dried coal conversion factor-reactivity distribution results; on the other hand, showed more regular trend and the highest maximum reactivity values were observed at 850°C and 900°C final temperatures (Figure 7-26).

For kinetic analysis of both coal samples, three data points giving the highest linear correlation coefficients as well as all data points of five temperature values were used in formation of $1/T$ (K) vs $\ln(R_{\max})$ graphs. Correspondingly, activation energy of washed and dried coal sample was found in between 13.88-15.16 kJ/ mole whereas it was found in the range of 72.46-84.68 kJ/mole for the as received coal sample (Figure 7-27-Figure 7-28). Post-gasification samples' SEM/ETD qualitative analyses were given in between Figure 7-30-Figure 7-31. Based on the results, samples formed after dry air gasification process were found to be composed of minerals formed mostly by silica (Si), Aluminum

(Al), calcium (Ca), molybdenum (Mo), iron (Fe), potassium (K), carbon (C) and oxygen (O) elements.

In general view, contrariety of some of the experimental results that made evaluation process difficult were tied to some reasons as experimental errors, complex structure and reactions as well as heterogeneity of the coal samples used throughout the experiments. To maintain the experimental errors at the minimum level, calibration of the thermogravimetry equipment was repeated once a month throughout the experiments. Moreover, margin of error for the sample amount parameter which was tried to be kept as constant in all of the conducted experiments (10 mg), was tried to be maintained as low as possible ($<3\%$). In order to see reproducibility of the experiments, Analyze 7 experiments were repeated and the figures were given in Appendix D and the tabulated results were given in Appendix E.

CHAPTER 9

RECOMMENDATIONS

Coal has a complex and heterogeneous structure which makes its analysis highly difficult. There are many parameters affecting its reactivity for any conversion process that's why many different techniques are needed in thermal characterization of coal.

In this study, two samples namely as received and washed and dried coals' isothermal gasification reactivities were evaluated mainly based on thermogravimetric analysis (TGA). Additionally, for optimum gasification conditions that were determined by TGA, XRD and SEM analyses were also performed which gave information about both chemical compositions and changes occurred in physical structures of the samples with different processes (pyrolysis and gasification).

For kinetic analyses of the samples, homogeneous model was used which assumes that pore structure of the coal samples did not change all through the reactions. For calculation of the activation energies of the samples, first order Arrhenius equality based on the maximum reactivity (R_{max}) and reactivity index (R_s) values was used.

This study, whose results will be used for pilot gasification plant that is planned to be built in Saray-Edirkoy region, can be evaluated for comparison of different gasification conditions formed by coal type, heating rate, gas flow rate, gas type, isothermal duration and final gasification temperature at laboratory conditions. Many combinations of the mentioned parameters are available and for sure, it requires an immense work to test all options experimentally.

Thus, in addition to used values of different parameters, this work should be extended with additional analyses. To illustrate, TG-FTIR, TG-MS for evolved gas analyses during pyrolysis and gasification stages should be determined to increase the accuracy of the thermogravimetric analyses results.

Moreover, by Brunauer–Emmett–Teller (BET) theory which defines the mesoporous and macro pore structures of the sample by gas (either N₂ or CO₂) adsorption methods, changes occurred in pore structure of the samples should be determined under different conditions in addition to visual inferences made by using SEM analyses which were conducted only for one experimental condition.

In results and discussion part of the thesis, it was mentioned that cleaning coal is an advantageous process for any coal conversion processes based on more appealing results of thermal and kinetic parameters of washed and dried coal sample. However, coal washing is a deep subject and there are many different technologies used for that process. Thus, it is really important to select the optimum methodology in which coal loss during cleaning can be decreased as much as possible and which is economically feasible. Otherwise, even the post washing conditions give an idea of cleaning coal before conversion process is favorable, the economy behind the process and some technical disadvantages of the process can lead a contrary situation. Thus, based on the washing technique that will be applied in the plant, technical and economical sides should also be evaluated detailedly not to cause any loss.

For kinetic analysis part, except for homogeneous model that assumes that the reaction is under chemical control rather than being under diffusion control, since coal gasification reactions are highly complex and the pore structure of coal samples is not stationary and it changes with conversion of coal with progress of the reactions, different non-homogeneous kinetic models as shrinking core model (SC), random pore model (RPM) and volumetric model (VM) should also be used to obtain much more accurate values for kinetic parameters.

Finally, in order to avoid from experimental errors and in order to check the reproducibility of experiments performed on non-homogeneous coal samples, all of the experiments should be repeated at least two times and since the TGA Q500 equipment limited the set final temperature of the experiments to 950 °C, it is highly recommended to experience higher temperature values to check their applicability on Saray-Edirkoy coal samples' gasification process.

All in all, it can be concluded up that, results of this study gives general opinion about gasification reactivity dependence of coal on type (run of mine/ washed), heating rate, gas flow rate, gas type, isothermal duration and final gasification temperature based on the given experimental procedures which should be further studied by experimental, modelling and simulation analyses.

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APPENDIX A

INSTRUMENT PROPERTIES

Table A- 1: TGA instrument characteristics (Thermogravimetric Analyzer, 2006)

TGA Instrument Characteristics		
Dimensions	Depth	55.9 cm (22 in.)
	Width	47 cm (18.5 in.)
	Height	52.1 cm (20.5 in.)
Weight		30,9
Weight of Transformer		8.18 kg (18 lbs.)
Power		120 Vac, 50/60 Hz, standard
Energy consumption		1.5 kVA
Room Operating Temperature		15°C to 35°C (non-condensing)
Temperature control range		ambient +5°C to 1000°C
Thermocouple		Platinel II*
Heating rate with standard furnace		0.1 to 100°C/min
Sample Pans		
Type		Platinum
Volume Capacity		
Balance Mechanism		
Weighing capacity (sample)		1.0 g
Resolution		0.1 µg

Table A- 1: TGA instrument characteristics (Thermogravimetric Analyzer, 2006)
(Continued)

Accuracy	< + 0.1%
Ranges	200 mg range: 0.1 µg — 200mg 1000 mg range: 1 µg — 1000 mg
Mass Flow Controller (MFC) Furnace Atmosphere For Q500	
Purge gases	Helium, nitrogen, oxygen, air, argon
MFC Purge rate Up to	200 mL/min
Operating Environment	
Ambient temperature range °C	15 – 35
Altitude	Less than 2 km

APPENDIX B

CALIBRATION RESULTS

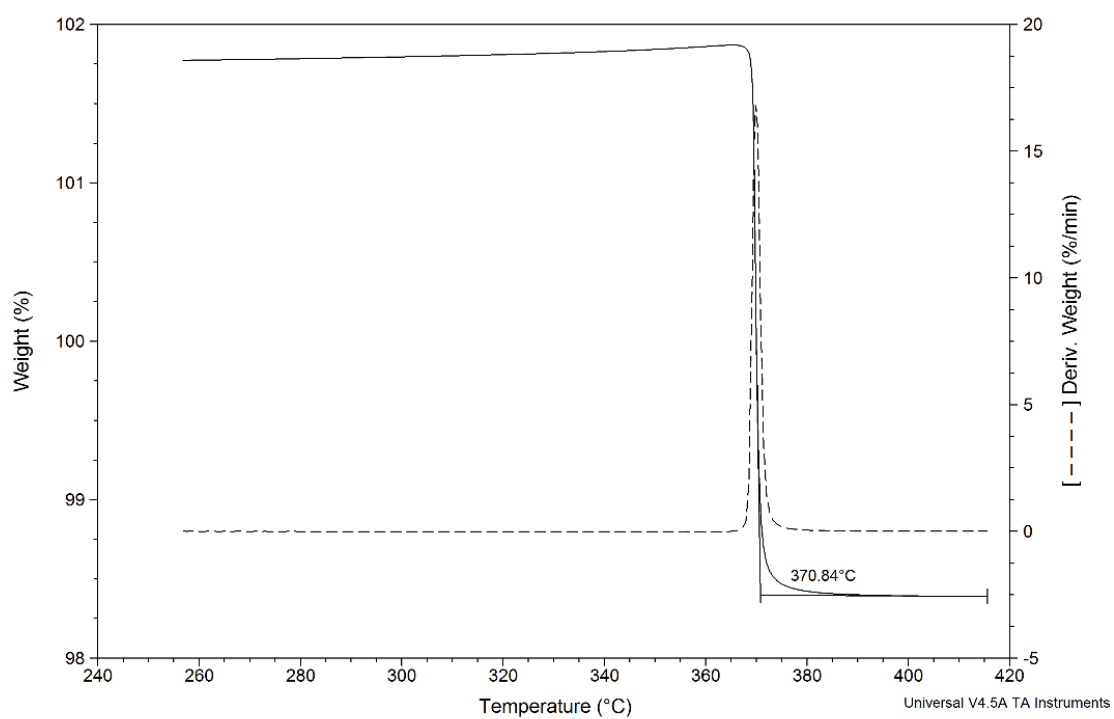


Figure B- 1: Example of temperature calibration of TGA instrument

APPENDIX C

TGA RESULTS OF EXPERIMENTS

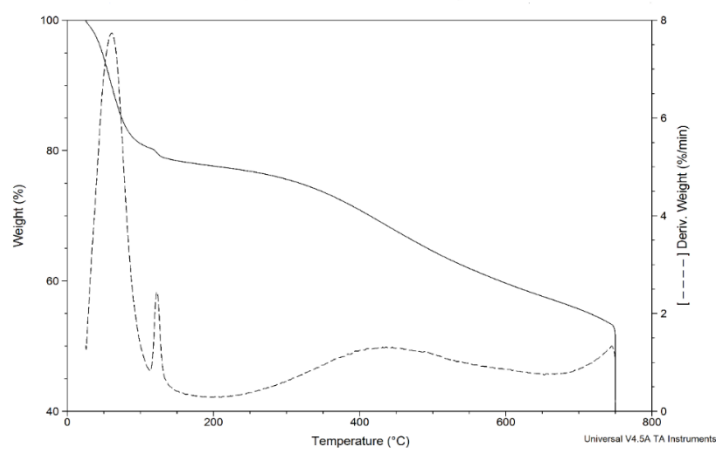


Figure C- 1: TG/DTG curve of as received coal under Analyze 1 Group 1 experimental conditions

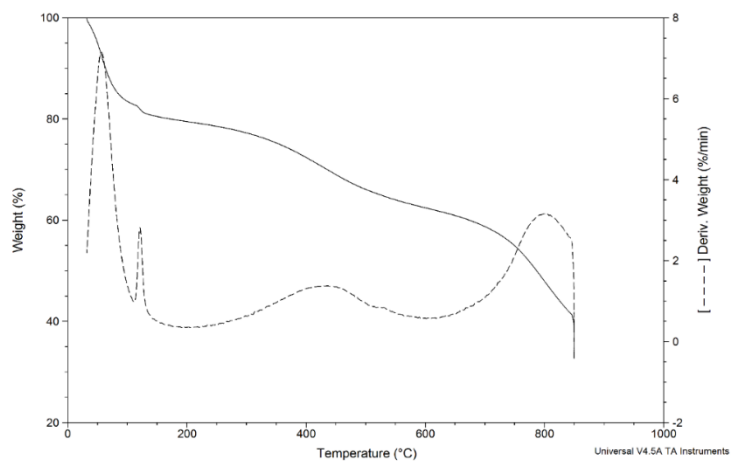


Figure C- 2: TG/DTG curve of as received coal under Analyze 1 Group 2 experimental conditions

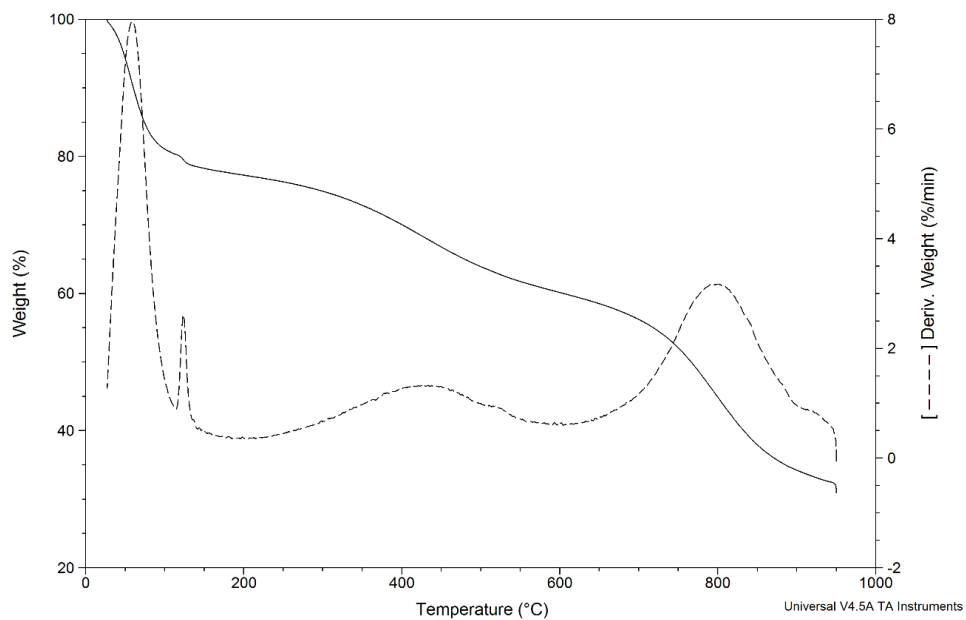


Figure C- 3: TG/DTG curve of as received coal under Analyze 1 Group 3 experimental conditions

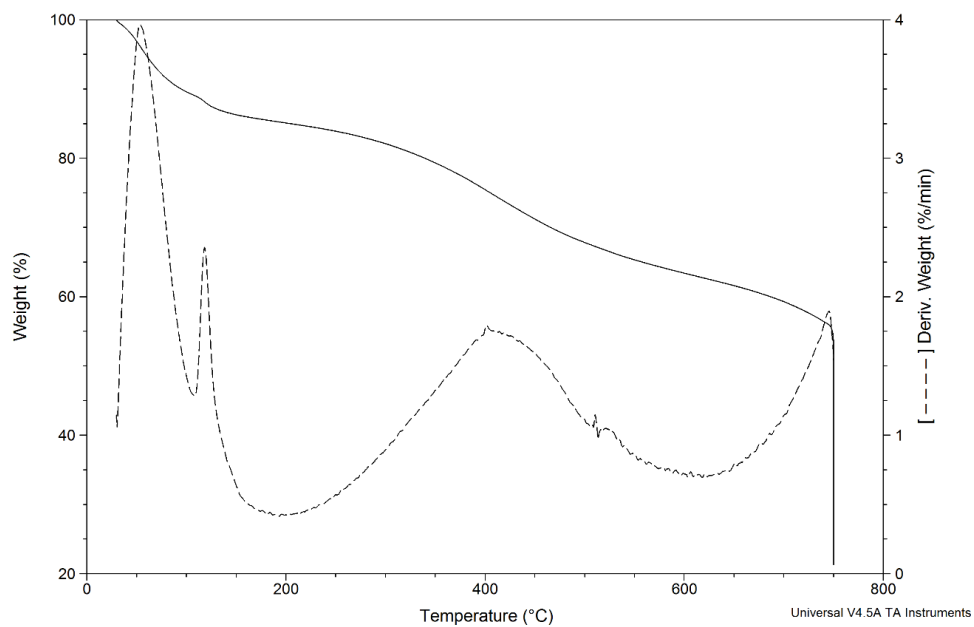


Figure C- 4: TG/DTG curve of washed and dried coal under Analyze 1 Group 1 experimental conditions

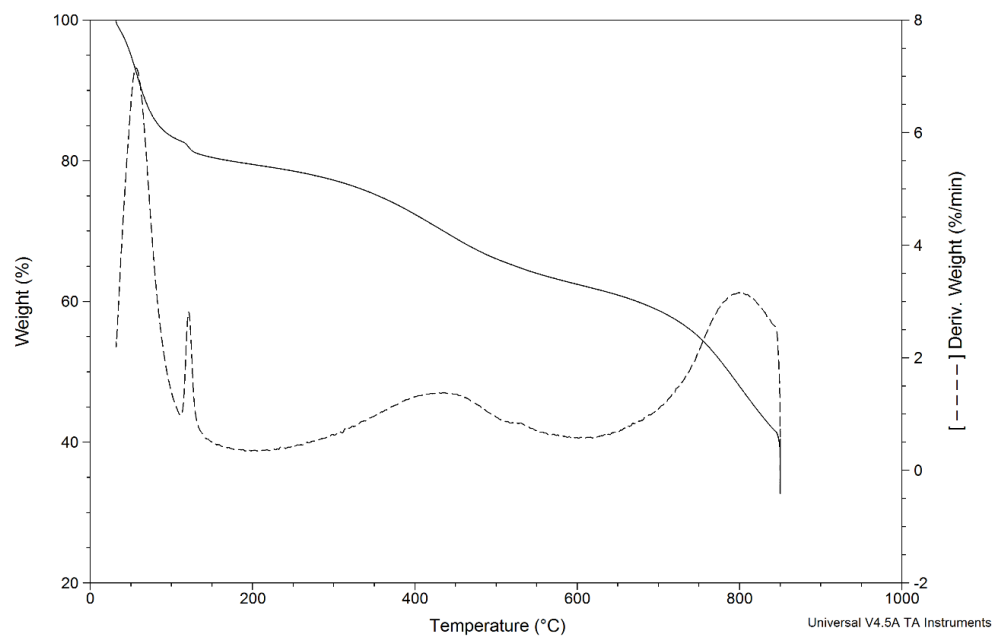


Figure C- 5: TG/DTG curve of washed and dried coal under Analyze 1 Group 2 experimental conditions

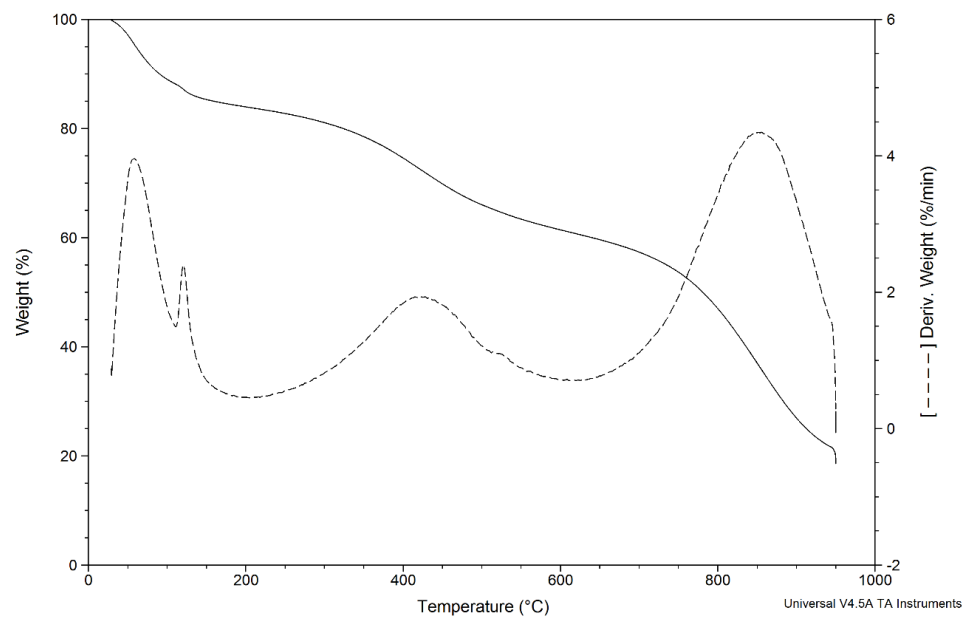


Figure C- 6: TG/DTG curve of washed and dried coal under Analyze 1 Group 3 (Analyze 2, Group 1) experimental conditions

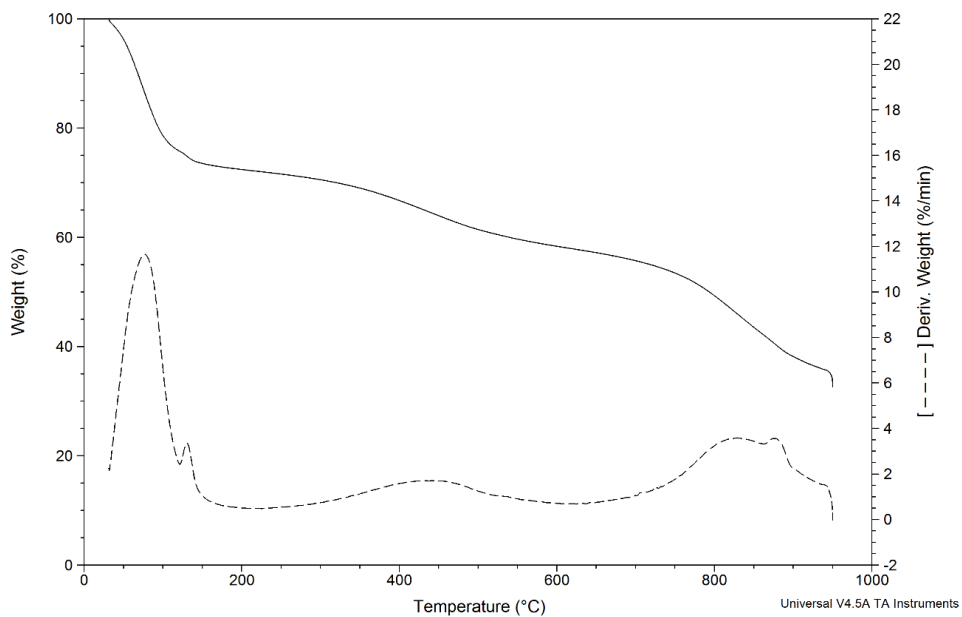


Figure C- 7: TG/DTG curve of as received mine coal under Analyze 2 Group 2 experimental conditions

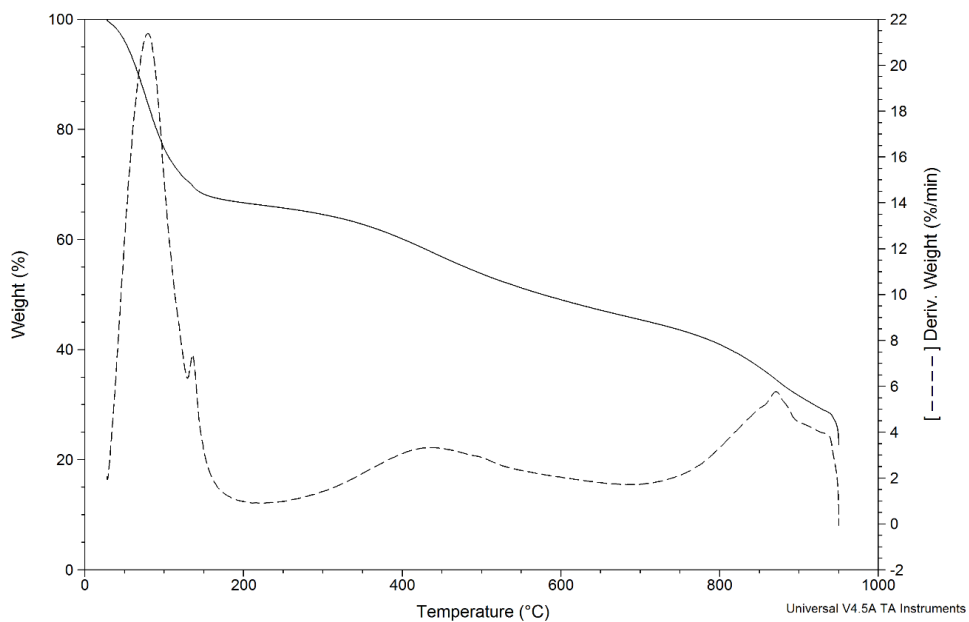


Figure C- 8: TG/DTG curve of as received coal under Analyze 2 Group 3 experimental conditions

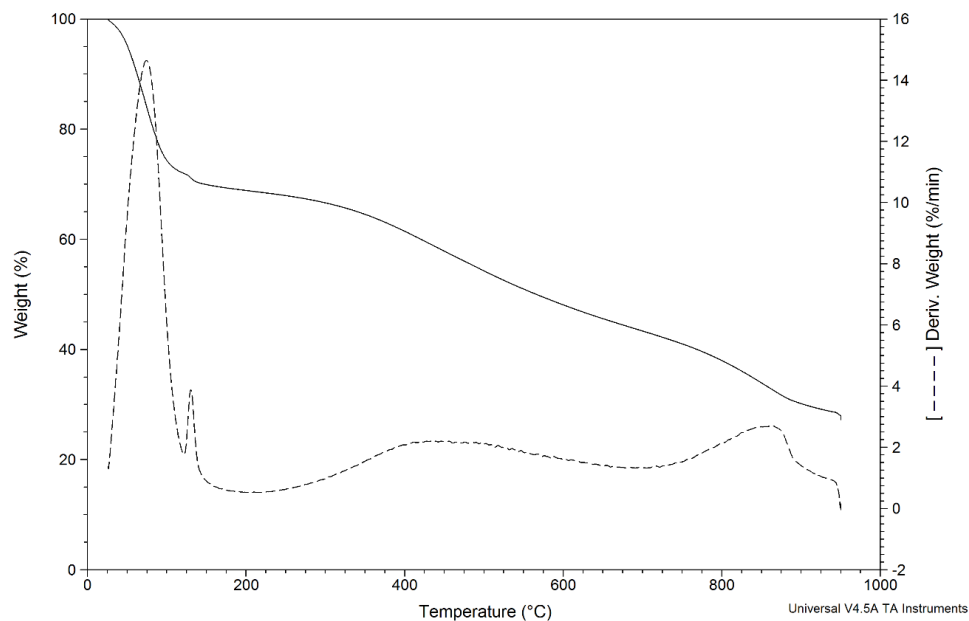


Figure C- 9: TG/DTG curve of washed and dried coal under Analyze 2 Group 2 experimental conditions

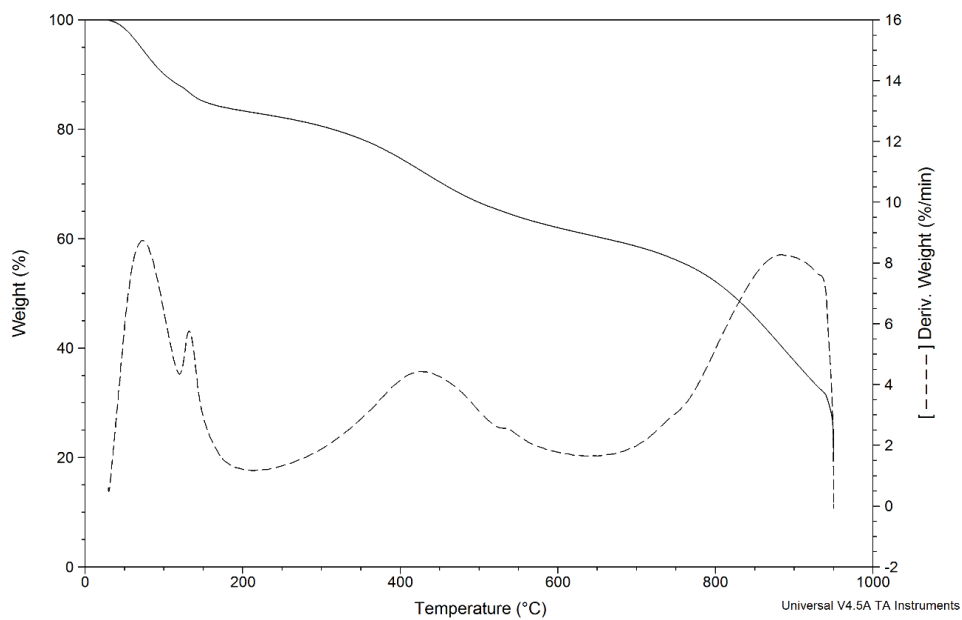


Figure C- 10: TG/DTG curve of washed and dried coal under Analyze 2 Group 3 experimental conditions

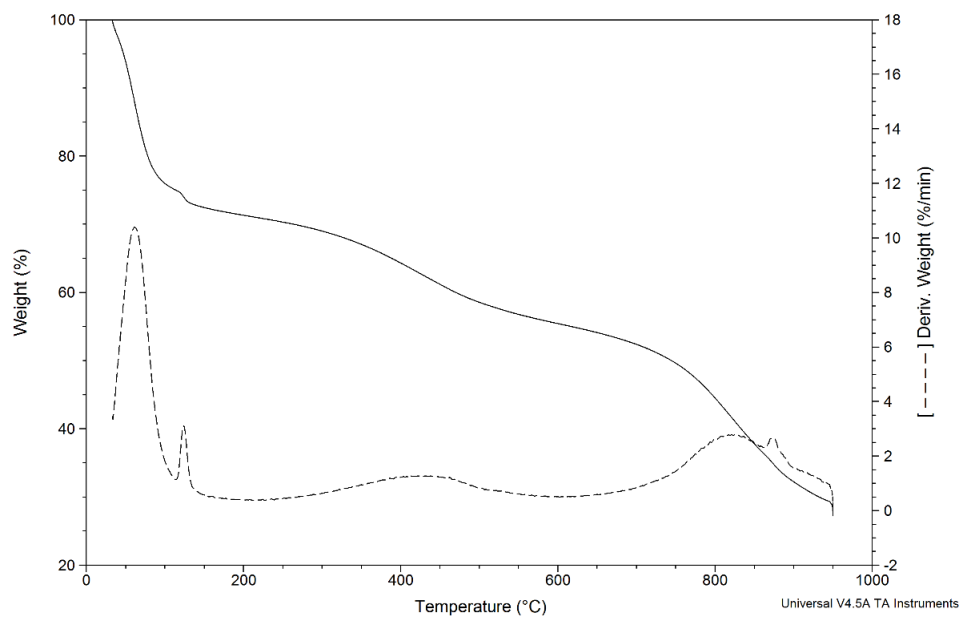


Figure C- 11: TG/DTG curve of as received coal under Analyze 3 Group 1 experimental conditions

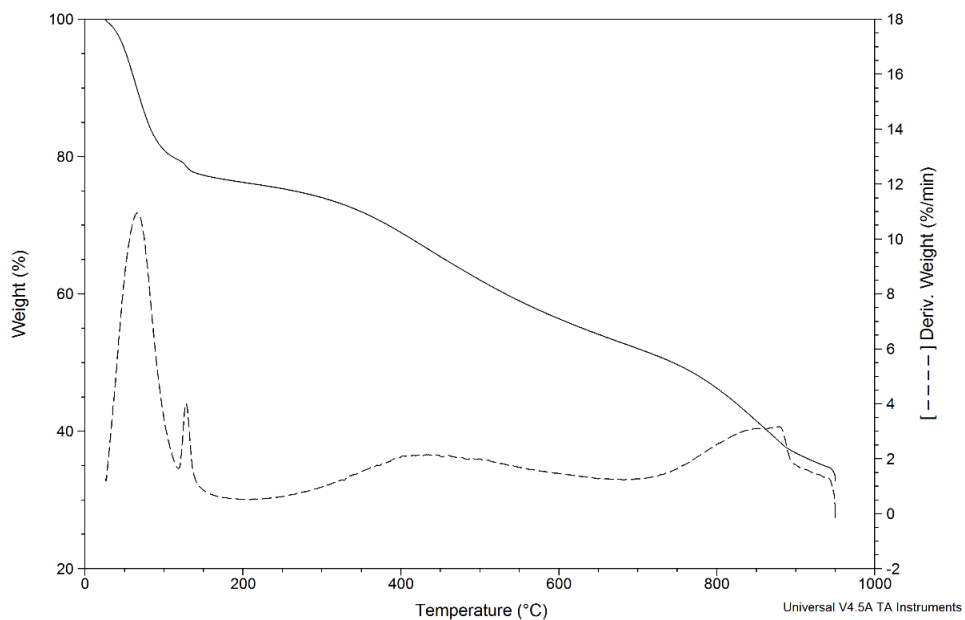


Figure C- 12: TG/DTG curve of as received coal under Analyze 3 Group 2 experimental conditions

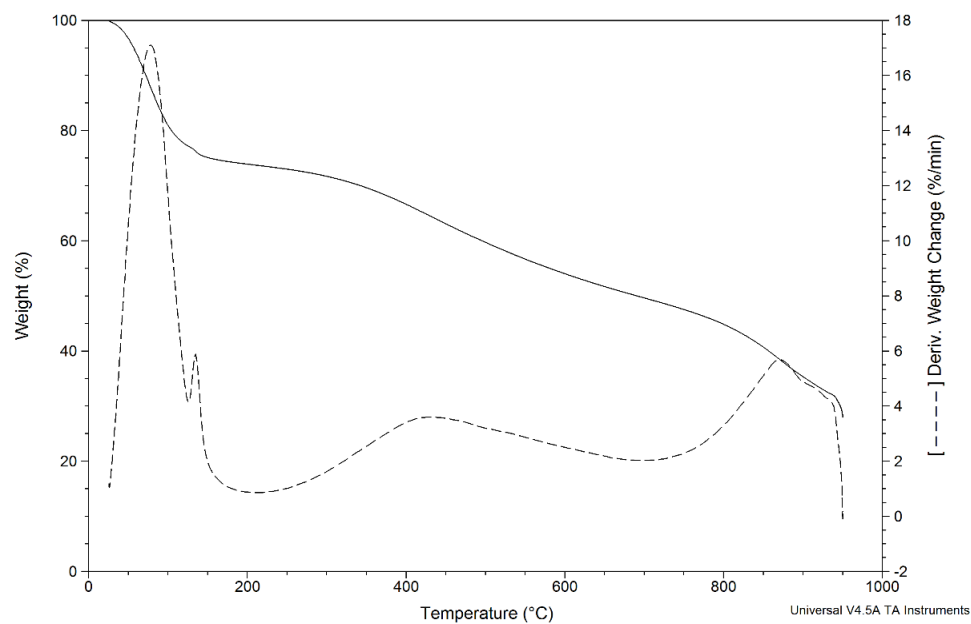


Figure C- 13: TG/DTG curve of as received coal under Analyze 3 Group 3 experimental conditions

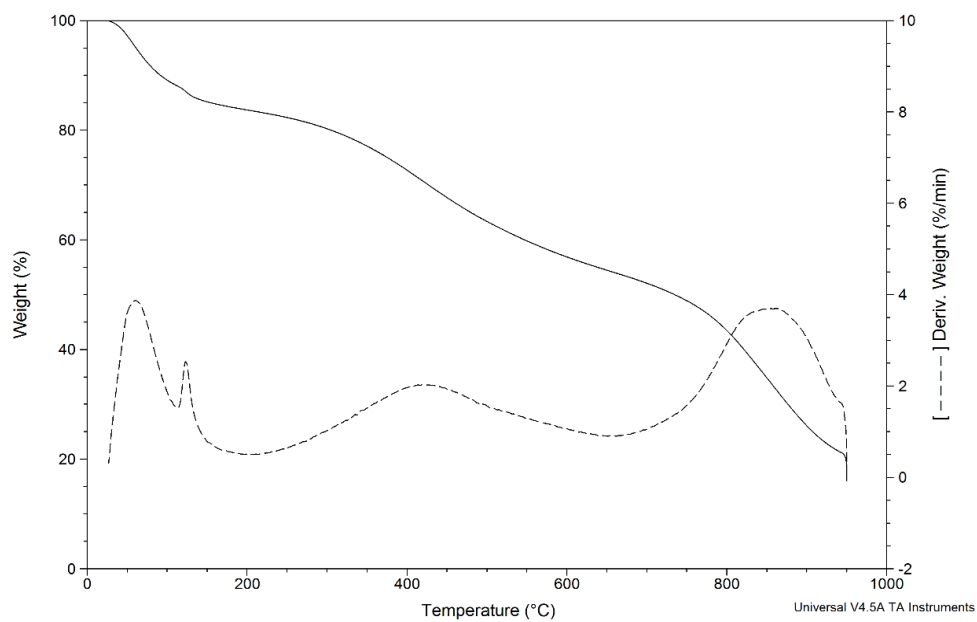


Figure C- 14: TG/DTG curve of washed and dried coal under Analyze 3 Group 1 experimental conditions

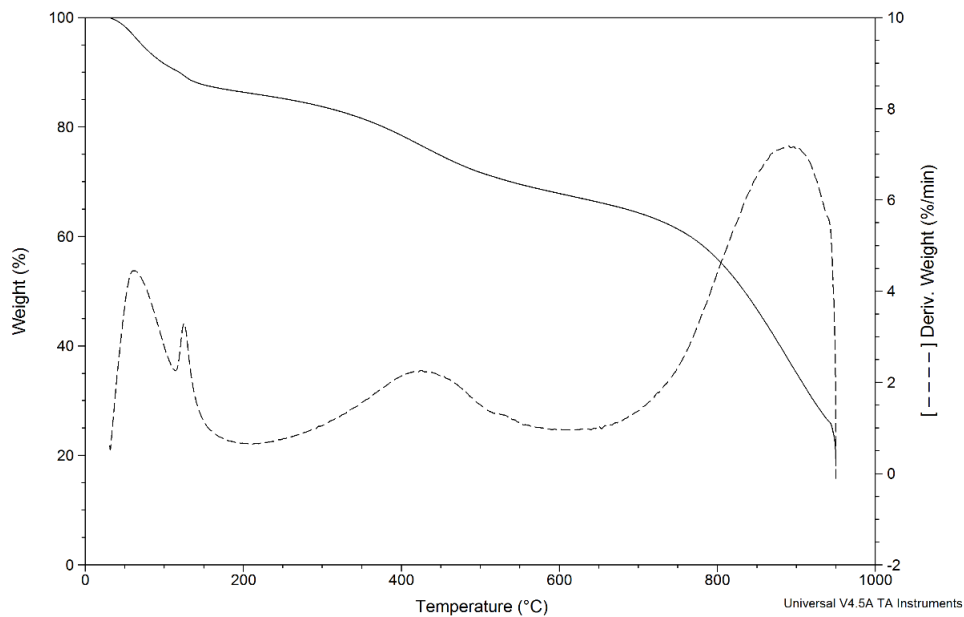


Figure C- 15: TG/DTG curve of washed and dried coal under Analyze 3 Group 2 experimental conditions

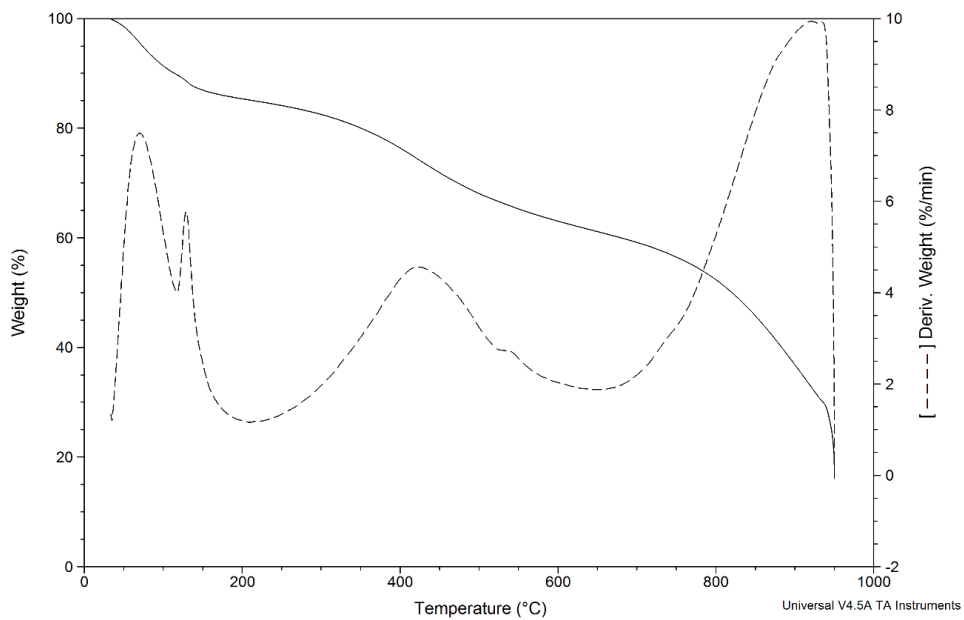


Figure C- 16: TG/DTG curve of washed and dried coal under Analyze 3 Group 3 experimental conditions

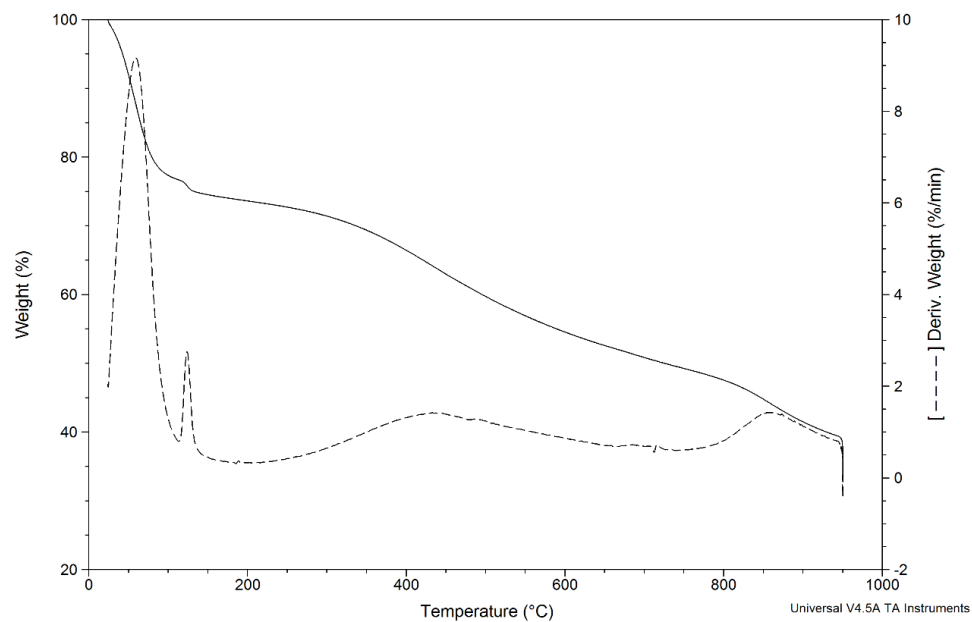


Figure C- 17: TG/DTG curve of as received coal under Analysis 4 Group 1 experimental conditions

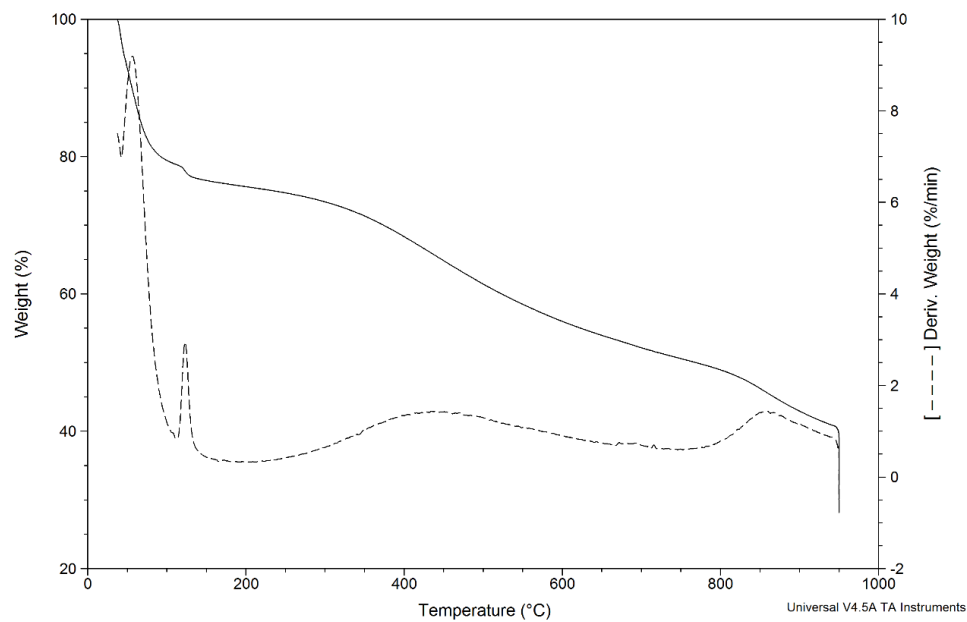


Figure C- 18: TG/DTG curve of as received coal under Analysis 4 Group 2 experimental conditions

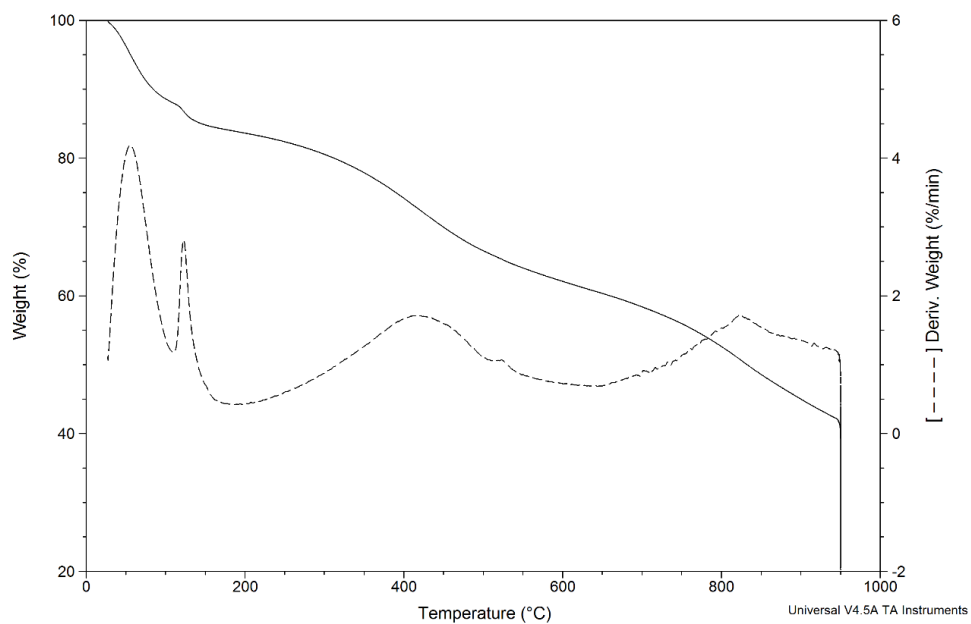


Figure C- 19: TG/DTG curve of washed and dried coal under Analysis 4 Group 1 experimental conditions

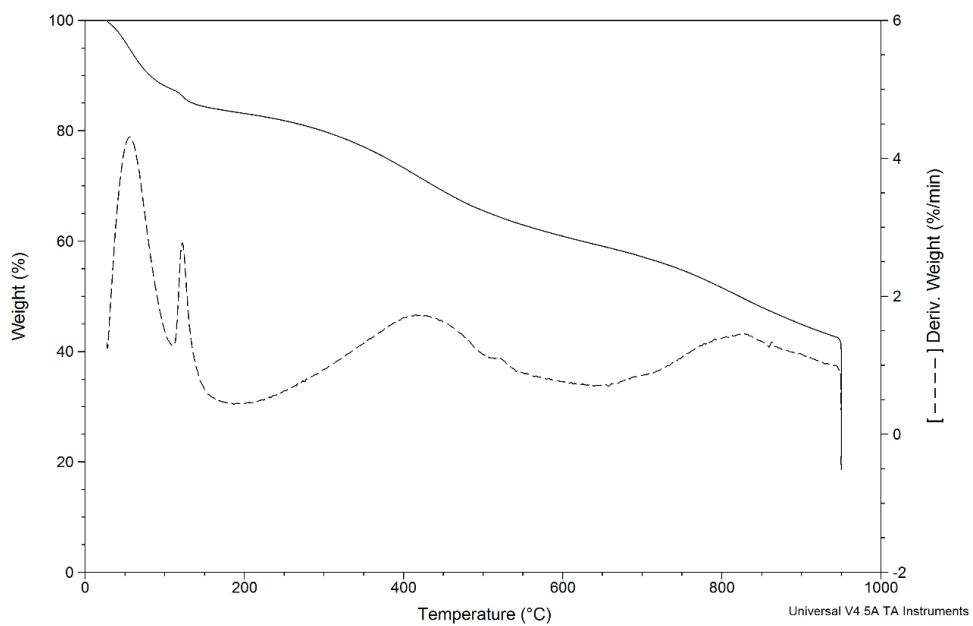


Figure C- 20: TG/DTG curve of washed and dried coal under Analysis 4 Group 2 experimental conditions

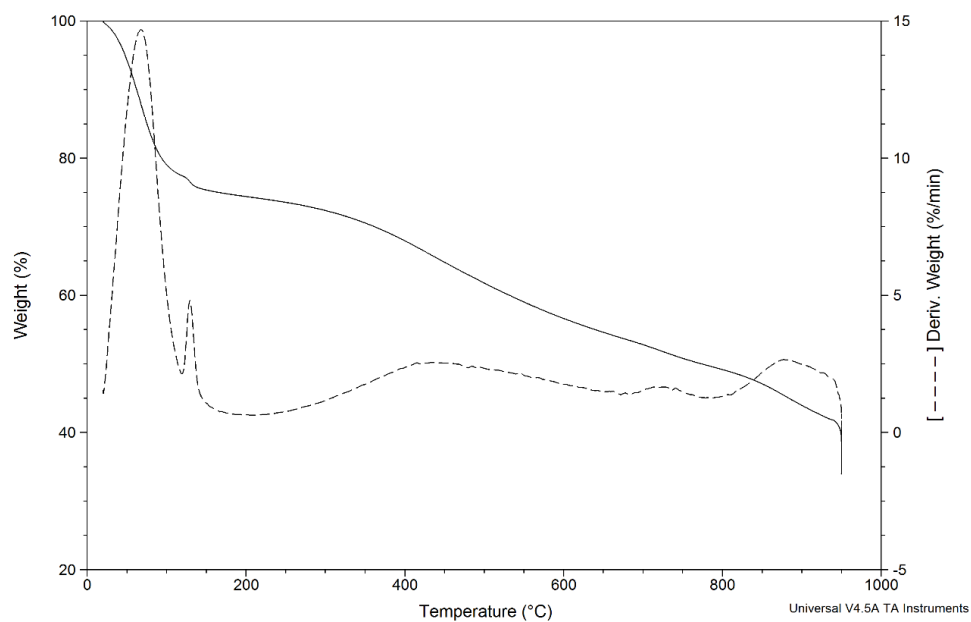


Figure C- 21: TG/DTG curve of as received coal under Analysis 5 Group 1 experimental conditions

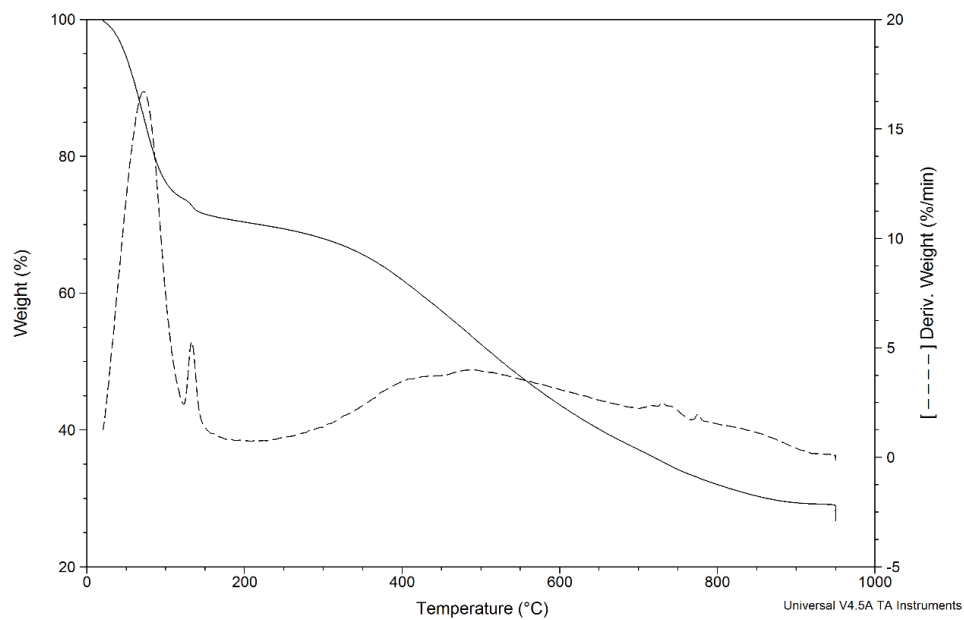


Figure C- 22: TG/DTG curve of as received coal under Analysis 5 Group 2 experimental conditions

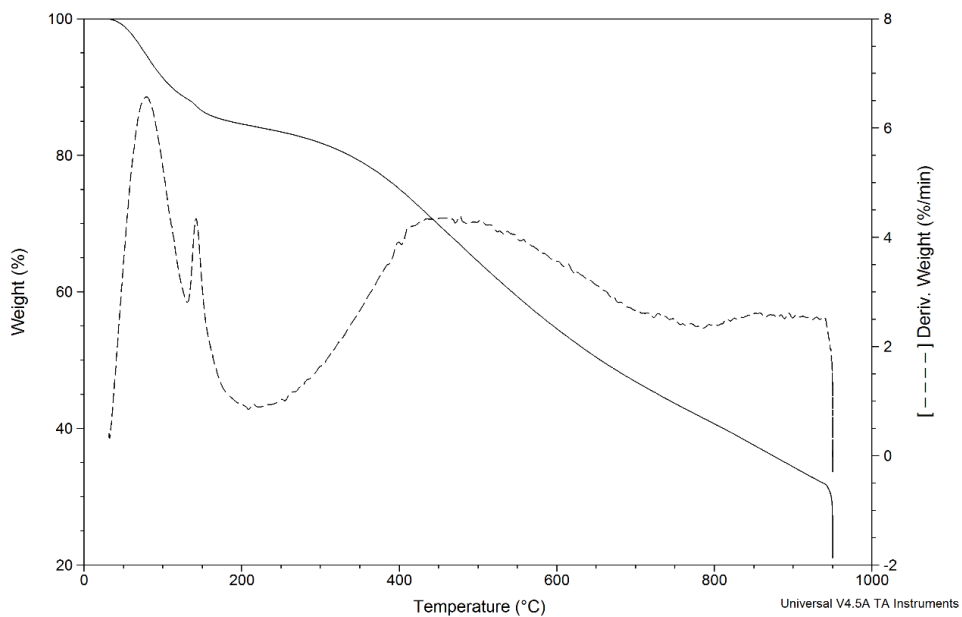


Figure C- 23: TG/DTG curve of washed and dried coal under Analysis 5 Group 1 experimental conditions

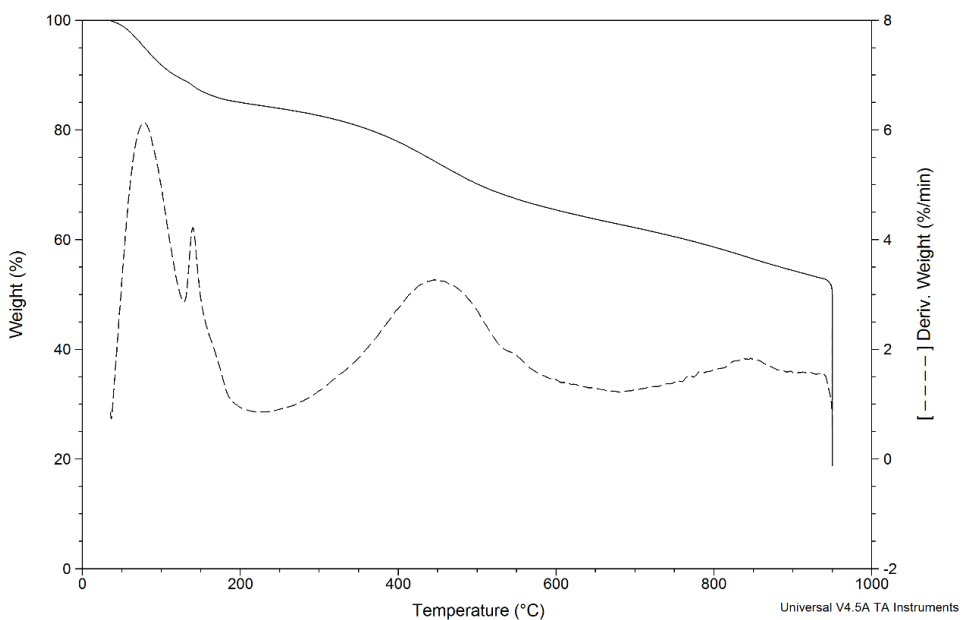


Figure C- 24: TG/DTG curve of washed and dried coal under Analysis 5 Group 2 experimental conditions

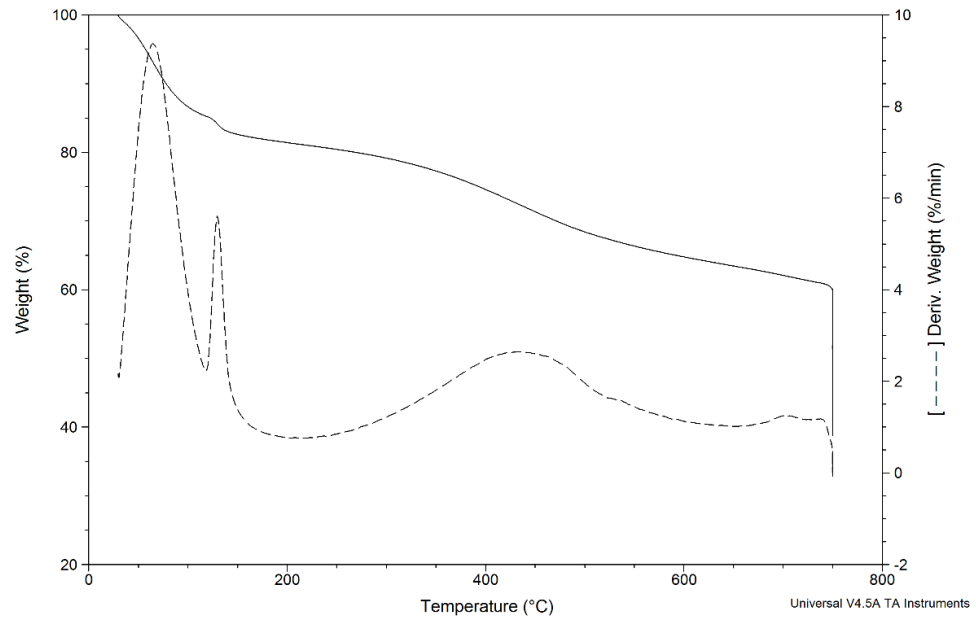


Figure C- 25: TG/DTG curve of as received coal under Analysis 6 Group 1 experimental conditions

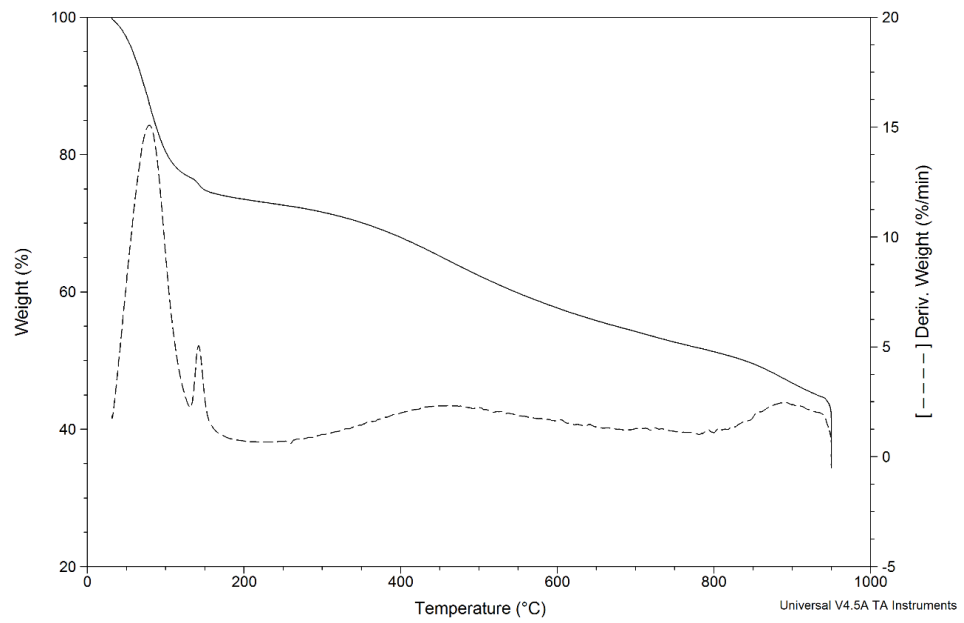


Figure C- 26: TG/DTG curve of as received coal under Analysis 6 Group 2 experimental conditions

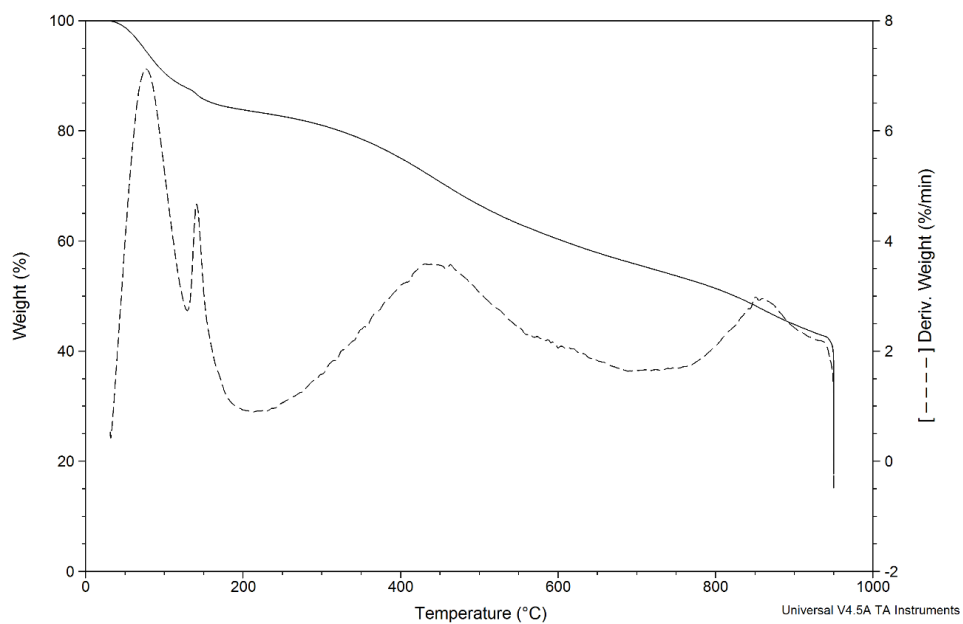


Figure C- 27: TG/DTG curve of washed and dried coal under Analysis 6 Group 1
Experimental conditions

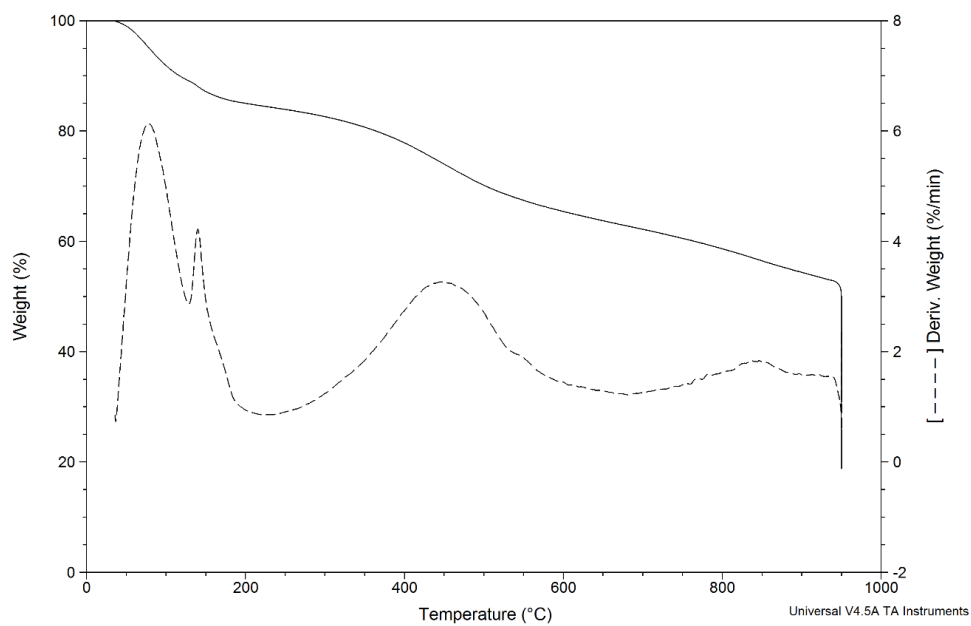


Figure C- 28: TG/DTG curve of washed and dried coal under Analysis 6 Group 2
experimental conditions

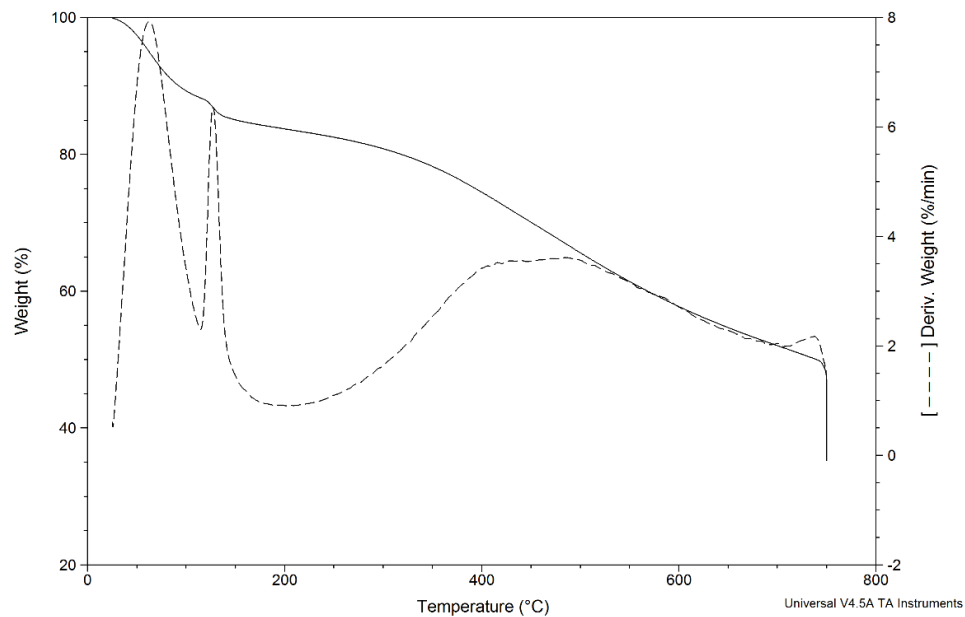


Figure C- 29: TG/DTG curve of as received coal under Analyze 7 Group 1 experimental conditions

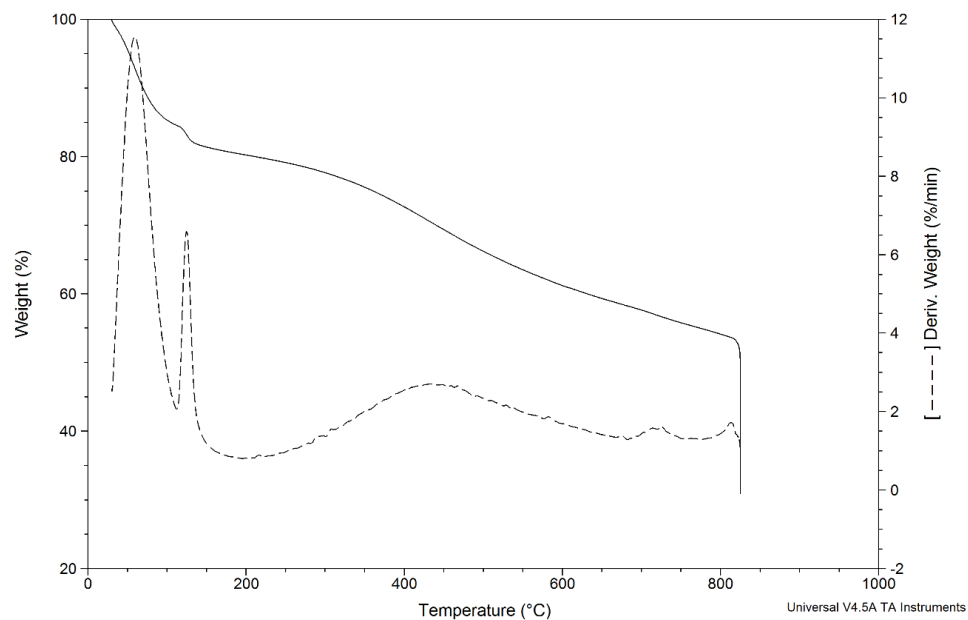


Figure C- 30: TG/DTG curve of as received coal under Analyze 7 Group 2 experimental conditions

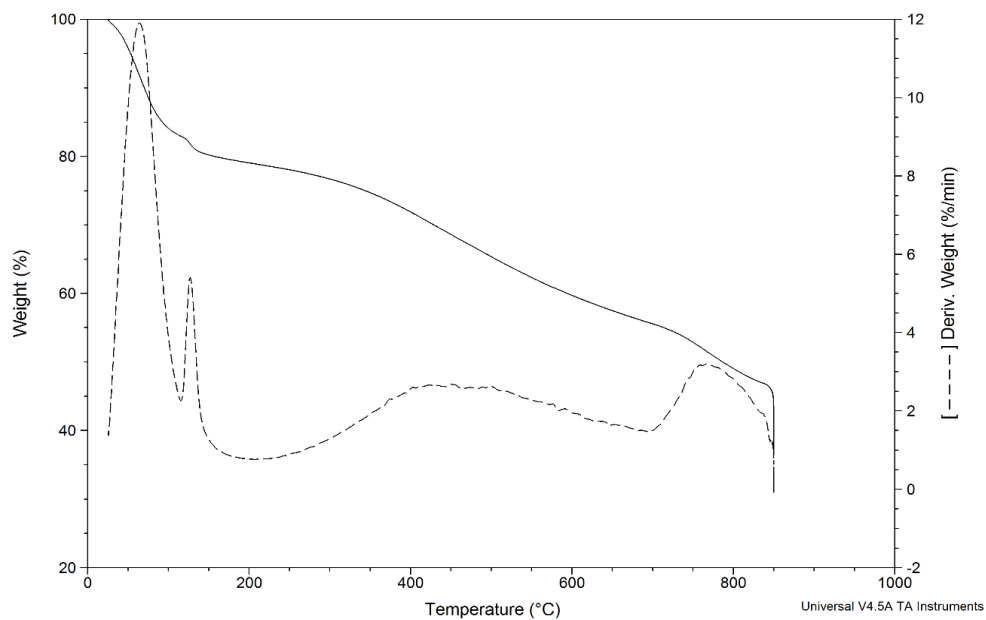


Figure C- 31: TG/DTG curve of as received coal under Analyze 7 Group 3 experimental conditions

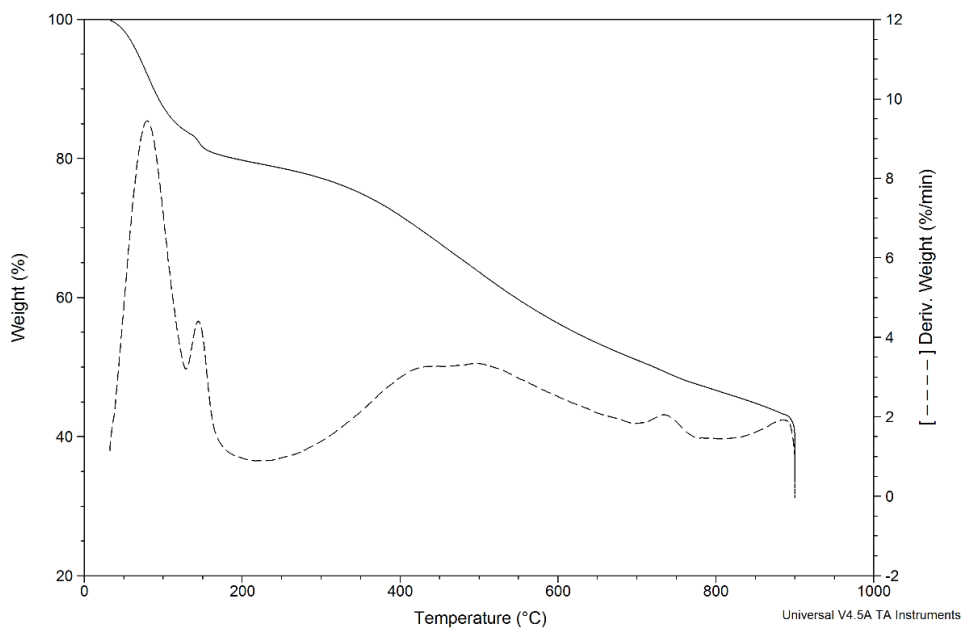


Figure C- 32: TG/DTG curve of as received coal under Analyze 7 Group 4 experimental conditions

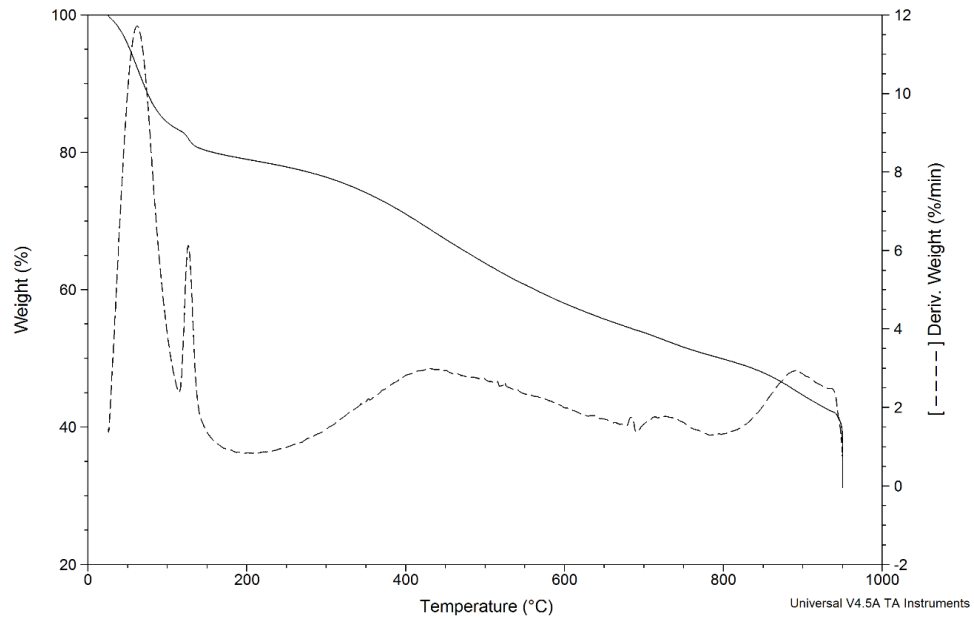


Figure C- 33: TG/DTG curve of as received coal under Analyze 7 Group 5 experimental conditions

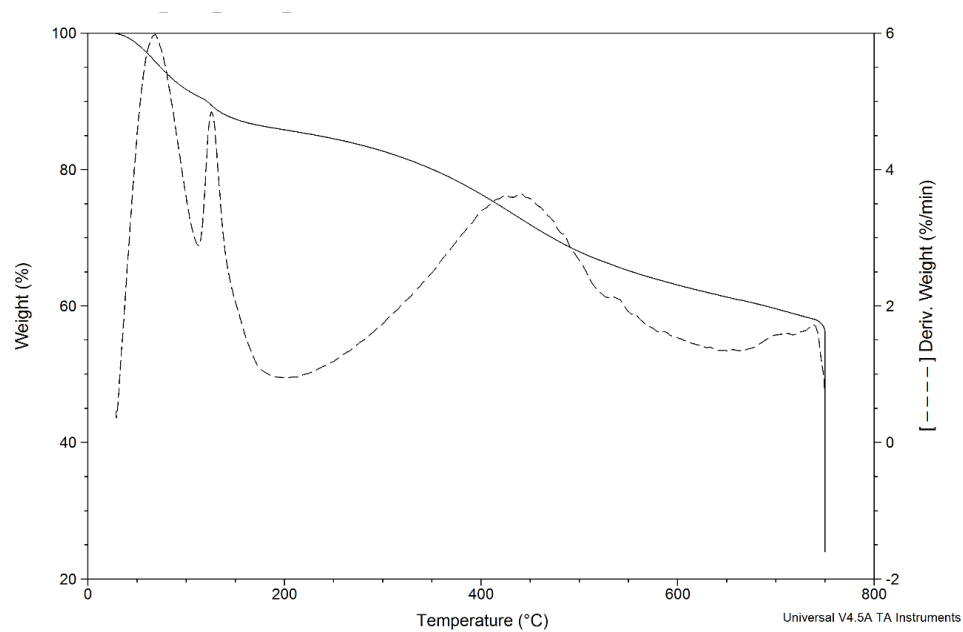


Figure C- 34: TG/DTG curve of washed and dried coal under Analyze 7 Group 1 experimental conditions

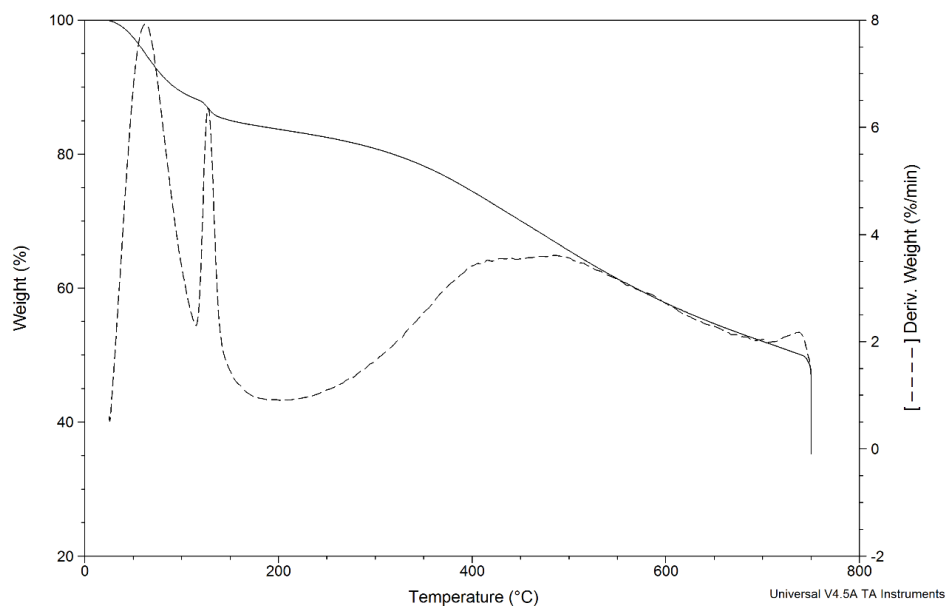


Figure C- 35: TG/DTG curve of washed and dried coal under Analyze 7 Group 1 experimental conditions

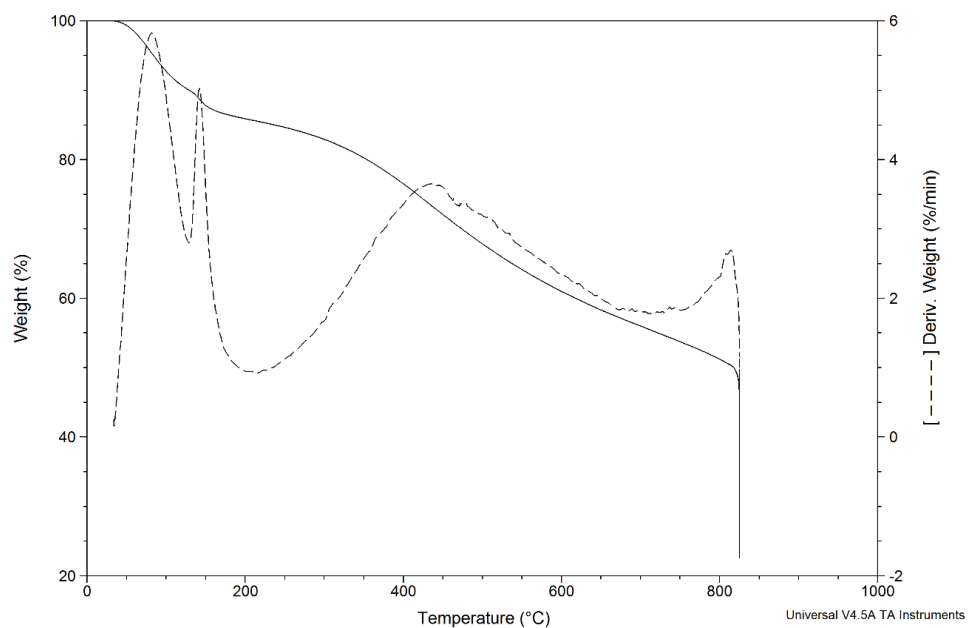


Figure C- 36: TG/DTG curve of washed and dried coal under Analyze 7 Group 2 experimental conditions

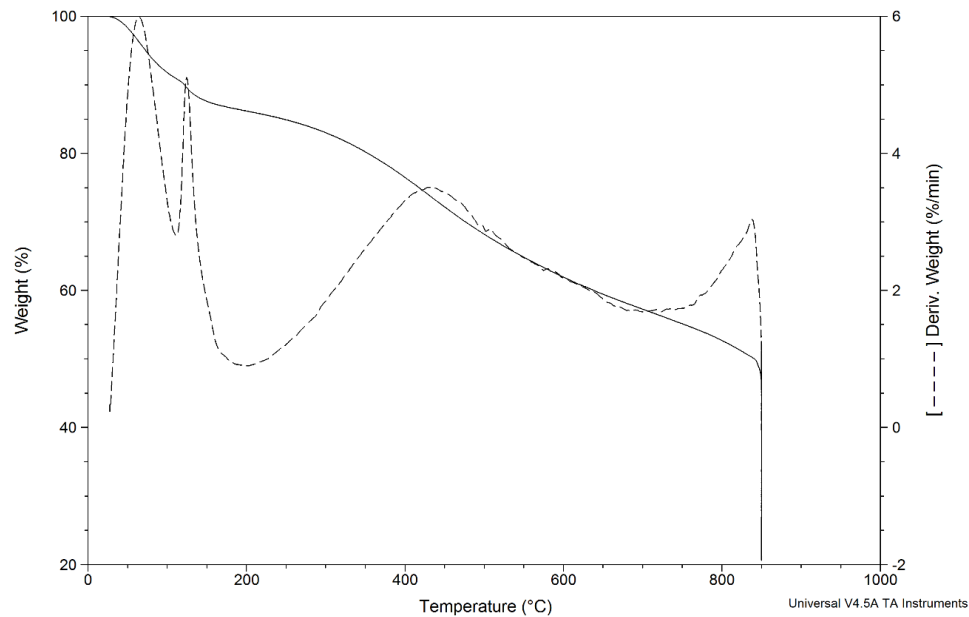


Figure C- 37: TG/DTG curve of washed and dried coal under Analyze 7 Group 3 experimental conditions

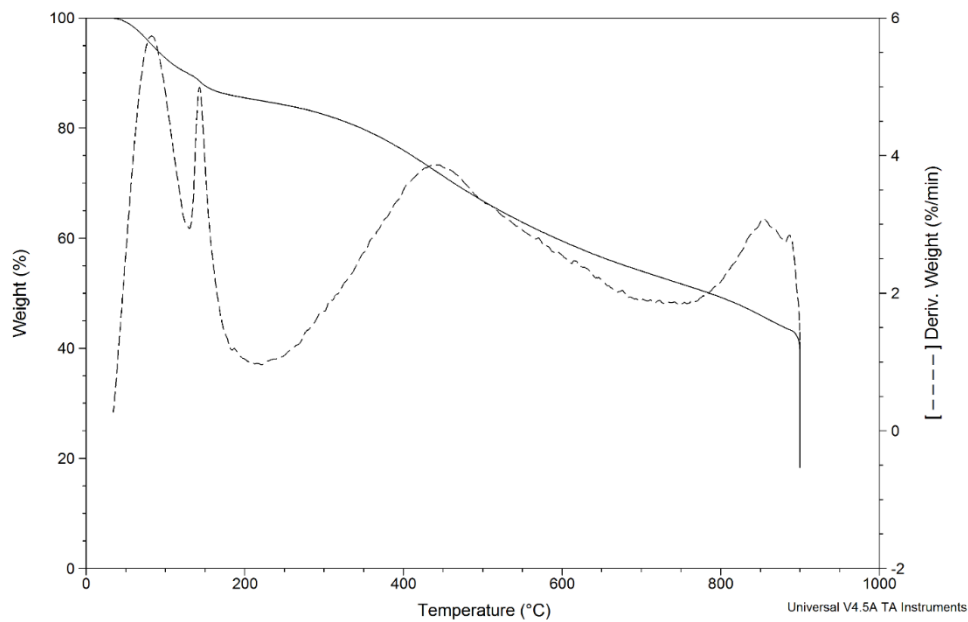


Figure C- 38: TG/DTG curve of washed and dried coal under Analyze 7 Group 4 experimental conditions

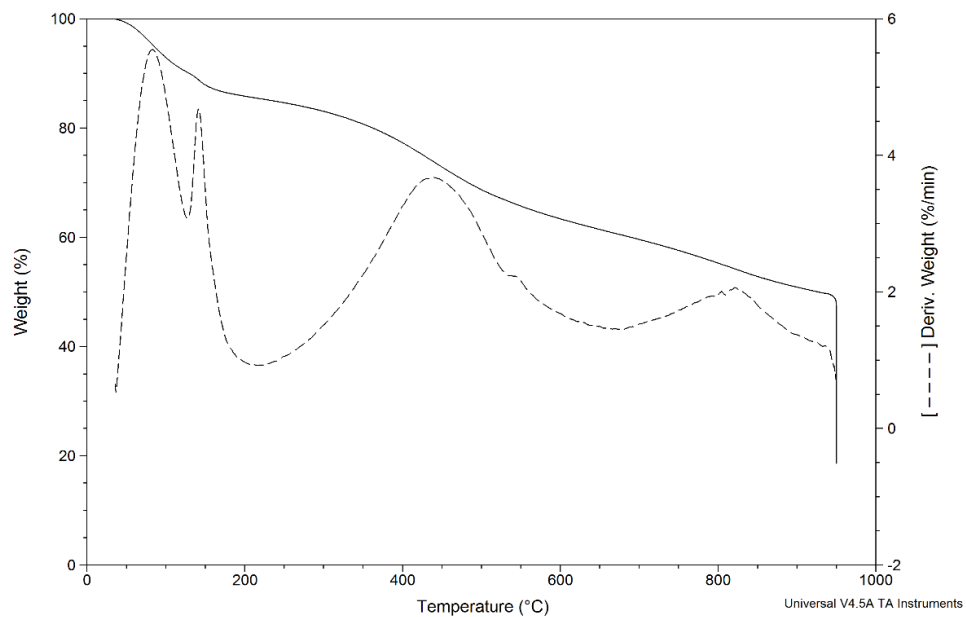


Figure C- 39: TG/DTG curve of washed and dried coal under Analyze 7 Group 5 experimental conditions

APPENDIX D

REPLICATED TGA RESULTS OF EXPERIMENTS

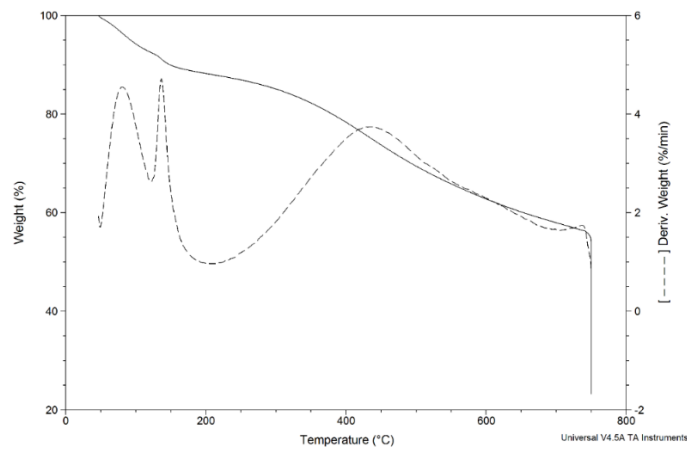


Figure D- 1: TG/DTG curve of as received coal under replicated Analyze 7 Group 1 experimental conditions

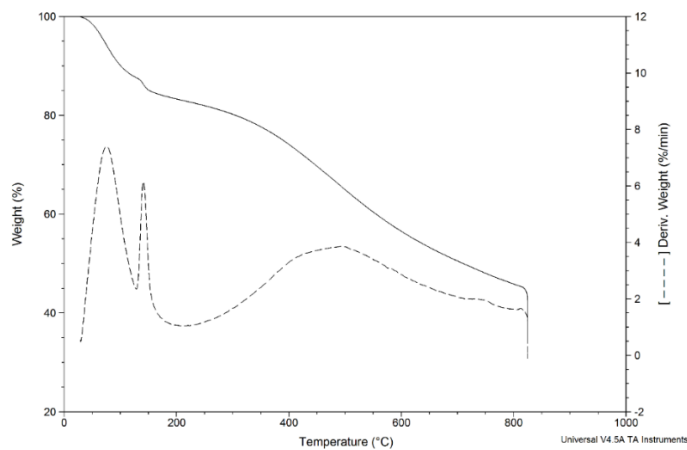


Figure D- 2: TG/DTG curve of as received coal under replicated Analyze 7 Group 2 experimental conditions

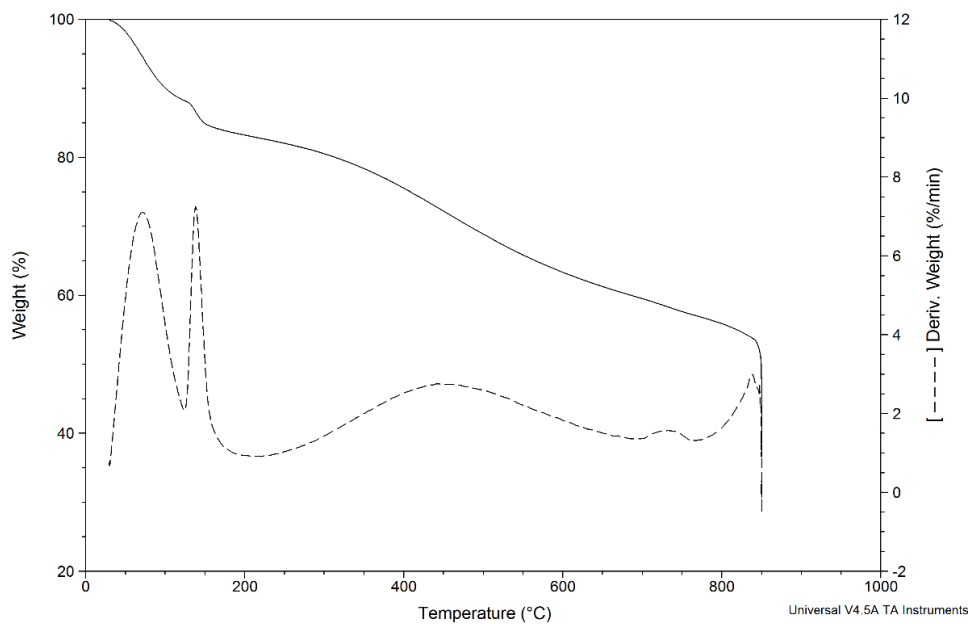


Figure D- 3: TG/DTG curve of as received coal under replicated Analyze 7 Group 3 experimental conditions

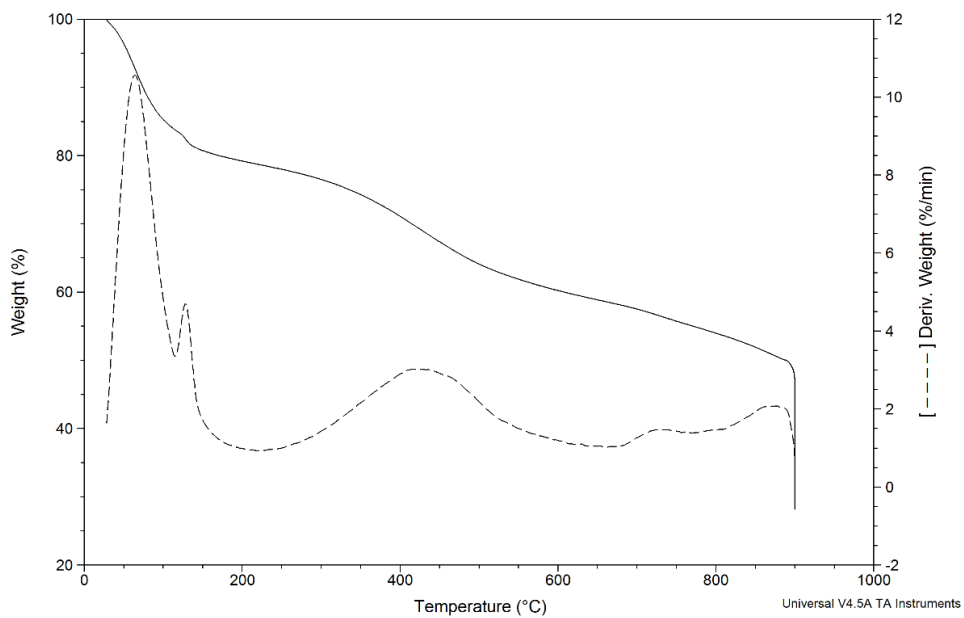


Figure D- 4: TG/DTG curve of as received coal under replicated Analyze 7 Group 4 experimental conditions

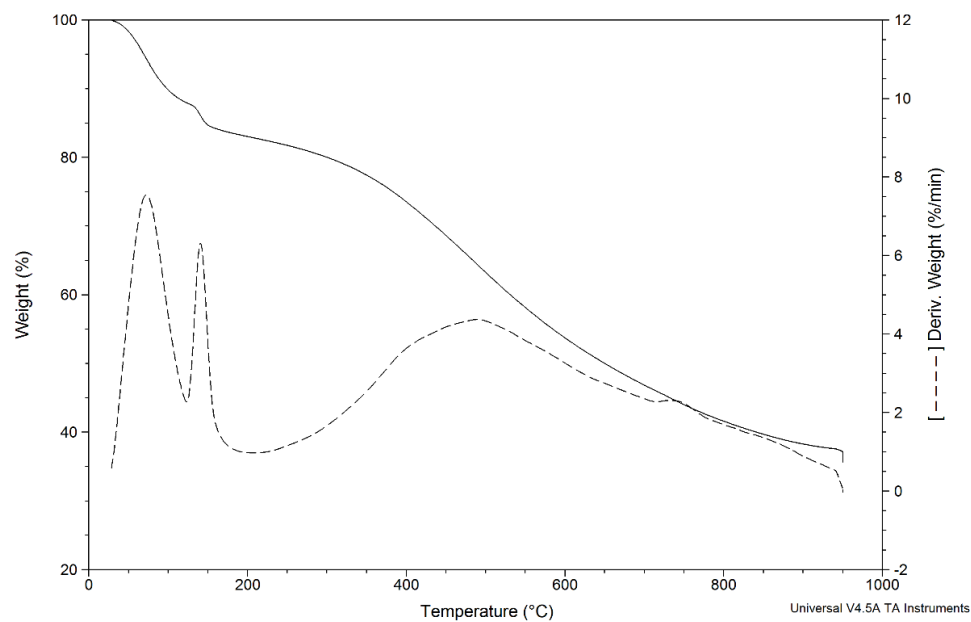


Figure D- 5: TG/DTG curve of as received coal under replicated Analyze 7 Group 5 experimental conditions

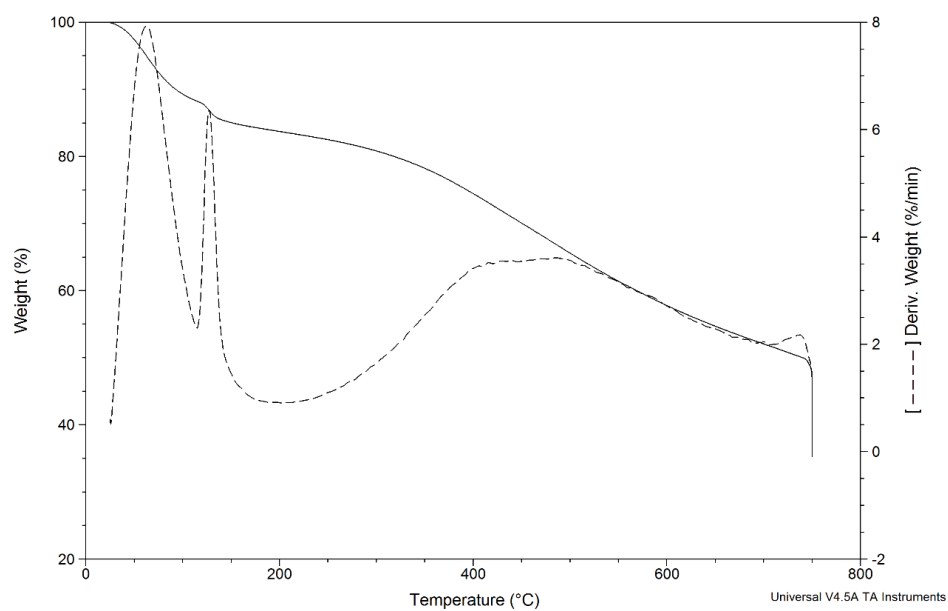


Figure D- 6: TG/DTG curve of washed and dried coal under replicated Analyze 7 Group 1 experimental conditions

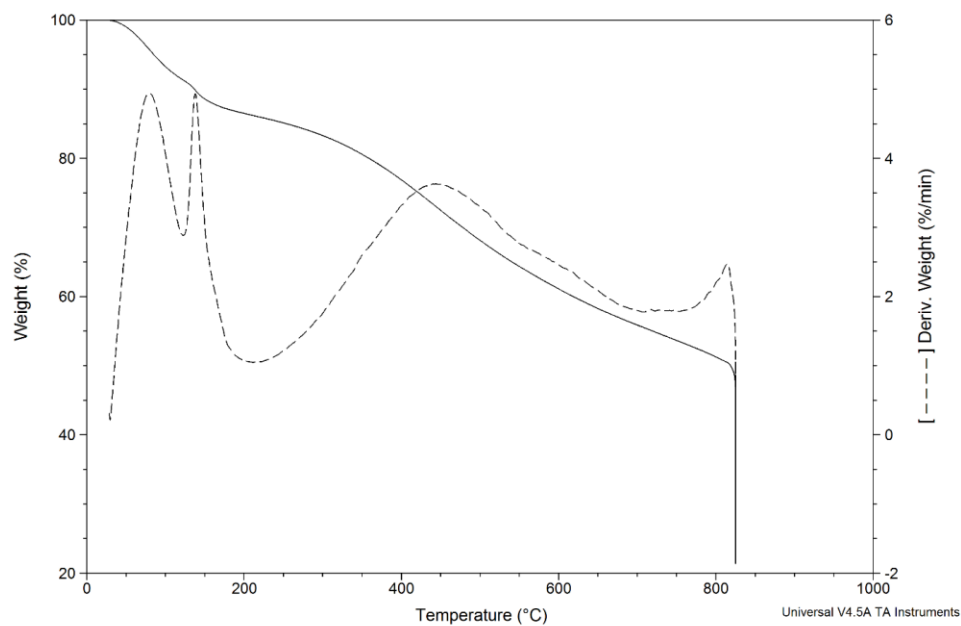


Figure D- 7: TG/DTG curve of washed and dried coal under replicated Analyze 7
Group 2 experimental conditions

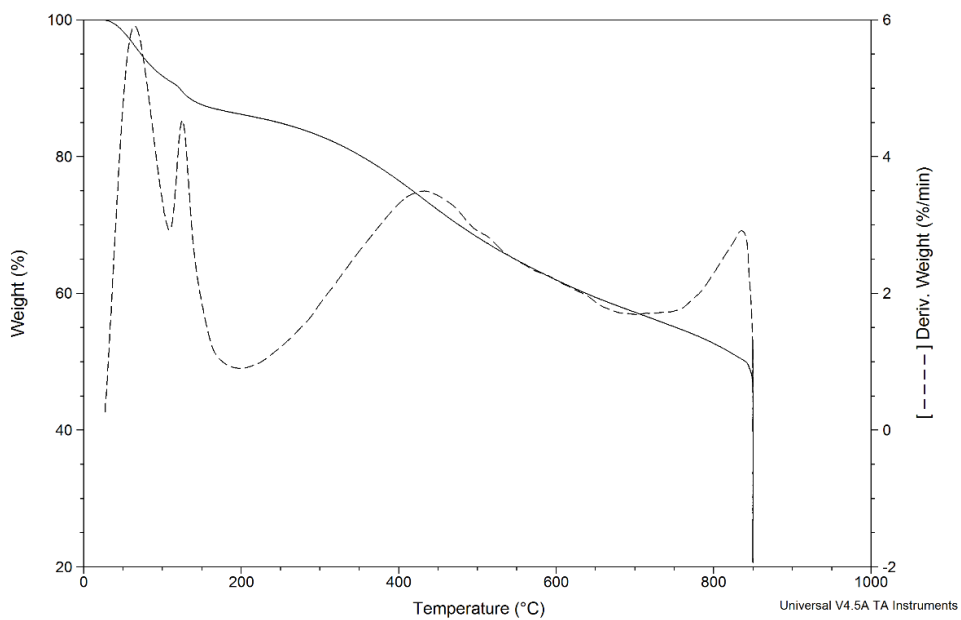


Figure D- 8: TG/DTG curve of washed and dried coal under replicated Analyze 7
Group 3 experimental conditions

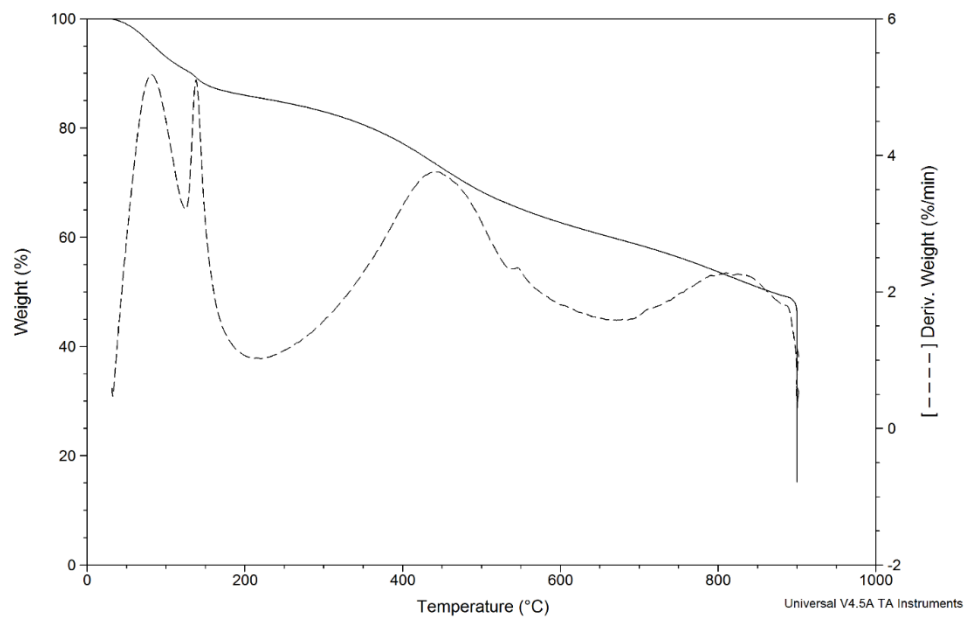


Figure D- 9: TG/DTG curve of washed and dried coal under replicated Analyze 7
Group 4 experimental conditions

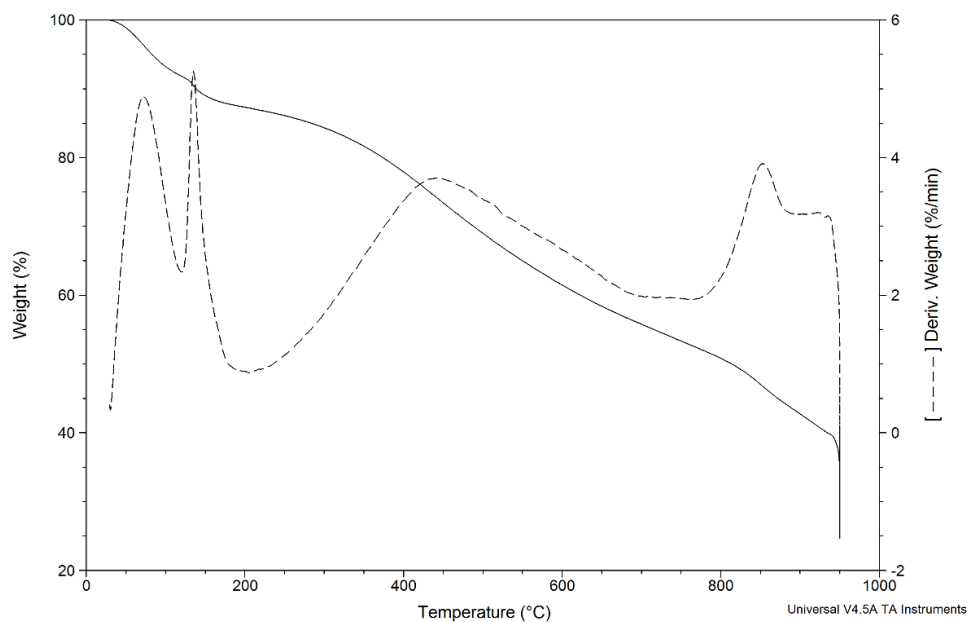


Figure D- 10: TG/DTG curve of washed and dried coal under replicated Analyze 7
Group 5 experimental conditions

APPENDIX E

TABULATED RESULTS OF EXPERIMENTS

Table E- 1: Tabulated results of Analyses
1-2-3 experiments

Coal Sample	Analyte-1						Analyte-2						Analyte-3					
	Final Temperature (oC.)	Reaction Interval (oC.)	Mass Loss (%)	Peak Temperature (oC.)	Maximum Mass Loss (%/min)	Residue %	Heating Rate (oC./min)	Reaction Interval (oC.)	Mass Loss (%)	Peak Temperature (oC.)	Maximum Mass Loss (%/min)	Residue %	Heating Rate (oC./min)	Reaction Interval (oC.)	Mass Loss (%)	Peak Temperature (oC.)	Maximum Mass Loss (%/min)	Residue %
As received coal	750	26-162	21.72	61.1	7.74	41.87	20	27-177	22.27	59.9	7.96	30.91	20	33-176	27.08	62.5	10.39	27.25
		162-567	17.03	436.5	1.31			177-597	17.44	426.1	1.33			176-643	18.53	426.1	1.27	
		567-750	19.27	745	1.33			597-950	29.38	801.7	3.17			643-950	27.14	825.9	2.79	
	850	25-153	19.54	57.1	7.14	32.71	30	31-201	21.6	77.9	11.64	32.6	30	26-177	23.19	66.6	10.95	32.8
		153-643	19.25	429.4	1.38			201-634	14.82	434.1	1.71			177-662	23.02	403.3	2.11	
		643-850	28.44	799.9	3.16			634-950	24.98	876.7	3.56			662-950	19.18	879.4	3.17	
	950	27-152	21.72	59.1	7.96	30.91	50	28-214	33.59	79.4	21.38	22.74	50	26-185	25.8	78.6	17.1	27.91
		152-634	19.12	426.1	1.33			214-682	20.34	438.1	3.33			185-673	23.45	422.7	3.59	
		634-950	28.17	801.7	3.17			682-950	23.33	871.4	5.77			673-950	22.59	871.9	5.68	
Washed and dried coal	750	30-158	13.72	53.9	3.96	27.84	20	29-164	15.08	58.3	3.96	18.54	20	27-171	15.46	60.9	3.87	16.76
		158-534	20.14	401.1	1.79			164-615	23.96	415.2	1.93			171-635	29.43	420.5	2.03	
		534-750	38.21	745.5	1.89			615-950	42.42	855.3	4.35			635-950	38.35	863.9	3.69	
	850	25-159	16.1	56.3	4.38	17.48	30	26-141	30.52	74.7	14.64	27.23	30	31-167	13.74	61.6	4.45	18.12
		159-532	23.73	415.7	1.97			184-618	21.96	434.3	2.21			167-647	19.9	425.3	2.26	
		533-850	42.41	843.7	3.48			618-950	20.29	864.8	2.7			647-950	48.24	896.4	7.17	
	950	29-164	15.12	58.4	3.96	18.54	50	30-214	16.94	72.3	8.74	20.33	50	34-200	14.6	69.9	7.49	16.14
		164-520	19.94	415.2	1.93			214-638	22.31	424.5	4.42			200-671	25.01	419.2	4.55	
		520-950	46.38	855.3	4.35			638-950	40.42	883.7	8.27			671-950	44.21	921.4	9.92	

Table E- 2: Tabulated results of Analyses 4-5-6 experiments

Analyze-4										Analyze-5					Analyze-6				
Coal Sample	Group	Reaction Interval (oC.)	Mass Loss (%)	Peak Temperature (oC.)	Maximum Mass Loss (%/min)	Residue %	Reaction Interval (oC.)	Mass Loss (%)	Peak Temperature (oC.)	Maximum Mass Loss (%/min)	Residue %	Reaction Interval (oC.)	Mass Loss (%)	Peak Temperature (oC.)	Maximum Mass Loss (%/min)	Residue %			
As received coal	1	25-227	26.06	59.67	9.163	33.35	25-232	25.46	67.82	14.69	33.94	28-179	24.66	69.51	14.12	31.4			
		227-720	23.72	432.25	1.42		232-783	24.8	415.29	2.54		179-697	26.23	431.28	3.139				
		720-950	16.87	855.34	1.424		783-950	15.8	876.85	2.65		697-950	17.71	739.83	2.648				
	2	35-246	24.44	57.53	9.173	34.08	26-247	30.52	72.6	16.7	26.72	32-214	26.53	79.09	15.09	34.38			
		246-756	25.09	434.57	1.435		247-710	32.99	488.84	4.016		214-805	22.09	448.07	2.311				
		756-950	17.39	855.75	1.429		710-950	9.79	733.58	2.421		805-950	17	892.85	2.456				
Washed and dried coal	1	27-212	16.43	55.71	4.187	20.96	32-220	15.85	78.44	6.568	21	32-203	16.2	76.48	7.123	18.36			
		212-657	22.41	415.25	1.713		220-707	37.8	433.69	4.334		203-751	30.11	430.25	3.581				
		657-950	40.2	822.51	1.715		707-950	25.35	733.64	2.568		751-950	35.33	850.96	2.983				
	2	28-219	17	56.18	4.312	18.62	37-235	15.47	77.86	6.141	18.71	32-224	16.45	79.54	6.876	20.05			
		219-665	24.34	415.06	1.732		235-697	22.11	447.01	3.266		224-698	24.3	436.96	3.309				
		665-950	40.04	829.39	1.449		697-950	43.71	836.43	1.836		698-950	39.2	839.44	2.522				

Table E- 3: Tabulated results of Analyze-7 and replicated Analyze-7 experiments

Coal Sample	Analyze-7					Residue %	Analyze-7 Replication					Residue %
	Final Temperature (oC)	Reaction Interval (oC)	Mass Loss (%)	Peak Temperature (oC)	Maximum Mass Loss (%/min)		Final Temperature (oC)	Reaction Interval (oC)	Mass Loss (%)	Peak Temperature (oC)	Maximum Mass Loss (%/min)	
As received coal	750	25.3-205.4	16.3	62.65	7.931	37.52	750	35-229.8	16.1	76.42	6.596	37.85
		205.4-698.2	31.5	428.74	3.355			229.8-697.7	26.2	434.61	3.096	
		698.2-750	14.7	738.1	2.171			697.7-750	19.8	738.61	1.893	
	825	30.4-211.7	19.8	59.5	11.28	36.05	825	29.7-226	17.3	75.42	7.307	36.05
		211.7-675.1	21.5	431.97	2.693			226-706.9	32.4	487.6	3.842	
		675.1-773.9	3.46	721.53	1.576			706.9-800.2	4.28	745.46	1.903	
	850	773.9-825	19.2	812.72	1.631	36.51	850	800.2-825	11.1	814.08	1.624	37.25
		25.6-212.7	21.1	64.43	11.79			29.4-221.14	17.2	70.16	7.095	
		212.7-687.6	22.8	422.73	2.65			221.14-699.18	23.2	422.15	2.753	
	900	687.6-850	19.6	770.16	3.173	33.47	900	699.18-775.94	2.84	770.16	1.568	28.2
		32.7-236.7	21.1	80.32	9.447			775.94-850	19.5	837.67	2.997	
		236.7-706.96	28.1	432.78	3.263			28.76-235.72	21.5	64.13	10.57	
Washed and dried coal	750	706.96-	4.61	736.3	2.072	31.48	750	235.72-670.04	20	416.97	3.023	35.62
		814.81-900	12.7	885.68	1.918			670.04-793.43	4.13	724.57	1.472	
		25.8-225.2	21.5	62.2	11.29			793.43-900	26.2	884.17	2.081	
	825	225.2-687.6	24.3	429.81	2.967	24.16	825	29-211.43	17.2	70.94	7.527	23.44
		687.6-793.1	4.04	730.38	1.748			211.4-713.8	36.7	484.21	4.362	
		793.1-950	18.7	887.41	2.884			713.8-789.6	4	744.77	2.279	
	850	29.2-202.6	14.2	68.25	5.892	22.64	850	789.6-950	6.4	867.86	1.224	25.45
		202.6-669.7	25.1	436.9	3.619			36-219.7	12.3	79.7	4.548	
		669.7-750	36.6	737.37	1.674			219.7-705.5	30	427.54	3.739	
	900	33.7-217.3	14.5	81.66	5.824	20.74	900	705.5-750	34.2	737.7	1.747	20.42
		217.3-747.8	31.7	433.68	3.651			29-213.37	13.8	76.06	4.911	
		747.8-825	31.2	814.52	2.696			213.37-761.37	33	439.42	3.627	
As received coal	750	28-200.7	13.8	63.92	5.9	18.49	750	761.37-825	31.6	814.6	2.471	34.91
		200.7-745.8	30.9	428.98	3.493			30-217.26	13	77.94	4.991	
		745.8-850	34.6	835.64	2.915			217.26-738.05	29.2	442.69	3.241	
	825	34.2-218.2	14.9	81.99	5.684	18.6	825	738.05-850	37.4	839.04	3.18	3.807
		218.2-745.8	33.2	439.22	3.857			32-220.2	14.5	78.27	5.082	
		745.8-900	33.4	852.72	3.033			220.2-694.33	26.7	439.75	3.746	
Washed and dried coal	950	35.90-221.1	14.6	82.54	5.522	3.67	950	694.33-900	43.4	829.81	2.249	3.707
		221.1-680.7	25	435.46	3.67			30-210.5	12.9	70.12	4.87	
As received coal	950	680.7-950	41.8	819.7	2.045	2.045	950	210.5-762.3	34.3	441.92	3.707	25.45
								762.3-950	27.3	851.6	3.807	