UNIVERSITY OF MARYLAND EASTERN SHORE
Department of Natural Sciences

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STUDIES OF THE SPONTANEOUS COMBUSTION OF LOW RANK COALS AND LIGNITES

FINAL TECHNICAL REPORT

Contract Number:	**DE-FG22-94MT94016**
Prepared for:	**USDOE, Federal Energy Technology Center**
FETC Project Officer:	**Dr. Karl T. Schroeder**
Authors:	**Dr. Joseph M Okoh, PI**
	Dr. Joseph N. D. Dodoo, co-PI

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Abstract

Spontaneous combustion has always been a problem in coal utilization especially in the storage and transportation of coal. In the United States, approximately 11% of underground coal mine fires are attributed to spontaneous coal combustion. The incidence of such fires is expected to increase with increased consumption of lower rank coals. The cause is usually suspected to be the reabsorption of moisture and oxidation.

To understand the mechanisms of spontaneous combustion this study was conducted to 1) define the initial and final products during the low temperature (10 to 60°C) oxidation of coal at different partial pressures of O_2, 2) determine the rate of oxidation, and 3) measure the reaction enthalpy. The reaction rate (R) and propensity towards spontaneous combustion were evaluated in terms of the initial rate method for the mass gained due to adsorbed O_2.

Equipment that was used consisted of a FT-IR (Fourier Transform-Infrared Spectrometer, Perkin Elmer), an accelerated surface area porosimeter (ASAP, Micromeritics model 2010), thermogravimetric analyzer (TGA, Cahn Microbalance TG 121) and a differential scanning calorimeter (DSC, Q1000, thermal analysis instruments). Their combination yielded data that established a relation between adsorption of oxygen and reaction enthalpy. The head space/ gas chromatograph/ mass spectrometer system (HS/GC/MS) was used to identify volatiles evolved during oxidation. The coal samples used were Beulah lignite and Wyodak (sub-bituminous).

Oxygen (O_2) absorption rates ranged from 0.202 mg O_2/mg coal hr for coal sample #20 (Beulah pyrolyzed at 300^oC) to 6.05 mg O_2/mg coal hr for coal sample #8 (wyodak aged and

pyrolyzed at 300°C). Aging of coal followed by pyrolysis was observed to contribute to higher

reaction rates. Reaction enthalpies ranged from 0.42 to 1580 kcal/gm/mol O_2.

1. BACKGROUND

In fulfillment of a key requirement for participating in the U.S. Department of Energy's fossil energy program for Historically Black Colleges and Universities and Other Minority Institutions, (HBCU/OMI), the University of Maryland Eastern Shore invited the Institute of Environmental Science, (IES) a private company based in Austin, Texas to collaborate on the project. The role to be played by the Institute of Environmental Science was to develop a semiconductor detector for gases such as CO, and C1 – C4 hydrocarbons. One year after the project commenced IES arbitrarily severed all contacts with the University of Maryland Eastern Shore. All attempts to contact the proprietor either by phone or certified mail failed. For this reason no deliverable is available from the Institute of Environmental Science.

A combined TG/MS/GC manufactured by Analytical Technologies incorporated (ATI), used in our study was for most of the project period, plagued by system outages. ATI service personnel had to be called on several occasions to service the unit. The net effect of this continuous failure of the equipment was slow progress. Towards the end of the three year project period the University of Maryland made funds totaling $125,000 available to upgrade our research equipment. This welcome opportunity resulted in the acquisition of Q1000 and DSC from Du Pont. With this new tool progress was again restored and the project was successfully completed.

2.   INTRODUCTION

Spontaneous combustion has always been a problem in coal utilization especially in the storage and transportation of coal. In the United States, approximately 11 % of underground coal mine fires are attributed to spontaneous combustion. The incidence of such fires is expected to increase with deeper mines, the introduction of longwall mining methods, and the increased consumption of lower ranked coals. The largest coal reserves in the United States are in the West, but these coals usually have high moisture contents. This makes it uneconomical to ship them. Even though huge amounts of money and work have gone into methods to beneficiate these coals (remove moisture, raise Btu content) to make shipment more economical, only little success has been realized. The culprit is usually suspected to be the reabsorption of moisture which leads to spontaneous combustion. Therefore, information on the mechanism of self-heating of low rank coals due to moisture absorption coming from this research will be of great benefit with respect to the utilization of low rank coals.

Spontaneous combustion occurs when the heat that is produced by the low temperature reaction of coal with oxygen is not adequately dissipated by conduction or convection, resulting in a net temperature increase in the coal mass. Under conditions that favor high heating rate, the coal attains thermal runaway and a fire ensues. The minimum initial temperature that will produce a sustained exothermic reaction, or thermal runaway in the initial stages of spontaneous combustion is defined as the minimum self heating temperature (SHT). Smith and Lazzara (1-2) have

established that the relative self-heating tendencies of coals, as measured by their minimum self-heating temperatures (SHT's) increases with decreasing rank. They suggested that coals especially sub-bituminous and lignite which have high spontaneous combustion potential have self heating temperatures less than 70 $^{\circ}$C, whereas those that demonstrate medium potential to spontaneous combustion have SHT's in the range of 70 $^{\circ}$C to 100 $^{\circ}$C. Other factors include humidity, temperature, ventilation, oxygen concentration, particle size of lower ranked coals.

A review of the literature [1-11] indicates that spontaneous combustion is likely to occur if :

(i)   Coal is dry and moisture is available in the prevailing atmosphere: In general coals containing less than their equilibrium moisture content are more prone to spontaneous combustion. Absorption of water by coal accelerates, and desorption retards, the process. These two processes depend on the inherent moisture content of coal. It is probably the heat produced during absorption of water vapor that causes the acceleration.

(ii)   Coal is present in a form such as fines which can be readily oxidized at ambient temperature: The exposed surface area contributes significantly to self heating. Decreasing the particle size increases the self-heating potential of the coal, down to critical diameter of 150 μm [1-2] even though Miron et.al. [9] couldn't find significant relation between particle size and amount of oxygen adsorbed on dry coals.

(iii) Oxygen is available to support the oxidation process : When air is allowed to come in contact with coal, oxygen is physically adsorbed to initiate the oxidation process. The step-by-step mechanism is very complex, but the reaction can formally be regarded as involving the (exothermic) conversion of carbon into carbon monoxide and dioxide. The oxygen adsorption

characteristics vary with the rank of coal, [12] and are generally higher with coals liable to spontaneous combustion most notably, the low rank variety.

(iv) The environment favors the accumulation of heat : The rate of heat dissipation from coal depends on its thermal conductivity. Coals with low thermal conductivity are more susceptible to spontaneous combustion (5). The possibility of spontaneous combustion will be negligible where the coal is spread out or the height of the stack is kept low. Adequate ventilation or a complete elimination of airflow will be essential.

(v) Mineral Impurities : Mineral impurities in a coal play substantial role in self-heating tendencies. Pyrites helps the process of swelling and causing disintegration of the coal mass, increasing the surface area available for oxidation. In addition, oxidation of pyrites produce heat.

3. SCIENTIFIC DISCUSSION

Reactions of carbon with the nominal constituents of air have been studied in detail, [7,8] The rates of these reactions may be diffusion controlled or reaction controlled or both. The chosen reactions conditions for this project are such that the rate is partially controlled by pore diffusion. This means that the gaseous reactant concentration will fall gradually to zero at some point in the pore system of the coal, putting the reaction into the Zone II kinetic regime, where the rate determining step becomes one of chemical control. While air is the reactant, it is the reaction with oxygen compared to that with carbon dioxide and steam, which predominates.

3.1   TG and HS/GC/ MS Studies

A TG and HS/GC/MS/ systems were successfully applied to the study of the reactions that occured during the slow heating of carbonaceous materials such as coal, and to relate the observed reactions to both temperature and mass change.

3.2   Kinetics and Mechanism

During the reaction of carbon with oxygen, the presence of a large number of pores, many of which arc interconnected, permits oxidation to proceed within the material as well as on the outer surface, [7, 13]. The following consecutive elementary processes describe the oxidation reaction :

(I) diffusion of reactants to the surface

ii) adsorption of reactants at the surface

iii) chemical reaction on the surface and within pores

iv) desorption of products

v) diffusion of products away from the surface and pores

Ignoring steps i and iv, the activation energy of the gasification reaction may be contributed to by (i) adsorption of oxidant gas, ii) chemical reaction and iii) desorption. The adsorption process may be considered as molecular involving an atom or a molecule from the gas phase and an active carbon atom on the carbon surface. The energy of activation required may be used to form an activated complex between the molecule or atom and the active carbon atom. Desorption

from an immobile layer involves an activated state in which a molecule attached to an adsorbing

center acquires the proper configuration and activation energy to permit it to escape form that

surface. The reaction rate (R) and propensity towards spontaneous combustion are easily evaluated

in terms of the rate of mass gain due to adsorbed oxygen using the thermogravimetric analyzer.

$$R = \frac{dm}{dt} = k_{air}\Sigma(O)P^n \qquad (1)$$

The rate of evolution of volatiles such as CO 2, CO, C 1 - C4 hydrocarbons and H 20 can be

measured on the mass spectrometer component of the TG/MS/GC system,[7,13,14]

where k_{air} is the reaction rate coefficient, P is the pressure of the reacting breathing air, n is the

$$R = \frac{dm}{dt} = \frac{k_{air}\Sigma(O)P^n_{CO}}{1 + k' P_{CO}{}^n + k'' P^n_{CO_2}} \qquad (2)$$

$$1 \ll k' P^n_{co} + k'' P^n_{co_2}$$

$$k = Ae^{-\frac{E_a}{RT}} \qquad (3)$$

reaction order and E (0) the surface area.

The equation above is based on the rate law proposed by Hinshelwood:
or the reaction between a porous solid and gas. Equation (2) becomes equation (1) if we assume
The temperature dependence of coal oxidation will be evaluated from the Arrhenius equation

where k is the rate constant, R is the universal gas constant and T is the absolute reaction temperature. This equation will enable us to calculate the respective values of the energy (Ea), entropy (ΔS), enthalpy (ΔH) of activation and the frequency factor A.   Using the absolute rate theory, a theoretical value of the frequency factor is obtained from the equation ,[15]:

$$AN_O = \frac{k_B T}{h} \frac{f^-}{f_a} \qquad (4)$$

where k_B is Boltzmann's constant, T; the absolute temperature, h;   Planck's constant and f* and f_a are partition functions of the transition state complex and the adsorbed species respectively. Since higher values of A which indicate more reactive sites on a coal surface and lower values of Ea both indicate higher coal reactivity, computation of these values (apparent global activation energies and pre-exponential factors), will enable a relative ranking of a coal's reactivity with respect to spontaneous combustion.

3.3   Prior Oxidation / Aging

Oxidation of a coal surface increases its oxygen functionalities which are hydrophilic in nature. Among these are carboxylic, phenolic, and carbonyl moieties. These groups attract moisture to the coal's surface through hydrogen bonding, their strong bond polarity facilitating the process. Since coal that has been oxidized to different degrees, exhibit different adsorption capacities for moisture - the probable trigger for spontaneous combustion, the amount of oxygen

that is sorped on coal (reflected by the weight gained by coal), in the initial stages of oxidation generally varies with the degree of oxidation.

3.4   Oxygen Concentration

When air comes in contact with coal, oxygen is physically adsorbed. The next initial interaction probably involving the interaction of the oxygen by-radical with a spin center in coal to form a peroxy radical occurs. The peroxy radical will have a certain mobility about its point of attachment, restricting the approach of other gas molecules. In the second stage of the adsorption process, an oxygen bridge is formed by the bonding of the localized radical to second active carbon site on the coal surface. The product from this second stage is the so-called solid coal/oxygen complexes- These may convert to more stable functional groups such as ether, lactone, carbonyl, carboxyl, and anhydride carbonate which eventually breakdown to gaseous products such as carbon dioxide, carbon monoxide and water.

4.   Experimental:

4.1   Coal Samples

The low rank coal samples (Wyodak (sub-bituminous) and Beulah (lignite) used in this project were obtained in sealed ampules from the USDOE Coal Repository Center at Penn State University.

4.2   Aging of Coal

Table 1 shows the coal samples used in our studies. The samples were aged i.e. pre-oxidized by passing air (research Grade, Air Products) over weighed samples in an oven that was preset to 45 $^{\circ}$C for 24 hours

Table 1 : Coal Samples Utilized

1. Wyodak Pyrolized at 400°C	17. Beulah Pyrolized at 450°C
2. Wyodak Pyrolized at 300°C	18. Aged Beulah Pyrolized at 200°C
3. Aged Wyodak Pyrolized at 250°C	19. Aged Beulah Pyrolized at 400°C
4. Aged Wyodak Pyrolized at 200°C	20. Beulah Pyrolized at 300°C
5. Wyodak Pyrolized at 250Â°C	21. Aged Coal (Beulah) Pyrolized at 200°C
6. Aged Wyodak	23. Pyrolized Beulah at 550°C
7. Wydoak Pyrolized at 400°C Aged for 4 Hrs.	24. Aged Beulah Pyrolized at 300°C
8. Aged Wyodak Pyrolized at 300°C	25. Pyrolized Beulah at 200°C
9. Wyodak Pyrolized at 350°C	26. Beulah Pyrolized at 350°C
10 Pyrolized Wyodak at 350°C	27. Beulah Pyrolized at 500°C
11. Dried Wyodak Coal	28. Aged Beulah
12. Pyrolized Wyodak at 200°C	29. Aged Beulah; Pyrolized 250 degrees
13. Pyrolized Beulah at 400°C	
14. Beulah Pyrolized at 250°C	
15. Aged Beulah at 350°C	

4.3   Coal Pyrolysis

Pyrolyzed Coal was prepared by heating coal samples under nitrogen in the thermogravimetric analyzer (TG) component of a TG/MS/GC system. About 50mg of coal powder were placed in the recording thermo analyzer chamber, and evacuated to

remove air. Nitrogen was flowed to flush the chamber and remove evolved gases as the temperature was raised at a controlled heating rate (20°C/min) until it reached the preset final pyrolysis temperature of 200, 250, 300, 350, 400, respectively. Pyrolysis was complete when no further weight loss was observed on the TG. Larger coal masses were pyrolyzed using a glass reactor system. Approximately 30 grams of coal were loaded into the reactor and nitrogen gas fed through a rotometer into the reactor for 24 hours. Pyrolyzed coal samples were then stored under nitrogen until needed.

4.4   Infrared Specral Analysis

A Perkin Elmer Spectrum FT-IR system equipped with a Diffuse Reflection Accessory, and a Dell/OptiPlex (Intel Inside) computer accessory including software capable of spectral addition/subtraction and deconvolution was used. Fourier Transform Infrared (FT-IR) spectra of aforementioned coal samples were taken to characterize processed coal.

4.5   Surface Area and Pore volume measurements:

A Micromeritics model 2000 accelerated surface area porosimeter (ASAP), was used to study the N_2 adsorption isotherms at 77 K of dried powdered samples i.e. pyrolysed, oxidized or untreated samples respectively. Approximately 3.5 gm of sample coal were evacuated at 250°C for 24 hours under dynamic vacuum of about 10-4 torr. After cooling the samples were kept in a N_2 atmosphere and later evacuated with a drag pump. The porosity characteristics including surface area, pore size distribution and pore volume were obtained from various data reduction methods contained in the apparatus software: Brunauer, Emmet and Teller (BET); Harkins and Jura (HJ); Horwarth and Kawazoe (HK); and Density Functional Theory (DFT) methods.

4.6   **Oxygen Adsorption Studies**

The reactivity in air i.e. oxygen adsorption of Untreated, Pyrolyzed and Aged Coals respectively were measured in a Cahn Thermograimetric Analyzer (TGA 121) and a Differential Scanning Calorimeter – Thermal Analysis Instruments – Q1000 with advantage software at 10, 20 40 and 60 ^{o}C for 12 hours respectively. Fresh samples were used for each run. The TGA was sensitive to 0.001 mg and the furnace was capable of temperatures up to 1100 ^{o}C. Runs on the TGA and Q1000 were initiated by first purging the reaction chamber with helium for 30 min before the temperature was raised to the desired reaction temperature. Approximately 50 mg (for the TGA) or 5mg (for the Q1000) of coal sample were weighed into the instruments. The temperature was raised at a controlled heating rate, 10 ^{o}C /min under nitrogen until it reached the preset final oxidation temperature. Once the set temperature was attained the flow of N_2 was discontinued and high purity, dry air was introduced at 50mL/min. The air temperature, sample weight and the time derivative of the weight gain (TGA) or reaction enthalpy, ΔH (Q1000) were continuously recorded.

4.7   **Coal Vapor Analysis**

Detection of evolved organic compounds during oxidation was accomplished using a Hewlett Packard (HP) head space analyzer (HS) attached to a HP 5973 gas chromatograph-mass spectrometer(GC/MS) system. Approximately 10 grams of untreated, pyrolyzed or aged and pyrolyzed coal samples were placed in 20-ml headspace vials and analyzed using an oil bath temperature of 200 degrees centigrade. Data were collected and analyzed using standard data processing software. Identification procedures included examination of the total ionization chromatograms (TIC) followed by the use of extracted ion profiles (EIP), manual inspection of data, and library searches using the NIST 98 PBM algorithm. Criteria for identification included recognition of the fragmentation pattern and existence of the molecular ion. Quality index information of the library search algorithm was another significant clue for positive identification; although lower quality indexes were accepted if the

associated and requisite molecular ion, fragmentation and retention time data were appropriate. These data summarize the results which were duplicated in successive runs.

Table 2: Analysis Conditions – Head Space/GC/MS:

HP Model7694 Headspace Analyzer 10 grams sample 200 degree bath temperature 200 degree loop temperature 210 degree transfer temperature 2.5 ml loop size equilibration time: 10 minutes pressurization time: 0.13 seconds injection time 0.10 minutes	HP Model 5973MSD 30 meter HP-5 Fused Silica Capillary Column (HP p/n 19091S-433) 250 um diameter 0.25 um film thickness constant flow; initial flow 0.8 ml/min inlet pressure: 4.28 psi linear velocity: 32 cm/sec splitless injection; 1.0 min purge time temp1: 50 degrees time 1: 5 minutes rate: 12 degrees/min temp 2: 250 degrees time 2: 10 minutes scanning mode: 350/500 Dalton 1.6 cycles/second autotune+200 EMV

5 Results and Discussion:

5.1 Spectral Analysis

FTIR spectra [13] were used to confirm results of treatments of coal samples and low temperature oxidation. Pyrolysis was confirmed by decreased intensity of the broad triangular-shaped band arising from the hydrogen-boned hydroxyl stretches within the amorphous coal matrix. This band normally spans ca. 3600 to near 2500 wave numbers. Aging/oxidation on the other hand was confirmed by increased intensity of a small, but prominent, band at ca. 2730 wave numbers due to the carbon-hydrogen stretch vibrations of the aldehyde components of the coal and carbonyl bands resulting in various modes ranging from 1650 to 1850 wave numbers, depending on the degree of oxidation of the surfaces of the coal particles

5.2 Surface Area Measurements

Table 3: Correlation of Coal Surface Area with Treatment.

Coal Samples	Treatment	Surface Area Langmuir m^2/g	Pore Diameter A°
4	Wyodak aged and pyrolysed d at 200°C	4.4496	125.7095
5	Wyodak Pyrolysed at 250°C	4.9467	130.5802
18	Beulah aged and pyrolysed at 200°C	0.9564	167.9572
20	Beulah Pyrolysed at 300°C	1.408	116.7401

Surface areas were estimated by adsorption of nitrogen at 77 K. It is generally accepted that for coals, the surface area accessible to nitrogen at 77 K is to some degree a measure of the macro and transitional pores. These pores, in processes which involve

mass transport, act as 'feeder' pores for reactant gases. Their distribution determines the ease with which a reactant can enter the micro porous substructure of the solid, where reaction predominantly occurs. Since the rate of oxidation will necessarily be determined by the extent of available surface and by the rate at which oxygen can be supplied to these surfaces, the apparent connection between the 'reactivity' of a coal and the probability of it igniting spontaneously and surface area is readily understood.

The effect of particle size or surface area on the self-heating of coal was examined by measuring the weight gain of coal on exposure to dry air in the TG component of the TG/MS/GC system and correlating the same with coal surface area using samples 4,5,18 and 20 selected at random. This correlation also enabled the evaluation of the impact of treatment on the propensity of the coal samples towards oxidation since the surface area varied with treatment.

Surface area and porosity results for representative coal samples (4, 5,18 and 20) are listed in Tables 3. Experimental adsorption-desorption isotherms of these samples which revealed porosity were analyzed by the t-plot method devised by deBoer and co-workers [14-15], in which the volume of adsorbed gas is plotted vs. film thickness, calculated from the Harkins and Jura equation [16]. The t curves of the coal samples showed deviations from linearity which also suggest that they are porous. BJH adsorption pore size distribution reports indicated that no pores were open at both ends. Surface areas for Wyodak coals were generally higher than those of Beulah. Also aging/oxidation increased average pore diameters and decreased observed surface areas.

Table 4 also lists the active surface Areas (ASA), of our coal samples 1 through 29, measured by prolonged exposure to O_2 at 10, 20, 40 and 60 ^{o}C respectively. As the coal gained weight in this temperature range, we propose that the O_2 reacted with the coal surface, forming carbon- oxygen complexes and negligible amounts of gaseous CO and CO_2. Using O_2 adsorption, values of active sites of carbon which ranged from a high of 2725.24 µgm/gmCoal (aged Wyodak pyrolized at 523°K) to 85.16µgmC/gmCoal (Beulah pyrolized at 773°K **)** were computed for all the coal samples analyzed. Compared to Active Surface Areas (15.6 µ gm activeC/gmC) of purer forms of carbon such as graphite [17]**,** we concluded that O_2 adsorption occurred on catalytic sites, primarily those that are metallic or metallic oxide.

Table 4: Reactivity of Coal Samples

Coal Samples	Treatment	gmCoal	mg O_2/gmC	μ gm activeC/gmC	mL O_2	mL O_2/gmC
6	Aged Wyodak	0.06	5.68	2129.09	0.30	4.85
28	Aged Beulah	0.05	2.14	802.97	0.11	1.83
8	Aged Wyodak Pyrolized at 300 C	0.06	6.65	2494.08	0.35	5.68
24	Aged Beulah Pyrolized at 300 C	0.05	3.94	1478.20	0.21	3.37
3	Aged Wyodak Pyrolized at 250 C	0.06	7.27	2725.24	0.38	6.21
29	Aged Beulah Pyrolized at 250 C	0.05	5.87	2202.09	0.31	5.02
4	Aged Wyodak Pyrolized at 200 C	0.06	5.65	2116.93	0.30	4.82
18	Aged Beulah Pyrolized at 200 C	0.05	0.68	255.49	0.04	0.58
12	Pyrolized Wyodak at 200 C	0.06	5.03	1885.77	0.26	4.30
25	Pyrolized Beulah at 200 C	0.05	0.34	127.75	0.02	0.29
5	Pyrolized Wyodak at 250 C	0.06	6.15	2305.50	0.32	5.25
14	Pyrolized Beulah at 250 C	0.05	0.70	261.57	0.04	0.60
2	Pyrolized Wyodak at 300 C	0.05	9.62	3607.29	0.51	8.22
20	Pyrolized Beulah at 300 C	0.06	1.09	407.57	0.06	0.93
1	Pyrolized Wyodak at 400 C	0.06	5.45	2043.93	0.29	4.66
13	Pyrolized Beulah at 400 C	0.06	0.81	304.16	0.04	0.69
11	Dried Wyodak Coal	0.05	3.23	1210.54	0.17	2.76
21	Aged Beulah Pyrolized at 200 C	0.06	4.72	1770.19	0.25	4.03
10	Pyrolized Wyodak at 350 C	0.06	6.49	2433.25	0.34	5.54
15	Aged Beulah at 350 C	0.06	3.36	1259.21	0.18	2.87
19	Aged Beulah Pyrolized at 400 C	0.05	3.62	1356.54	0.19	3.09
23	Beulah Pyrolized at 550 C	0.06	0.23	85.16	0.01	0.19

5.3   Kinetics and Mechanism

5.3.1 O_2 adsorption

Apart from adiabatic calorimetry, the other test that is widely used to measure

the reactivity of coal is static O_2 adsorption. In this test, a coal sample is placed in a

sealed flask and gas samples are withdrawn daily for analysis. The results are then used

for the determination of the rates of O_2 adsorption. This method has the drawback that

when the volume of the flask is small, frequent removal of samples depletes available

O_2 and also complicates calculations.   In this work, O_2 adsorption rates were

continuously measured at thermal equilibrium on the thermogravimetric analyzer

(TGA, Cahn Microbalance) and differential scanning calorimeter (DSC, Q1000, thermal analysis instruments). O_2 adsorption rates were used as a relative measure of the reactivity of the coal. In general, Wyodak coals were more reactive than lignite. Of the twenty nine coal samples used, the order of reactivity for Wyodak was : Wyodak pyrolyzed at 300 ^{o}C > aged Wyodak pyrolise at 250 ^{o}C > aged Wyodak pyrolyzed at 300 ^{o}C. The order for Beulah was : aged Beulah pyrolyzed at 250 ^{o}C > aged Beulah pyrolyzed at 300 ^{o}C > aged Beulah pyrolyzed at 350 ^{o}C. Aging of coal followed by pyrolysis was observed to increase coal reactivity.

Table 5: Alkane (C9-C18) Detection and Rate of Oxygen Adsorption on Coal.

Coal Samples	Type	Pyrolysis Temp	Treatment	Hydrocarbon Carbon	R_{O2} Ads mgO_2/mg coal.sec.
1.	Wyodak	400		No alkanes	7.42×10^{-4}
2.	Wyodak	200		No alkanes	6.67×10^{-4}
3.	Wyodak	250	Aged	C 10-12	4.93×10^{-4}
4.	Wyodak	200	Aged	C11-13	1.41×10^{-3}
5.	Wyodak	250		C11-12	2.64×10^{-4}
6.	Wyodak		Aged	C11-13	2.78×10^{-4}
7.	Wyodak	400	Aged	No alkanes	
8.	Wyodak	300	Aged	No alkanes	1.68×10^{-3}
9.	Wyodak	350		No alkanes	
10.	Wyodak	350		No alkanes	2.46×10^{-4}
11.	Wyodak		Dried	C11-14, 16	
12.	Wyodak	200	Pyrolized	C9-13	2.44×10^{-4}
13.	Beulah	400		No alkanes	9.78×10^{-5}
14.	Beulah	250		No alkanes	9.77×10^{-5}
15.	Beulah		Aged - 350		2.33×10^{-4}
17.	Beulah	450			5.58×10^{-4}
18.	Beulah	200	Aged	No alkanes	9.51×10^{-5}
19.	Beulah	400	Aged	No alkanes	
20.	Beulah	300		No alkanes	5.61×10^{-5}
21.	Beulah	200	Aged	C16-18	3.74×10^{-4}
23.	Beulah	500		No alkanes	
24.	Beulah	300		No alkanes	
25.	Beulah	200	Aged	No alkanes	2.8×10^{-4}
26.	Beulah	350		No alkanes	
27.	Beulah	500		No alkanes	6.1×10^{-4}
28.	Beulah		Aged	No alkanes	
29.	Beulah	250	Aged	No alkanes	4.65×10^{-4}

The reaction rate (R) and propensity towards spontaneous combustion was evaluated in terms of the initial rate method for the mass gained due to adsorbed O_2. The coals used for the current studies had O_2 absorption rates which ranged from 0.202 mg O_2/mg coal hr for coal sample #20 (Beulah pyrolyzed at 300^oC) to 6.05 mg O_2/mg coal hr for coal sample #8 (Wyodak aged and pyrolyzed at 300^oC). Aging of coal followed by pyrolysis was observed to contribute to higher reaction rates. The Representative selection of the

heat flow against time spectra for the coals analyzed are shown in figure 1. In the the examples shown oxidation was carried out at O_2 concentrations of 5% and 21% respectively.

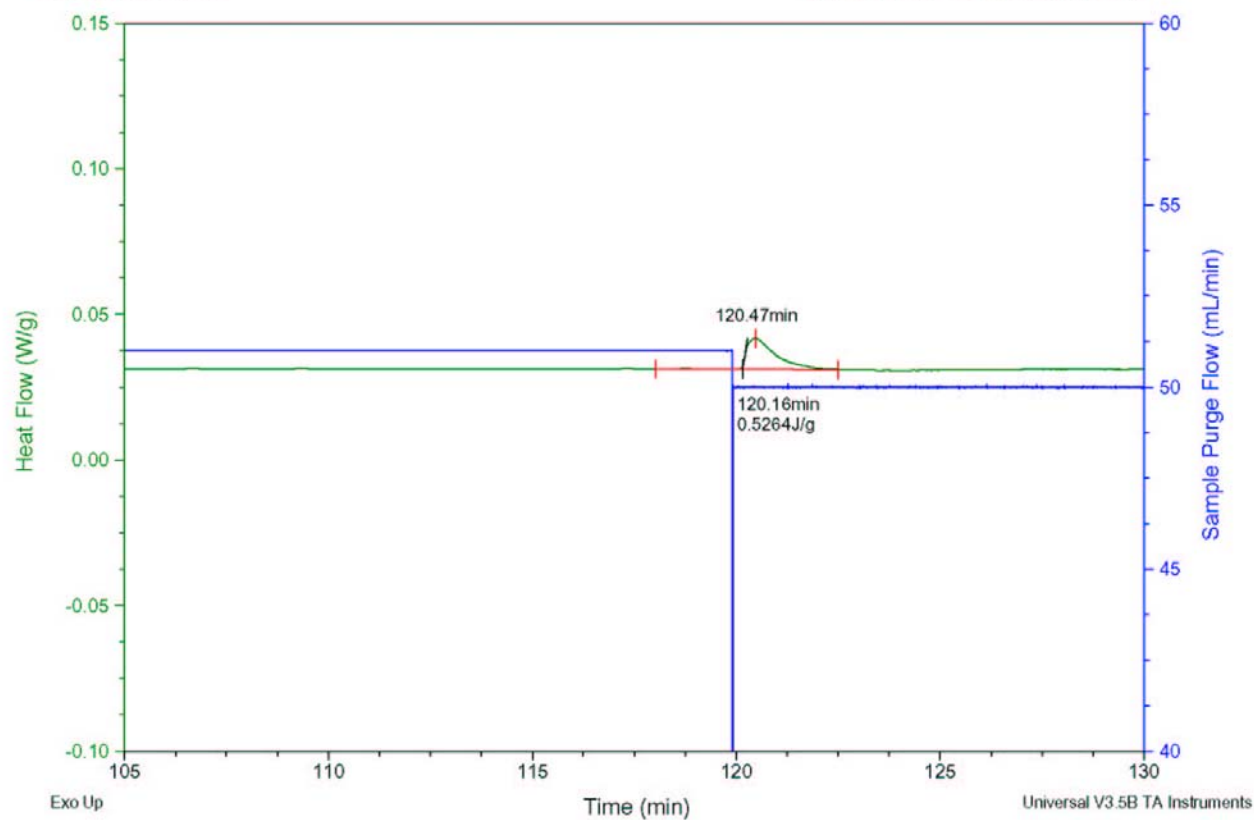Figure 1 Heat flow versus time plots from DSC measurements[1]

Sample: Figure 28b (5% Oxygen)
Size: 5.5000 mg
Comment: Coal Test
DSC
File: D:\COAL.058
Operator: Tia
Run Date: 11-Aug-02 19:28
Instrument: DSC Q1000 V5.1 Build 191

121.08min
120.31min
0.1559J/g

Exo Up
Time (min)
Universal V3.5B TA Instruments

---
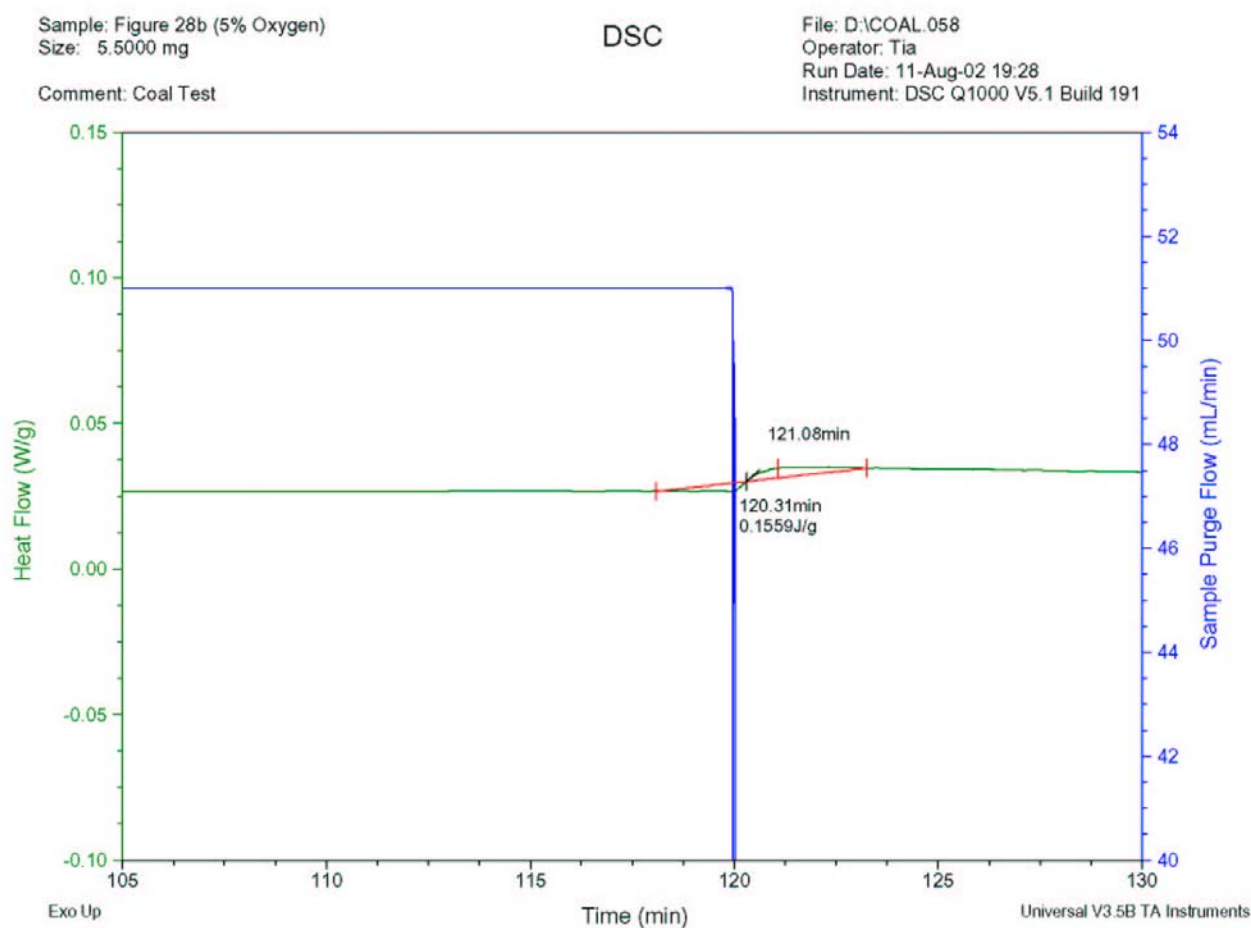
[1] The complete set of spectra from our analysis is placed on a CD and included with this report. Also available upon request.

Sample: Coal #8 Figure 8d 5%O2 40C
Size: 5.1000 mg

Comment: Coal Test

DSC

File: D:\COAL.090
Operator: Tia
Run Date: 27-Aug-02 00:45
Instrument: DSC Q1000 V5.1 Build 191

120.47min

120.16min
0.5264J/g

Exo Up

Time (min)

Universal V3.5B TA Instruments

Sample: Figure 29a (21% Oxygen)
Size: 5.1000 mg

Comment: Coal Test

DSC

File: D:\COAL~1.033
Operator: Tia
Run Date: 08-Aug-02 07:38
Instrument: DSC Q1000 V5.1 Build 191
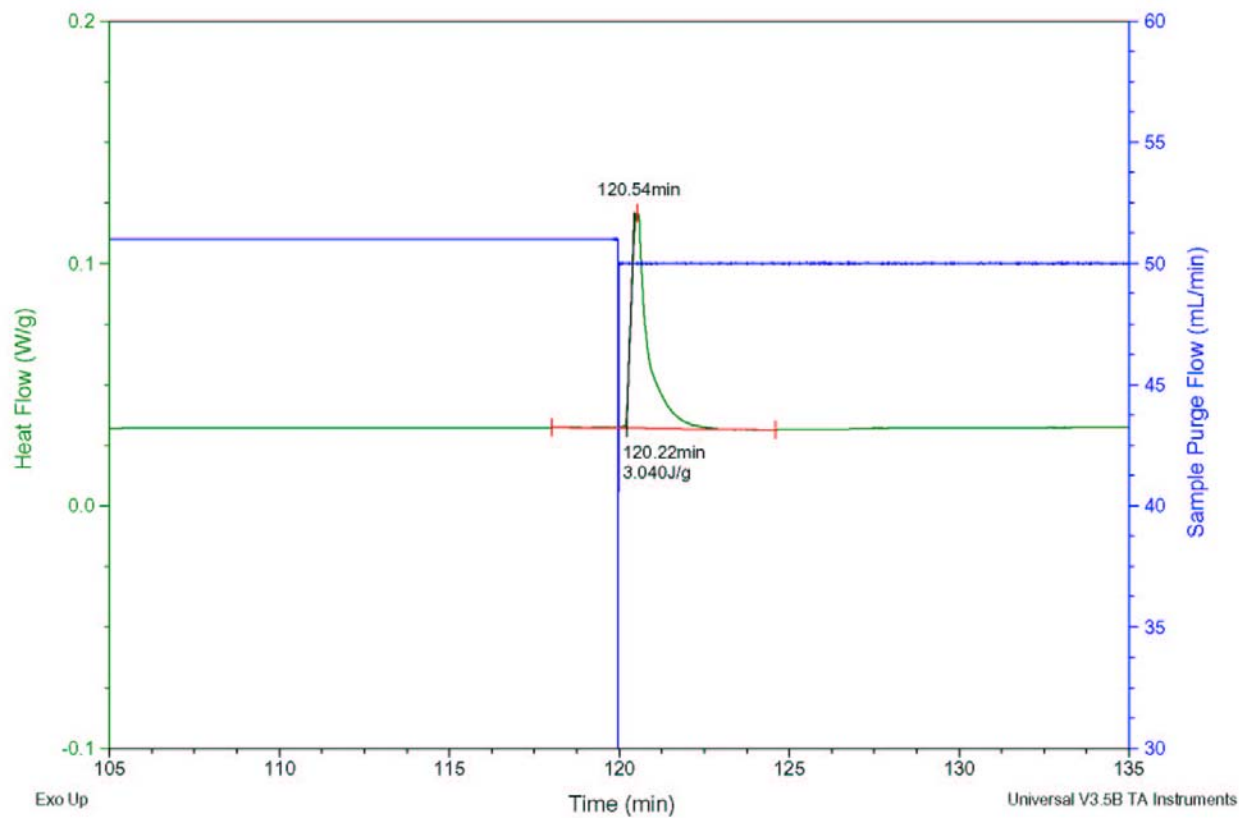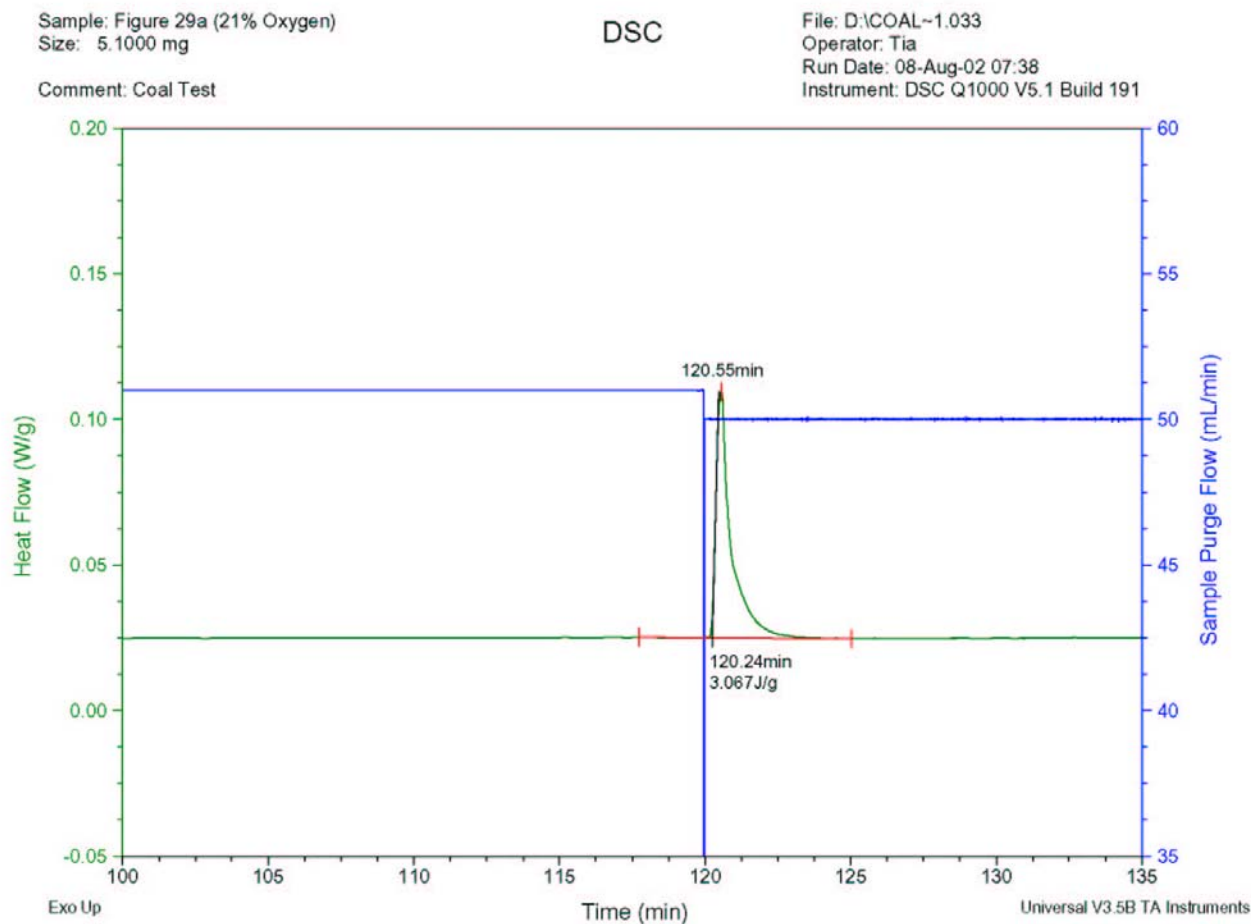
5.4 Analyses using Head Space (HS) and GC/MS

HS/GC/MS chromatograms of coal samples which had been oxidized and pyrolized at various temperatures were evaluated as a means of identifying key chemical markers indicative of samples prone to self ignition phenomena. Results are presented in table 5. Coal samples chromatograms were characteristic of treatment. Samples which had been aged and or pyrolyzed at 200 to 250 ^{o}C contained trace

amounts of identifiable linear straight chain hydrocarbons over the C9 to C13 range and a myriad of organic saturated and unsaturated components. Samples which had been pyrolyzed at 400 degrees produced seemingly transparent chromatograms devoid of the linear alkane indicators and significant amounts of other identifiable organic material. Using split injection techniques with no scan start delay, a volatile component with a low flash point was detected. Trace amounts of acetone was flagged in selected samples---primarily those with the lower (200 to 250 degree) pyrolysis temperature and corresponding to those samples with the alkane qualitative prescence indicated earlier. Those samples containing acetone (chromatograms 29-48) above threshold values were compared to those samples with significant oxygen adsorption profiles again with remarkable coincidence since a peroxy intermediate has been suggested. The collective chromatograms are shown in figure 2.

Figures 2 Choromatograms of Coal Samples 29 through 48

Coal Sample #29
Figure
49
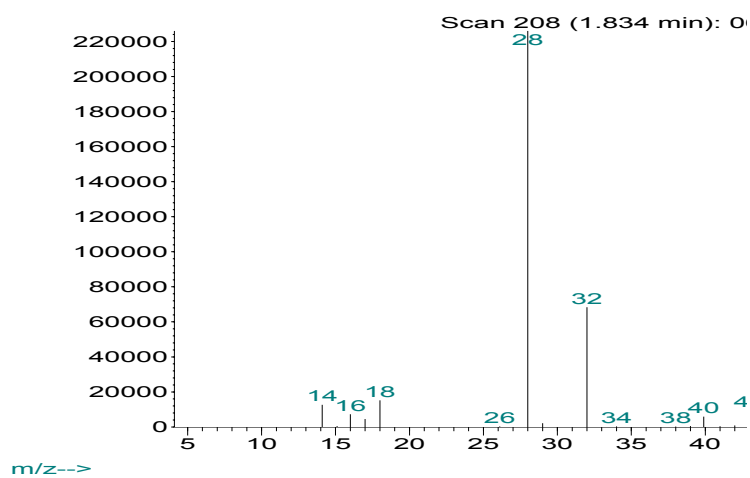
Coal Sample #2
Figure
30
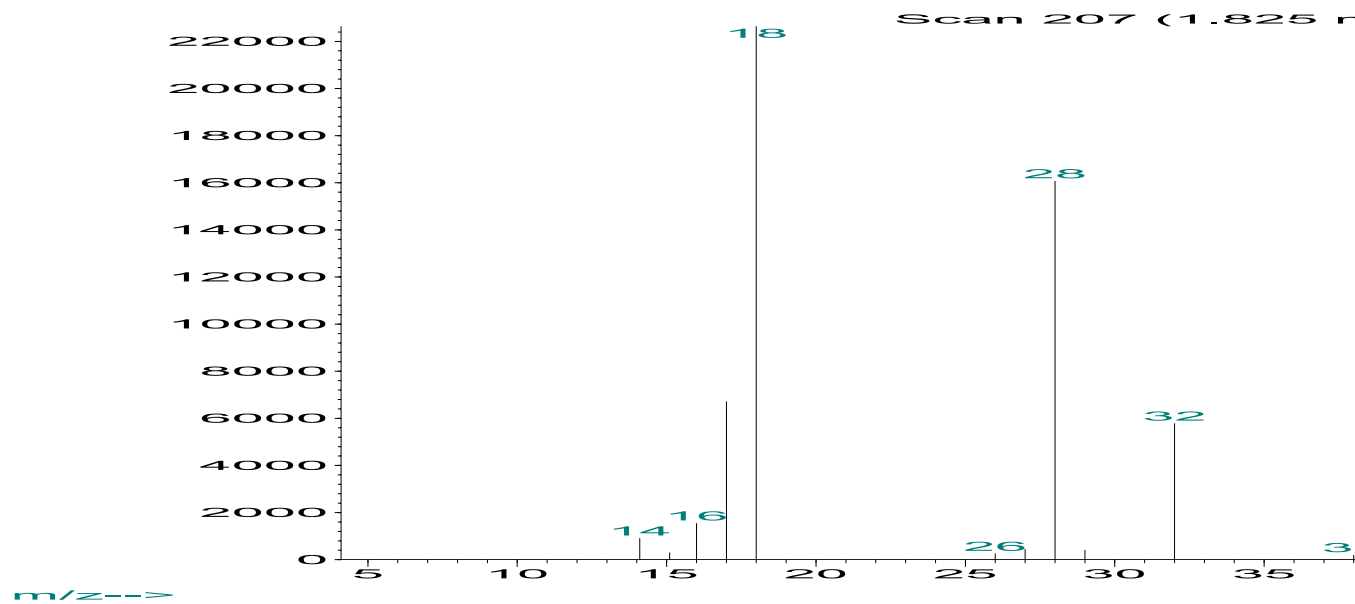
Coal Sample #3
Figure
31
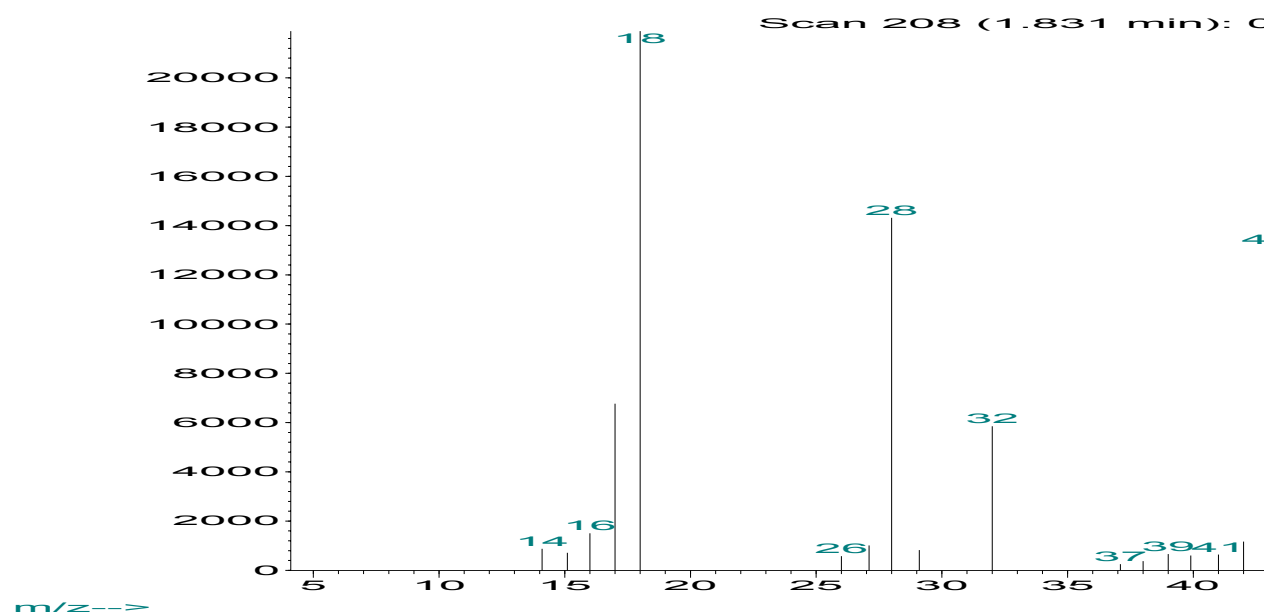
Coal Sample #5
Figure
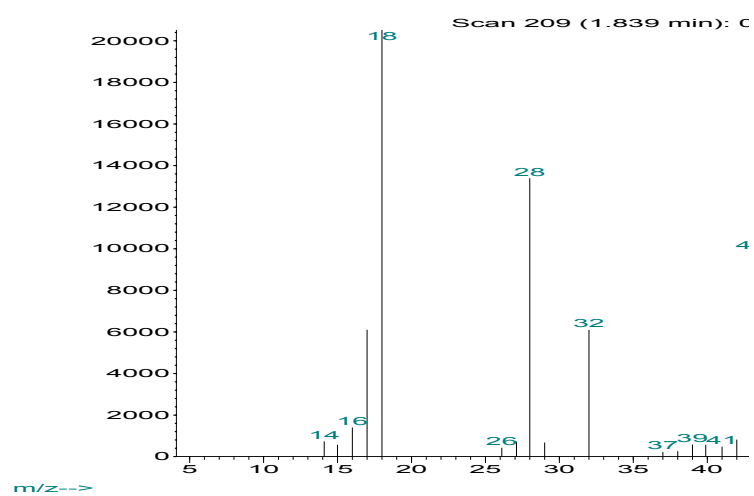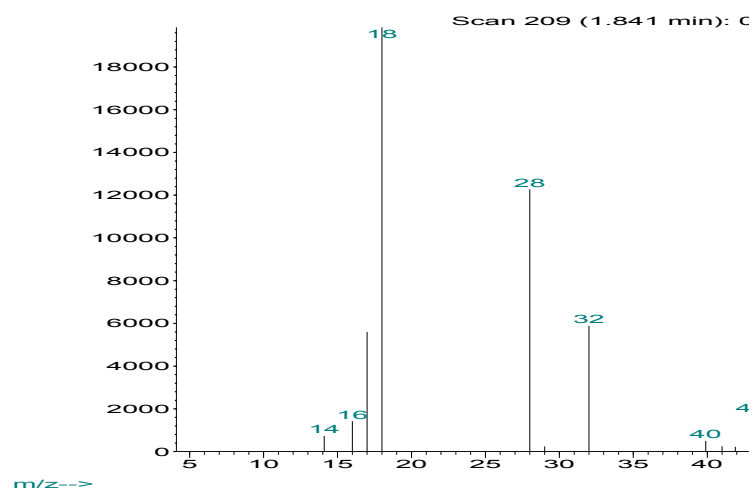32

Coal Sample#6

Figure

33
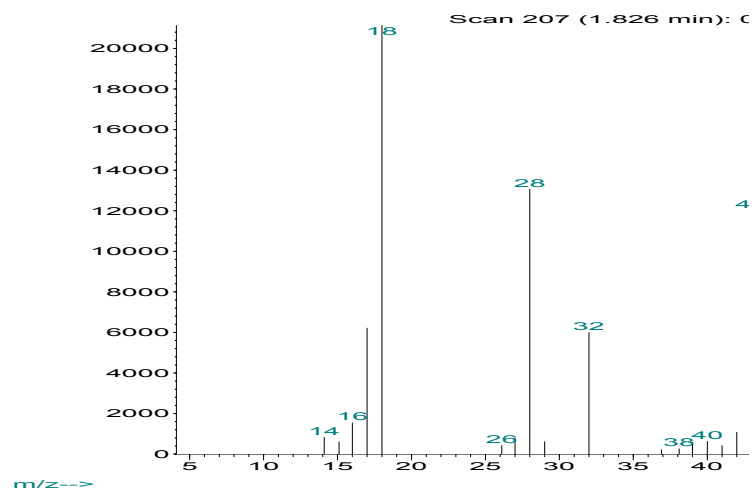
Coal Sample #8

Figure

34

Coal Sample # 9

Abundance
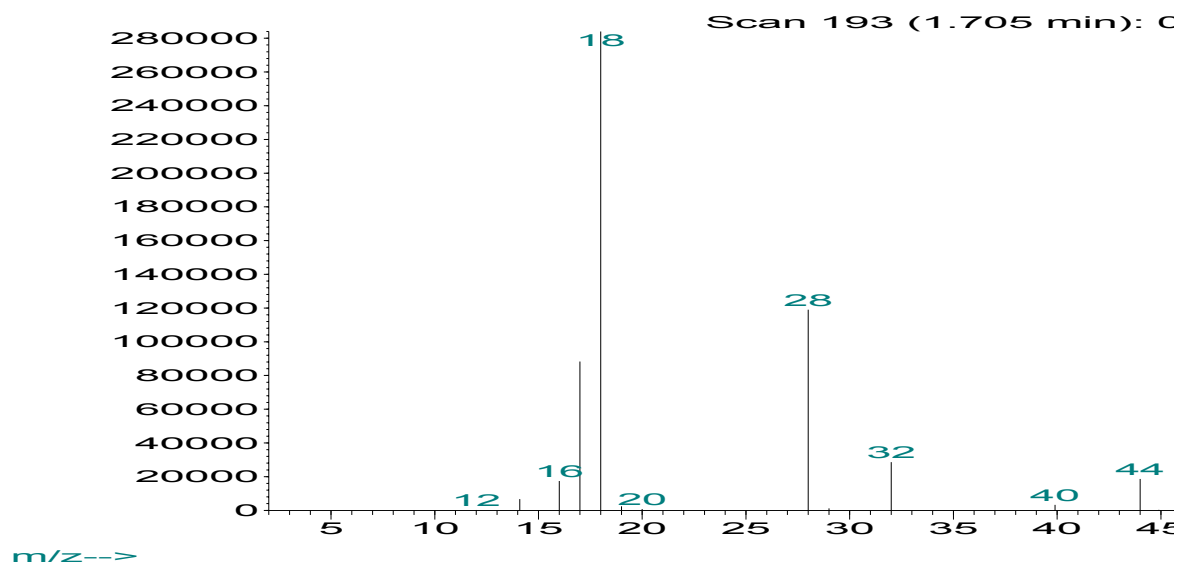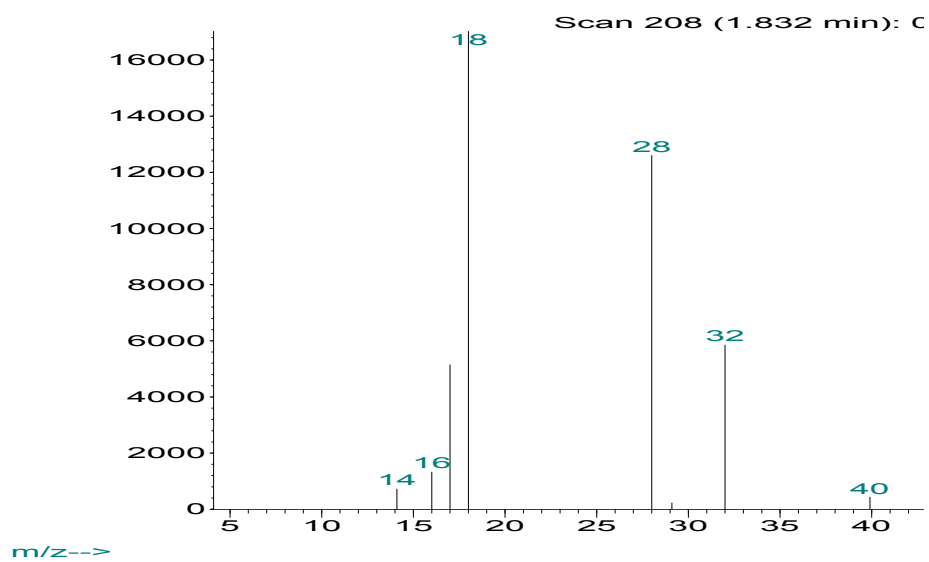

Figure 35

Coal Sample#10

Figure

36

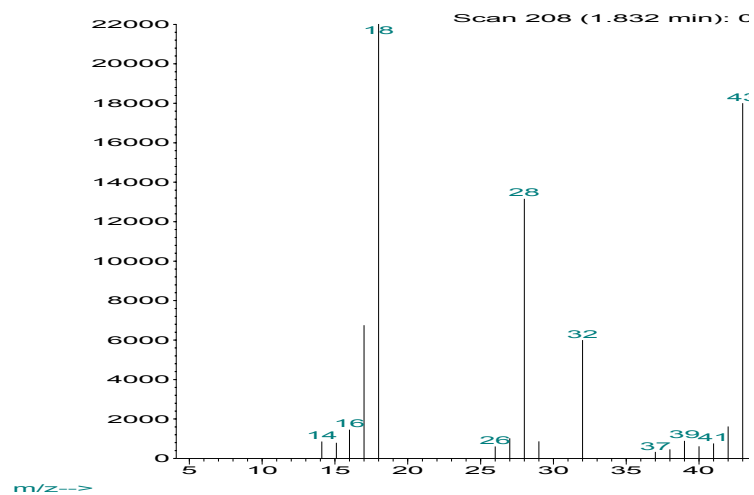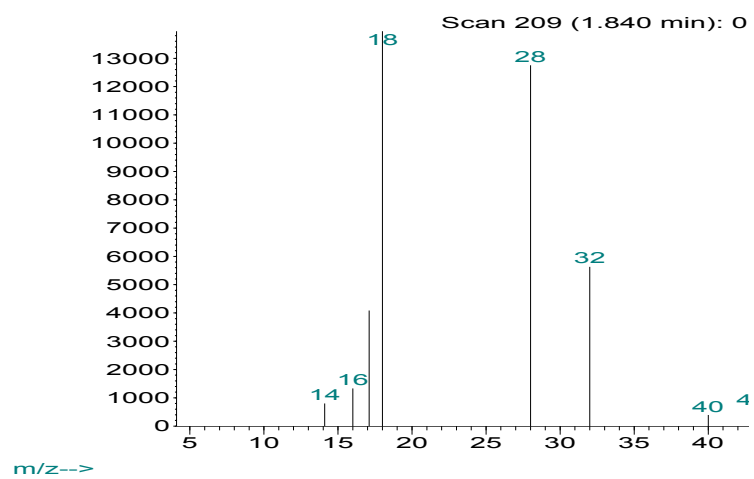Abundance

Coal Sample#11

Figure#37

Coal Sample#13

Figure

38

Coal Sample#14

Figure

39

Abundance

Scan 209 (1.842 min): 0...
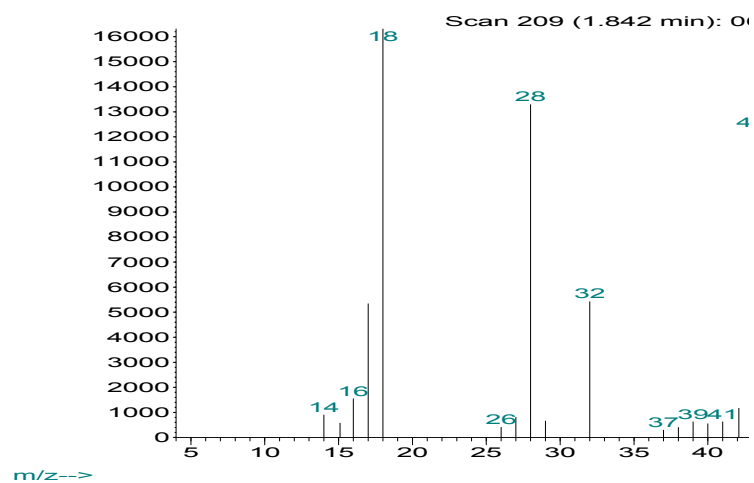
Coal Sample# 15

Figure

Abundance

Scan 209 (1.842 min): 0...
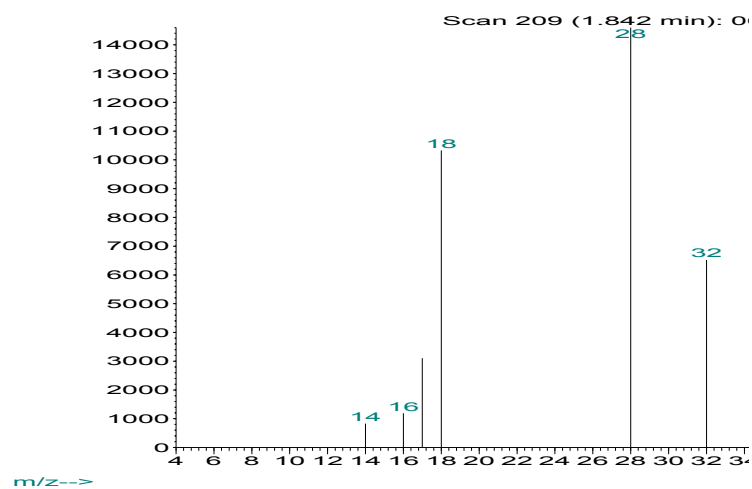
40

Coal Sample#17
Figure
41

Scan 176 (1.562 min): 060316.
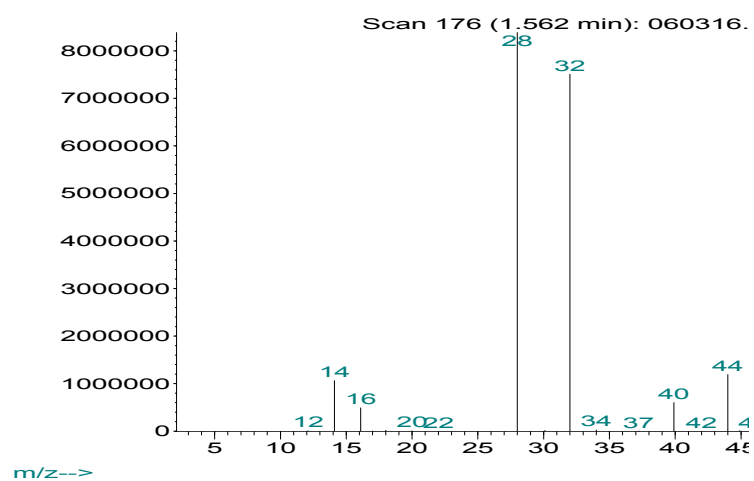
Coal Sample #18
Figure
42

Scan 208 (1.833 m
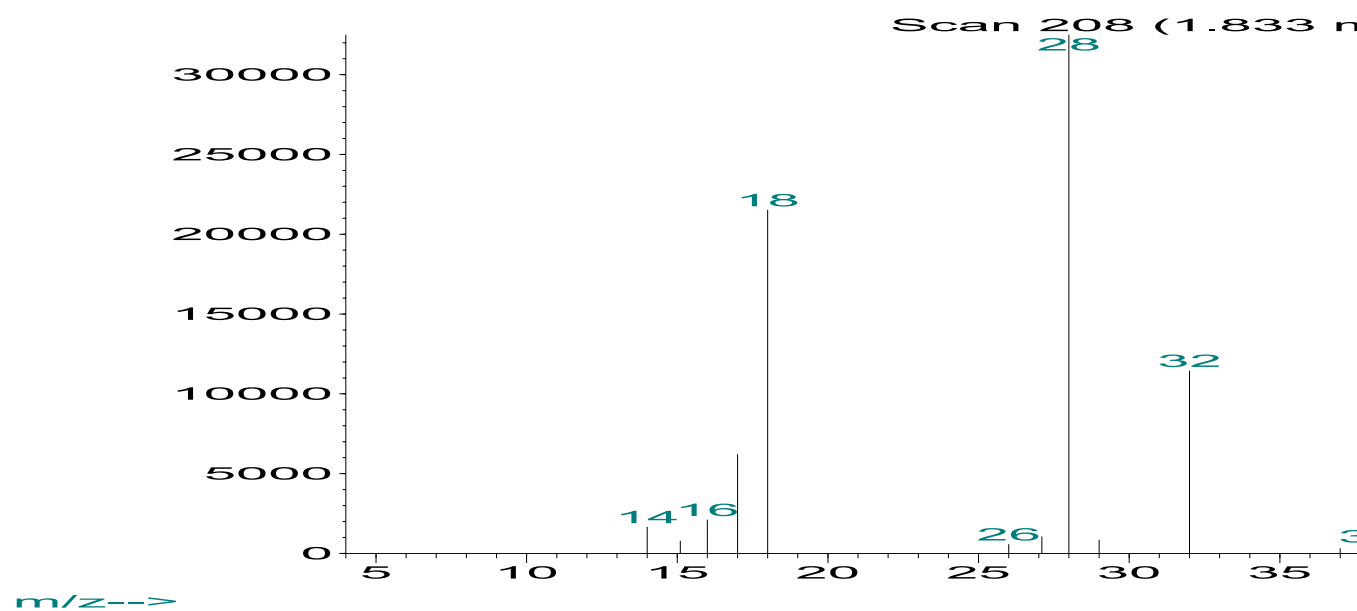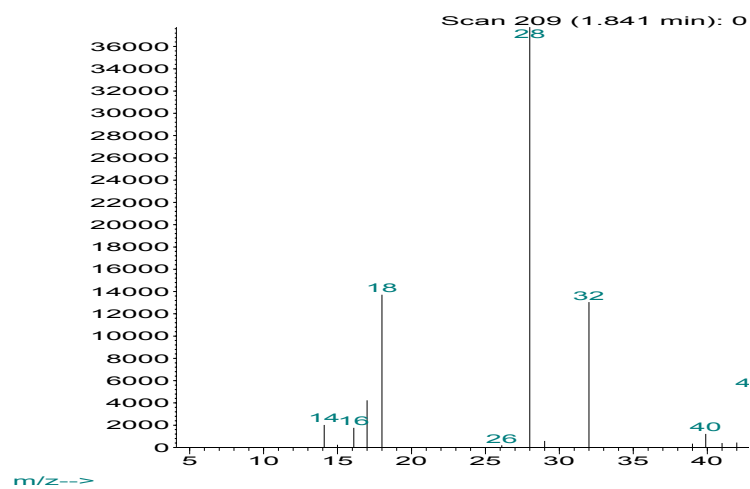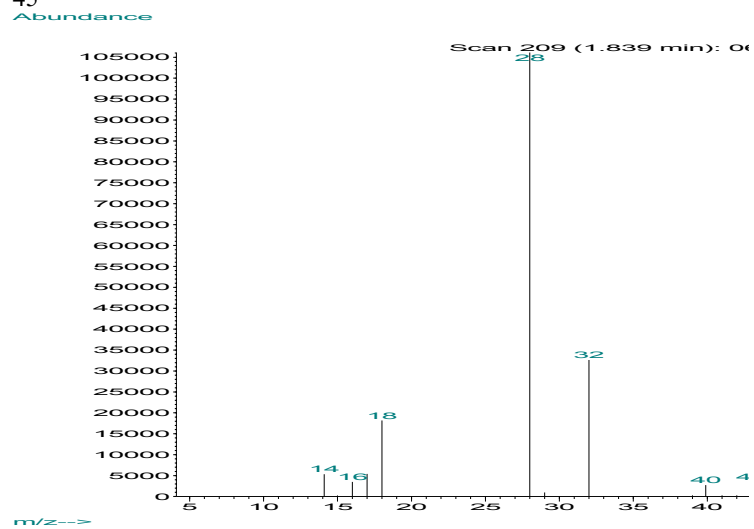
Coal Sample#19
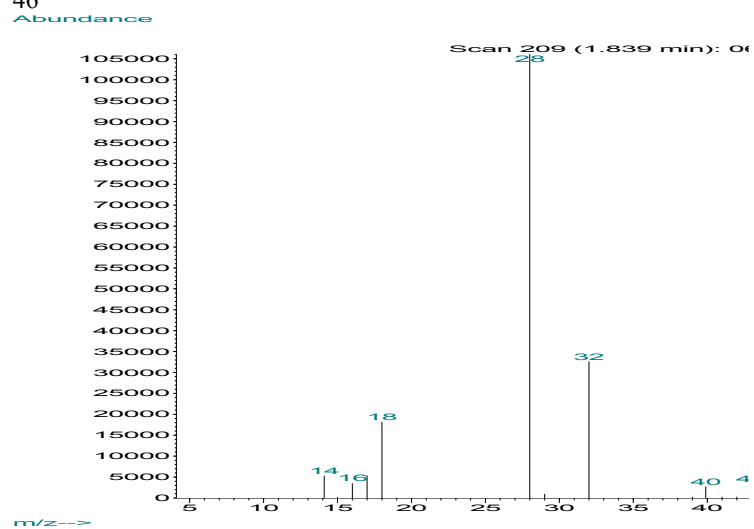Figure
43
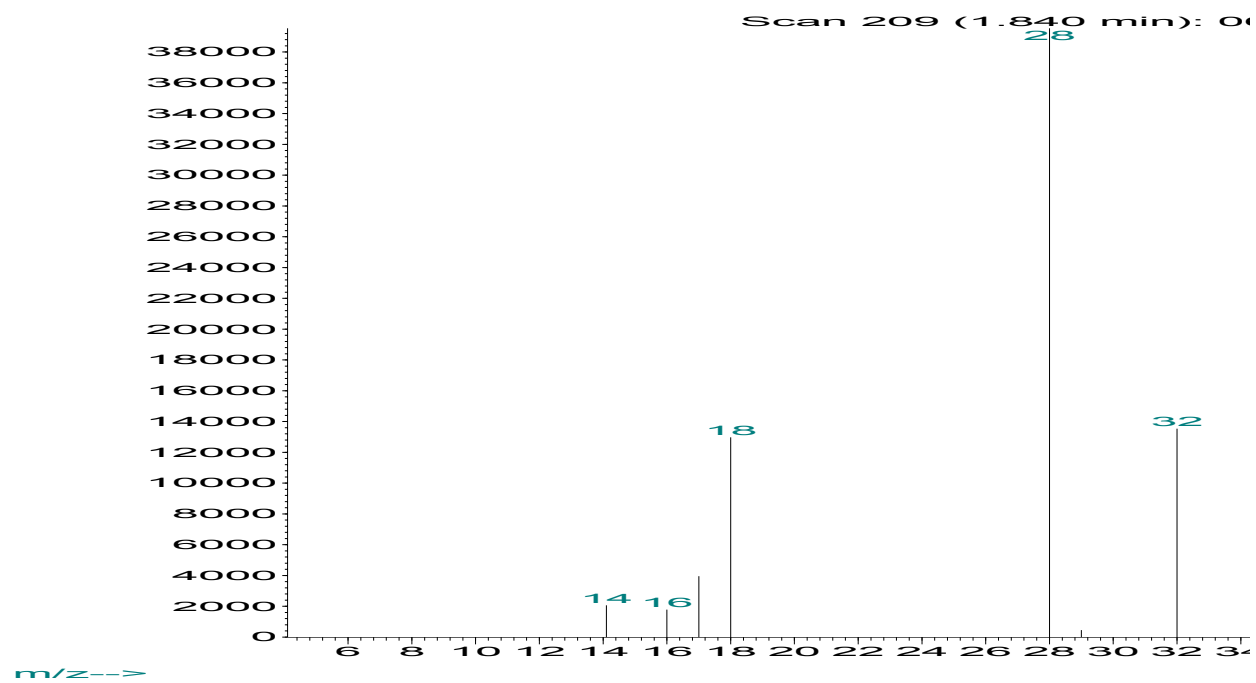
Coal Sample#23
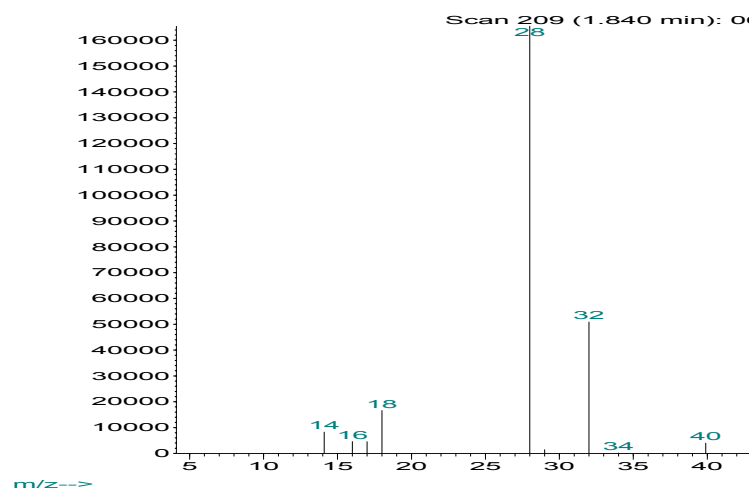Figure
44

Coal Sample # 24
Figure
45

Coal Sample # 26
Figure
46

Coal Sample #27

Figure

47
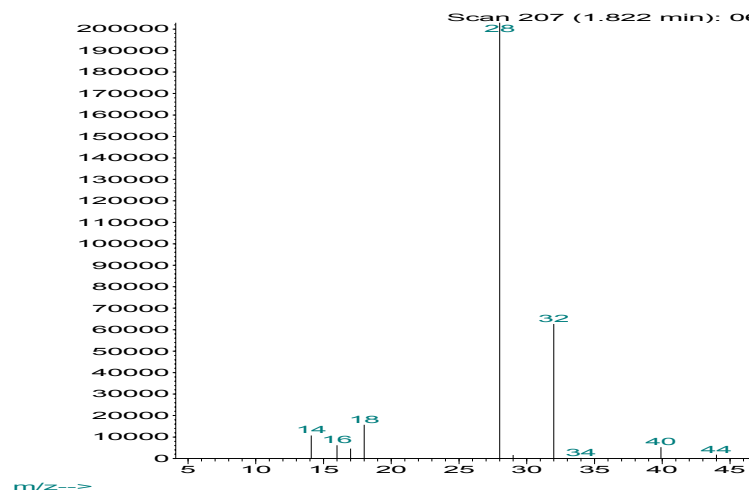

Coal Sample #28

Figure

48

5.5   Activation Energies

The temperature dependence of rates of coal oxidation was evaluated from the Arrhenius equation

$$k = A \ e^{-Ea/RT}$$

here k is the rate constant, R is the universal gas constant and T is the absolute reaction temperature. This equation enabled the calculation of the respective values of the energy of activation (Ea), and the frequency factor (A). A and E_a were calculated to enable a relative ranking of coal reactivity with respect to spontaneous combustion Higher values of A (pre-exponential factor) and lower values of E_a (apparent global activation energies) indicated higher reactivity of coals used in this study. Rates for Arhenius plots were calculated by measuring the initial rates of heat released (dQ/dt), as a function of temperature. Our measured rate values for the formation of coal - oxygen complex and its breakdown to give products were validated by application of the absolute rate theory[19]. According to this theory, the pre-exponential factor is given by:

$$A = \frac{k_B T \ f^*}{h \ f_a}$$

Where k_B is the Boltzmann constant; T, the absolute temperature; h, Planck's constant; and f* and f_a the partition functions of the transition state complex and the adsorbed species C(O), respectively. The value of A at 301 K (mean temperature in this study) has a value of 6.33 x 10^{12} sec^{-1}. The values 1.44 x 10^{11} for aged Wyodak; 3.03 x 10^{10} for aged Beulah and 1.45 x 10^{10} for aged Beulah pyrolized at 773 K with partition functions 0.02, 0.005 and 0.002 respectively and aged Wyodak coal pyrolized at 573 K

with an A value of 3.27 x 10^{15} and partition function 517   identifies Wyodak coal

pyrolized at 573 K as the most reactive towards oxidation. By using partition functions

the reactivities of the coal samples used for the current studies can be listed in

the following order: Wyodak coal pyrolized at 573 K > aged Wyodak; > aged Beulah >

aged Beulah pyrolized at 773 K.

5.6   Mechanism

When air is allowed to come in contact with coal, oxygen is physically

adsorbed. The next initial interaction probably involving the interaction of the oxygen

by-radical with a spin center in coal to form a peroxy radical occurs. The peroxy radical

will have a certain mobility about its point of attachment, restricting the approach of

other gas molecules. In the second stage of the adsorption process, an oxygen bridge is

formed by the bonding of the localized radical to second active carbon site on the coal

surface. The product from this second stage is the so-called solid coal/oxygen

complexes. These may convert to more stable functional groups such as ether, lactone,

carbonyl, carboxyl, and anhydride carbonate which eventually breakdown to gaseous

products such as carbon dioxide, carbon monoxide and water. The detection of acetone,

a carbonyl, on the GC/MS analytical system employed in our study confirms the

mechanism above for the low temperature oxidation of our coal samples.

From the foregoing, we can infer that the activation energy of our coal oxidation

reaction is contributed to by i) adsorption of O_2, ii) chemical reaction and iii)

desorption of trace amounts of products. The adsorption process involves a molecule of

O_2 from the gas phase and an active carbon atom on the carbon surface. The energy of activation required may be used to form an activated complex between the molecule and the active carbon atom. Desorption of trace amounts of acetone or hydrocarbons from the coal surface involves an activated state in which either may be attached to an adsorbing center on the coal surface and must acquire the proper configuration and activation energy to permit it to escape form that surface.

Activation energies ranging from 70 to 90 kcal/mole have been reported by Strange and Walker [17] Wicke[18], Armington [19], Meyer[20] and Turkdogan and Vinters[21], Blyholder and Eyring[22] for the breakdown of the oxygen complex in the reaction of purer forms of carbon such as graphite with oxygen. These investigators studied the breakdown of carbon surface complex C(O) to give CO(g) in the graphite C-O_2 reaction. A number of other workers [23,24] have found that these values compare with the energies (72 to 83 kcal/mole) required to split a carbon-carbon bond on the graphitic surface

Many workers [25-28] have reported that the global activation energies for the self-heating of highly reactive lower rank (bituminous) coals fall in the 3- to 20-kcal/mole range and less than 10 kcal/mole between 30° to 70° C. These values are lower than those of graphite because of the catalytic sites in coal. Oreshko [29], reported that the initial step of self heating is the chemisorption of oxygen with an activation energy of 3 to 4 kcal/mole, followed by the decomposition of the chemisorbed oxygen complex with an activation energy of about 6 kcal/mole. The subsequent oxidation step reportedly involves the formation of an "oxycoal" compound

with an activation energy of the order of 16 kcal/mole. Reznik [30] reported that the

activation energy is approximately 5 kcal/mole for the low-temperature state (20° to 70°

C) and 30 kcal/mole for the high-temperature stage ($>70^o$ C).

Values of activation energy for the current studies are listed in Table 6.

Table 6: Activation Parameters.
Two sets of Activation Energy values are apparent

Sample #	Treatment Type *	Slope	Intercept	Ea kcal/mole	Log A	A
6	AW	9057	25.7	18.01	11.16	1.44E+11
28	AB	8674	24.14	17.25	10.48	3.03E+10
8	AWP300	11936	35.73	23.74	15.51	3.27E+15
19	ABP400	8392	23.4	16.69	10.16	1.45E+10
6	AW	5488	16.07	10.92	6.98	9.50E+06
28	AB	4360	11.46	8.67	4.98	9.40E+04
8	AWP300	6479	19.1	12.89	8.29	1.97E+08
19	ABP400	4596	12.15	9.14	5.28	1.89E+05

*

 AW   Aged Wyodak
AB   Aged Beulah
AWP300   Aged Wyodak Pyrolized @ 573 K
ABP400   Aged Beulah Pyrolyzed @ 773 K

The rate constants for the oxidation of the Wyodak and Beulah coals are shown in

figure 3

Figure 3   Rate constants for oxidation of Wyodak and Beulah coals

Temperature Dependence of Reaction Rate of Coal Oxidation
AW

Temperature Dependence of Reaction Rate of Coal Oxidation
AB

**Temperature Dependence of Reaction Rate of Coal Oxidation
AWP300**

**Temperature Dependence of Reaction Rate of Coal Oxidation
ABP400**
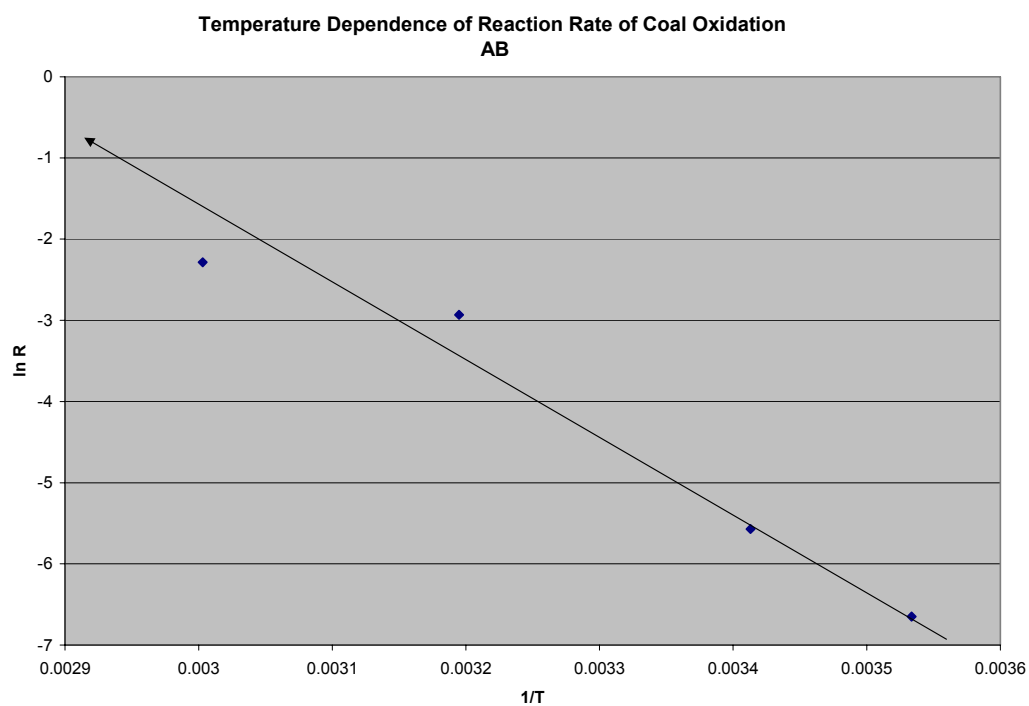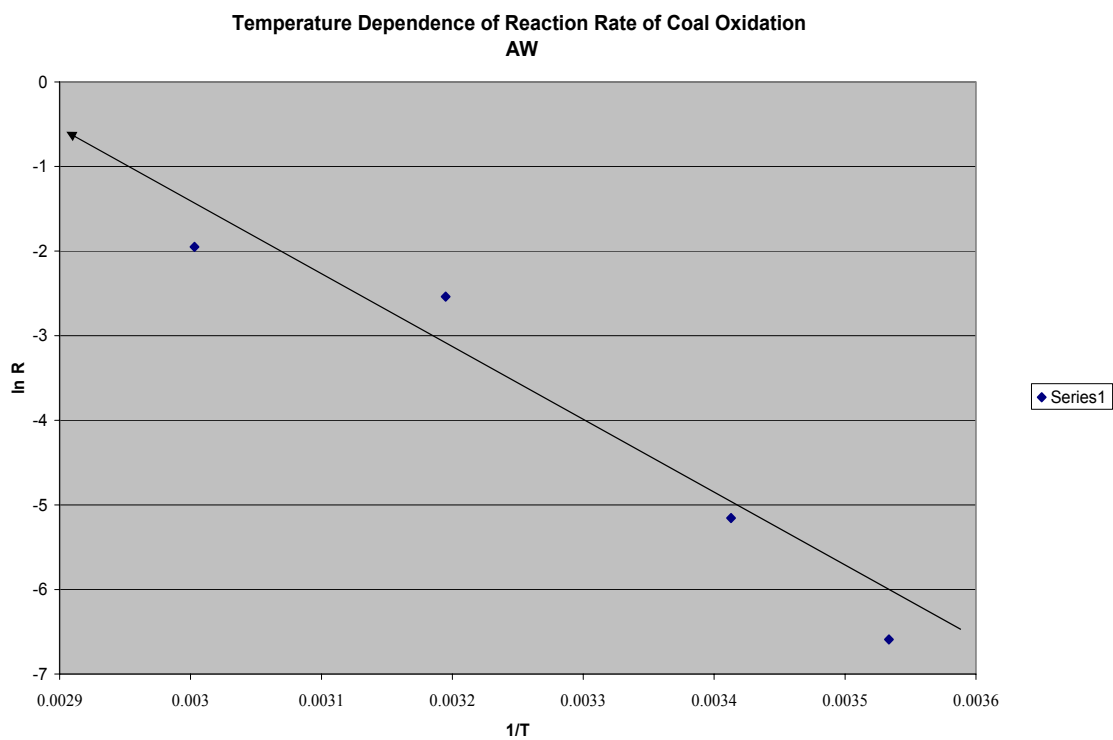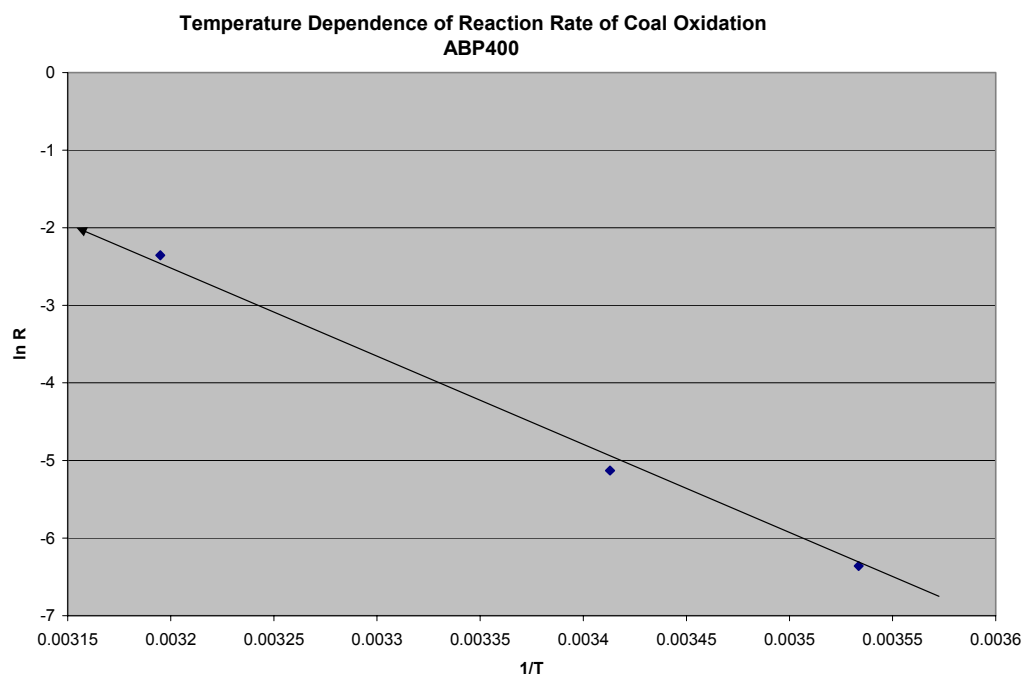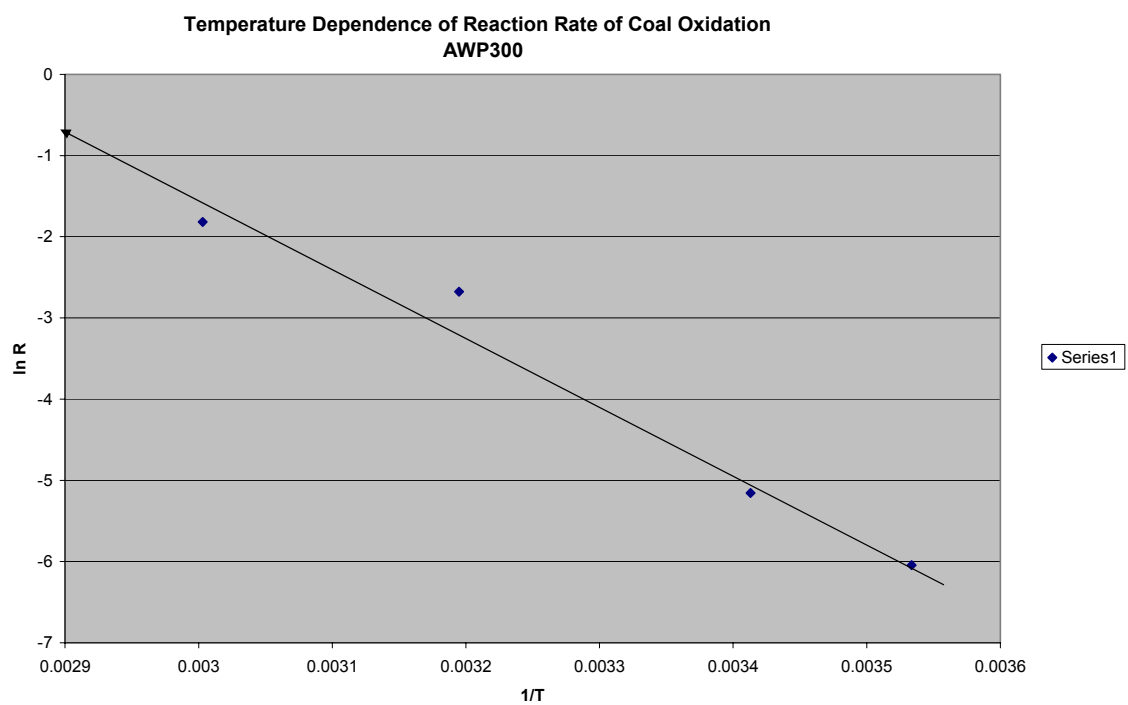
Two sets of values (16.7 – 23.74 6 kcal/mole and 8.67 – 12.89 6 kcal/mole) are apparent and based on them, we suggest that oxygen chemisorption on coal samples occured on two discrete types of sites with an abrupt change in activation energy when chemisorption proceeds from one type of site to another [6].

5.7 Reaction Enthalpy

Enthalpies of reaction (ΔH) in kcal/gmole O_2, for the most reactive coal samples : Aged Wyodak Pyrolized at 250^oC (#3), Aged Beulah Pyrolized at $250\ ^oC$ (#29), Wyodak Pyrolized at $300\ ^oC$ (#2), Aged Wyodak Pyrolized at $300\ ^oC$ (#8) and Aged Beulah Pyrolized at $350\ ^oC$ (#15) are presented in table7.

Table 7: Dependence of $\Delta H(kcal/gC/molO_2)$ on O_2 Concentration and Temperature

Sample #	Treatment	21 % O_2				5% O_2			15 % O_2
		10C	20C	40C	60C	20C	40C	60C	60C
3	Aged Wyodak Pyrolized at 250C	416.00	479.00	209.00	45.00	323.00	6.93	0.82	45.80
29	Aged Beulah Pyrolized at 250C	794.00	603.00	559.00	64.90	0.00	8.19	0.42	0.00
2	Wyodak Pyrolized at 300C	338.00	483.00	147.00	61.00	254.00	8.86	3.19	59.50
8	Aged Wyodak Pyrolized at 300C	563.00	621.00	382.00	92.00	0.00	9.84	3.84	0.00
15	Aged Beulah at 350C	1580.00	1300.00	851.00	133.00	1060.00	22.20	23.50	0.00

Enthalpies of reaction were found to be dependent on reaction time, temperature and oxygen concentration over the temperature range $10 – 60^oC$. Reactions were exothermic, with ΔH ranging from 1580 kcal/gmoleO_2 for the reaction of aged Beulah

Pyrolized at 350 ^{o}C (#15) with 21% O_2 at 10°C to 0.42kcal/ gmoleO$_2$ for the reaction

of aged Beulah Pyrolized at 250C (#29) with 5% O_2 at 60°C. These enthalpies of

interaction are significantly higher than the activation energy requirements (16.7 –

23.74 6 kcal/mole and 8.67 – 12.89 6 kcal/mole) computed in the current studies.

6   Conclusions

1) The low rank coals Wyodak (sub-bituminuos) and Beulah (lignite) employed in this study are susceptible to low temperature oxidation by oxygen.

2) Low temperature (10 to 60°C) oxidation formed surface oxygen complexes with trace evolution of hydrocarbons and acetone. The reaction led to increase in coal mass.

3) The surface oxygen complexes are precursors of spontaneous combustion and their activation energy of formation ranged from 8.67 to 23.74 kcal/mole.

4) The formation of these precursors was exothermic with values of ΔH, the reaction enthalpy ranging from 0.42 to 1580 kcal/gm/molO$_2$

5) Evolution of trace amounts of combustible gases coupled with heat during the formation of these precursors may facilitate spontaneous combustion of coals.

6) Aging of coal followed by pyrolysis made coal more reactive thereby facilitating the formation of these precursors. Thus heat treatment of coal with prior exposure to air increased coal reactivity and the value of ΔH.

7) The reaction of aged and pyrolyzed Beulah with oxygen was most exothermic, with a reaction enthalpy of 1580 kcal/gm/molO$_2$

8) Reaction enthalpies were temperature dependent and highest at 10°C compared to 40°C and 60°C.

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