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Experimental and Theoretical Studies of Kinetics and Quality Parameters to Determine Spontaneous Combustion Propensity of U.S. Coals

Xinyang Wang
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Experimental and Theoretical Studies of Kinetics and Quality Parameters to Determine Spontaneous Combustion Propensity of U.S. Coals

Xinyang Wang

Dissertation submitted to the
College of Engineering and Mineral Resources
at West Virginia University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy in
Mining Engineering

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Morgantown, West Virginia
2014

Keywords: spontaneous combustion of coal, adiabatic oxidation,
self-heating rate, self-heating temperature, activation energy

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ABSTRACT

Experimental and Theoretical Studies of Kinetics and Quality Parameters to Determine Spontaneous Combustion Propensity of U.S. Coals

Xinyang Wang

Spontaneous combustion is one of the most serious problems to mine safety and production in the global coal industry. It is considered to be the trigger for fires and explosions in underground coal mines especially for gassy mines. Such thermal events are not easily detectable since they normally occur in inaccessible gob and sealed area. It is also difficult to find the most likely hot point accurately. Admittedly, determination of the propensity for spontaneous combustion before mining activity should be a necessary step in the design of a mine and ventilation plan. However, due to the complexity of the chemical and physical properties of coal, spontaneous combustion has not been fully understood.

Many methods and techniques have been developed for studying self-heating of coal. Each of the methods has its unique characteristics and index for assessing the propensity of self-ignition. However, all the reasonable candidate factors causing spontaneous combustion could not be examined thoroughly by any single method. Accountable relationships among the propensity indices of different methods should be established. The certainty for assessing the propensity of spontaneous combustion will be greatly improved by using the combination of various methods. On the other hand, spontaneous combustion is affected by many factors. According to a proximate analysis of coal, it is believed that sulfur and volatile matter in coal are the main intrinsic factors that cause the self-heating of coal. Their oxidation at lower temperatures than that of fixed carbon to initiate coal's self-heating should be quantified.

In order for better understanding spontaneous combustion behavior, the following research has been done in this dissertation:

- Establishment of a coal spontaneous combustion testing facility that features adiabatic self-heating, thermogravimetric analyzer (TGA) and USBM self-heating temperature methods in the mine ventilation laboratory at West Virginia University.
- Correlation of U.S. coal rank and propensity for spontaneous combustion has been studied by classifying coal rank quantitatively. This quantified rank system provides a schematic view that reflects the relationship between rank and self-heating temperature of coal. As such, it can be used to serve as a quick estimate of self-heating potential of U.S. coals and as a cost effective way for initial risk assessment for any new mine development.
- Based on the law of energy conservation, a mathematical model has been developed to quantify the self-heating rate of coal and assist the adiabatic self-

heating test when the testing period becomes impractically long. Then improvements have been made to the model by enhancing the model's ability to consider the effects of sulfur, volatile matter and moisture contents in the coal – three important factors affecting a coal's self-heating process. Heat release rates for pyrite oxidation and moisture condensation are built into the model.

If you cannot measure it, you cannot improve it.

When you can measure what you are speaking about, and express it in numbers, you know something about it.

— *Lord Kelvin*

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LIST OF SYMBOLS

A	surface area of heat convection	m^2
A'	pre-exponential factor	s^{-1}
Bi_M	Mass transfer Biot number	
b	stoichiometric number	
C_A	gas concentration	mol/m^3
C_0	concentration of liquid moisture	mol/m^3
C_v	concentration of water vapor	mol/m^3
c	BET constant	
$C_c(T)$	specific heat capacity of coal	$kJ/kg \cdot K$
$C_f(T)$	specific heat of liquid water	$kJ/kg \cdot K$
$C_{fg}(T)$	specific heat for liquid water to evaporate	$kJ/kg \cdot K$
$C_g(T)$	specific heat capacity of dry air	$kJ/kg \cdot K$
$C_g(T, \omega)$	specific heat capacity of moisture air	$kJ/kg \cdot K$
$C_o(T_o, 0)$	specific heat of inflow dry oxygen	$kJ/kg \cdot K$
D_e	diffusion coefficient	m^2/s
E	activation energy	kJ/mol
F_c	fixed carbon of coal	%
f	heat convection coefficient	$W/m^2 \cdot K$
H_g	Heat of coal generated from reaction with oxygen	kJ

H_c	Heat used for heating the coal itself	kJ
H_l	Heat loss	kJ
H_p	heat generation from pyrite oxidation	kJ/mol
H_{vap}	Heat of moisture condensation	kJ/mol
$h(T)$	heat generation rate	kJ/kg·s
k	chemical reaction rate	s ⁻¹
k_g	mass transfer coefficient	m/s
k_p	reaction rate constant of pyrite	m/s
M_p	molar mass of pyrite	g/mol
$m_c(T)$	mass of coal sample	kg
$m_g(T)$	mass of the gases	kg
$\dot{m}_{O_2}$	mass flow rates of the oxygen	kg/s
$\dot{m}_e(t)$	mass flow rates of exhaust gases	kg/s
n_p	moles of pyrite	mol
p_v	saturation vapor pressure	Pa
Q	heating value of coal	kJ/kg
Q_1	oxygen inflow rate	m ³ /s
$Q_2(t)$	exhaust gases flow rate	m ³ /s
R	gas constant	J/mol·K
R_H	relative humidity	%

r	radius	m
$T_o(t)$	oven temperature	K
$T(t)$	temperature inside the test container	K
t	time	s
x_p	fractional conversion of pyrite	%
V	air volume inside the container	m ³
V_m	volatile matter of coal	%
$w_c(T)$	moisture content in the coal	%
α	fractional conversion	%
β	temperature increment rate	K/min
$\rho(T, \omega)$	specific weight of air	kg/m ³
$\rho(T_o, 0)$	specific weight of oxygen	kg/m ³
ρ_p	density of pyrite	kg/m ³
$\omega(t)$	relative humidity of the air	%
ϕ	coal quality in weight percent	%
θ	ratio of pressure	%

CHAPTER 1 INTRODUCTION

1.1 Definition of Spontaneous Combustion

Coal, as a fuel, has the potential to start burning itself without being artificially ignited when certain conditions are present. Such spontaneous combustion of a coal generally starts as a slow oxidation process that occurs without an external heat source. In a suitable environment the heat generated is accumulated inside the coal leading to a rise in temperature. It usually happens with sufficient oxygen supply but insufficient means to dissipate the heat generated. As the oxidation process of the coal continues, more and more heat released is stored by the coal making the temperature increase exponentially. This can eventually result in a thermal runaway and burning the coal.

1.2 The Impacts and Hazards of Coal Self-Heating Worldwide

Spontaneous combustion of coal has posed a serious safety threat in the coal industry and other related industries. It was reported that 65 coal mine fires in the U.S. were attributed to spontaneous combustion for the period from 1952 to 1969 (Table 1.1) and led to 3 injuries and 3 fatalities (Kuchta, 1980). Analysis of U.S. underground coal fires indicates that 21 mine fires were caused by spontaneous combustion during the period from 1978 to 1992 (Pomroy and Carigiet, 1995). It was responsible for 17% of 89 reportable mine fires which lasted 30 minutes or longer after being discovered or causing injury occurring in U.S. underground coal mines during the period 1990 to 1999 (DeRose, 2004).

According to the analysis of U.S. coal mine fires from United States Bureau of Mines (USBM) and National Institute for Occupational Safety and Health (NIOSH), Table 1.1 shows 97 underground coal fires were caused by coal self-heating from 1952 to 1999.

Spontaneous combustion creates not only safety problems to surface and underground coal miners, but also causes problems in storage and transportation worldwide. Statistics show that, in France and Great Britain, about seven to eight cases of spontaneous combustion in coal mines each year (Kuchta, 1980). In South African collieries spontaneous combustion of coal is the major cause of underground fires, which is responsible for more than one third of the 254 fires reported during the period from 1970

to 1990 (Gouws and Knoetze, 1995). Additionally, spontaneous combustion also occurs in surface mines in the Witbank and Sasolburg coalfields in South Africa burning the entire length of the main pit, about 4.5 km. This fire in turn led to poor fragmentation and difficult digging conditions for the draglines and shovels (Phillips et al., 2011). A total of 125 incidents resulted from coal self-heating occurred in the New South Wales state of Australia during the period from 1960 to 1991 (Cliff et al., 1996). Coal outcrops fires have spread over a large area of 720 km² resulting in 4.2 billion tons of coal burned in seven provinces of Northern China. Half of all the state-owned coal mines have the potential of spontaneous combustion leading to 5 billion yuan (about \$782 million) financial losses every year (Xu, 2001). In a recent series of four Coal Age articles (Gambrel, 2010), an explosion on an ocean-going coal ship as a result of coal's spontaneous combustion has caused a serious safety concern for the shipping industry.

Table 1.1 Number of fires for underground coal mines by ignition source and time period, 1952-1969¹, 1978-1992², 1992-1999³

Ignition source	Time period								Total
	1952-69	1978-82	1983-87	1988-92	1992-93	1994-95	1996-97	1998-99	
Welding and flame cutting	-	10	10	6	2	3	2	2	35
Electrical	602	27	20	10	7	9	1	6	682
Spontaneous combustion	65	8	9	4	2	4	3	2	97
Friction	91	8	13	11	1	1	-	-	125
Other	-	3	1	-	-	-	-	1	5
Total	758	56	53	31	12	17	6	11	944

¹ Derived from Spontaneous Combustion Susceptibility of U.S. Coals, USBM Report, 1980

² Derived from Analysis of Underground Coal Mine Fire Incidents in the United States from 1978 through 1992, USBM, 1995

³ Derived from Analysis of Mine Fires for all U.S. Underground and Surface Coal Mining Categories: 1990-1999, NIOSH, 2004

Fires caused by the spontaneous combustion can cause explosions. In June 1991, a coal bunker at coal-fired plant experienced an explosion which is believed to have been triggered by spontaneous combustion. The fire ignited coal dust that eventually resulted in a massive explosion (Hossfeld, R.J. and R. Hatt, 2005).

Spontaneous combustion causes enormous economic losses and environmental problems. It can result in a direct loss of valuable resources through the undesired burn-

ing of coal reserves. In addition, it interrupts the mining operation which in turn results in indirect loss of coal resources when the underground working areas must be shut down. The unmined coal seams will be blocked and the coal reserves not involved in the fire cannot be extracted. Equipment and personnel will stand idle. It was estimated that 353 million tons of unexploited coals were reserved in Wuda coal basin, Inner Mongolia, China but 100 million tons of the coal reserve have been blocked by coal fires (Stracher et al., 2005). Coal fires release various harmful pollutants which are toxic for the human body. Carbon monoxide, nitrogen oxides, sulfur oxides and volatile organic compounds are those toxic pollutants produced by burning coal. Carbon dioxide also contributes to the greenhouse effect.

1.3 Statement of Problems

However, the mechanisms of spontaneous combustion are not fully understood due to the complex chemical structure and physical condition of the coal. Under the interaction between the chemical and physical properties, the same rank coals or even the same coals existing in different conditions will have different potentials of spontaneous combustion. For instance, the low ranking coals are relatively young at an immature metamorphic stage in the long process of formation. This type of coal has high volatile matter content, plentiful porous structures and large internal surface and contains a great amount of moisture. If drying and rewetting occur during handling, heat of wetting will be generated through the effect of water vapor condensation when the coal adsorbs the humidity from the surrounding environment. Although a small amount of heat is generated in this process, it provides the initial heat for coal self-heating. Once the heat accumulates gradually without fully dissipating, coal self-heating will occur. With the indispensable initial heat and sufficient oxygen, coal will be oxidized by oxygen on the surface of the porous structure and more heat will release. Since these factors influencing the potential of self-heating are controlled by physical conditions, chemical properties and ambient situation, both experimental and theoretical methods are needed to analyze and quantify the oxidation process.

In addition, self-heating incidents in underground coal mines often occur in gob or sealed areas and may not be easily detectable. In storage and shipment conditions, spontaneous combustion normally starts under the surface of the coal storage pile and

may not be detected initially. Therefore, a better understanding about the propensity of spontaneous combustion of coal could greatly benefit the scheduling of these coal handling operations, design of the ventilation system as well as mining operations in coal mines.

Up until now, the propensity of spontaneous combustion of coals can be evaluated using a wide variety of laboratory testing methods with different techniques. R_{70} adiabatic test is a widely accepted standard method in Australia. Critical self-heating temperature (CSHT) method is first developed from USBM. Thermal gravimetric analyzer (TGA) test is a relatively new quantitative method. It can measure temperature and weight changes in a short testing period. Each of the methods has its unique characteristics and index for classifying the propensity of self-ignition of coals. Accountable relationships among the propensity indices of different methods should be established. The certainty for assessing the propensity of spontaneous combustion will be greatly improved by using the combination of the three widely used methods. On the other hand, improvement of a theoretical basis should be another very important advancement to unveil the mechanism of spontaneous combustion. In this regard, sound scientific experimental techniques and setups and a mathematical model that takes into account the relevant factors should be developed to assist managing the coal spontaneous combustion prevention tasks.

To sum up, methods for accurate measurement of spontaneous combustion behavior needs to be established. Additionally, a mathematical model developed to both quantify the factors that influence the potential of coal self-heating and simulate the temperature changes over time in an adiabatic condition is needed. This experimental and theoretical combined approach can be used to improve the mine safety management and provide helpful guidance for the ventilation system design and mining operation planning.

1.4 Research Plans and Study Objectives

This research work will contribute to improve the ability to understand and analyze the mechanism of spontaneous combustion to improve mine safety. The major objectives of this research are:

1. Improve the certainty of assessment for propensity of spontaneous combustion by drawing strengths from three widely used methods. Samples from U.S. coal mines will be collected and tested using the newly established R_{70} and TGA testing setups in our ventilation laboratory. Through a relatively short time, the TGA equipment can measure the temperature and weight of the sample with high precision, which can then be used to determine the important kinetic parameters, activation energy and exponential factor of the coal for the mathematical model. Under a specific experimental design, the TGA technique can perform the proximate analysis for deriving the coal quality parameters (e.g., moisture, volatile matter, fixed carbon and ash content). These parameters can be used in an empirical equation derived from USBM method for assessing the potential of coal self-ignition. Then the same samples are tested in a temperature controllable oven with R_{70} method to evaluate the self-heating rate in an adiabatic condition.
2. Develop a mathematical model based on energy conservation law to simulate the coal temperature changes over time in an adiabatic condition. This model can serve as a tool to assist the test plan design and to generate a complete self-heating curve when an experiment becomes impractically long.
3. Quantify: (a) the effect of moisture condensation under different humidified environment with a mobile core model, (b) the effect of pyrite oxidation with a shrinking core model, and (c) the effect of volatile matter oxidation with a distributed activation energy model. The developed mathematical model is the first theoretical description that correlates coal and the effects of pyrite and moisture to the propensity of spontaneous combustion. It is also the first mathematical model using coal quality results (moisture, volatile matter, fixed carbon and pyrite content) as input parameters which can be easily obtained through proximate analysis.
4. Calibrate the mathematical model with experimental results.

1.5 Structure of the Dissertation

In this research effort, spontaneous combustion of U.S. coals has been studied experimentally and theoretically. The dissertation is organized in 7 chapters. In Chapter 1, hazards, accidents and impacts of spontaneous combustion of coal as current global scenarios is introduced. The existing problems and research scope has been presented. The understanding of the spontaneous combustion phenomenon is reviewed in Chapter 2 including the causal factors for coal self-heating in terms of intrinsic and extrinsic properties of coal, experimental techniques for testing tendency of spontaneous combustion and mathematical model developed for predicting this phenomenon. Then, Chapter 3 is mainly focused on the proposed adiabatic method, including experimental procedure, apparatus and materials used, to deal with this issue. The coal samples are collected from U.S. coal mines from major coal producing states. As reference and control groups, some coal samples are also collected and shipped from a few coal mines in China. Three methods, adiabatic R_{70} method, TGA method and USBM self-heating method have been proposed for evaluating the propensity of spontaneous combustion. The adiabatic method to investigate coal self-ignition characteristics is based on the thermodynamic properties of coal.

Testing procedures, instruments and testing results of coal samples with TGA and USBM methods are presented and discussed in specific details in Chapters 4, and 5. TGA method explains coal spontaneous combustion in the aspects of kinetics. USBM self-heating method mainly considers the role of coal quality parameters in the potential of coal self-heating. Thermal gravimetric analyzer (TGA) and temperature controllable oven are used as main apparatus for the experiments. For application of USBM self-heating method, coal proximate analysis results including moisture content, volatile matter and fixed carbon should be provided in advance. TGA, on the other hand, could provide an alternative way with rapid and reliable testing procedure to determine coal quality parameters which could be only determined traditionally by ASTM testing procedure. In Chapter 5, a quantified coal ranking system is proposed. It enables to classify the traditional ranks of coal quantitatively. Based on the SHT testing data, the USBM method is improved through multiple linear regressions for each rank of coal. Schematic view of relationship between quantified ranks and SHT was developed in this chapter.

Each of the mentioned methods has its own pros and cons. R_{70} testing results are most direct and easy for testers, researchers and engineers to understand, but this method is time consuming, tedious and the experimental procedure will become impractically long when the coal sample for testing has a low potential. TGA testing period is relatively short and this method has a sound theoretical background which can be used to explain the mechanism of spontaneous combustion but this concept is new and needs further verification. USBM self-heating method is the first method that points out the causative factors affecting self-heating of coal but it is highly empirical. In this consideration, a mathematical model is developed in Chapter 6 with the following purposes: (1) this model is developed based on adiabatic method and the modeling outcome is shown in form of the relationship between time and temperature, (2) combining the three experimental methods into a theoretical model, (3) considering the contribution of influential factors in coal self-ignition, and (4) providing an assistant for the testing results for determining propensity of spontaneous combustion.

Finally, the dissertation is ended with Chapter 7, presenting the main conclusions, findings of the whole research, and some recommendations and research ideas for the further work.

The main structure of the dissertation can be seen in Figure 1.1.

Figure 1.1 Flowchart for the main structure of the dissertation

CHAPTER 2 LITERATURE REVIEW

2.1 Coal Properties Affecting Spontaneous Combustion

Coal was formed from decomposed plant material which had accumulated in waterlogged places (Speight, 1983). Through burial and metamorphism under elevated temperature and pressure for millions of years, it was formed as layers within the surface rocks of the earth. Coal contains the elements (e.g. C, H, O and N) and sun's energy that the plants collected into their own constituent compounds when they grew many millions of years ago as shown in Figure 2.1 (Edmunds, 2002). The plant debris consisted of several thousand species. The relative amounts of similar types of plants vary considerably in different ranks of coals. On this basis, coal differs markedly in composition from one location to another. As a result, coal has many properties that affect its ability to combust and to spontaneously ignite.

Figure 2.1 Source of the chemical elements and energy stored in coal (Edmunds, 2002)

Davis and Reynolds (1928) proposed the classifications of factors affecting spontaneous combustion. They classified the factors into two groups, chemical and physical properties.

The chemical properties are:

- presence of pyrites
- rank of coal
- weathering
- moisture
- organic sulfur
- chemical deterrents

The physical properties are:

- particle size
- oxygen supply
- temperature
- ventilation

Later Guney (1968) classified the factors into intrinsic and extrinsic categories as shown in Table 2.1.

Table 2.1 Factors affecting spontaneous combustion of coal (Guney, 1968)

Intrinsic factors (nature of coal)	Extrinsic factors (atmospheric, geologic and mining)
Pyrites	Temperature
Moisture	Barometric pressure
Particle size and surface area	Oxygen concentration
Rank and petrographic constituents	Bacteria
Miner matter	Ventilation system

2.1.1 Intrinsic Properties

Kaymakci and Didari (2002) investigated the intrinsic properties that affect the potential of coal self-heating. In their survey, pyrite, moisture content, particle size and ash content are analyzed as the main factors. Their respective influences to self-heating are:

- Pyrite content may accelerate spontaneous combustion.
- Changes in moisture content, i.e. the drying or wetting of coal, have apparent influence on the propensity for coal to self-heat.
- As the particle size decreases and the exposed surface area increases, the tendency of coal towards spontaneous combustion increases.

- It is widely recognized that lower rank coals are more susceptible to spontaneous combustion than higher rank coals. Ash content generally decreases the propensity of coal to spontaneously heat. Certain constituents of the ash, such as lime, soda and iron compounds, may have an accelerating effect, while others, such as alumina and silica, produce a retarding effect. However, chemical structure of coal as another important intrinsic property was never mentioned by the authors in the literatures above.

2.1.1.1 Chemical Structure

The widely accepted reason for self-ignition is the chemical adsorption between activated functional groups of coal macro-molecule and oxygen molecules resulting in exothermic chemical reaction (Xu, 2001). Investigation of the original constituents' chemical structures of the coal will provide a better comprehension of this phenomenon. Precursors of coal are the organic portions of plants including lignin, carbohydrates and proteins as well as other polymers. These polymers are considered contributors to the organic matter of coal, but the relative amount of each of these elements varies greatly with the particular species of a plant. It is this reason that determines the complexity of the final chemical structure of a coal molecule (Work Package, 2000).

- **Lignin**

Lignin has been considered one of the most important substances involved in the transformation of plant constituents into coal. The molecular structure of lignin is regarded as a polymer of coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol as shown in Figure 2.2. Coniferyl alcohol is the main constituent of the lignin of conifers. Sinapyl alcohol is contained in the lignin of deciduous trees. Lignin of grasses contains the p-coumaryl alcohol. All of these alcohols have the same structural elements with the phenyl propane skeleton. One of the first substantial steps of the coalification of woody tissue is the transformation of lignin in wood into xylite in lignite (Bowes, 1984).

- **Carbohydrates**

The simple sugars, or monosaccharides (i.e. glucose and xylose), are the building blocks of the more complex carbohydrates (Speight, 1983). Carbohydrates have the general formula $C_n (H_2O)_m$.

Figure 2.2 Monomeric units in lignin: (1) coniferyl alcohol; (2) sinapyl alcohol; (3) p-coumaryl alcohol (Speight, 1983)

Although the monosaccharides do occur in nature, it is more common to find them occurring as high molecular weight polysaccharides. It is the polysaccharides that most probably contribute to the source material, especially the two well-known polysaccharides cellulose and starch. The fibrous tissue in the cell wall of plants and trees contains cellulose, and starch also occurs throughout the plant kingdom in various forms but usually as a food reserve.

The structural chemistry of many polysaccharides, especially cellulose and starch, is fairly well defined, for example, the simplified structures for cellulose and starch as shown in Figure 2.3.

Figure 2.3 Simplified structures for cellulose (I) and starch (II)

Generally speaking, cellulose and starch have the general formula $(C_6H_{10}O_5)_n$, where n may represent several hundreds or even several thousand units. These two high molecular weight polysaccharides may have been incorporated into the plant debris and thus were eventually incorporated in an altered form into the coal structure.

- Proteins

Proteins are nitrogen-containing organic substances which occur in the protoplasm of all plant and animal cells. The composition of proteins varies with the source, but a general range for protein composition is usually of the order

Carbon (C)	47-50%	by weight
Hydrogen (H)	6-7%	by weight
Nitrogen (N)	15-18%	by weight
Oxygen (O)	23-26%	by weight
Sulfur (S)	<1%	by weight

The characteristic structural feature of proteins is a chain of amino acids joined together by amide linkages as shown in Figure 2.4.

Figure 2.4 Simplified representation of part of a protein chain

Proteins occur throughout nature in a wide variety of sizes and shapes. Many proteins contain metals such as iron (Fe), zinc (Zn) and copper (Cu) which, in turn, are involved in the physiological functions of the molecules to which they are bound.

Coal as a macro-molecule has many different components derived from its precursors. Each of the components has their own reactivity. Figure 2.5 depicts a typical model structure. It shows that coal contains a wide range of functional groups including aldehyde, alcohol, ketone, ether, ester and carboxylic acid. These functional groups are much more reactive than the pure hydrocarbon groups (Cliff, 2009). The numbers and activity of these functional groups play an important role in low temperature oxidation of coal (Zhang et al., 2011).

Figure 2.5 Coal Model (Wells and Smoot, 1991)

2.1.1.2 Coal Quality Parameters

General coal quality parameters are moisture, volatile matter, fixed carbon, ash content, sulfur content, calorific value, size and Grinding Hardgrove Index, as well as

other parameters such as elemental analysis in the ash content (SiO_2 , Al_2O_3 , P_2O_5 , Fe_2O_3 , etc.), analysis of the composition of sulfur (pyritic sulfur, sulfate sulfur, organic sulfur), and the melting point of ash (ash fusion temperature) (About Everything Website, 2011). The composition of a coal is usually reported in terms of its proximate analysis and its ultimate analysis. The proximate analysis consists of four items: fixed carbon, volatile matter, moisture and ash, all on a percentage of weight basis. The ultimate analysis provides an element-by-element composition of the coal's organic fraction, namely: carbon, hydrogen, oxygen and sulfur, all on a percentage of weight basis.

USBM researchers Litton and Page (1994) proposed an empirical equation to link some of the quality parameters, moisture, volatile matter and fixed carbon determined from proximate analysis to the critical self-heating temperature (CSHT) for assessing the potential of self-heating of coal. Studies have also been done by many other researchers on quality parameters. They used different methods and techniques to investigate the influence of each parameter such as, moisture, volatile matter, ash content and sulfur on spontaneous combustion independently (Guney 1971; Bhattacharyya 1972; Kaymakci and Didari 2002; Sweeny et al. 1988; Beamish and Blazak 2005).

- Moisture

The effect of moisture on the self-ignition of coal is two-step process (Nordon and Bainbridge, 1983). The first heating step occurs when water vapor condenses into liquid. The heat it gained is called heat of vaporization or the latent heat of condensation from vapor to liquid, H_v . The second heating step occurs when the heat is generated from the physical adsorption between coal and water and is called heat of wetting, H_w . It evolved when a solid is wetted by a liquid.

The total or integral heat of adsorption is

$$H_t = H_v + H_w \quad (2-1)$$

When the coal is pre-dried, a promotion of self-ignition process by the wetting of coal can be expressed by

Water adsorption is not essential stage but provides initial heat and eventually leads to self-heating, especially for low rank coals (Berkowier and Schein, 1951). Low rank coals have much higher heat of wetting than the higher rank coals as shown in Table 2.2. The heat of wetting is proportional to the internal surface of coal such that one calorie of heat is equivalent to 10 m², and the low rank coals have large internal surfaces. For example, a sub-bituminous coal having 77.5% carbon on dry and mineral matter-free basis (dmmf) or 45% VM can generate over 25 cal/g of wetting heat. For lignite this heat may raise the temperature of coal by about 80 °C (Das and Hucka, 1986). Water plays an important role in the coal oxidation process. However, so far there has been no conclusive information on whether it participates in the chemical reactions or just acts as a catalyst during coal oxidation.

Table 2.2 Heat of wetting for different ranks of coal (Das and Hucka, 1986)

Coal rank	Volatile matter (dmmf) %	Fixed carbon (dmmf) %	Heat of wetting	
			cal/g	kcal/mole
Sub-bituminous	45	77.5	25	52.5
High volatile bituminous	35	82.5	10-15	9-13.5
Medium volatile bituminous	30	85.0	3-6	2.7-5.4
Low volatile bituminous	20	89.0	2	1.34
Semi anthracite	12	91.5	3-4	-
Anthracite	5	93.3	6-9	-

- **Volatile Matter**

The volatile matter consists mainly of combustible gases such as hydrogen, carbon monoxide, methane plus other hydrocarbons. The composition of the volatile matter evolved from coal is substantially different for the different ranks of coal. The proportion of incombustible gases increases as the coal rank decreases (James, 1994).

The higher the amount of volatile material in coal, the more likely the coal will suffer from spontaneous combustion (McSherry, 1998). At least to a certain extent the process of coal oxidation might be attributed to an increase in volatile matter content (Working Group, 2006).

- **Ash**

Ash is the residue derived from the mineral matter during complete incineration

of the coal. It is quantitatively and qualitatively different from the mineral matter originally present in the coal. The ash content has been considered as having retardant effects on coal self-ignition. R_{70} index decreases significantly with increasing ash content (Beamish and Blazak, 2005). This effect is due to the mineral matter in the coal acting as a heat sink. The authors proposed an empirical equation (Eq. 2-2) to fit the testing data as shown in Figure 2.6.

$$R_{70} = 0.0029 \times Ash^2 - 0.4889 \times Ash + 20.644 \quad (2-2)$$

Figure 2.6 Relationship between ash content and R_{70} self-heating rate of coal samples

2.1.1.3 Presence of Pyrites

Pyrite (FeS_2) and the related mineral marcasite exist frequently in coal (Speight, 1983). Pyrite oxidation takes place when the mineral is exposed to air and water. The process is complex because it involves chemical, biological (Lorenz and Stephan, 1967), and electrochemical reactions (Scott, 1965), and varies with environmental conditions. Factors that determine the rate of oxidation are pH value, specific surface and morphology of pyrite, presence or absence of bacteria and/or clay minerals, as well as hydrological factors.

The real cause of spontaneous combustion cannot be attributed to presence of pyrite, since it does not account for the numerous cases of the spontaneous combustion of coal in which sulfur is not present (Barr, 1900). But it is an important factor in the spontaneous ignition of coal and cannot be discarded in an off-hand way (Parr and Kressmann, 1910). Under suitable conditions the pyrites in coal will oxidize rapidly and may be a dominating factor in certain cases for the self-heating of coal (Li and Parr, 1926).

The low temperature oxidation of pyrite is exothermic and the heat liberated is found as follows (Parr and Kressmann, 1910):

Among the possible reaction paths, the ones with H₂O involved generally produces much more heat than those without H₂O. Thus, storing coal where it would be repeatedly wetted by rain may favor pyrite oxidation. In underground coal mines, the relative humidity of the air is high, for the ventilating current picks up moisture from the walls and the coal dust. When the outside air is colder than the mine air, as in winter, the entering air is rapidly warmed to the mine temperature. Consequently its relative humidity is low. Thus, during cold weather the effect of the ventilating current is to dry the mine. However, in hot weather, relative humidity of mine air will become higher. That will be helpful for pyrite oxidation and generation of heat of wetting for the coals remained in gob area, eventually leading to self-heating of coal.

Beamish, et al., (2012) conducted a test to investigate the influence of reactive pyrite on self-heating of a high volatile bituminous coal containing sulfur content from

0.62% to 17.95% with a moist coal adiabatic oven. Dry air or oxygen does not promote the oxidation of the pyrites (Li and Parr, 1926). They concluded that as the pyritic sulfur content increased the time needed for thermal runaway to occur decreased.

A well-known shrinking core model was used to describe pyrite oxidation and pollutant leaching processes in waste dump sites (Levenspiel 1999; Cathles and Apps 1975; Singh and Ardejani 2004). This model combined surface reaction with accumulation of product layer on the surface. It is assumed that the reaction rate is first-order with respect to the principal gas reactant and the surface area of remaining solids, and that the reaction rate is also controlled by the steady-state diffusion of the reactant gas through the accumulated layer of product on the unreacted core (Evangelou, 1995).

The time required for a specified quantity (X) of pyrite to oxidize can be expressed as a function of the reaction rate constant of pyrite (K_p), the effective diffusion coefficient for O_2 through any ash layer on surface of pyrite particle (D_e), and the concentration (C_{Ag}) of O_2 as follows:

$$t = \frac{1-3(1-X)^{\frac{2}{3}}+2(1-X)}{D_e \cdot C_{Ag}} + \frac{1-(1-X)^{\frac{1}{3}}}{K_p \cdot C_{Ag}} \quad (2-9)$$

The first term accounts for the effect of increased thickness of surface coating on the reaction rate, while the second term accounts for the effect of the decreased amount of pyrite on the reaction rate. During oxidation of pyrite by O_2 alone, the first term is omitted and it turns to

$$t = \frac{1-(1-X)^{\frac{1}{3}}}{K_p \cdot C} \quad (2-10)$$

Thus, Eq. 2-10 describes first-order kinetics with respect to FeS_2 . Therefore, as expected, the plot of t versus $[1 - (1 - X)^{\frac{1}{3}}]$ should display a straight line.

2.1.1.4 Porosity

Coal is a material with a complex pore structure and very high surface area. The nature of American coals' porosity in a number of 40×70 (i.e. – 40 + 70) mesh size, varying in rank from anthracite to lignite, has been studied (Gan et al., 1972). In the lower rank coals, porosity is primarily due to the presence of macropores, whereas in the coals of higher rank microporosity predominates.

Falcon (1985) mentions that porosity is a characteristic of extreme importance to

spontaneous combustion. Firstly, it provides an indication of the total surface area, which may be subjected to oxidation. Secondly, it provides an indication of the total volume of the voids or spaces, a factor directly proportional to the amount of moisture and gas which may be stored in such a coal.

Mercury intrusion method was used to study pore structure in coal (Dai, 2010). The results showed that total pore volume and specific surface area decrease as coal rank increases. In the coal oxidation process, the rate of temperature increase and the rate of heat release decrease when pore volume and specific surface area of the coal decrease.

If all pores were filled with water in nature, the inherent seam moisture would give direct information on the pore volume, as shown in Figure 2.7. Pores in coal usually contain small amounts of gaseous and liquid hydrocarbons and CO_2 , but as a first approximation, the natural moisture content can be assumed to fill most of the pore space of a coal (Thomas and Damberger, 1976).

Figure 2.7 Relation between inherent moisture content and volume-percent porosity in Illinois coals

When the coal is dried, the internal moisture will be removed. The internal surface area which was occupied initially by internal moisture will be available for oxygen. The oxygen absorbed by the coal will impose high potential for self-heating.

2.1.1.5 Coal Rank

It is generally accepted that self-ignition is a rank-related phenomenon. Kim (1977) demonstrated that coal rank has a major influence on coal self-ignition. Low rank coals are more susceptible to self-heating than high rank coals. Beamish (2005) used an adiabatic oven to assess the effect of rank on the R_{70} self-heating rate of coal. He concluded that sub-bituminous coals have the highest R_{70} self-heating rates which are 20 times that of high volatile A bituminous coals on a dry mineral matter free basis.

- Coalification

Coal rank is the degree of transformation or coalification. Coalification is the alteration of vegetation to form peat, followed by the transformation of peat through lignite, sub-bituminous, bituminous, semi-anthracite to anthracite coal as shown in Figure 2.8.

Figure 2.8 Schematic representation of the coalification process

As the process of progressive transformation takes place, the heating value and the fixed carbon content of the coal increase and the amount of volatile matter in the coal decreases. The method of ranking coals used in the United States and Canada was developed by the American Society for Testing and Materials (ASTM). The ASTM ranking system is presented in Table 2.3.

Table 2.3 Simplified classification of coals by rank (ASTM D388, 2005)

Class and group	Fixed carbon (dmmf, %)		Volatile matter (dmmf, %)		Calorific value (moist mmf, Btu per lb)	
	Equal or greater than	less than	Greater than	Equal or less than	Equal or greater than	less than
Anthracite						
1. Meta-anthracite	98	-	-	2	-	-
2. Anthracite	92	98	2	8	-	-
3. Semi-anthracite	86	92	8	14	-	-
Bituminous						
1. Low volatile bituminous coal	78	86	14	22	-	-
2. Medium volatile bituminous coal	69	78	22	31	-	-
3. High volatile A bituminous coal	-	69	31	-	14000	-
4. High volatile B bituminous coal	-	-	-	-	13000	14000
5. High volatile C bituminous coal	-	-	-	-	11500	13000
Sub-bituminous						
1. Sub-bituminous A coal	-	-	-	-	10500	11500
2. Sub-bituminous B coal	-	-	-	-	9500	10500
3. Sub-bituminous C coal	-	-	-	-	8300	9500
Lignite						
1. Lignite A	-	-	-	-	6300	8300
2. Lignite B	-	-	-	-	-	6300

Peat is an organic sediment. Burial, compaction and coalification will transform it into coal, a rock. Peat has a carbon content of less than 60% on a dry ash-free basis as shown in Figure 2.9 (<http://geology.com/rocks/coal.shtml>).

Lignite is the lowest rank of coal as shown in Figure 2.10. It is a peat that has been transformed into a rock that is a brown-black coal. By definition it has a heating value of less than 8300 British Thermal Units (BTU) per pound on a mineral matter free basis. It has a carbon content of between 60% and 70% on a dry ash-free basis.

Sub-bituminous coal is a lignite that has been subjected to an increased level of organic metamorphism. This metamorphism has driven off some of the oxygen and hydrogen in the coal. That loss produces coal with a higher carbon content (71% to 77% on a dry ash-free basis). Sub-bituminous coal has a heating value between 8,300 and

13,000 BTU/pound on a mineral matter free basis. On the basis of heating value it is subdivided into sub-bituminous A, B and C ranks.

Figure 2.9 Sample of peat

Figure 2.10 Samples of lignite

Bituminous is the most abundant rank of coal. It accounts for about 50% of the coal produced in the United States. Bituminous coal is formed when a sub bituminous coal is subjected to increased levels of organic metamorphism. It has a carbon content of between 77% and 87% on a dry ash-free basis and a heating value that is much higher than lignite or sub-bituminous coal. On the basis of volatile content, bituminous coals are subdivided into low-volatile, medium-volatile and high-volatile bituminous.

Anthracite is the highest rank of coal as shown in Figure 2.11. It has a carbon content of over 87% on a dry ash-free basis. Anthracite coal generally has the highest heating value per ton on a mineral matter free basis. It is often subdivided into semi-anthracite, anthracite and meta-anthracite on the basis of carbon content.

Figure 2.11 Sample of anthracite

Baughman (1978) graphically illustrated the relationship of the data from proximate analysis and the calorific value to coal rank in Figure 2.12 and Figure 2.13.

Figure 2.12 Variation of proximate analysis data with coal rank (Baughman, 1978)

Figure 2.13 Variation of calorific value with coal rank

Suggate (1982) proposed the Suggate rank (S_r) for New Zealand coal as shown in Figure 2.14. This coal ranking method is a quantitative classification for coal rank distribution based on coal quality parameters of volatile matter and calorific value on dry mineral-matter and sulfur-free basis or the atomic O/C and H/C ratios of the coal on a mineral matter-free basis. Rank of lignite is equal to 0-3, sub-bituminous is 3-8, bituminous is 8-16, semi-anthracite is 16-20, and anthracite is 20-25.

Figure 2.14 Suggate rank for New Zealand coal

In order to correlate the R_{70} values to Suggate rank, the coal has to be dried first before the adiabatic tests and converted to a mineral matter-free basis. An equation for this conversion has been developed (Humphreys, et al., 1981). Beamish (2005) defined a non-linear relationship for coals between R_{70} self-heating rate and Suggate rank as shown in Figure 2.15. As the figure shows sub-bituminous coals have the highest R_{70} self-heating rate of more than 21°C/h indicating sub-bituminous coals have the highest potential of self-heating. The propensity of high volatile bituminous coals varies greatly from about 14°C/h to 0.5°C/h . Higher rank coals have lower potential of self ignition than

the lower rank coals. From this relationship, an initial risk assessment can be obtained by estimating the R_{70} value of a new coal as long as its Suggate rank is known.

Figure 2.15 Relationship between Suggate Rank (Sr) and R_{70} self-heating rate of New Zealand and Australian coals

However, the R_{70} -Suggate rank correlation curve is on a mineral matter-free, moisture-free basis. This can create a misleading result of self-heating rate of coal in reality, since the in-situ coal is neither mineral matter-free nor dry. These two parameters strongly affect the R_{70} value (Beamish B. and Beamish R., 2012).

- **Geology**

Basin geology is related to coalification and coal rank and thus has an indirect influence on propensity of coal self-heating. A better understanding of geology on coal reserve distribution could provide a general idea about coal properties in different locations. The Pennsylvanian age coals were formed during the Carboniferous period approximately 334 to 384 million years ago. The major coal basins in U.S. include Appalachian basins in the east, Illinois and western interior basins in the central U.S., and sev-

eral western basins such as the San Juan and Powder River basins as shown in Figure 2.16. The six coal zones formed in that great coal age located within the northern Appalachian coal basin are the Brookville-Clarion, Kittanning, Freeport, Pittsburgh, Sewickley, and the Waynesburg (EPA, 2004). These coal units are contained within the Pottsville, Allegheny, and the Monongahela Groups as shown in Figure 2.16.

Figure 2.16 Major coal basins in United States and generalized stratigraphic column of the Northern Appalachian Coal Basin (Kelafant et al., 1988)

- Depth

As you travel from the earth's surface toward the center, temperature increases. This geothermal gradient averages about a 1.5 °F increase per 100 feet of depth. As coal is buried deeper and deeper by accumulating sediments, much of the water and volatile components are extruded (de-volatilization) leaving behind fixed carbon, ash, sulfur often in the form of pyrite and other trace elements. The normal geothermal gra-

dient will produce bituminous coals at burial depths between 8,500 and 20,000 feet and anthracite between 20,000 and 25000 as shown in Figure 2.17 (http://www.geocraft.com/WVFossils/coal_rank.html).

Figure 2.17 Coal burial depth changing with temperature and rank

2.1.2 Extrinsic Properties

Extrinsic factors classified by Guney (1986) are: temperature, moisture, barometric pressure, oxygen concentration, bacteria, coal seam and surrounding strata, method of working, ventilation system and flow rate, timbering, and roadways.

Chakravorty and Kolada (1988) grouped the critical factors contributing to spontaneous combustion into intrinsic, i.e. those that cannot be controlled (coal properties and geological features), and extrinsic, i.e. those that can be controlled (mining practices). Table 2.5 shows these factors.

The extrinsic properties that will mainly influence the experiments on testing propensity of spontaneous combustion in this proposal are environmental humidity, particle

size, and aging effect.

Table 2.4 Critical factors contributing to spontaneous combustion

Coal Properties	Geological Features	Mining Practices
High volatile matter	Thick seams	Leaving roof and floor coal during mining
High moisture	Presence of inferior pyrite bands and carbonaceous shale	Poor maintenance of roadways and old districts
High pyrites	Presence of faults	Inadequate measures to prevent air leakage through air crossings, doors, mine seal
High exinite	Weak and disturbed strata conditions	Caving to surface under shallow overburden
High friability	High strata temperature	Close proximity to multi-seam working
		Poor ventilation management

2.1.2.1 Environmental Humidity

The moisture that contributes to the problem of spontaneous combustion comes from humidity or from other coals. For example, when new coal added over old coal may create more heat at their interface (Hossfeld, and Hatt, 2005). Coal drying is an endothermic process, in which heat is absorbed by the moisture to evaporate, and the temperature of the coal is lowered. The adsorption of moisture on a dry coal surface is an exothermic process generating heat. If the coal partially dried during its mining, storage, or processing, with the potential to reabsorb moisture from environmental humidity, the coal will produce heat. Therefore, the higher the moisture contents of the coal, the greater the potential for this to occur. The most dangerous scenario for spontaneous combustion is when wet and dry coals are combined. The interface between wet and dry coal becomes a heat exchanger (Smith, et al, 1991).

2.1.2.2 Particle Size

The rate of coal oxidation has a linear relationship to the surface area of coal (Sujanti et al., 1999). Therefore, the smaller particle size of the coal, the greater the surface area exposed to oxidation, thus releasing more heat per unit volume of coal. Although particle size of coal shows an effect on the rate of oxidation for some types of coal, the nature of this effect is still not fully understood.

Sondreall and Ellman (1974) indicated that the effect of particle size was represented by the following equations:

$$r = \frac{k}{m} \cdot (1 - e^{-5.5m}) \quad (2-11)$$

$$m = \frac{1.22}{s} \quad (2-12)$$

where, r is oxidation rate in kg/h, k is an oxidation rate constant, m is the mean sieve size in inches, s is specific surface area of coal particles excluding internal pore area in ft²/lb.

2.1.2.3 Aging Effect

The aging of coal refers to the physical and chemical changes when coal is exposed to air and oxidized by oxygen. The changes can affect the behavior and properties of coal, and therefore affect the coal as it is processed and utilized.

Aging can affect the propensity of the coal's spontaneous combustion in the following three ways: (1) slow oxidation at ambient temperature to increase the retardant in the coal, (2) reaction and consumption of the active chemical fractions of the coal making the coal intrinsic properties inert, and (3) evaporation of the coal moisture. Based on the parameters considered in the USBM CSHT method, these three coal quality parameters could retard the coal's self-heating process.

As the coal cores are stored in ambient environment, the self-heating rate value decreases noticeably as the storage time increases. Many tests have been conducted by Beamish to show the aging effect on self-heating potential of coal (Beamish, et al, 2000). Coal samples were collected from Huntly East, BBL and New Vale coal mines in New Zealand. The tests were performed with different time lengths after the samples were taken as shown in Figure 2.18. Huntly East coals have been stored for 2, 7, 14 and 33 days before the R_{70} tests and marked as HE1, HE4, HE8 and HE10, respectively. It was found that as the storage time increased the self-heating rate decreased. The HE1 coal sample with a storage time of only 2 days has the most rapid self-heating rate, 19.53°C/h (Table 2.5) and the earliest thermal runaway. The HE10 coal sample with a 33-day storage time has a self-heating rate of 13.47 °C /h. This is also confirmed by the results for the repeat tests on samples from BBL and New Vale mines as shown in Figure 2.19 and Figure 2.20, respectively. In Figure 2.19, BBL samples have a considerable drop in R_{70} of 6.05 °C/h over a 56 day period between tests. In Figure 2.20, the coal sample from New Vale only has 1.89°C/h self-heating rate after 609 days storage.

Table 2.5 Self-heating rate test results of New Zealand coals due to aging effect

Samples	Days Elapsed Since Sampled	R ₇₀ (°C/h)
<i>Huntly East</i>		
HE1	2	19.53
HE4	7	15.12
HE8	14	14.39
HE10	33	13.47
<i>BBL</i>		
BBL1	21	14.91
BBL2	77	8.86
<i>New Vale</i>		
NV1	600	2.26
NV2	609	1.89

Figure 2.18 Repeat self-heating profiles for Huntly East samples

Figure 2.19 Repeat self-heating profiles for BBL samples

Figure 2.20 Repeat self-heating profiles for New Vale sample

From the testing results above, it can be seen that aging of coal samples has a strong effects on their self-heating rates. This aging effect is even more noticeable as storage time increases from 2 days to 609 days. Consequently, the self-heating rate significantly decreases from 19.53 °C /h to 1.89 °C /h.

2.2 Methods to Determine Spontaneous Combustion

A wide variety of methods have been developed for assessing the propensity of spontaneous combustion (Beamish and Arisoy, 2008; Banerjee et al., 1972; Mohalik et al., 2009). The methods have been used are as follows:

- USBM CSHT method

USBM researchers proposed this method. Two empirical equations were derived from adiabatic testing results to predict the minimum self-heating temperature based on proximate analysis and ultimate analysis. In the test, grounded dry coal samples were placed in an adiabatic vessel and then exposed to a continuous steady flow of moist air of predetermined temperature. The experiment was repeated at various temperatures with fresh samples for each run. The lowest heating temperature demonstrating thermal runaway was termed as the minimum self-heating temperature of the coal

- Adiabatic method

Adiabatic methods, sometimes called adiabatic oxidation methods, are considered to be good at simulating the initial stages of coal oxidation in situ. The heat generated at the beginning of oxidation was made to be stored by the coal itself without losing heat to the surroundings. A reaction container holding a certain amount of coal sample is placed in an adiabatic oven. After the sample is preheat and dried in the nitrogen atmosphere, pure oxygen as the major reaction gas is used to pass through the sample. A thermometer is buried inside the coal sample while another is used to measure the oven temperature. Ideally, the oven temperature should be controlled to be equal to that of the coal sample to avoid heat exchange between the coal sample and its testing surrounding. Through such control, it is ensured that only and all the heat generated by the oxidation of the coal sample is used to sustain the reaction and to raise the temperature of the coal. For example, R₇₀ test is one of the typical adiabatic methods.

- Adiabatic R₇₀ method

The R₇₀ self-heating rate was first introduced by Humphreys (1981). It is used to

measure the coal's propensity to ignite spontaneously. The R_{70} self-heating index is defined as the average temperature increasing rate in an adiabatic oven for the temperature to reach 70°C from a starting temperature of 40°C. The units of R_{70} are °C/h. Once the temperature increases past 70°C, the rate of temperature rises dramatically leading to a thermal runaway.

- Differential thermal analysis (DTA) and thermal gravimetry (TG)

DTA can be used to study the self-heating phenomenon of coals by following the heat generation during the experiment. DTA-TG curves have been used to characterize the propensity for spontaneous combustion and determine the kinetic parameters (Wang, et al., 2008).

- Differential scanning calorimetry (DSC)

DSC is a non-isothermal method, in which the environment temperature is usually increased at a constant rate. In DSC equipment, two pans are used for tests. One contains a coal sample and the other is empty. The two pans are maintained at the same temperature. The difference in the amount of heat required to achieve this is measured as a function of the changing environment temperature. This allows endothermic and exothermic processes to occur within the coal, both of which are related to self-heating processes (Garcia, 1999).

- Isothermal methods

Isothermal can be classified into two methods. One is a static isothermal method and another is dynamic isothermal method. The static isothermal method measures the rate of reaction of coal under conditions in which the oxygen concentration is effectively a constant (Smith and Glasser, 2005). In the dynamic method, oxygen was allowed to flow into the coal with a constant flow rate at a constant temperature. The amount of oxygen adsorbed by the coal was determined by desorption of the oxygen when the coal was flushed with nitrogen (Xu, J.C., 2001).

- Crossing-point temperature (CPT) method

In the CPT method, 30-60 g samples are contained in a reaction vessel which is placed in a programmed oven or temperature bath. Dry air is preheated to the oven's temperature before it flows into the reaction vessel. The temperature of the oven increases at a constant rate that raises the inlet gas temperature. The temperatures of the

oven and the reaction vessel are recorded continuously. The crossing-temperature is defined as the temperature at which the coal is equal to that of the oven (Qi, et al., 2011).

2.3 Mathematical Models

2.3.1 Models for Coal Stockpiles

Prediction of the temperature rise in a coal stockpile has been developed. Smith and Glasser (2005a) developed the heat transfer model using parameters such as specific heat capacity, heat of reaction, reaction rate, and activation energies determined from the experimental data (Smith and Glasser, 2005a). Dick et al (1984) developed a one-dimensional model to describe the spontaneous heating process for dry coal at relatively low temperatures ($<100^{\circ}\text{C}$). The influence of moisture transfer on the maximum temperature rise has been analyzed using the simplified one-dimensional differential equations by Chen (1992). Mathematical models developed for this purpose are based on heat balance and energy conservation equations. However, the chemical kinetic reactions and the heat generation by coal oxidation are significantly simplified. In addition, some physical and chemical properties affecting coal oxidation, such as the moisture content, presence of pyrite, and volatile matter content are not taken into account. Consequently, the prediction results of the temperature rise in a coal stockpile at specific conditions are of great uncertainty and are questionable for conditions such as wet coal, extra environmental humidity, and high volatile matter content.

2.3.2 Kinetics

Several kinetic models have been developed to describe coal oxidation at low temperature. Krishnaswamy et al. (1996) assumed an external diffusion-control regime in coal oxidation at temperatures between 27 and 60 $^{\circ}\text{C}$, and considered two simplified reaction steps in the model development. Wang, et al. (2002) proposed a kinetic model for determining the rate of oxygen consumption and production of carbon oxides during the oxidation of coal at temperatures below 100 $^{\circ}\text{C}$. Kam et al. (1976) proposed a model for coal oxidation at temperature between 175 and 225 $^{\circ}\text{C}$, based on the mass balance between external diffusion of oxygen and oxygen consumption by chemical reaction. Karsner and Perlmutter (1982) developed a model for coal oxidation at temperature be-

tween 200 and 257 °C, on the basis of coal oxidation being controlled by chemical kinetics. Das et al. (2006) developed a mathematical model to predict the yield and composition of volatile matter as a function of temperature.

Kinetic parameters, such as activation energy (E) and exponential factor (A) of oxidation were obtained from heat-release rate measurements and self-heating curves of adiabatic tests using Arrhenius and heat balance equations (Beamish, et al., 2003; Jones et al., 1996; Jones et al., 1998). Reliable values of E and A will enhance the prediction of the propensity of coals to combust spontaneously (Beamish, et al., 2003).

These models and kinetic parameters serve to gain additional insight into the oxidation process of chemical reaction. However, the heat contributed to the self-heating and spontaneous combustion of coal derives not only from chemical reactions, but also from physical processes, such as water condensation.

2.3.3 Ignition Time

The model for predicting the ignition time for coal from low temperature self-heating to ignition has been developed. The model for ignition time proposed by Jones (2000) is shown in Eq. 2-13.

$$t_{ab} = \frac{RT_R^2}{E} \frac{c}{QA} e^{\frac{E}{RT_R}} \quad (2-13)$$

In this equation, c is the specific heat, Q the heating value, R the gas constant and T_R is the initial temperature of the coal. A value of 1,260 J/kg·K was used for c and 25 MJ/kg for Q . The prediction model was derived from an adiabatic condition. Therefore, the values of t_{ab} calculated for the coals will be the lower limit of the actual times the coal needed to ignite. Ignition temperatures of six coals have been calculated using the ignition model at initial temperature of 300K. The shortest time for coal to ignite is 2 days and the longest one is 73 days. However, the activation energy and pre-exponential factor used in the model have to be determined from adiabatic testing results. If the coal has low potential of self-heating, it will be very difficult to obtain a complete self-heating curve to determine these two parameters. As a result it is impossible to calculate the ignition time.

CHAPTER 3 ADIABATIC METHODS FOR EVALUATION OF COAL SPONTANEOUS COMBUSTION

3.1 Introduction

Many factors can affect the spontaneous combustion process of coal as it is mined, stored and transported. These factors include the self-heating potential of the coal, coal rank, geologic and mining conditions, mining practices, ventilation, etc. Among these factors, the self-heating potential is most important. However, spontaneous combustion events in underground coal mines often occur in gob or sealed areas and may not be easily detectable. In storage and shipment conditions, spontaneous combustion normally started under the surface of the coal storage pile and may not be detected initially. Therefore, a better understanding about the propensity of the spontaneous combustion of coal could greatly benefit the planning of these coal mining and handling operations.

Various basic and practical studies for determining the self-heating potential of coal have been developed for more than a hundred years. Up until now, the propensity of spontaneous combustion of coals can be evaluated qualitatively in laboratories by a wide variety of methods with different techniques. Three widely used methods, R_{70} , TGA and USBM will be introduced to assess the propensity for coal's spontaneous combustion. The testing facilities that feature these three methods are established in the mine ventilation lab as shown in Figure 3.1.

The experiments performed with TGA and USBM methods will be presented and discussed in the following chapters. In this chapter, methodology, experimental instruments, testing procedures and testing results of R_{70} adiabatic oxidation method are demonstrated and discussed specifically.

Adiabatic oxidation method is considered to be a good method to simulate the initial stage of the coal oxidation process at a relatively low temperature. It becomes a standard way in Australia to assess the intrinsic properties of self-heating propensity of coal. The adiabatic test of coal is conducted in a reaction vessel which has been designed to minimize heat exchange and ideally act as a perfect insulation (Beamish, et al, 2000). The reaction vessel is placed inside an adiabatic oven with its temperature being controlled automatically to equal to that of the coal in the reaction vessel. Consequently,

there is no heat exchange between the oven environment and the coal sample. This requires the use of a data logging thermometer to monitor the temperatures of the coal and the oven. The inlet gas, oxygen, is preheated before it flows into the reaction vessel. These controls ensure that only and all the heat generated by the oxidation of the coal sample is used to sustain the reaction and to raise the temperature of the coal itself. The self-heating rate is measured by monitoring the temperature development of the coal sample in the reaction vessel. The average hourly temperature increase rate for the coal to self-heat from 40 °C to 70 °C under an adiabatic condition is used to classify the self-heating risk (Humphreys, 1981) as shown in Figure 3.2. Once the temperature increases above 70 °C, the rate of temperature could accelerate leading to a possible thermal runaway.

Figure 3.1 Coal self-heating testing system

3.2 Samples Collection

3.2.1 Samples Collected from U.S. Coal Fields

Coal samples from the Upper Freeport, Pittsburgh and Sewickley coal seams and Pow-

der River Basin were shipped to the ventilation laboratory in the Department of Mining Engineering of West Virginia University on May 19, 2011 and August, 11, 2011, respectively. The first arrived samples were from the Upper Freeport coal seam. The coal samples were obtained from boreholes 2, 9 and 10 drilled in 2008 and 2009 and labeled as FR0802, FR0809 and FR0910 on the packages, respectively. The coal samples in the second delivery were from the Upper Freeport, Pittsburgh, Sewickley coal seams and from the Powder River Basin (PRB). The Upper Freeport samples obtained from borehole 1, 3, 4, and 13/14 were drilled in 2008 and 2009 and labeled as FR0801, FR0803, FR0804 and FR0913/14. The Sewickley coal samples from borehole 12, 13 were drilled in 2010 and labeled as GM1012, GM1013. The coal samples from the Pittsburgh seam and from the Powder River Basin were drilled in, 2010 and July 21, 2011, respectively. The cores have been stored in core boxes before being shipped to our laboratory. The samples from central Indiana (marked as KM3 and KM4) were drilled in late November of 2010 and shipped to our laboratory in mid-December of 2010. The samples from Trapper, New Elk and BBCC mines in Colorado were drilled more than one year before they arrived on September 10, 2012. After the coal samples were received, they are kept in sealed plastic bags and placed in refrigerator to prevent oxidation and aging effect. All the samples are listed in Table 3.1.

Figure 3.2 Typical R_{70} self-heating curve of coal (Humphreys, 1981)

Table 3.1 Samples collected from U.S. coal mines

Samples	States
Powder River Basin coal (PRB)	PRB
SPE	Montana
Trapper	Colorado
New Elk	Colorado
BBCC	Colorado
WR	Utah
KM 3	Indiana
KM 4	Indiana
ME	Ohio
Sewickley coal seam GM 10-12 (GM1012)	Pennsylvania
Sewickley coal seam GM 10-13 (GM1013)	Pennsylvania
Pittsburgh coal seam in Waynesburg (Pitt)	Pennsylvania
Upper Freeport coal seam 08-01 (FR0801)	Pennsylvania
Upper Freeport coal seam 08-02 (FR0802)	Pennsylvania
Upper Freeport coal seam 08-03 (FR0803)	Pennsylvania
Upper Freeport coal seam 08-04 (FR0804)	Pennsylvania
Upper Freeport coal seam 09-10 (FR0910)	Pennsylvania
Upper Freeport coal seam 09-13 (FR0913)	Pennsylvania
Upper Freeport coal seam 09-14 (FR0914)	Pennsylvania
RB	West Virginia
Sewickley coal seam	West Virginia

3.2.2 Samples Collected from Chinese Coal Fields

Coal samples were also collected from Chinese mines located in Inner Mongolia, Shanxi and Hebei provinces. They are the main coal producing provinces in China and have the problems of spontaneous combustion in their mining history. The samples from Inner Mongolia were collected from face No. 4 and development No. 6 in Suancigou mine in Xuejiawan Town. Samples collected at panel No. 3 and face No. 4 were from Nanyangpo mine, owned by China Coal Co. in Shuozhou, Shanxi province. The last sample was from Xuandong mine in Zhangjiakou, Hebei province. All these Chinese samples were shipped internationally from China and received on November 20, 2012. It should be noted that those samples are drilled in 2011 before they arrived. Samples from Chinese coal fields are listed in Table 3.2.

For this research, coal samples collected from U.S. and Chinese coal mines were tested using adiabatic, TGA and USBM methods to investigate their potential of spontaneous combustion.

Table 3.2 Samples collected from Chinese coal mines

Samples	Locations
Face No.4, Suancigou mine	Inner Mongolia
Development No. 6, Suancigou mine	Inner Mongolia
Panel No. 3, Nanyangpo mine	Shanxi
Face No. 4, Nanyangpo mine	Shanxi
Seam No. 3, Xuandong mine	Hebei

3.3 Experimental Instruments

In the R₇₀ method, testing instruments for the experiment includes temperature controllable oven, thermos bottle as the reaction vessel, coil copper tubing, flow meter, data logging thermal anemometer, nitrogen and oxygen cylinders.

3.3.1 Temperature Controllable Oven

Binder heating oven, FD 53, is used in this testing setup. This oven is designed with mechanical convection. Thanks to its fully homogeneous temperature distribution, quick dynamics and powerful fan, this heating oven guarantees uniform inside temperature and can reach the set temperature quickly to maintain temperature equilibrium between the coal sample and the oven.

The oven has an exterior dimension of 25 (W) x 24.4 (H) x 22.6 (D) inch (635 x 620 x 575 mm) as shown in Figure 3.3. Plus door handle and connection is 4.1 inch (105 mm). Wall clearances of rear and side are 3.9 (100 mm) and 6.3 inch (160 mm) . Diameter of exhaust duct is 2.1 inch (52 mm). The width, height and depth of the interior dimension are 15.8x15.8x13.4 inch (400 x 400 x340 mm) and the interior volume is 1.9 ft³.(53 L)

Temperature range is approximate 5 °C (9 °F) above ambient temperature to 300 °C (572 °F). Specific temperature data are list in Table 3.3

In the experiment, the oven temperature is adjusted to the coal's temperature manually with a resolution of 1 °C.

3.3.2 Reaction Vessel

The reaction vessel is a 16-oz (473ml) aluminum vacuum thermo-bottle that is fitted with a rubber plug for sealing. It further prevents heat exchange between the coal sample placed inside the bottle and the interior space of the oven when a minor tem-

perature imbalance exists. Two copper tubes pass through the rubber plug. The longer one used for gas flow, either oxygen or nitrogen into the vessel as inlet airway has a 3/8 inch inner diameter and is 150 mm long. It has a point end with small holes drilled around it for gas inlet. The purpose of such a design is to allow the longer tube to be easy to insert through the ground coal samples and the inlet gas to spread uniformly in the middle of the sample. The shorter tube is used as an outlet for the exhaust air from the upper portion of the vessel above the coal sample and connects to a longer exhaust tube which allows the gases pass through it to flow out of the oven.

The rubber plug is held in place for preventing gas leaks by a specially designed clamp with four nuts and bolts on the top and bottom ends for tightening or loosening the clamp as shown in Figure 3.4. One thermocouple passes through the rubber plug and is fastened at the end of the longer tube to monitor the temperature of the coal.

Figure 3.3 Binder heating oven, FD 53

3.3.3 Coil Copper Tubing

For the inlet and outlet of gas, 20 feet copper tube with 3/8 inch inner diameter was used. The copper tubing winds in a coil to minimize temperature difference between inlet gas and oven as shown in Figure 3.6 (the right one).

The copper tube was also used as air flow path with one end connected with the oxygen or nitrogen cylinder and the other end connected with longer pipe in the vessel.

Another shorter copper tube was used as exhaust airway connecting the shorter pipe in the vessel.

Table 3.3 Temperature data of Binder oven, FD 53

Temperature data	
Temperature range approx. 5 °C (9 °F) above ambient temperature to (°C/°F)	300 / 572
Temperature variation	
at 70 °C (158 °F) ($\pm$ K)	0.8
at 150 °C (302 °F) ($\pm$ K)	2
at 300 °C (572 °F) ($\pm$ K)	3.7
Temperature fluctuation at 70 °C (158 °F)($\pm$ K)	0.3
Heating up time	
to 70 °C (158 °F) (min.)	7
to 150 °C (302 °F) (min.)	24
to 300 °C (572 °F) (min.)	60
Recovery time after doors were open for 30 sec.	
at 70 °C (158 °F) (min.)	2
at 150 °C (302 °F) (min.)	5
at 300 °C (572 °F) (min.)	9

Figure 3.4 Reaction vessel for R₇₀ test

3.3.4 Thermometer

Extech thermocouple data logging thermometer is used for measuring the inner temperature of the oven and recording the coal temperature in the reaction vessel. It has seven thermocouple input types K, J, T, E, R, S and N. Type T with measurement range between $-150\text{ }^{\circ}\text{C}$ and $400\text{ }^{\circ}\text{C}$ and resolution of $0.1\text{ }^{\circ}\text{C}$ is chosen as the appropriate measurement type. This meter accepts two thermocouples with spade plugs (sub-miniature type with one spade wider than the other). T_1 (thermocouple 1) is the primary display and T_2 (thermocouple 2) is the lower display on the screen the thermometer as shown in Figure 3.5. In the experiment, one of the thermocouples is attached on the longer copper pipe inserting in the middle of the sample in the vessel. The other thermocouple is put in the oven to measure the inner temperature of the oven. The testing temperatures are stored in the PC using the supplied software through the automatic datalogging function of the device. The storage interval rate is programmable from 3 to 255 seconds.

Figure 3.5 Thermocouple data logging thermometer

The complete configuration of experimental instruments for R_{70} method is shown in Figure 3.6. The spontaneous combustion experiments are conducted in the reaction vessel which is designed to minimize heat loss. The reaction vessel is placed inside the temperature-controllable oven. The temperature of the oven is controlled to equal to that of coal in the reaction vessel so that no heat transfer is occurring between the oven and

the coal. In the R_{70} test, the temperature of the coal samples is traced by a data logging thermometer. As the coal temperature increases, the oven temperature will be simultaneously adjusted to equal the coal temperature. The copper tubing coil for the gas inlet is used to minimize the temperature difference between inlet gas and the coal.

Figure 3.6 A modified adiabatic oxidation testing setups

3.4 Experimental Procedures

3.4.1 Experimental Procedures of R_{70} Test

In the testing procedure, 150 grams of coal crushed to size smaller than $212\ \mu\text{m}$ is dried at $110\ ^\circ\text{C}$ under nitrogen for 16 hours. After the coal is cooled down to $40\ ^\circ\text{C}$ under a nitrogen atmosphere, oxygen is switched to pass through the container at 50ml/min . A coal having a high R_{70} index indicates that it is easier to lead to spontaneous combustion.

3.4.2 Experimental Procedures of Moist R_{70} Test

In the moist R_{70} test, approximately 200 grams of coals were crushed to less than $212\ \mu\text{m}$ and then dried in nitrogen at $110\ ^\circ\text{C}$ for 16 hours. Still under nitrogen, the coal was cooled down to $40\ ^\circ\text{C}$ before being oxidized. In order to reduce the cooling effect, oxygen flow rate was adjusted to $10\ \text{ml/min}$. Differing from the previous testing procedure, the dry oxygen was made to pass through a vacuum trap with water in it before entered into the reaction container as shown in Figure 3.7. The oxygen is moisturized in such a way as it flows into vacuum trap, goes through the water from the bottom and exit on the top. This modification from previous testing procedure could enable the test to investigate the effect of heat of wetting during the initial stage of self-heating process.

Figure 3.7 Vacuum trap for testing heat of wetting

In order to investigate the specific humidity effects on the spontaneous combustion behavior of the coal, the moist adiabatic testing facilities are continuously updated. In this specially designed test, a digital water bath was used to incubate the water in the vacuum trap at three different temperature, 25 °C, 35°C and 42 °C as shown in Figure 3.8. Through such a way, the oxygen passing through the water in the vacuum trap will be saturated at those three temperature levels and carry different amount of water vapor into the reaction container. The amount of water vapor can be determined by barometric pressure, dry ball and wet ball temperatures.

Figure 3.8 Updated moist adiabatic oxidation testing setups with water bath

3.4.3 Determination of Heat Convection of the Reaction Vessel

Heat convection is one of the indispensable parameters used in the mathematic model for predicting self-heating rate of coal. It may vary depending on the dimension, texture and structure of the reaction vessel applied. In order to provide the basic parameter for the model, an experiment is specially designed to determine the heat convection of the reaction vessel.

In the test, water is heat up to 100 °C in an electric kettle first. Then 450 g of the hot water is poured into the reaction vessel. After that, the reaction container is covered and placed in an oven kept at a constant temperature that is lower than that of water. The water in the vessel is then allowed to cool down naturally in the oven. Two thermocouples of thermometer are used for recording the temperatures of water and oven. Variation of the water temperature with respect to time is recorded by the data logging thermometer for further data analysis.

Specific enthalpy of water is a function of temperature. This functional relationship can be seen in Figure 3.9. It is found that specific enthalpy and temperature has a perfect linear relationship with $R^2 = 1$. Therefore, specific enthalpy of water can be determined by the following equation,

$$E_w = 4.185T + 0.141 \quad (3-1)$$

Heat loss rate of water in the container can be determined as

$$H_r = \frac{E_w}{t} \quad (3-2)$$

Then heat convection of the reaction vessel with surface area A can be determined by

$$f \cdot A = \frac{H_r}{T_w - T_o} \quad (3-3)$$

Based on the testing data, heat lost rate through the bottle insulation at varying temperature difference between inside and outside of the bottle is shown in Figure 3.10. Through linear regression, it is found these two parameters have fairly good linear relationship with $R^2 = 0.95$. Then heat convection of the reaction vessel was determined by slope of the straight line which is equal to 0.2×10^{-5} .

Figure 3.9 Specific enthalpy of water against temperature

Figure 3.10 Heat loss rate against temperature

3.5 Results and Discussion

Because the adiabatic oven needs to be adjusted manually to follow the temperature of the coal, it is difficult to obtain complete temperature rise before thermal runaway when the tests become impractically long for the coals with low tendency of self-heating. Therefore, not all the samples are tested with this method. One or two representative samples from the same rank are chosen to test.

3.5.1 Upper Freeport Coal Samples

The Upper Freeport coal samples FR0802 and FR0809 in the first batch of shipment to ventilation lab have been tested with the R_{70} test setups. For checking the repeatability of the newly established experimental setups, the sample FR0802 has been tested twice.

The R_{70} self-heating curves of these samples are shown in Figure 3.11. Tests have been performed for 45 hours on each of the samples. None of them show a significant temperature rise but only 1 °C to 2.5 °C increases above the initial temperature. The temperatures did not increase but even slightly decreased after 30.5 hours test. At the end of the 45-hour testing period, the coal temperatures were still far less than the required 70 °C. For FR0802-1 and FR0809, effort was even made to prompt self-heating by setting the oven temperature slightly higher than the coal's. It was still hard for the coal temperatures to catch up or exceed the oven temperature. These tests showed that the tested Upper Freeport coal samples have low potential for spontaneous combustion.

It should be pointed out that the geological cores for the FR0802 and FR0809 samples were not fresh and had been exposed to atmosphere for three years before the tests. The aging effect on coal samples is significant and the slow oxidation might have taken place during the core storage and consequently reduced the potential of self-heating of the Upper Freeport coal samples. Therefore, it is difficult to use the tests performed on the aged coal samples in making reliable conclusions about their propensity of spontaneous combustion.

Figure 3.11 Self-Heating Curve for Coal Sample from Upper Freeport

3.5.2 Indiana Coal Sample

A coal sample from Indiana was tested with R₇₀ method. From the testing results, it is found that the Indiana coal sample (KM4) had a complete self-heating curve in a 45-hour testing duration as shown in Figure 3.12. This coal sample reached the required temperature of 70 °C after about 35 hours of test. The coal sample demonstrated a thermal run-away characteristics and the temperature reached 110 °C at the end of the 45-hour testing period. The lower rank of the Indiana coal and much shorter storage life (2 to 3 months) can explain the higher potential for self-heating of this coal sample than the Upper Freeport samples.

Comparison of the self-heating curves among Upper Freeport and Indiana samples was shown in Figure 3.13. No matter how flat the curves were in comparison to the Indiana coal, all the Upper Freeport samples appeared a temperature acceleration stage at the beginning of the tests. Actually, the temperatures reached around 41.5°C and then essentially stopped increasing afterwards. According to R₇₀ standard, if there is no apparent temperature rise within 36 hours, the coal samples can be classified to be low propensity of spontaneous combustion.

Figure 3.12 Self-Heating Curve for Coal Sample from Indiana KM4

Figure 3.13 Comparison of Self-Heating Curves among Coal Samples from Indiana KM4 and Upper Freeport FR0802 and FR0809

3.5.3 PRB, Pittsburgh and Sewickley Coal Seam Samples

The R_{70} self-heating tests were conducted on the Power River Basin (PRB), Pittsburgh and Sewickley coal seam samples after the second batch of coal samples were received. Figure 3.14 shows the temperature development curves of these samples. At the beginning of the test, PRB sample exhibited the fastest self-heating rate and the temperature increased about 4 °C within one hour. Then the temperature of this sample stopped increasing eventually after 21 hours of testing. The Pittsburgh and Sewickley coal samples reached to 40.5 °C in 5 hours, and then the temperature remained constant without going through significant changes until the tests were terminated. Actually, they experienced less than 1°C temperature rise in about 20 hours. Sewickley sample's temperature even decreased in the later stage of the test.

Figure 3.14 Self-Heating Curves for Coal Samples from PRB, Pittsburgh and Sewickley Coal Seams

It should be noted that most of the tested samples could not reach the required 70 °C due to the low propensity of spontaneous combustion or due to aged samples. In such cases, R_{70} self-heating rates for these samples could not be determined based on

the partial self-heating data and their self-heating risk could not be evaluated using the R_{70} method. For the completeness of the data, initial temperature (T_0), highest temperature (T_1), time spend to reach the highest temperature and tests durations were listed in Table 3.4.

Table 3.4 Results of R_{70} Self-Heating Test for Samples

Sample	Initial Temperature, T_0 (°C)	Highest Temperature, T_1 (°C)	Time from T_0 to T_1 (h)	Test Duration (h)	Ages (days)
FR 0802	40	41.6	28	45	1095
FR 0809	40	41.4	14	41	534
Pittsburgh	40	40.7	12	20	349
Sewickley GM 1012	40	40.7	3	25	21
PRB	40	46.4	21	23	230
KM4	40	110	45	45	230

3.5.4 BBCC and PRB Samples with Moist Oxygen

In order to investigate the effect of moisture condensation on low rank coals, the moist adiabatic tests were conducted on sub-bituminous coals, from Colorado (sample BBCC) and PRB. With the contribution of moisture condensation, both BBCC and PRB coal reached 100 °C only within 5 hours after reacted with moist oxygen, around 3 hours for one and 4.2 hours for another as shown in Figure 3.15.

Figure 3.16 shows the temperatures of the samples and their testing environment. Since the oven was not automatically controlled and needed to be adjusted manually, the oven temperature rising curves were slightly noisier than those of the samples. However, it is still good enough to minimize the heat loss during the test.

Figure 3.15 Self-Heating curves of coal samples from BBCC and PRB with moist oxygen

Figure 3.16 Temperatures of samples and oven

Figure 3.17 shows the comparison of self-heating curves of samples from BBCC, PRM and Indiana. BBCC and PRB samples reached 70 °C only within approximately 2 hours, while the KM4 sample spent 38 hours to the same temperature. The R_{70} self-heating rate of BBCC and PRB samples were 20°C/h and 15°C/h, respectively and 0.86 °C/h for Indiana sample.

Figure 3.17 Comparison of self-heating curves of samples from BBCC, PRM and Indiana

Oxidized with moist oxygen, the self-heating curve of PRB coal increased very rapidly and only 4.2 hours was spent to reach 100 °C. Without the heat of wetting, the coal only experienced about 5 °C rise in temperature from 40 °C as shown in Figure 3.18. After 15 hours, no apparent temperature rise was observed indicating the heat generated from coal oxidation could hardly further sustain self-heating of the coal. Moisture condensation played very important role in initiating the spontaneous combustion. Therefore, it should be alerted the possibility for low rank coals to have spontaneous combustion increases considerably when they were rewetted after dried.

Figure 3.18 Comparison of self-heating curves of PRB sample with moist and dry oxygen

3.5.5 Suancigou No.4 Sample with Dry and Moist Oxygen

The coal sample, Suancigou No.4, from Chinese mine was also tested as reference with adiabatic and moist adiabatic testing procedures. Shown in Figure 3.19 are the self-heating curves of this sample oxidized in dry and moist oxygen. Without moisture effect, the sample reached 50.3 °C in 11 hours and then the temperature leveled off and even slightly dropped in the following 10 hours. Oxidized by the moist oxygen, self-heating curve of the sample reached 53 °C in 11 hours but also kept nearly stable for the remaining test period. Although the moisture condensation contributes the temperature rise 3 °C higher than that of the sample tested in dry oxygen, it is still hardly to promote the coal self-ignition due to the low potential of spontaneous combustion. Different from the moisture content of PRB sample, only 4.4% moisture condensed could contribute the heat for the initial oxidation stage for this sample.

Figure 3.19 Comparison of self-heating curves of Suancigou No.4 sample with moist and dry oxygen

3.5.6 BBCC Sample Tested with Three Temperature Incubation Levels

The testing results of BBCC sample tested with moist oxygen incubated at three temperature levels are plotted in Figure 3.20. Since the oxygen is saturated when it passes through the water in the vacuum trap, then the dry ball and wet ball temperatures for each testing conditions are equal to each other. The results of specific humidity, weight of water vapor, heat of wetting and temperature changes of the sample for the tests at three incubation levels are summarized and presented in Table 3.5. With the barometric pressure, 29.24 in-Hg, dry ball and wet ball temperatures for each test, the specific humidity at saturation per dry air are 0.0206, 0.0375 and 0.0563 lb/lb dry air. As shown in Figure 3.20, the average testing duration of the three tests is 3.5 hours. During this time period, the weight of water vapor carried with inlet dry oxygen at flow rate of 10ml/min is determined to be 0.06, 0.11 and 0.16 g. Heat of wetting generated by each amount of water absorbed by coal are 0.15, 0.27 and 0.40 kJ. With the heat of water condensation, temperature changes of coal for each test are 0.6, 1.0 and 1.5 °C.

For the test performed at 42 °C incubation temperature, the sample shows the highest self-heating rate at the beginning of the test among all the three self-heating

curves due to the highest weight of water vapor absorbed by the coal. After 75 °C, its temperature increasing rate is slightly lower than the sample tested at incubation temperature of 25 °C. This could be caused by heat consumed to heat up the water. The resulting curve from the test incubated at 35 °C shows an average self-heating rate among them. Since the temperature changes of the sample are slightly different for each testing condition due to the small temperature interval for incubation, they show highly similar pattern and the differences of self-heating rate among them are not significant.

Table 3.5 Calculation results for three incubation temperature levels

Temperature		Relative Humidity, %	Specific Humidity @ Saturation, lb/lb dry air	Weight of Water Vapor, g	Heat of Wetting, kJ	Temperature Changes of Coal, °C
Dry Ball	Wet Ball					
25 °C (77 °F)	25 °C (77 °F)	100	0.0206	0.06	0.15	0.6
35 °C (95 °F)	35 °C (95 °F)	100	0.0375	0.11	0.27	1.0
42 °C (107.6 °F)	42 °C (107.6 °F)	100	0.0563	0.16	0.40	1.5

Figure 3.20 Self-heating curves of BBCC sample tested at three temperature levels

3.6 Summary

In the R₇₀ self-heating tests in which coals reacted with dry oxygen, the highest temperatures for the Upper Freeport, Pittsburgh, Sewickley and PRB coal samples to reach are far less than the required 70 °C at the end of testing period compared to the Indiana sample.

However, when consider the effect of moisture condensation for the coal oxidized with moist oxygen, BBCC and PRB coals show the most rapid temperature rise in all the samples. For PRB coal, the self-heating curve grew more rapidly and reached 100 °C within a much shorter time when oxidized by moist oxygen than dry oxygen.

Due to the low capacity of moisture condensed and low potential of spontaneous combustion, even reacted with moist oxygen, self-heating curve of the sample, Suancigou No. 4 didn't show obvious temperature rise but even slightly decreased after 11 hours testing duration.

Although the oven needs to be controlled manually during the test all the time, it is still fairly good to minimize the heat loss and keep an adiabatic environment for self-heating tests.

CHAPTER 4 KINETICS ANALYSIS OF COAL PROPERTIES ON SELF-HEATING

4.1 Introduction

The kinetic method is also called thermal gravimetric analysis (TGA) method. The thermal gravimetric analysis (TGA) is a relatively new quantitative method in studying coal's self-heating potential with a sound theoretical basis. In a relatively short period of experiment on a small coal sample, the oxidation process of coal can be simulated in a precisely controlled environment. Through processing the testing data with kinetic theory, the measured temperature and weight can be used to calculate pre-exponential factor and activation energy of the coal which in turn is a good indicator for the propensity of spontaneous heating.

4.1.1 Experimental Instruments

In the experimental setup using the TGA method, a TA Q 50 thermogravimetric analyzer as shown in Figure 4.1 is used for determining the kinetic parameters. The TA Instruments, thermogravimetric analyzer (TGA), a thermal weight-change analysis instrument in conjunction with thermal analysis controller and associated software was used to make up a thermal analysis system. The TGA measures the amount and rate of weight change in a material, either as a function of increasing temperature, or isothermally as a function of time, in a controlled atmosphere. It can be used to characterize the sample that exhibits a weight change and to detect phase changes due to decomposition, oxidation, or dehydration. This information helps the scientist or engineer identify the percent weight change and correlate chemical structure, processing, and end-use performance.

The TGA instrument has the following six major components:

- The balance, which provides precise measurement of sample weight. The balance is the key to the TGA system as shown in Figure 4.2.
- The sample platform, which loads and unloads the sample to and from the balance.
- The furnace, which controls the sample atmosphere and temperature. Inside the furnace there are platinum pan and thermocouple as shown in Figure 4.3 and Figure 4.4.

- The cabinet, where the system electronics and mechanics are housed.
- The heat exchanger, which dissipates heat from the furnace.

Figure 4.1 Thermogravimetric analyzer (TGA) Q50 (TGA Q50 Manual)

Figure 4.2 The balance part of TGA (TGA Q50 Manual)

4.1.2 Experimental Procedures

The collected coal sample was ground to less than 297 μ m and stored in sealed plastic bags in a refrigerator to minimize the effects of oxidation. In the tests, a 13-14 mg crushed sample were placed on the platinum pans and loaded into the furnace. The test is run with a constant flow of O₂ 10 ml/min and N₂ 40ml/min passing through the

coal sample. The rate of temperature increase in the furnace is precisely controlled to 10°C/min starting from ambient temperature of 18.5 °C. The test continued until no more weight change is measured. Each of the tests only needs about an hour to complete – a significant advantage over the R₇₀ method.

Figure 4.3 Furnace part of TGA (TGA Q50 Manual)

Figure 4.4 Pan and thermocouple parts of TGA (TGA Q50 Manual)

The temperatures and weights of the specimen are precisely measured by the

analyzer during the process and plotted as shown in Figure 4.5. Typically, a complete oxidation process can be divided into three stages according to the changing pattern of the T-G curve. In the initial stage, the specimen loses its weight due to the evaporation of the contained moisture and this stage ends at the inflection point t_1 . Then the specimen could experience a weight gain stage as the low-temperature oxidation occurs before ignition point t_2 . Point t_1 and t_2 are two inflection points to define the weight loss and weight gain stages. The third stage is the combustion process of the specimen during which the weight of the specimen decreases rapidly and this stage ends at t_{end} when all the combustibles in the coal specimen are fully consumed (Wang, et al, 2008).

Figure 4.5 A typical thermal gravimetric experiment Curve (T-G)

The most useful part of the resulting T-G curve to assess the propensity of a coal's spontaneous combustion is between the inflection points t_1 and t_2 . If a coal has the tendency of self-ignition, the weight gain process from m_1 to m_2 (weights measured at t_1 and t_2 , respectively) would be significant and the value of Δm will be larger as

shown by the T-G curve in Figure 4.6. On the other hand, the coal with low potential for spontaneous combustion will experience no or insignificant weight gain and the value of Δm will be smaller.

Figure 4.6 A typical T-G curve showing the moisture loss and weight gain process

The activation energy (an indicator of spontaneous combustion propensity) as an independent kinetic parameter of a coal can be obtained from a data analysis procedure of the TGA testing results. If a coal has self-ignition potential, the weight gain process would be significant. Only a little activation energy is needed for the coal to be oxidized. Therefore, the less activation energy the coal needs, the higher is the potential of self ignition and vice versa.

4.2 Determination of Activation Energy

For a chemical reaction involving substance A and B to produce C (Victor, 1985), the reaction form and the reaction rate are expressed as

$$\frac{dc}{dt} = k(T) \cdot f(c) \quad (4-1)$$

In Eq. 4-1, dc is the differential concentration of substance C within a time duration of dt , $k(T)$ is reaction rate constant that quantifies the speed of a chemical reaction, $f(c)$ is the function of reaction mechanism

In Eq. 4-1, the reaction rate constant can be expressed by Arrhenius equation:

$$k(T) = Ae^{-\frac{E}{RT}} \quad (4-2)$$

In this equation, A is the pre-exponential factor in unit of s^{-1} , R is the gas constant and equals to 8.314 J/mol·K, E is the activation energy in kJ/mol. When Eq. 4-2 is substituted into Eq.4-1, it becomes

$$\frac{dc}{dt} = Ae^{-\frac{E}{RT}} \cdot f(c) \quad (4-3)$$

Eq. 4-3 denotes the homogeneous and isothermal reaction in gas or liquid state. Since the oxidation of coal is a solid-state and non-isothermal reaction, the fractional conversion (α) in % for solid reaction is introduced to replace c . Temperature increment rate (β) in K/min is introduced for non-isothermal reaction.

$$\beta = \frac{dT}{dt} \quad (4-4)$$

Substitute Eq. 4-4 into Eq. 4-3, and it becomes

$$\frac{d\alpha}{dT} = \frac{1}{\beta} Ae^{-\frac{E}{RT}} F(\alpha) \quad (4-5)$$

Rearrange above equation

$$\frac{d\alpha}{F(\alpha)} = \frac{1}{\beta} Ae^{-\frac{E}{RT}} dT \quad (4-6)$$

Integrate both sides of Eq. 4-6

$$\int_0^{\alpha} \frac{d\alpha}{F(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{-\frac{E}{RT}} dT \quad (4-7)$$

Let

$$y = \frac{E}{RT} \quad (4-8)$$

then

$$T = \frac{E}{Ry} \quad (4-9)$$

Take the first derivative of T with respect to y

$$\frac{dT}{dy} = -\frac{E}{Ry^2} \quad (4-10)$$

then

$$dT = -\frac{E}{Ry^2} dy \quad (4-11)$$

$$\frac{A}{\beta} \int_{T_0}^T e^{-\frac{E}{RT}} \left(-\frac{E}{Ry^2}\right) dy = \frac{AE}{\beta R} \int_{\infty}^y \frac{-e^{-y}}{y^2} dy \quad (4-12)$$

Let

$$P(y) = \int_y^{\infty} \frac{e^{-y}}{y^2} dy = \frac{e^{-y}}{y^2} \left(1 - \frac{2!}{y} + \frac{3!}{y^2} - \frac{4!}{y^3} + \dots\right) \quad (4-13)$$

Rearranging,

$$\int_{T_0}^T e^{-\frac{E}{RT}} dT = \frac{E}{R} \frac{e^{-y}}{y^2} \left(1 - \frac{2!}{y} + \frac{3!}{y^2} - \frac{4!}{y^3} + \dots\right) \quad (4-14)$$

Reserve the first and second terms

$$\int_{T_0}^T e^{-\frac{E}{RT}} dT = \frac{E}{R} \frac{e^{-y}}{y^2} \left(1 - \frac{2!}{y}\right) = \frac{RT^2}{E} \left(1 - \frac{2RT}{E}\right) e^{-\frac{E}{RT}} \quad (4-15)$$

Let

$$F(\alpha) = (1 - \alpha)^n \quad (4-16)$$

then

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \begin{cases} -\ln(1-\alpha), n = 1 \\ \frac{(1-\alpha)^{1-n}-1}{n-1}, n \neq 1 \end{cases} \quad (4-17)$$

When $n \neq 1$

$$\frac{(1-\alpha)^{1-n}-1}{n-1} = \frac{ART^2}{\beta E} \left(1 - \frac{2RT}{E}\right) e^{-\frac{E}{RT}} \quad (4-18)$$

Take the logarithm of both sides

$$\ln \left[\frac{(1-\alpha)^{1-n}-1}{T^2(n-1)} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT} \quad (4-19)$$

When $n = 1$

$$\frac{-\ln(1-\alpha)}{T^2} = \frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) e^{-\frac{E}{RT}} \quad (4-20)$$

Take the logarithm of both sides

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT} \quad (4-21)$$

$$\frac{E}{RT} \gg 1, E \gg RT, \frac{2RT}{E} \approx 0, 1 - \frac{2RT}{E} \approx 1$$

So

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (4-22)$$

In this research, the second assumption $n = 1$ is chosen for data process and kinetic parameters determination. Based on Eq. 4-22, the plotting of $\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right]$ against $1/T$ within the temperature range from T_1 and T_2 would produce a quasi-straight line of slope $-E/R$ and intercept of $\ln(AR/\beta E)$ as shown in Figure 4.7.

$$\alpha = \frac{m_0 - m}{m_0} = \frac{\Delta m}{m_0} \times 100\% \quad (4-23)$$

where m_0 is initial mass of the sample, m is mass of the sample at time t .

Figure 4.7 Linear regression of the testing data from TGA to determine activation energy

4.2.1 TGA Tests on Upper Freeport Coal Samples

Figures 4.8-4.14 show the TGA testing curves of the coal samples from the Upper Freeport coal seam. The two inflection points (t_1 and t_2) defining the weight gain

stage for each of the resulting T-G curves are shown on the curves along with the weight changes. Between the two inflection points the weight gain values of Δm are also shown on the curves. For example, for coal sample FR0801, the initial inflection point is defined as temperature of $t_1 = 223.08$ °C and $m_1 = 98.23\%$ of the original sample weight. The second inflection point is defined at $t_2 = 303.50$ °C and $m_2 = 98.43\%$. The sample's weight increases 0.20% in the weight gain stage of slow oxidation process. From Figures 4.8 to 4.14, it is found that all the Upper Freeport samples showed marginal weight gain less than 1% between the inflection points t_1 and t_2 on the resulting T-G curves and the samples have the similar development patterns during the process of heating. The activation energy of each sample was derived based on the testing data from the T-G curve between the two inflection points using a special data transformation process and a regression method. The characteristic points and the derived activation energy for each of the tests performed are listed in Table 4.1. The large activation energies indicate that Upper Freeport samples have low potential of spontaneous combustion which is reasonably agreed with the results from R_{70} self-heating test.

Table 4.1 Results of TGA test for samples from Upper Freeport coal seam

Sample	t_1 (°C)	t_2 (°C)	m_1 (%)	m_2 (%)	Weight Gain % Δm	E (kJ/mol)
FR 0801	223.08	303.50	98.23	98.43	0.20	153.9
FR 0802	231.09	304.20	97.24	97.41	0.18	166.0
FR 0803	205.40	305.43	98.29	98.87	0.58	125.2
FR 0804	198.91	307.41	98.24	99.03	0.79	123.9
FR 0809	207.05	312.87	98.19	98.66	0.48	124.6
FR 0910	219.94	303.92	98.25	98.45	0.20	138.2
FR 0913/14	190.77	303.09	98.33	99.27	0.95	120.4

Figure 4.8 T-G curve for coal sample from Upper Freeport FR0801

Figure 4.9 T-G Curve for coal sample from Upper Freeport FR0802

Figure 4.10 T-G curve for coal sample from Upper Freeport FR0803

Figure 4.11 T-G curve for coal sample from Upper Freeport FR0804

Figure 4.12 T-G curve for coal sample from Upper Freeport FR0809

Figure 4.13 T-G curve for coal sample from Upper Freeport FR0910

Among all the samples, the Indiana coal marked as KM4 has an obvious weight gain stage and a largest weight gain amount of T-G curve in the TGA test as shown in Figure 4.15. This sample has a significant weight gain of $\Delta m = 3.26\%$ between the inflection points of $t_1 = 112.78\text{ }^{\circ}\text{C}$ and $t_2 = 286.12\text{ }^{\circ}\text{C}$. Consequently the derived activation energy of $E = 63.3\text{ kJ/mol}$ for this sample is notably lower than those of the Upper Freeport coal samples. It should be noted that the KM4 sample shows a fast self-heating rate and a complete self-heating curve within a reasonable testing duration in the R_{70} tests.

Figures 4.16 - 4.19 show the T-G curves of the PRB, Pittsburg and Sewickley samples. The PRB sample has the least weight gain of $\Delta m = 0.04\%$ between the inflection points of $t_1 = 189.73$ °C and $t_2 = 206.57$ °C. Its weight gain stage is the shortest among the samples. This sample has the most moisture content and the most of the

weight loss in the first stage occurred before the temperature reached to 100°C. However, it does not necessarily indicate that the PRB coal has low potential for self-heating. It was evidenced by the testing results obtained from moist adiabatic test in Chapter 3.

Figure 4.15 T-G curve for coal sample from Indiana KM4

The Pittsburgh and Sewickley GM1012 and GM1013 samples experience insignificant weight gain of $\Delta m = 1.24\%$, 1.27% and 1.03% , respectively. The measured weight gain ($\% \Delta m$) and the determined activation energy (E) during oxygen adsorption process from m_1 to m_2 are listed in Table 4.2.

From the TGA test, it is found that Indiana sample has the most significant weight gain and the lowest activation energy. The descending order of the potential of self-ignition classified based on the derived activation energies for the coal samples are as follows: KM4 > GM1012 > Pittsburgh > GM1013 > FR0913/14 > FR0804 > FR0809 > FR0910 > FR0801 > FR0802. The PRB sample should be treated as a special case.

Table 4.2 Results of TGA Test for Coal Samples from Indiana, PRB, Pittsburgh and Sewickley

Sample	t ₁ (°C)	t ₂ (°C)	m ₁ (%)	m ₂ (%)	Weight Gain % Δm	E (kJ/mol)
Indiana KM4	112.78	286.12	96.26	99.53	3.26	63.3
PRB	189.73	206.57	79.41	79.45	0.04	148.6
Pittsburgh	172.73	301.69	98.25	99.49	1.24	89.2
Sewi GM 1012	159.56	302.74	98.73	100.00	1.27	87.8
Sewi GM 1013	167.42	303.54	98.83	99.85	1.03	96.7

Figure 4.16 T-G curve for coal sample from Powder River Basin

4.2.4 TGA Tests on All the Other Samples

Apart from the samples that already tested in previous sections, the TGA results of all the other samples in sample bank are listed in Table 4.3. However, the samples marked as SPE, Trapper and BBCC have no weight gain stage in T-G curve. They cannot be evaluated by TGA method. In Chapter 3, BBCC sample has been tested and has very high potential in moist environment. The other two samples will be tested using improved USBM method in the following Chapter.

Figure 4.17 T-G curve for coal sample from Pittsburgh coal seam

Figure 4.18 T-G curve for coal sample from Sewickley coal seam GM1012

Figure 4.19 T-G curve for coal sample from Sewickley coal seam GM1013

Table 4.3 Results of TGA Tests for all the other samples in sample bank

Sample	t ₁ (°C)	t ₂ (°C)	m ₁ (%)	m ₂ (%)	Weight Gain % Δm	E (kJ/mol)
WR	176.29	303.92	98.69	99.84	1.15	91.8
RB	185.56	305.35	98.36	98.90	0.54	105.0
Swei WV	155.45	310.78	98.75	100.30	1.55	86.8
KM3	121.58	288.72	95.48	99.08	3.60	65.9
Murray	165.54	298.93	98.10	99.19	1.09	91.4
SPE	-	-	-	-	-	-
Trapper	-	-	-	-	-	-
New Elk	163.27	317.13	98.88	100.00	1.12	84.0
BBCC	-	-	-	-	-	-
Suancigou No.4	155.05	283.34	95.76	96.65	0.89	84.7
Suancigou No.6	161.78	294.18	96.62	97.20	0.58	83.1
Nanyangpo No.3	158.61	294.58	96.84	97.76	0.92	90.1
Nanyangpo No.4	157.54	291.51	96.60	97.48	0.88	85.6
Xuandong No.3	128.29	314.76	98.31	99.34	1.03	89.6

4.3 Summary

In the TGA tests, Indiana sample has more significant weight gain stage and smallest activation energy than the other samples. The order for the potential of self-ignition classified based on activation energy is: KM4 > KM3 > Suancigou No.6 > New Elk > Suancigou No.4 > Nanyangpo No.4 > Sewi WV > Sewi GM1012 > Pittsburgh > Xuandong No.3 > Nanyangpo No.3 > Murray > WR > Sewi GM1013 > FR0913/14 > FR0804 > FR0809 > FR0803 > FR0910 > FR0801 > FR0802. For the low rank coals, PRB, SPE, Trapper, BBCC, will be treated as special cases and tested using other two methods. In Chapter 3, the testing results have indicated that PRB and BBCC samples have very high tendency of self-heating in moist oxygen condition.

The mechanism of spontaneous combustion can be explained by kinetic theory. A coal contains various functional groups. The abilities for these substances to be oxidized are different. The substances which are more easily oxidized will be activated first with a very small amount of energy with the heat released from physical and chemical adsorption. Then the chemical reaction will occur between activated substances and oxygen. As more oxygen is adsorbed and heat accumulated, temperature of the coal will increase. The functional groups which are easier to be activated become more sensitive and more prone to be activated. Some substances which are difficult to be activated are not consumed at low temperature (40-70°C). They can only be activated by more energy as the temperature continues to increase.

CHAPTER 5 ANALYSIS OF COAL QUALITY PARAMETERS

5.1 Introduction

Coal quality parameters, such as moisture, volatile matter, fixed carbon and ash content are normally determined by proximate analysis. These coal quality parameters have been used to link the self-heating temperature of coal to assess the propensity of coal spontaneous combustion.

The critical self-heating temperature (CSHT) method was first developed by the USBM researchers in 1987 (Smith and Lazzara, 1987). The CSHT is a laboratory determined quantity from an adiabatic test of coal. In the test, grounded dry coal samples were placed in an adiabatic vessel and then exposed to a continuous steady flow of moist air of predetermined temperature. The experiment was repeated at various temperatures with fresh samples for each run. The lowest heating temperature demonstrating thermal runaway was termed as the minimum self-heating temperature of the coal.

Two different critical self-heating temperatures have been identified. One was based on the amount of oxygen which was then linked to CSHT through regression. The CSHT can be determined using the following equation.

$$CSHT_{OX} = 139.74 - 6.57 \times O_{DAF} \quad (5-1)$$

In this equation, $CSHT_{OX}$ is the critical self-heating temperature in °C and O_{DAF} is the oxygen content on a dry, ash-free basis in %.

Another method was based upon a combination of the water adsorption capability of the coal and the amount of carbon and volatiles (Litton and Page, 1994). These last three values were incorporated into a quantity defined as “moist fuel ratio”. An empirical equation developed based upon curve fitting of the testing data extracted from Smith and Lazzara’s experiments was proposed as shown in Eq. 5-2

$$CSHT_{VOL} = 117(1 - e^{-2.6x}) \quad (5-2)$$

where $CSHT_{VOL}$ is critical self-heating temperature in °C, x is the “moist fuel ratio” and is

expressed as:

$$x = \frac{\left(\frac{\% \text{ fixed carbon}}{\% \text{ volatile matter}} \right)}{\% \text{ moisture}} \quad (5-3)$$

If the CSHT is less than 70 °C, the coal will be classified as having a high potential for spontaneous ignition. Coals having a CSHT at or above 70 °C, but less than 100 °C, are considered as having a moderate potential for spontaneous ignition. For coals having a CSHT equal to or greater than 100 °C, the potential for spontaneous ignition will be low.

The proximate analysis results of 6,679 coal samples are obtained from USGS coal quality database. Using the second empirical equation, the $CSHT_{OX}$ values of the 6,679 samples are calculated and marked on the U.S. geological map shown in Figure 5.1. The 413 lignites out of 6679 samples have the smallest CSHT values, between 2 and 37°C indicating that lignite has the highest potential of self-ignition. The 994 sub-bituminous coals have the CSHT value between 5 and 58°C. Only 3 sub-bituminous samples' CSHT are more than 70°C and 4 samples' CSHT are in the 108-115°C range. The CSHT's of more than 3,000 bituminous samples are between 70 and 117°C. The 50 semi-anthracite and anthracite have the highest CSHT values between 110 and 117°C. However, the USBM method overstates the moisture effects on the potential of spontaneous combustion. Based on the calculation results, the more moisture the coal contains, the lower CSHT the coal has. It is evidenced by the CSHT results in the U.S. map as shown in Figure 5.1. Actually, it is impossible for lignite to burn at the temperature of 2°C. In other words, the potential of spontaneous combustion of those low rank coals cannot be determined merely rely on the amount of moisture they contained. This method needs to be improved and will be studied in the following sections.

5.2 Determination of Coal Quality Parameters with TGA

The propensity of coal's spontaneous combustion can be assessed using the coal quality parameters of moisture, volatile matter, and fixed carbon that are normally obtained from proximate analysis of coal. Traditionally, the various proximate analysis determinations process is guided by ASTM standards. However, these determinations are time consuming and require a significant amount of laboratory equipment. TGA

technique, on the other hand, could provide an alternative method to perform the proximate analysis with a faster procedure to determine the coal quality parameters (TA Brief). In addition, not all coal samples tested in our laboratory had been tested for the proximate analysis or the analysis results are not provided. The TGA can also be used to fill the data voids.

Figure 5.1 CSHT_{ox} distribution of 6,679 samples on US map

The coal sample is ground and screened with US standard sieve No. 50 to particle size less than 297 μm before the test was conducted. An approximately 40 mg of the sample was placed in the platinum pans and loaded into the furnace of the equipment.

The sample is heated to 110 $^{\circ}\text{C}$ at a constant ramp rate of 85 $^{\circ}\text{C}/\text{min}$ with a constant nitrogen gas supply of 60 ml/min. Then the sample is kept in isothermal condition for 3 min. The weight loss during this process is the amount of moisture in the coal. The sample continues to be heated to 900 $^{\circ}\text{C}$ at a rate of 80 $^{\circ}\text{C}/\text{min}$ in pure nitrogen environment. Then the temperature is maintained at 900 $^{\circ}\text{C}$ for 7 min. The weight loss during this process is the amount of volatile matter in the coal.

After a 7 min isothermal condition, with the temperature still maintained at 900°C the gas supply is switched to pure oxygen at a flow rate of 60 ml/min. The process will continue for 5 min and no further weight loss is observed on the sample. The weight loss during this process is the fixed carbon content of the coal. The residual weight at the end of the test is the ash content of the coal (Ottaway, 1982). The testing environment and the test results of one of the tests (Coal O) are shown in Figure 5.1. Three plateaus are apparent on the weight-time curve. The test results in Figure 5.1 shows that the tested coal sample contains 1.41% moisture content, 37.40% volatile matter, 48.28% fixed carbon and 12.91% ash content. TGA-based proximate analysis results for all the samples in the sample bank are listed in Table 5.1.

Figure 5.2 T-G curve for proximate analysis of coal

5.3 Quantification of U.S. Coal Rank

Spontaneous combustion continues to pose a safety hazard and significant interruption to mining operation. Two major thermal events have recently taken place in WV and CO, resulting in coal mine shutdown and longwall mining machine abandon. Therefore, considering this dramatically increased thermal incidents, reliable methods for

classifying the spontaneous combustion of coal are of great importance for risk assessment and hazard management.

Table 5.1 TGA-based proximate analysis results for all the samples in the sample bank

Coal Sample	TGA (Wt %)			
	Moisture Content	Volatile Matter	Fixed Carbon	Ash Content
WR	1.6	36.0	57.1	5.3
RB	1.8	34.5	42.7	21.0
Sewickley WV	1.2	33.4	52.5	12.8
KM3	9.8	35.3	48.1	6.8
KM4	9.5	32.1	52.9	5.5
Murray	2.0	39.0	48.7	12.3
Pittsburgh coal seam	2.1	37.7	52.2	8.0
Sewickley GM1013	1.4	34.9	37.3	26.4
Sewickley GM1012	1.4	37.4	48.3	12.9
FR0801	1.2	34.8	58.5	5.5
FR0802	1.1	39.3	52.5	7.1
FR0803	1.5	40.0	52.2	6.3
FR0804	1.5	40.0	52.6	5.9
FR0809	1.4	32.4	58.9	7.3
FR0910	1.4	36.1	56.5	6.0
FR0913/14	1.5	39.4	53.2	5.9
PRB	25.9	37.7	31.9	4.5
SPE	13.2	44.2	38.4	4.2
Trapper	11.2	33.5	43.1	12.2
New Elk	1.9	27.4	38.8	31.9
BBCC	18.9	49.8	26.9	4.4
Suancigou No.4	4.4	34.0	39.8	21.8
Suancigou No.6	3.5	19.4	28.1	49.0
Nanyangpo No.3	3.2	26.7	47.5	22.6
Nanyangpo No.4	3.4	32.1	49.5	15.0
Xuandong No.3	1.2	29.3	53.1	16.4

Coal rank, one of the most important factors has a significant influence on coal self-heating (Beamish, 2005 and Nugroho et al, 2008). As it is widely known, low rank coals have high potential for self-ignition, and vice versa. However, this description is still highly qualitative. The definite relationship between rank and propensity of spontaneous combustion needs further study in a quantitative manner.

In general, coal metamorphism or coalification, denoted as the coal rank, is marked by a progressive decrease in moisture and volatile matter with a consequent increase in the carbon content of the coal. Coal rank involves the physical and chemical transformation from peat through bituminous coal, anthracite and meta-anthracite to graphite. Many of the fundamental properties of coal that are important for industrial us-

es are rank dependent. Classification of coal by rank has developed for 150 years from simply introducing some order into different coals to primarily intending to aid scientific studies. The basis for classification that facilitates scientific studies of coal and its use in different industrial operations was well recognized (Grout 1849 and Ralston 1915). But the full development of such classification is mainly due to Seyler and Mott (Seyler 1938 and Mott 1948). Suggate scale (S_r) as a maturity index for coals from Australia and New Zealand, creatively proposed by Suggate, is an updated method that allows classifying the coal rank quantitatively (Suggate 2000). The core of Suggate system is a coal band that defines itself both in carbon-hydrogen (C-H) and calorific value-volatile matter (CV-VM) plots, and then the coal band is scaled from 0 to 25 according to the burial depth of different ranks of coal. This scale can then be used to explore relationships quantitatively between rank and coal properties. Strictly speaking, this diagram is specifically developed for Australia and New Zealand coals. The boundaries of the major coal classes and the connections between carbon contents and other parameters can not reflect general coal behavior.

Jo used crossing-point temperature (CPT) and gas chromatography (GC) methods to evaluate the spontaneous combustion and correlate it to coal ranks (Jo, et al., 2013). However, only lignite and bituminous coals were selected for their study. Sahu et al. presented an approach for classification of coal seams with respect to their spontaneous heating susceptibility. In their study, a number of coal samples of various ranks have been tested with CPT, differential thermal analysis (DTA), differential scanning calorimetry (DSC), however, there was no quantitative relationship between ranks and those classification indexes (Sahu, et al. 2009). Beamish quantified the relation between self-heating and rank of coal using R_{70} index determined by an adiabatic self-heating method and Suggate ranking scale, but the relationship was built on limited sample data and rank range (Beamish, 2005). SHT index proposed by USBM was another method for evaluation of self-heating of coal. The advantage of this method is SHT of coal can be determined easily by data which is also the essential information for rank determination, from proximate analysis, but the SHT prediction equation is highly empirical and each rank, improved prediction equations for SHT is proposed. A chart with visualized relationship of quantified coal rank (QCR) and SHT can be used as an engineering tool

to evaluate the risk of spontaneous combustion and illustrate the effect of has large deviation against the testing results.

In this section U.S. coal rank and SHT of coal is proposed. A Suggate ranking system-based method is used to scale the coal band which consists of 4543 coal quality data extracted from USGS database to quantify the rank. Depending on the testing results for rank on coal critical self-heating temperature.

5.3.1 Coal Band

Because carbon contents vary directly or inversely with several other parameters, such as VM and CV, the choice of principal coordinates for classifying coal by rank is a matter of convenience and usually depends on the purposes which the scheme is to serve.

For schemes mainly intended to facilitates scientific studies of coal classifications, the basic rectangular coordinates, always expressed on a dry, ash-free (daf) or dry, mineral-matter-free (dmmf) basis, are normally as follows:

1. percentage carbon versus percentage hydrogen or in certain cases, atomic O/C versus H/C ratios,
2. percentage VM versus CV,

Suggate's New Zealand Coal Band was illustrated on charts with CV-VM axes (Suggate, 1959). Data point of each New Zealand coal on the chart was determined by the equations of Eq. 5-4 and Eq. 5-5 which allowed the calculation of CV and VM from proximate and ultimate analysis of those samples on dry, mineral-matter and sulfur-free (dmmsf) basis. All the scattered points located on the chart with CV as X-axis and VM as Y-axis formed a distribution range of coal. This range which was then bounded graphically with two lines as upper and lower boundaries was defined as coal band. Although sometimes it is in idealized form, the boundary lines show how the composition of a coal changes when its rank altered.

Determination of the analytical point of a coal located in the coal bend is as follows:

$$CV_{dmmsf} = \frac{\frac{CV}{1 - \frac{M}{100}} - 50S}{1 - 0.0108A - 0.0055S} \quad (5-4)$$

$$VM_{dmmsf} = \frac{\frac{VM \times 100}{VM + FC + A} - 0.08 - 0.4S}{1 - 0.0108A - 0.0055S} \quad (5-5)$$

Where, CV_{dmmsf} is calorific value on dry, mineral-matter and sulfur-free basis in Btu/lb, CV is calorific value in Btu/lb, M is moisture content in %, S is sulfur in %, A is ash in %, VM_{dmmsf} is volatile matter on dry, mineral-matter and sulfur-free basis in %, VM is volatile matter in %, FC is fixed carbon in %.

For determination of U.S. coal band, a total of 4,543 coal composition data which was derived from proximate and ultimate analysis of coal was extracted from USGS coal quality database. Those data points represent the coal from most of the mining field all over the U.S. with all kinds of rank from lignite, sub-bituminous, bituminous, semi-anthracite to anthracite. Then the as received coal quality data was processed with Eq. 5-4 and Eq. 5-5 to adjust to dmmsf basis for CV and VM . All the 4,543 data points including lignite (259 samples), sub-bituminous (571 samples), bituminous (3,673 samples), semi-anthracite (8 samples) and anthracite (32 samples) were plotted in a diagram with CV - VM coordinates. The ASTM rank ranges legend was attached as reference into the plot. Although it has been used for the coal original standard classification and can only be applied approximately, it provides useful general terms indicating rank increase. Distribution of the sample points forms the U.S. coal band which is graphically bounded with boundary lines as shown in Figure 5.3. It should be noted that since the CV and VM are adjusted to dmmsf basis, the determined CV_{dmmsf} and VM_{dmmsf} will be higher than the actual ones.

In the coal band, it can be seen that lignite has the lowest calorific values on dmmsf basis (10,000-11,750 Btu/lb) and the highest volatile matter on dmmsf basis (40-60%). Sub-bituminous follows with CV_{dmmsf} (11,750-13,500 Btu/lb) and VM_{dmmsf} (38-55%), and then are bituminous coals with CV_{dmmsf} (13,500-16,000 Btu/lb) and VM_{dmmsf} (17-52%) and semi-anthracite with CV_{dmmsf} (15,300-15,800 Btu/lb) and VM_{dmmsf} (10-16%). However, as the coal rank increases, the CV_{dmmsf} and VM_{dmmsf} of all ranks of coal are not changing linearly with the fact that anthracite is on the top of the rank and has the lowest VM_{dmmsf} (<10%) but does not have the highest CV_{dmmsf} (13,900-15,600 Btu/lb) which is lower than that of bituminous coal.

Figure 5.3 U.S. coal band

5.3.2 Rank Scale for U.S. Coals

Rank scale for New Zealand coal type was first proposed by Suggate through defining equal rank lines based on the plot of serial samples' analysis results in coal band diagram with CV-VM coordinates on a dmmsf basis (Suggate 1959). Coals of equal rank appear as collinear points on plots of CV-VM on a dmmsf basis. The slope of defined lines was determined by distribution trends of serial sample sets empirically. The slope keeps constant from lignite to mid-bituminous coals but show progressive changes from higher rank bituminous coals to anthracite. The rank scale for all ranks of coal was defined based on the burial depth of coal as shown in Figure 2.17. With every 1,000 ft increasing depth of original burial at the time coal was formed, the rank scale of coal increases 1 accordingly. Therefore, refer to approximate ASTM rank ranges, the proposed ranks scale for coals are: 0-5 for lignite, 5-10 for sub-bituminous, 10-16 for bituminous, 16-20 for semi-anthracite, 20-25 for anthracite.

Similarly, considering the data points plotted in the coal band, quantified rank for U.S. coals is expressed with rank scale using the same principle as Suggate rank (Sr)

from 0 to 25 with 1 increment for rank increase as shown in Figure 5.4. However, the slope of the rank lines is determined empirically based on the distribution trends of different ranks of coal.

Figure 5.4 Rank scale for U.S. coals

The procedure for quantification of U.S. coal rank is

1. Adjust the received sample data to dmmsf basis for CV and VM using Eq. 5-4 and Eq. 5-5
2. Build a diagram with CV-VM coordinates and plot all the data points in it
3. Bound the upper and lower range of data distribution as boundaries
4. Build the coal band based on the boundaries in last step
5. Determine the equal rank lines and draw them on the coal band
6. Determine rank scale for each rank based on the burial depth of the coal

For determination of quantified coal rank of a particular coal sample, the procedure is

1. Perform the proximate and ultimate analysis of coal

2. Adjust the as received coal quality results to dmmsf basis for CV and VM
3. Plot the interest data points of coal in the diagram developed in last procedure
4. Determine the quantified rank of the coal based on the position where the data point located on the rank scale

5.4 Improvement of CSHT Method

Advantages of CSHT method are it is easy to determine the self-heating temperature using the empirical equation as long as the proximate analysis data are provided and it reflects the effects of affecting factors, such as moisture, volatile matter and fixed carbon, on the propensity of spontaneous combustion. The second USBM empirical equation is used for prediction of SHT not only because it classifies potential of self-heating quantitatively and provides risk index for rating but also it reveals the most likely causes of this phenomenon. In addition, those essential coal composition data can be determined easily and rapid through the TGA instrument in the lab. However, this method still has some limitations and can be improved further.

Firstly, Mazumdar pointed out that the term “moist fuel ratio” appears to be misleading (Mazumdar, 1995). The ratio of fixed carbon to volatile matter is meaningful and well-understood. However, why this ratio should be divided by moisture and the resultant expression called moist fuel ratio is not readily apparent. Secondly, the exponential relationship between moist fuel ratio and SHT suffers from a large deviation between the experimental and calculated values. The correlation is not applicable to the lignite samples evidenced by the large root-mean-square deviation (RMSD), 23. For sub-bituminous coal RMSD is 14, 12 for high volatile bituminous and 11 for medium to low volatile bituminous as shown in Table 5.2.

In the improved approach, correlations could be expressed as multiple linear relationships, essentially in the form of $y = a_0 + a_1x_1 + a_2x_2$, where the variables y , x_1 and x_2 are the self-heating temperature, moisture and the ratio of fixed carbon to volatile matter, respectively. The improved correlations are developed based on the variation of coal quality along with ranks. As rank increases, moisture and volatile matter decrease and fix carbon increases. The correlations for the prediction of SHT are as follows:

$$SHT = \begin{cases} 0.22M - 6.31\frac{C}{V} + 29.0 & 25 < M \leq 35 \\ 0.13M + 2.36\frac{C}{V} + 25.5 & 10 < M \leq 25 \\ -4.95M + 2.66\frac{C}{V} + 88.3 & 1 < M \leq 10 \\ 36.1M - 5.29\frac{C}{V} + 108.3 & 0 < M \leq 1 \end{cases} \quad (5-6)$$

In Eq. 5-6, M is moisture content in weight %, C is fixed carbon in wt %, V is volatile matter in wt %.

Table 5.2 Proximate analysis, self-heating temperature, ASTM and quantified coal rank of samples

Sample	Proximate Analysis, %				Sulfur, %	Calorific Value, Btu	SHT, °C	Calculated SHT, °C				ASTM Rank	QCR
	Moisture	Volatile Matter	Fixed Carbon	Ash				USBM	Dev.	Proposed Method	Dev.		
Lignite													
Beluga	24.5	31.1	28.9	15.5	0.1	7000	32	11	-21	31	-1	Lignite	2.6
Gascoyne	34.0	29.5	30.2	6.3	1.3	7150	30	9	-21	30	0	Lignite	4.4
Husky	34.1	30.7	29.0	6.2	0.6	7280	30	8	-22	31	1	Lignite	4.9
Center	32.0	32.5	30.9	4.6	0.4	7660	30	9	-21	30	0	Lignite	4.6
								RMSD	23	RMSD	0.6		
Sub-bituminous													
Darco	31.1	30.5	32.5	5.9	1.0	7850	30	10	-20	29	-1	SubC	6.1
Sandow	21.1	39.5	29.1	10.3	1.0	8940	30	10	-20	30	0	SubB	6.2
Rosebud	22.0	32.5	39.4	6.1	0.5	9330	30	16	-14	31	1	SubA	8.4
Stray	18.5	33.5	37.8	10.2	0.8	9460	30	17	-13	31	1	SubA	8.9
Bridger	15.7	31.6	49.9	2.8	0.4	10740	32	27	-5	31	-1	SubA	9.9
Dr. No. 80	11.7	38.0	46.9	3.4	0.6	11190	30	28	-2	30	0	SubA	9.3
								RMSD	14	RMSD	0.8		
High Volatile Bituminous													
F	11.4	40.9	45.3	2.4	0.3	11561	45	26	-19	35	-10	Hvcb	9.6
No. 80-2	11	39.5	43.9	5.6	0.7	11353	40	27	-13	37	-3	Hvcb	10.1
No. 80-1	7.6	38.3	44.1	10	0.4	11236	35	38	3	53	18	Hvbb	10.3
Prince	3.2	35.1	52.4	9.3	4.7	12580	70	82	12	76	6	Hvab	12.9
No. 6	2.2	41.8	42.7	13.3	4.2	11914	70	82	12	80	10	Hvab	11.4
B-1	2.8	38.3	49.6	9.3	0.5	13029	70	82	12	77	7	Hvab	10.7
B-2	3.9	40.1	53.8	2.2	0.5	13920	75	69	-6	73	-2	Hvab	12.8
Clarion	4.8	43	44.4	7.8	3.5	12888	75	50	-25	67	-8	Hvab	12.4
D-1	2.1	43.9	47.8	6.2	0.5	13734	90	87	-3	81	-9	Hvab	12.5
D-2	2.7	44.2	47.3	5.8	0.4	13480	80	75	-5	77	-3	Hvab	12.2
E-1	3.9	39.7	54.6	1.8	0.7	13784	65	70	5	72	7	Hvab	12.6
E-2	3.2	40.5	54.4	1.9	0.7	13823	65	78	13	76	11	Hvab	12.6
Kittanning	1	31.7	44.9	22.4	3.9	11055	100	114	14	87	-13	Hvab	13.2
L. Sunny-1	3.2	36.2	54.2	6.4	0.5	13318	85	82	-3	76	-9	Hvab	13.1
L. Sunny-2	2.3	38.6	56.2	2.9	0.4	14097	80	94	14	81	1	Hvab	13.1
Pittsburgh	1.7	38.8	53.9	5.6	1.3	13947	90	103	13	84	-6	Hvab	13.3
								RMSD	12	RMSD	8.8		
Medium to Low Volatile Bituminous													
CB-1	0.7	22	70.4	6.9	0.7	14616	120	117	-3	117	-3	Mvb	15.3
CB-2	0.9	21.6	69.5	8	0.5	14350	120	117	-3	123	3	Mvb	15.2
Bluecreek	1.1	19.2	72.7	7.0	0.5	14276	135	117	-18	128	-7	Lvb	15.4
Mary Lee	1.3	20.2	71.3	7.2	0.6	14381	135	117	-18	136	1	Lvb	15.4
P 3-1	0.9	18.7	73.2	7.2	1.7	14419	115	117	2	120	5	Lvb	15.6
P 3-2	0.6	17.6	67.5	14.3	1.1	13279	110	117	7	110	0	Lvb	15.5
								RMSD	11	RMSD	3.9		

These correlations are developed based upon the results of self-heating tests conducted by Kuchta in 1980 and Smith and Lazzara in 1987, for different ranks of coal including lignite, sub-bituminous coal, high volatile bituminous and medium to low volatile bituminous. The predictions of SHT with various moisture contents and the ratios of fixed carbon and volatile matter ($C/V = 0.7, 0.8, \dots, 13, 16$) determined by Eq. 5-6 are plotted in Figure 5.5. With assistance of this figure, the SHT of various types of coal can be determined easily based on coal quality data. For example, if a coal has the ratio of $C/V = 4$ and $M = 8\%$, then the SHT of 60°C for the coal will be directly pointed out in the chart.

Figure 5.5 Variations of SHT with moisture and ratio of fixed carbon and volatile matter

The improved correlation gives more accurate predictions than the USBM correlation. The RMSDs are 0.6 and 0.8 for lignite and sub-bituminous coals compared with 23 and 14 for the USMB correlation. For high volatile bituminous and medium to low bituminous, its performance is still better and keeps the RMSDs within 8.8 and 3.9 for both type of coals. A similar approach was once developed by Mazumdar in 1995. In his method, only moisture and volatile matter were taken into account for the correlations of

SHT prediction. Comparisons among the USBM method, Mazumdar method, improved method and experimental data are made and plotted in Figure 5.6. The RMSD of USBM method and improved method against experimental results for each type of coal are listed in Table 5.2. The RMSDs of Mazumdar method are 11.6 for lignite, 12 for sub-bituminous coal, 9.3 for high volatile bituminous, and 9.1 for medium to low bituminous.

Figure 5.6 Comparisons of the USBM method, Mazumdar method and improved method for SHT prediction against experimental data

5.5 Correlation of Quantified Coal Rank and Self-Heating Temperature

5.5.1 Rank of U.S. Samples

The proposed quantified ranking scheme is applied to U.S. samples extracted from two reports of USBM for using as much data as possible, listed in Table 1 (Kuchta, 1980; Smith and Lazzara, 1987). Those sample data were processed for both calorific value and volatile matter to a dry mineral matter and sulfur free basis (dmmsf) based on the provided proximate and ultimate analysis of the samples. Then those values are

plotted in the ranking scale chart and the rank distribution of the samples can be seen in Figure 5.7.

The ranks of the available samples include lignite, sub-bituminous, high volatile bituminous and medium to low volatile bituminous. However, for the higher rank coals such as semi-anthracite and anthracite, there are no testing data available because of the low potential of self-heating for such ranks of coal. Therefore, they were not considered in those two literatures. It can be seen from Figure 5.7, quantified rank range for lignite is 2.5-5, sub-bituminous is 6-10, for high volatile bituminous is 9.5-14 and for medium to low volatile bituminous is 15-16.

Figure 5.7 Rank scale for coal samples used in this study

5.5.2 Relationship between QCR and SHT

A plot of the SHT values against their respective quantified coal rank (Figure 5.8) clearly shows that the relationship is non-linear. Sub-bituminous coal has the lowest self-heating temperature among all ranks of coal. Although lignite has the lowest rank,

its SHT is slightly higher than that of sub-bituminous coal. As for high volatile bituminous C, B, A and medium to low volatile bituminous coals, higher rank has the higher SHT. However, there is no data for semi-anthracite and anthracite.

Figure 5.8 Relationship between quantified coal rank and SHT of U.S. coal

The overall shape of the curve is similar to that proposed by Mazumdar (1996) and Beamish (2005) for two other self-heating index parameters, crossing point temperature (CPT) and R_{70} self-heating rate. However, the SHT of sub-bituminous coal doesn't decrease significantly in comparison to that of lignite, different from the findings of Beamish (2005), where the R_{70} self-heating rate values increase dramatically from lignite to sub-bituminous coal. It may be due to the different test methods applied. In SHT method, moist air was used, but for R_{70} method, the reactant oxygen was dry. Moisture condensation may play an important role on lignite self-heating due to its capacity of containing more moisture than sub-bituminous coal.

Additional samples' SHTs which were determined by the improved method were

also plotted in the Figure 5.7. It can be seen that the determined results follow the same trend of the trendline.

5.6 Summary

Propensity of coal's spontaneous combustion can be determined by proximate analysis results through using USBM method. The TGA setup can be used as an alternative method for proximate analysis for coal quality parameters which in turn can be used to determine critical self-heating temperature through a specially designed testing procedure.

Quantified coal rank system has been developed for U.S. coals based on the Suggate ranking principle. A total of 4,543 coal samples with their coal quality data, extracted from USGS database, were used for establishment of the system. All the data were adjusted into dmmsf basis for CV and VM and plotted into a diagram. The rank scale was defined as 0 to 25 for all ranks of coal from lignite to anthracite.

The original USBM method for predicting SHT has been improved with testing results derived from two USBM technical reports. The improved SHT correlations have been developed upon the targeted samples for each rank including lignite, sub-bituminous coal, high volatile bituminous and medium to low volatile bituminous coals. The improved prediction correlation has the lowest RMSD among all the methods against experimental results.

The relationship between rank and SHT of U.S. coals is non-linear. There is a slight decrease in the SHT values in the rank range of sub-bituminous coals. By calculating the CV and VM on dmmsf basis and SHT with the standard coal quality data obtained from proximate analysis during exploration, a quick estimate of the self-heating temperature of U.S. coals can be obtained through the relationship diagram. Therefore, it is a very cost effective way for initial risk assessment for any new mine development.

The R_{70} , activation energy, SHT results from the three methods and quantified coal rank for all the samples in the sample bank are listed in Table 5.3. From this table it can be seen that sub-bituminous coal has high tendency of self-heating than that of bituminous coals. For example, the SHT of PRB sample (SubA) is 29.4 °C which is lower than 45.6 °C of KM4 sample (HvCb). The testing data also indicate that the index value determined by these three methods agree fairly well with each other. For example, the

KM4 sample, which has lower SHT, has lower activation energy and higher self-heating rate than other HvAb and HvBb samples.

Table 5.3 All the samples testing results with the three methods

Coal Sample	TGA (Wt %)				USBM SHT (°C)	Modified SHT (°C)	Activation Energy (KJ/mol)	R ₇₀ /Moist (°C/h)	ASTM Rank	Coal Rank	Age (days)
	Moisture Content	Volatile Matter	Fixed Carbon	Ash Content							
WR	1.6	36.0	57.1	5.3	109	84.6	91.8	-	HvAb	12.6	180
RB	1.8	34.5	42.7	21.0	98	82.7	105.0	-	HvAb	11.8	120
Sewi WV	1.2	33.4	52.5	12.8	113	86.5	86.8	-	HvAb	12.5	150
KM3	9.8	35.3	48.1	6.8	35	43.4	65.9	-	HvCb	12.0	230
KM4	9.5	32.1	52.9	5.5	42	45.6	63.3	0.86	HvCb	12.0	230
Murray	2.0	39.0	48.7	12.3	94	81.7	91.4	-	HvAb	12.4	90
Pittsburgh	2.1	37.7	52.2	8.0	97	81.6	89.2	0.06	HvBb	12.2	534
Sewi GM1013	1.4	34.9	37.3	26.4	102	84.2	96.7	-	HvAb	11.5	349
Sewi GM1012	1.4	37.4	48.3	12.9	106	84.8	87.8	0.23	HvAb	12.0	349
FR0801	1.2	34.8	58.5	5.5	114	86.8	153.9	-	HvAb	13.8	1095
FR0802	1.1	39.3	52.5	7.1	112	86.4	165.9	0.06	HvAb	13.4	1095
FR0803	1.5	40.0	52.2	6.3	104	84.3	125.3	-	HvAb	13.1	1095
FR0804	1.5	40.0	52.6	5.9	105	84.4	123.9	-	HvAb	13.2	1095
FR0809	1.4	32.4	58.9	7.3	113	86.2	124.6	0.03	HvAb	13.9	1095
FR0910	1.4	36.1	56.5	6.0	111	85.5	138.2	-	HvAb	13.5	730
FR0913/14	1.5	39.4	53.2	5.9	105	84.5	120.4	-	HvAb	13.3	730
PRB	25.9	37.7	31.9	4.5	9.5	29.4	148.6	0.29/15	SubA	10.1	21
SPE	13.2	44.2	38.4	4.2	18.4	29.3	-	-	HvCb	10.6	730
Trapper	11.2	33.5	43.1	12.2	30.2	30.0	-	-	HvCb	11.4	730
New Elk	1.9	27.4	38.8	31.9	100.1	82.7	84.0	-	HvAb	12.1	730
BBCC	18.9	49.8	26.9	4.4	8.5	19.2	-	-/20	SubA	8.8	365
Suancigou No.4	4.4	34.0	39.8	21.8	58.4	69.6	84.7	0.95/1.18	HvBb	11.3	730
Suancigou No.6	3.5	19.4	28.1	49.0	77.1	74.8	83.1	-	HvBb	11.4	730
Nanyangpo No.3	3.2	26.7	47.5	22.6	89.4	77.2	90.1	-	HvBb	12.0	730
Nanyangpo No.4	3.4	32.1	49.5	15.0	81.1	75.6	85.6	-	HvBb	12.2	730
Xuandong No.3	1.2	29.3	53.1	16.4	114.7	87.2	89.6	-	HvAb	12.1	730

From the table it can be seen that the samples from Pittsburgh coal seam (Pittsburgh) and Upper Freeport coal seam (FR0802) have the same R₇₀ self-heating rate but different activation energy. It should be noted that the R₇₀ results shown in the table only reflect the rate of sample reaching the highest temperature it could from the initial temperature, 40 °C. They are not the values that determined by the standard way partly due to the significant aging effects. Since both of them were pre-oxidized for 534 and 1095 days before test, aging effect greatly reduced the activity of the samples, making the self-heating rate hardly to reflect the real activity of the coal.

CHAPTER 6 MATHEMATICAL MODEL DEVELOPMENT TO ESTIMATE POTENTIAL OF SELF-HEATING

6.1 Introduction

A mathematic model has been developed to link the three methods for testing the propensity of coal's spontaneous combustion theoretically. In other words, the mathematic model is developed based on adiabatic energy conservation due to the fact that the R_{70} method is considered as the most reliable experimental technique to determine the propensity of coal's spontaneous combustion. Heat generation rate is determined by kinetic parameters and heating value, which is considered to be generated by volatile matter and fixed carbon as the only sources for coal to generate heat. These kinetic and coal quality parameters can be determined using TGA equipment under different testing procedures. The model development process is shown in the flow chart Figure 6.1. The R_{70} self-heating test has been used as one of the major laboratory methods for testing the intrinsic properties of coal that influences its propensity for spontaneous combustion. The R_{70} test is conducted in an artificially created adiabatic environment so that only and all the heat generated by the coal sample is used to prompt the oxidation process and to increase the temperature of the sample. The key to create such an artificial adiabatic testing environment is to eliminate any heat exchange between the coal sample in the testing container and the outside environment through a precise temperature control. Even a minor amount of heat exchange in the testing duration could produce unreliable testing results, especially for the coals having low propensity.

Based on the law of energy conservation, a mathematical model has been developed to quantify the effects of any imperfection of the testing adiabatic environment on the testing results for a R_{70} self-heating test setup and the testing procedure. The model considers the heat losses and gains caused by coal moisture, inlet oxygen flow and exhaust air, conduction and convection heat transfers between coal and outside, and heat diffusion in the sample. The mathematical model can be applied to correct the testing results in terms of the heat generation rate at a given temperature caused by the system imperfection. Coupled with the experimentally determined parameters such as the specific heat of coal, heating value of various combustibles in the coal, etc. the accuracy of the R_{70} testing could be greatly improved. The mathematical model also al-

lows the determination of heating value, activation energy and pre-exponential factor from the experiment-generated temperature development curves.

This model can serve as a tool to simulate the coal self-heating behavior with respect to time and temperature in an adiabatic condition. For coal having very low propensity of spontaneous combustion, the model can provide a complete self-heating curve which is unable to be obtained experimentally using the R₇₀ method.

It is well known that sulfur, moisture content and volatile matter can greatly influence the process of coal's spontaneous combustion. Their effects are quantified and incorporated into the developed mathematical model. It enhances the model's ability to consider the effects of these three important properties in the coal. Sulfur exists in coal primarily in the form of pyrite which will be oxidized rapidly under suitable conditions. Shrinking core model is used to quantify the oxidation of pyrite. Heat of moisture condensation which provides initial energy for low temperature oxidation is incorporated into the model. Volatile matters, higher in low rank coals, are more easily oxidized. The activation energy distribution as function of temperature during the volatile matter oxidation process are taken into account and also incorporated into the model.

6.2 Model Developed Based on Adiabatic Testing Procedure

Adiabatic oxidation method is considered to be a good method to simulate the initial stage of the coal oxidation process at a relatively low temperature. It becomes a standard way to assess the intrinsic properties of self-heating propensity of coal. The adiabatic test of coal is conducted in a reaction vessel which has been designed to minimize heat loss and ideally act as a perfect insulation (Beamish, et al, 2000). The reaction vessel is placed inside an adiabatic oven which can be controlled automatically for adjusting the temperature to be equal to that of the coal in the reaction vessel. Consequently, there is no heat transfer between the oven environment and the coal sample. This requires the use of a data logging thermometer to monitor the temperatures of the coal and the oven. The inlet gas of oxygen is preheated before it flows into the reaction container. Through such control, it is ensured that only and all the heat generated by the oxidation of the coal sample is used to sustain the reaction and to raise the temperature of the coal. The self-heating rate is measured by monitoring the temperature development of the coal sample in the reaction vessel. The average hourly temperature in-

crease rate for the coal to self-heat from 40 °C to 70 °C under an adiabatic condition is used to classify the self-heating risk (Humphreys, 1981) as shown in Figure 3.1. Once the temperature increases above 70 °C, the rate of temperature change could accelerate leading to a possible thermal runaway. However, to maintain a perfect adiabatic condition is a difficult task for the adiabatic test methods. A best way to avoid heat loss is to minimize the temperature differences among the coal sample, the oven environment and inlet oxygen gas during the test.

Figure 6.1 Flow chart of model development

Although mathematical models have been developed to analyze the heat transfer in the coal, most of them are about coal stockpiles and few of them are developed for

adiabatic experimental condition. Beamish (2008) proposed a specific self-heating rate prediction equation for a high volatile bituminous coal. However, this empirical equation was about the calculation of R_{70} value using ash and sodium (Na_2O) contents. Smith and Glasser (2005) developed the heat transfer model using parameters such as heat capacity, heat of reaction, reaction rate, and activation energies determined from the experimental data (Smith and Glasser, 2005). Dick et al (1984) developed a one-dimensional model to describe the spontaneous heating process for dry coal at relatively low temperatures ($< 100\text{ }^\circ\text{C}$). The influence of moisture transfer on the maximum temperature rise has been analyzed using the simplified one-dimensional differential equations by Chen (1992). All of these mathematical models for describing the self-heating process were developed for coal stockpiles.

In this section, a mathematical model is developed to describe the heat generation and consumption in a R_{70} self-heating test setup and to quantify the elements that influence the accuracy of adiabatic testing method. Sensitivity of the imperfection in the testing setup and process is analyzed using the program under the condition that the oven temperature is lower, equal to or higher than the temperature of the coal. Temperature development curves predicted through mathematical model for samples from different coal seams are presented.

6.2.1 Energy Conservation Law

In the artificial adiabatic environment, the heat generated (H_g) by the coal will be consumed in terms of either heating the coal itself (H_c) or losing to the surroundings that is not used to heat up the coal (H_l). This heat generation and consumption forms obey the energy conservation law and can be expressed by the following equation

$$H_g = H_c + H_l \quad (6-1)$$

6.2.2 Conditions and Assumptions

Figure 6.2 shows the schematic diagram of the setup for R_{70} self-heating test. A 16-oz (473ml) aluminum vacuum thermo-bottle with excellent thermal insulation is used as the container for the coal sample to minimize the heat exchange through conduction. In order to increase the insulation, the container is wrapped with a 2-inch (50mm) thick

fiber glass insulation layer. The bottle is placed in a temperature-controlled oven. A crushed coal sample of mass m_c is placed in the bottle with one-half of its inside space occupied by coal. The coal sample is pre-dried in pure nitrogen environment before the self-heating process. During the self-heating test, oxygen is introduced through a coiled brass tube to the coal at a flow rate of Q_1 . The coiled tube is to keep the temperature of the oxygen flowing into the bottle at the oven temperature of T_0 . Two precise temperature sensors are used to measure the temperature of the coal sample T and that of the oven environment T_0 , respectively. Constant adjustment of the oven temperature is made to keep it as close to the coal temperature as possible. However, since the minimum adjustment to the oven temperature is 1°C , the temperature difference between the coal and oven could be up to 1°C .

Figure 6.2 Schematic diagram of R_{70} self-heating test setup

Based on the energy conservation law and the testing setup, the conditions and assumptions of the testing environment and test samples at a given time t for the mathematical model are as follows,

1. The temperature inside the test container at the given time t is $T(t)$ in K and the oven temperature is $T_o(t)$ in K.
2. The mass of coal sample at a given temperature is $m_c(T)$ in grams. It should be noted that as the coal oxidizes and the liquid water evaporates as the temperature increases, the mass of the coal sample will change.
3. The moisture content in the coal is $w_c(T)$ in percent of coal sample by weight.
4. The specific heat capacity of the coal at a given temperature is $C_c(T)$ in kJ/kg·K. It changes with temperature T and can be determined through a test and other method.
5. The air volume inside the container is V and is assumed to be constant. Its specific weight, $\rho(T, \omega)$ in kg/m³, depends on barometric pressure, temperature and relative humidity (ω).
6. The relative humidity of the air in the container is a function of temperature $\omega(t)$.
7. The steady oxygen inflow rate is Q_1 in m³/s containing no water content. Its specific weight is $\rho(T_o, 0)$ in kg/m³.
8. The flow rate of the exhaust gases is $Q_2(t)$ in m³/s and the psychrometric property is the same as that in the container.
9. The temperature of coal inside the reaction vessel is uniform and the thermocouple used to measure the temperature of the coal locally could represent the whole.
10. Since pure oxygen is used as reactant gas, it assumes the reaction is zero-order reaction.

6.2.3 Heat Generation and Consumption

The heats generated and consumed in a time interval between t and $t + dt$ are described as follows:

The total heat generated by the coal oxidation

$$dH = m_c(T) \cdot [1 - w_c(T)] \cdot h(T) \cdot dt \quad (6-2)$$

The total heat used to raise temperature of the coal

$$dH_1 = C_c(T) \cdot m_c(T) \cdot [1 - w_c(T)] \cdot dT \quad (6-3)$$

The heat to raise temperature of liquid water

$$dH_2 = C_f(T) \cdot w_c(T) \cdot m_c(T) \cdot dT \quad (6-4)$$

The heat to evaporate dw (in percent) of the liquid water into vapor at a given temperature T depends the heat of vaporization (h_{fg}) of water.

$$dH_3 = h_{fg}(T) \cdot w_c(T) \cdot m_c(T) \cdot dw \quad (6-5)$$

The heat to raise the temperature of moist air in the container

$$dH_4 = V \cdot \rho(T, \omega) \cdot C_g(T, \omega) \cdot dT \quad (6-6)$$

The heat lost to or gained from the incoming oxygen flow

$$dH_5 = Q_1 \cdot \rho(T_o, 0) \cdot C_o(T_o, 0) \cdot (T - T_o) \cdot dt \quad (6-7)$$

The heat carried away by the exhaust air

$$dH_6 = Q_2(t) \cdot \rho(T, \omega) \cdot C_g(T, \omega) \cdot (T - T_o) \cdot dt \quad (6-8)$$

The heat gained from or lost to the atmosphere inside the oven

$$dH_7 = f \cdot A \cdot (T - T_o) \cdot dt \quad (6-9)$$

6.2.4 Heat Generation Rate

Based on the law of energy conservation (Eq. 6-1), the heat generated by the coal (Eq. 6-2) should be equal to that used and lost (Eqs. 6-3 to 6-9).

$$dH = dH_1 + dH_2 + dH_3 + dH_4 + dH_5 + dH_6 + dH_7 \quad (6-10)$$

The heat generation rate of the coal at a given temperature can be determined as

$$h(T) = \left\{ C_c(T) + \frac{C_f(T) \cdot w_c(T)}{[1 - w_c(T)]} + \frac{V \cdot \rho(T, \omega) \cdot C_g(T, \omega)}{m_c(T) \cdot [1 - w_c(T)]} \right\} \cdot \frac{dT}{dt} + \frac{h_{fg}(T) \cdot w_c(T)}{[1 - w_c(T)]} \cdot \frac{dw}{dt} + \left\{ Q_1 \cdot \rho(T_o, 0) \cdot C_o(T_o) + f \cdot A + Q_2(t) \cdot \rho(T) \cdot C_g(T) \right\} \cdot \frac{(T - T_o)}{m_c(T) \cdot [1 - w_c(T)]} \quad (6-11)$$

Since the coal has been pre-dried with nitrogen, there is no or very insignificant amount of moisture left in coal during the self-heating process. The terms related to moisture in the equation can be dropped or ignored. The resulting equation for the heat generation rate becomes

$$h(T) = \left[C_c(T) + C_g(T) \frac{V \cdot \rho(T)}{m_c(T)} \right] \frac{dT}{dt} + \left[Q_1 \cdot \rho(T_o) \cdot C_o(T_o) + f \cdot A + Q_2(t) \cdot \rho(T) \cdot C_g(T) \right] \frac{T - T_o}{m_c(T)} \quad (6-12)$$

In equation 6-12, term $V \cdot \rho(T)$ is the mass of the gases in the container and is

denoted with $m_g(T)$; Term $Q_1 \cdot \rho(T_o)$ is the mass flow rate of oxygen entering the container and is rewritten as $\dot{m}_{O_2}$; Term $Q_2(t) \cdot \rho(T)$ is the mass flow rate of exhaust air and is replaced with $\dot{m}_e(t)$. Equation 6-12 is further shortened into Eq. 6-13.

$$h(T) = \left[C_c(T) + C_g(T) \frac{m_g(T)}{m_c(T)} \right] \frac{dT}{dt} + \left[C_o(T_o) \cdot \dot{m}_{O_2} + f \cdot A + C_g(T) \cdot \dot{m}_e(t) \right] \frac{T-T_o}{m_c(T)} \quad (6-13)$$

When the slow oxidation of coal occurs, heat generation rate from the coal per unit mass itself is determined by Eq. 6-14.

$$h(T) = Q \cdot k \quad (6-14)$$

In the equation, Q is the heating value of the coal per unit mass while k is the oxidation reaction rate that can be determined by the Arrhenius equation (Eq. 6-15).

$$k = A' e^{-\frac{E}{RT}} \quad (6-15)$$

Combining Eqs. 6-13, 6-14 and 6-15 will result in Eq. 6-16.

$$\left[C_c(T) + C_g(T) \frac{m_g(T)}{m_c(T)} \right] \frac{dT}{dt} + \left[C_o(T_o) \cdot \dot{m}_{O_2} + f \cdot A + C_g(T) \cdot \dot{m}_e(t) \right] \frac{T-T_o}{m_c(T)} = Q \cdot A' e^{-\frac{E}{RT}} \quad (6-16)$$

In the first part on the left side of Equation 6-16, the mass of the gases in the container, $m_g(T)$, is considerably smaller than that of coal, $m_c(T)$. The mass of the gases in the empty space inside the reaction vessel is in the order of 0.2 gram. The mass flow rates of the oxygen, $\dot{m}_{O_2}$ and exhaust gases, $\dot{m}_e(t)$, should be in the order of 0.06 gram/min. The property to reflect the heat convection from the reaction vessel to the oven environment, the product of $f \cdot A$, is determined to be 0.2×10^{-5} kJ/kg.s using a specially designed experiment.

In Eq. 6-16, only $C_c(T) \frac{dT}{dt}$ is the part of the heat generated from the coal that is used for heating the coal itself. It depends on the specific heat capacity of the coal and

can be determined from an experiment or other empirical method. The derivative $\frac{dT}{dt}$ is the temperature change rate of the coal at a given time determined by Eq. 6-17. In order to make $C_c(T)\frac{dT}{dt}$ truly represent the heat from coal oxidation, efforts should be made to minimize the other heat consumptions. The most direct way to minimize the heat exchange in the second part on the left side of Eq. 6-16 is to reduce the temperature difference between oven environment and the coal or $T - T_o$.

$$\frac{dT}{dt} = \frac{Q \cdot A' e^{-\frac{E}{RT}} - [C_o(T_o) \cdot \dot{m}_{O_2} + f \cdot A + C_g(T) \cdot \dot{m}_e(t)] \frac{T - T_o}{m_c(T)}}{C_c(T) + C_g(T) \frac{m_g(T)}{m_c(T)}} \quad (6-17)$$

6.2.5 Oxidation Time

The oxidation time ($\Delta t = t_2 - t_1$) is defined as the required time for a coal sample to reach from an initial temperature (T_1) to a temperature of interest (T_2) when the self-heating oxidation process occurs in an actual R₇₀ testing environment.

Rearranging Eq. 6-17 to separate time (t) and temperature (T) terms and then integrating both sides, the oxidation time is determined by Eq. 6-18.

$$\int_{t_1}^{t_2} dt = \int_{T_1}^{T_2} \frac{C_c(T) + C_g(T) \frac{m_g(T)}{m_c(T)}}{Q \cdot A' e^{-\frac{E}{RT}} - [C_o(T_o) \cdot \dot{m}_{O_2} + f \cdot A + C_g(T) \cdot \dot{m}_e(t)] \frac{T - T_o}{m_c(T)}} dT \quad (6-18)$$

Due to the difficulty for finding the close-form solution from Eq. 6-18, the numerical integration method, Simpson's 1/3 rule, is applied. A computer program based on the mathematical model has been developed.

6.2.6 Case Study

The coal sample obtained from the central Indiana has been tested for assessing the self-heating potential of its intrinsic property with the R₇₀ method. The cores were drilled in late November 2010 and shipped to our laboratory in mid-December of 2010. The coal samples were kept in sealed plastic bags and placed in refrigerator. The specific heat capacity, heating value, activation energy and pre-exponential factor for this sample were determined previously for the mathematical model. The methods to de-

termine a number of important input parameters describing the coal intrinsic property are discussed in this section.

- Heating Value

Among the coal proximate analysis parameters (i.e., moisture, volatile matter, fixed carbon and ash), volatile matter and fixed carbon could be the only sources for coal to generate the heat. The heating value of a coal can be determined using an empirical equation (Eq. 6-20) in which the volatile matter and fixed carbon in weight percent are independent variables. This empirical equation is derived from the USGS coal quality database. A total of 126 Indiana coal sample data were selected from the database to perform the multiple regression analysis. The resulting R^2 of the regression is 0.91 showing a good fit to the original data.

$$Q = 158.162 \cdot V_m + 146.853 \cdot F_c - 878.01 \quad (6-20)$$

Again, the volatile matter and fixed carbon can be determined experimentally using the TGA setup (Wang and Luo, 2011b).

- Activation Energy and Pre-exponential Factor

The activation energy and pre-exponential factor can be determined using TGA experimental procedure (Wang and Luo, 2011a). The TGA test on a coal would generate a complete weight-temperature curve. Based on the generated test curve, the activation energy and pre-exponential factor of the coal can be determined using Eq. 6-21. It is believed that the same treatment can be used to determine the activation energy and pre-exponential factor using the R_{70} self-heating test data in the section from the initial temperature 40 °C to thermal runaway point.

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left(\frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (6-21)$$

6.2.7 Results and Discussions

The R_{70} self-heating test has been conducted on the collected Indiana sample with the experimental setups as mentioned previously. Figure 6.3 shows the complete

self-heating curve in the 45-hour testing duration. It took about 35 hours for the temperature of this coal sample to increase from 40 °C to 70 °C giving a self-heating rate of 0.86 °C/hr. The coal sample demonstrated a thermal run-away characteristic afterwards and the temperature reached 105 °C at the end of the 45-hour testing period.

Figure 6.3 R₇₀ self-heating test and modeling results of coal from Indiana

The mathematical model of R₇₀ self-heating test developed is calibrated using the self-heating temperature development curve for the Indiana sample. The experimentally determined parameters to be used in the mathematical model are listed in Table 6.1.

Table 6.1 Parameters for the mathematical model

Parameters	Value	Unit
Air specific heat, C_g	1	kJ/kg·K
Sample weight, m_c	150	g
Coal heating value, Q	27,835.5	kJ/kg
Gas constant, R	0.008314	kJ/mol·K
Pre-exponential factor, A'	17,200	1/s
Activation energy (40-50 °C), E_1	62.5	kJ/mol
Activation energy (50-70 °C), E_2	65.0	kJ/mol

Using the mathematical model, the required oxidation time in a R_{70} test to reach a given temperature is determined and the results are shown in Table 6.2. In this table, the variation of specific heat capacity which is determined by empirical equation is also listed.

The coal experiences a fairly rapid self-heating process in the temperature range from 40 °C to 50 °C showing a convex curve. Actually, at the beginning of the test, physical and chemical adsorptions between coal and oxygen occurred first and generated a significant amount of heat. The activation energy E_1 (Table 6.1) deducted in this temperature range is smaller than the activation energy E_2 in the temperature range of 50 °C to 70 °C and in the later thermal runaway process. The values of E_1 and E_2 were experimentally determined by TGA in the two temperature ranges using Eq. 6-21. The simulation results are also plotted in Figure 6.3. Although the temperature development curves between the simulation and experiment still deviates to some degree, the general trends at the early and late stages agreed well. The model predicts the required time for the sample to reach from 40 °C to 70 °C to be 37.1 hours. The predicted R_{70} self-heating rate is 0.81 °C/hr agreeing fairly well with the test results.

Table 6.2 Results predicted by the mathematical model

Time (h)	Temperature (°C)	Specific Heat Capacity of Coal (kJ/kg·K)
0.00	40	1.23
4.85	45	1.24
21.26	50	1.25
27.34	55	1.26
31.67	60	1.26
34.80	65	1.27
37.11	70	1.28
38.86	75	1.29
40.20	80	1.30
41.25	85	1.30
42.10	90	1.31
42.81	95	1.32
43.40	100	1.33
43.91	105	1.33

Using the coal property parameters determined by TGA, the self-heating processes under adiabatic testing condition for the samples from the Pittsburgh and

Sewickley coal seams are also simulated. The simulation results are shown in Figure 6.4. The temperature rise in the early 30 hours testing stage agreed well with the laboratory test results. However, it shows the excessively long required time for conducting a complete R_{70} test for these two coals is impractical in laboratory condition. Another R_{70} self-heating test data of high rank coal, low volatile bituminous coal from Australia (Beamish, 2008b) was also plotted in Figure 6.4. The activation energy for the Australian coal in the self-oxidation process determined from the testing data is 71.4 kJ/mol which is less than that of 89.2 kJ/mol for Pittsburgh and 96.7 kJ/mol for Sewickley coals respectively resulting in the coal to be the earliest one to reach the thermal runaway.

Figure 6.4 . R_{70} Predicted self-heating curves of samples from the Pittsburgh and Sewickley coal seams

6.2.8 Sensitivity Analysis

Since the minimum adjustment to the oven temperature is 1 °C, the temperature difference between the coal and oven could be up to 1 °C. If the oven temperature is consistently 1 °C higher than that of the coal, the oven will add heat to the coal and it

forces the coal temperature to increase faster than it supposed to do. In this case, the self-heating curve will be the shaper one in Figure 6.5 shown as $T < T_0$. However, if the adjusted oven temperature is 1 °C lagging the coal temperature in the reaction container, part of the heat generated by the coal will be lost to the environment. The lost heat will make the self-heating process slower as shown in the figure as the one marked as $T > T_0$. Therefore, the imperfect testing environment could result in inaccurate self-heating rate.

6.3 Distributed Activation Energy Model

The R_{70} self-heating index test is considered to be a reliable method to evaluate the potential of coal self-ignition. However, for a coal with low propensity it is difficult to obtain a complete self-heating curve for the investigation of its thermal runaway characteristics - the critical information for assessing coal's spontaneous combustion.

Figure 6.5 Sensitivity analysis with different oven temperatures

The activation energy, as one of the input parameters in this model, plays an important role in the accuracy of the simulation results. Thermal gravimetric analysis

(TGA) test, requiring a short testing duration, can be used to determine the activation energy. The weight-gain stage is considered to be the initial stage of coal oxidation reaction. Activation energy in this stage is determined by the integral method based on the testing data. Differing from the current practice to only determine an average activation energy in the weight-gain stage, the relationship between temperature and activation energy can be determined. By assuming that the process consists of a set of irreversible first-order reactions with varying activation energy and a constant frequency factor, the complete R₇₀ self-heating process can be more accurately simulated with the mathematical model.

To calibrate the model, coal samples with self-heating propensity from low to moderate are tested on both R₇₀ and TGA setups. For the TGA tests, coal samples are tested on a TGA machine in an automatically and precisely controlled system with specified constant rates of temperature increment at 5, 10, 20 °C/min, respectively. The weight-temperature relation is recorded during the entire forced oxidation process of the coal and the data are used to derive the temperature - activation energy relationships. These relationships are used in the mathematical model to generate the simulated R₇₀ self-heating curves.

The distributed activation energy model (DEAM) has been widely used to analyze reactions as pyrolysis of fossil fuels. When the model is used to analyze coal pyrolysis, it can be expressed by Eq. 6-22

$$1 - \frac{V}{V^*} = \int_0^\infty \exp\left(-k_0 \int_0^t e^{-\frac{E}{RT}} dt\right) \cdot f(E) dE \quad (6-22)$$

where V^* is the total volatile matter of coal, V is the reacted volatile matter by time, $f(E)$ is the normalized distribution curve of the activation energy representing the differences in the activation energies of many reactions, k_0 is the frequency factor related to the E value which is assumed to be a constant.

Making the exponential expression in Eq. 6-22 equal to $\Phi(E, t)$, thus

$$\Phi(E, t) = \exp\left(-k_0 \int_0^t e^{-\frac{E}{RT}} dt\right) \quad (6-23)$$

with temperature increment rate β

$$T = T_0 + \beta t \quad (6-24)$$

$$dt = \frac{dT}{\beta} \quad (6-25)$$

Then $\Phi(E, t)$ becomes,

$$\Phi(E, T) = \exp\left(-\frac{k_0}{\beta} \int_0^T e^{-\frac{E}{RT}} dT\right) \quad (6-26)$$

where

$$\int_0^T e^{-\frac{E}{RT}} dT = \frac{RT^2}{E} e^{-\frac{E}{RT}} \quad (6-27)$$

$$\Phi(E, T) = \exp\left(-\frac{k_0 RT^2}{\beta E} e^{-\frac{E}{RT}}\right) \quad (6-28)$$

Eq. 6-28 was approximated by a step function at $E=E_s$ for a selected temperature T and the E_s was chosen to satisfy $\Phi(E_s, T) \approx 0.58$ then

$$\frac{0.545 \beta E_s}{k_0 RT^2} = e^{-\frac{E_s}{RT}} \quad (6-29)$$

Eq. 6-22 was then simplified to Eq. 6-30

$$\frac{V}{V^*} = 1 - \int_{E_s}^{\infty} f(E) dE = \int_0^{E_s} f(E) dE \quad (6-30)$$

This conversion approximates that only a reaction having E_s occurs at the specified T and β . For an actual reaction system, E can be estimated by Eq. 6-31 from the Arrhenius plot of β/T^2 at the selected V/V^* for different β .

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{k_0 R}{E}\right) + 0.6075 - \frac{E}{R T} \quad (6-31)$$

The procedure to estimate $E(T)$ using this method is as follows:

1. Measure V/V^* vs T relationships at three different heating rates.
2. Calculation the values of β/T^2 at selected V/V^* from the V/V^* vs T relationships obtained for different heating rates.
3. Plot $\ln(\beta/T^2)$ vs $1/T$ at the selected V/V^* values, and determine the E values from the Arrhenius plots at different V/V^* values using the relationship in Eq. 6-31. The E values corresponding to the V/V^* values can be obtained from the slope and the intercept in each Arrhenius plot.

As such, the KM4 sample was tested with TGA at three different heating rates at

5, 10, 20 °C/min. The selected V/V^* are from 0.1, 0.2, ... to 0.8. The Arrhenius plots at different V/V^* values are shown in Figure 6.6.

Figure 6.6 Linear regression of testing data at three heating rates for determination of activation energy

Through regression of the data E and T , the relationship between them is expressed in Eq. 6-35

$$E(T) = \frac{1}{(0.49917 - 0.38572 \cdot T^{0.039278})} \quad (6-35)$$

In this improved model, the variations of weight and air specific heat against temperature are also considered through regression analysis of TGA test data in the weight gain stage and air specific heat property from tool box. The regression analyses of those two parameters are shown in Figures 6.7 and 6.8. The corresponding equations are expressed as Eqs. 6-36 and 6-37. Then Eqs. 6-35, 36, 37 are substituted into Eq. 6-18 to calculate the self-heating curve with the improved model. Figure 6.9 shows the self-heating curve and testing data after incorporate these three equations. Unlike

the results with a big difference in the middle section of temperature rise determined by the previous model, it can be seen that the self-heating profile has a fairly good agreement with the testing data with the improved model.

Sample weight variation with temperature is expressed as follows:

$$m_c(T) = 151.454 + 1.421 \cdot \cos(0.021 \cdot T + 1.783) \quad (6-36)$$

Air specific heat variation with temperature can be determined as:

$$C_g(T) = 3.01 \times 10^{-7} \cdot T^2 + 4.32 \times 10^{-5} \cdot T + 1.0037 \quad (6-37)$$

Figure 6.7 Regression of weight variation against temperature

Figure 6.8 Regression of air specific heat variation against temperature

Figure 6.9 Comparison between the modeling results and testing data after improvement

6.4 Model Developed for Quantifying the Effects of Coal Quality Parameters

It is believed that sulfur and volatile matter contents in coals are the main intrinsic properties to cause the self-heating of coal. Their oxidation at lower temperatures than that of fixed carbon to initiate coal's self-heating should be quantified. This study is aimed to improve the previous mathematical model developed by the authors for studying the coal's propensity for spontaneous combustion. It enhances the model's ability to consider the effects of sulfur, volatile matter and moisture contents in the coal – three important factors affecting the coal's self-heating process. Sulfur exists in coal primarily in the form of pyrite which will be oxidized rapidly under suitable conditions. Volatile matters, higher in low rank coals, are more easily to be oxidized than the fixed carbon. The heat of water condensation provides initial energy for low temperature oxidation. The heat release rates for pyrite oxidation and moisture condensation are built in the model. Finally, the simulation results in terms of time versus temperature on pyrite oxidation and moisture condensation are validated with the adiabatic testing data respectively.

The R_{70} self-heating adiabatic test is considered to be a reliable method to evaluate the potential of coal self-ignition. However, for a coal with low propensity it is difficult to obtain a complete self-heating curve for the investigation of its thermal runaway characteristics - the critical information for assessing coal's spontaneous combustion. In this regard, a mathematic model has been developed by the author to simulate the coal's self-heating process in a R_{70} testing environment (Luo and Wang, 2012). This model can serve as a tool to assist the test plan design and to generate a complete self-heating curve when an experiment becomes impractically long. It can also quantify the effects of any imperfection of the testing adiabatic environment on the testing results for a R_{70} self-heating test setup. However, the previous model was developed base on the standard R_{70} testing procedure in which the coal was totally dried in nitrogen and then oxidized with oxygen at the initial temperature of 40 °C. In addition, it is simplified by assuming that the self-heating rate was not affected by other chemical and physical properties, such as, the oxidation of pyrite and volatile matter, moisture condensation, relative humidity and initial ambient temperature.

The primary role of water condensation was to supply an initial heat of adsorption which raised the temperature to a point where the oxidation reactions are self-sustaining (Guin, et al., 1986). The adsorption of moisture on a dry coal surface is an exothermic process generating heat. If the coal has been partially dried during its mining, storage, or processing, it has the potential to re-absorb moisture from environmental humidity and absorbs the condensation heat. This phenomenon is called heat of wetting. The higher the moisture contents of the coal, the greater the potential for this to occur, especially for low rank coals (Berkowier and Schein, 1951). Since low rank coals have larger internal surface which is proportional to the heat of wetting (Das and Hucka, 1986). The effects of moisture content and humidity on porous medium or stockpiled coal have been simulated using numerical modeling techniques (Gong, 2000; Gray et al., 2002, Zarrouk, 2004; Ejlali et al., 2011). An improved analytical model is developed based on mobile core theory, different from the Arrhenius kinetics on moisture condensation used in the numerical modeling.

Pyrite (FeS_2) and the related mineral marcasite exist frequently in coal (Speight, 1983). Pyrite oxidation takes place when the mineral is exposed to air and water (Li and Parr, 1926). The real cause of spontaneous combustion cannot be attributed to presence of pyrite, since it does not account for the numerous cases of the spontaneous combustion of coal in which sulfur is not present (Barr, 1900). However, it is an important factor in the spontaneous ignition of coal and cannot be disregarded in an off-hand way (Parr and Kressmann, 1910). It appears that pyrite may play a role in raising the temperature to a critical point (75-85 °C) at which the oxidation rate is sufficiently high to support further spontaneous heating and eventual ignition at a higher temperature (Li and Parr, 1926). Beamish, et al., (2012) conducted a test to investigate the influence of reactive pyrite on self-heating of a high volatile bituminous coal containing sulfur content from 0.62% to 17.95% with a moist coal adiabatic oven. It is found that as the pyritic sulfur content increases the time needed for thermal runaway to occur decreases.

The higher the amount of volatile material in coal, the more likely the coal suffers from spontaneous combustion (McSherry, 1998). At least to a certain extent the process of coal oxidation might be attributed to an increase in volatile matter content. Nordon et

al. (1979) found that an 8-fold decrease in volatile matter content caused a 3- to 5-fold decrease in the oxidation rate.

In this section, the mathematical model has been improved by quantifying the effects of pyrite and volatile matter oxidation, moisture condensation, and relative humidity variation on the process of coal self-ignition. Heat release rates of pyrite oxidation and moisture condensation have been derived theoretically with shrinking core and mobile core models. The improved model is considered to be the first mathematical description that correlates coal and the effects of pyrite and moisture to the propensity of spontaneous combustion. Experiments were performed with specially designed procedures to verify the improved model.

6.4.1 Quantification of Pyrite Oxidation

The shrinking core model has been used to describe pyrite oxidation and pollutant leaching processes in waste dump sites (Levenspiel 1972, Cathles and Apps 1999, Singh and Doulati Ardejani 2004). This model combined surface reaction with accumulation of product layer on the surface. The following major assumptions have been made in applying the shrinking core model:

1. The reaction rate is first-order with respect to the principal gas reactant and the surface area of remaining solids.
2. Chemical reaction governs the pyrite oxidation. The ash layer has a structure with high porosity. The progress of reaction is unaffected by ash layer.
3. Pyrite particle is isothermal, and the reaction process is in a pseudo-steady-state, in which the diffusion rate of gaseous reactant through the ash layer outside the unreacted core is much faster than the rate of core shrinkage.
4. All the pyrite particles are in the shape of spherical without changing size during the reaction.

Concentration gradients of reactants and shrinkage of the unreacted core are illustrated as shown in Figure 6.10. The pyrite particle with radius r_{ps} is partially oxidized having an unreacted core with radius r_{pc} inside. The particle is exposed to the gaseous environment. The gas in the bulk phase with highest concentration C_{Ag} gradually decreases to C_{As} at the surface of the particle through the gas film and eventually to concentration C_{Ac} at the moving reaction surface through the ash layer. Moving along with

the shrinkage of the core, the ash layer becomes thicker and thicker resulting in the decrease of gas concentration before it reaches the unreacted core.

Figure 6.10 Representation of reactants and products for the reaction, $A(g)+bB(s) \rightarrow \text{products}$ for a shrinking core model

In a pseudo steady-state, the rate of oxygen diffusion into the particle from the bulk phase is equal to the rate of oxygen diffusion to the unreacted core through the ash layer which is also equal to the rate of reaction of oxygen with the unreacted core. The rate of oxygen diffusion is

$$-\frac{dn_p}{dt} = 4\pi r_{ps}^2 \cdot k_g \cdot (C_{Ag} - C_{As}) \quad (6-38)$$

In Eq. 6-38, k_g is the mass transfer coefficient between fluid and particle, n_p is moles of pyrite. The negative sign means the depletion of the pyrite in the reaction. The rate of oxygen diffusion to the unreacted core through the ash layer is

$$-\frac{dn_p}{dt} = 4\pi r_{pc}^2 \cdot D_e \cdot \left(\frac{dC_A}{dr} \right)_{r=r_{pc}} \quad (6-39)$$

where D_e is the diffusion coefficient, C_A is the gas concentration at any radius of r in the ash layer.

The rate of reaction of oxygen with the unreacted core is

$$-\frac{dn_p}{dt} = 4\pi r_{pc}^2 \cdot k_p \cdot C_{Ac} \quad (6-40)$$

where k_p is reaction rate constant of pyrite.

In general, the rate of oxygen diffusion in the region $r_{pc} \ll r \ll r_{ps}$ is determined by the following equation

$$\frac{d}{dr} \left(r^2 \cdot D_e \cdot \frac{dC_A}{dr} \right) = 0 \quad (6-41)$$

Integrate the Eq. 6-41 with the boundary conditions, $C_A = C_{As}$ at $r = r_{ps}$, $C_A = C_{Ac}$ at $r = r_{pc}$, the following equation is obtained to represent the function of gas concentration C_A at any radius r .

$$C_A - C_{Ac} = (C_{As} - C_{Ac}) \frac{1 - \frac{r_{pc}}{r}}{1 - \frac{r_{pc}}{r_{ps}}} \quad (6-42)$$

Take the first derivative of Eq. 6-42 at $r = r_{pc}$, then it becomes

$$\left(\frac{dC_A}{dr} \right)_{r=r_{pc}} = \frac{C_{As} - C_{Ac}}{r_{pc} \left(1 - \frac{r_{pc}}{r_{ps}} \right)} \quad (6-43)$$

Substitute Eqs. 6-38, 6-39 and 6-40 into Eq. 6-43 to eliminate the unknowns C_{As} and C_{Ac} , then

$$-\frac{dn_p}{dt} = 4\pi r_{ps}^2 \cdot C_{Ag} \left[\frac{1}{k_g} + \frac{r_{ps}(r_{ps} - r_{pc})}{D_e r_{pc}} + \frac{r_{ps}^2}{k_p r_{pc}^2} \right]^{-1} \quad (6-44)$$

The fractional conversion of pyrite can be written as

$$x_p = 1 - \left(\frac{r_{pc}}{r_{ps}} \right)^3 \quad (6-45)$$

Substitute Eq. 6-45 into Eq. 6-44 and then integrate Eq. 6-44. We find the time required for conversion is

$$t = \frac{\rho_p}{b \cdot M_p \cdot C_{Ag}} \left\{ \frac{r_{ps}}{3k_g} x_p + \frac{r_{ps}^2}{6D_e} \left[1 - 3(1 - x_p)^{\frac{2}{3}} + 2(1 - x_p) \right] + \frac{r_{ps}}{k_p} \left[1 - (1 - x_p)^{\frac{1}{3}} \right] \right\} \quad (6-46)$$

where M_p is molar mass of pyrite, ρ_p is density of pyrite.

Take the first derivative of Eq. 6-46, the reaction rate of pyrite is

$$\frac{dx_p}{dt} = \frac{3b \cdot M_p \cdot C_{Ag}}{\rho_p \cdot r_{ps}} \left[\frac{1}{k_g} + \frac{2r_{ps}}{D_e(1-x_p)^{\frac{1}{3}}} + \frac{1}{k_p(1-x_p)^{\frac{2}{3}}} \right]^{-1} \quad (6-47)$$

Since the particle size of the samples in the test are all less than or equal to 212 μm , it assumes the pyrite oxidation process are chemical controlled according to assumption 2. In other words, pyrite can be oxidized thoroughly without ash layer accumulated outside the particle. Therefore, the oxidation rate of the unreacted core becomes

$$\frac{dx_p}{dt} = \frac{3b \cdot k_p \cdot M_p \cdot C_{Ag}}{\rho_p \cdot r_{ps}} \left(1 - \frac{t \cdot b \cdot k_p \cdot M_p \cdot C_{Ag}}{\rho_p \cdot r_{ps}} \right)^2 \quad (6-48)$$

For n moles, the heat generation rate by the oxidation of pyrite is

$$n \frac{dx_p}{dt} H_p = \frac{3\phi_p \cdot m_t \cdot b \cdot k_p \cdot C_{Ag}}{\rho_p \cdot r_{ps}} \left(1 - \frac{b \cdot k_p \cdot M_p \cdot C_{Ag}}{\rho_p \cdot r_{ps}} \cdot t \right)^2 H_p \quad (6-49)$$

In Eq. 6-49, $n = \frac{\phi_p \cdot m_t}{M_p}$ and $C_{Ag} = \frac{P}{RT}$. ϕ_p is pyrite content in the coal, P is the standard atmospheric pressure, H_p is the heat generated in the pyrite oxidation. The heat production of the oxidation of pyrites has been studied by Parr and Kressman (1910). The reaction could generally be presented by the following equation:

6.4.2 Quantification of Volatile Matter Effects

Considering the coal proximate analysis parameters (i.e., moisture, volatile matter, fixed carbon and ash), volatile matter and fixed carbon could be the main sources for coal to generate the heat. An empirical equation (Eq. 6-51) related to volatile matter ϕ_v and fixed carbon ϕ_c in weight percent has been developed based on USGS coal qual-

ity database (Luo and Wang, 2012). On the one hand, higher volatile matter creates higher heating value which contributes to the rate of temperature increased.

$$Q = 2.326 \cdot (158.162 \cdot \phi_v + 146.853 \cdot \phi_c - 878.01) \quad (6-51)$$

On the other hand, at the beginning of coal oxidation, volatile matter is more easily to be oxidized than fixed carbon with a small amount of activation energy. The less the activation energy is needed, the easier the volatile matter will be oxidized. Low rank coals contain more volatile matters which increase the chances for the coal to be oxidized with small amount of activation energy. Therefore, the low rank coals have higher potential of self-heating. Up till now, there have been no investigations reported on how the volatile matter affects the spontaneous combustion. Therefore, activation energy provides an additional way to quantify the effect of volatile matter on the coal self-ignition.

The activation energy and pre-exponential factor can be determined by Eq. 6-52 through TGA experimental procedure (Wang and Luo, 2011).

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left(\frac{A'R}{\beta E_c} \right) - \frac{E_c}{RT} \quad (6-52)$$

where α is the fractional conversion, R is the gas constant, E_c is the activation energy, β is temperature increment rate, A' is the pre-exponential factor.

6.4.3 Quantification of Moisture Condensation Effects

In the adiabatic condition, an isothermal coal particle with radius r_0 and temperature T is presented in a gaseous environment at the same temperature. Evaporation or condensation takes place on the surface of core with radius r_c . Water vapor concentration in the bulk phase is C_{vb} which is affected by the relative humidity, RH. Water vapor concentration inside the coal is C_{vc} , as shown in Figure 6.11. In a pseudo steady-state, the liquid moisture in the core is in equilibrium with moisture in the form of vapor. The rate for water vapor to diffuse into the particle from the bulk phase is equal to rate of moisture concentration gradient in the core.

Bhat and Agarwal (1996) developed a mobile core model to quantify the effect of moisture condensation on the rate of oxidation of coal. In this dissertation, Eq. 6-53 is

proposed and incorporated into the model. . It relates the moisture content to the radius of the inner core and the coal particle and assumes the radius of the core equals zero as the initial condition. When the radius of the inner core is $r_c = 0$, the moisture content is $\phi_m = 0$. When moisture condensed, both r_c and ϕ_m gradually increase to $r_c = r_0$.

$$\frac{r_c}{r_0} = \phi_m^{\frac{1}{3}} \quad (6-53)$$

Figure 6.11 Single coal particle with a moisture core

The heat generation rate by water condensation in N particles is

$$N \frac{d}{dt} \left(\frac{4}{3} \pi r_c^3 C_0 \right) H_{vap} = \frac{(1-\phi_p) \cdot m_t}{\rho_p} \frac{3\phi_m^{\frac{1}{3}}}{r_0^2} \frac{D_e \cdot Bi_M \cdot (C_{vb} - C_{vc})}{Bi_M \cdot \left(1 - \phi_m^{\frac{1}{3}} \right) + \phi_m^{\frac{1}{3}}} H_{vap} \quad (6-54)$$

In the above equation, C_0 is the concentration of liquid moisture, H_{vap} is the heat of moisture condensation, Bi_M is mass transfer Bi_{ot} number, $Bi_M = 2k_g \cdot r_0 / D_e$.

The equilibrium relation between liquid moisture in the core and water vapor at the surface of the core within the coal is assumed to follow the Brunauer-Emmett-Teller (BET) equation. The ratio of the equilibrium and saturation vapor pressures can be written as

$$\theta = \frac{\sqrt{c}-1}{c-1} \quad (6-55)$$

In this equation, c is BET constant which is listed in Table 6.3. Then the concentration of water vapor in the bulk phase and on the surface of the core is determined as

$$C_{vb} = \frac{R_H \cdot P_v}{RT} \quad (6-56)$$

$$C_{vc} = \frac{\theta P_v}{RT} \quad (6-57)$$

The Antoine equation is used to represent the saturation vapor pressure,

$$P_v = \ln \left(A_1 - \frac{A_2}{T - A_3} \right) \quad (6-58)$$

In the equation, A_i is Antoine constants and $A_1=10.196$, $A_2=1730.63$, $A_3=-39.574$. Base on the energy conservation law, the energy balance of the coal in the adiabatic condition can be written as

$$\left[c_c(1 - \phi_p - \phi_m)m_t + m_g c_g \right] \frac{dT}{dt} = (1 - \phi_p - \phi_m)m_t k_c Q + n \frac{dx_p}{dt} H_p + N \frac{d}{dt} \left(\frac{4}{3} \pi r_c^3 C_0 \right) H_{vap} \quad (6-59)$$

6.4.4 Solutions and Discussions

The ordinary differential equation, Eq. 6-59, was solved using the fourth-order Runge-Kutta method with the fixed parameters listed in Table 6.3 to obtain the relationship between temperature variation and time with initial condition, $T = T_{initial}$ at $t = 0$.

Table 6.3 Fixed parameters used in the model

Parameter	Value	Reference
Coal specific heat, c_c	1.38 kJ/kg·K	Tool Box
Air specific heat, c_g	1 kJ/kg·K	
Standard atmospheric pressure, P	1.01×10^5 Pa	
Gas constant, R	8.314 J/mol·K	
Pyrite density, ρ_p	5.01×10^3 kg/m ³	
Molar mass of pyrite, M_p	120 g/mol	
mass of the gases, m_g	0.2 g	Luo and Wang, 2012
Activation energy of coal, E_c	63 kJ/mol	
Stoichiometric number, b	1/7	Parr and Kressman, 1910
Heat generation per mole from pyrite oxidation, H_p	268.6 kJ/mol	
Pyrite reaction rate constant, k_p	9.91×10^{-3} m/s	Clark, 1965
Radius of pyrite particle, r_{ps}	1.06×10^{-4} m	Testing procedure
Radius of coal particle, r_0	1.06×10^{-4} m	
Heat of moisture condensation, H_{vap}	44.3 kJ/mol	Hartman, et al., 1998
Molecular diffusivity of water vapor, D_e	1.78×10^{-5} m ² /s	Bhat and Agarwal, 1996
Mass transfer Biot number, Bi_M	2	
BET constant, c	12	

Moisture content, volatile matter, fixed carbon, pyrite content in weight percent and total mass of the coal are independent variables in the model and can be changed as input to perform the self-heating simulation. This model is considered to be the first theoretical description that facilitates adiabatic test to generate a complete self-heating curve using coal quality test data as input parameters which can be easily obtained through proximate analysis. Comparison of the simulation results between the previous model and the improved model is shown in Figure 6.12. As the solid line indicates, without consideration of the effect of pyrite and moisture condensation, the self-heating curve simulated by the previous model spends more than 225 hours to reach 160°C from initial temperature of 30°C. For comparison, the self-heating process of a sample with 10% of pyrite and 15% of moisture condensation with the same fixed parameters listed in Table 6.3 is simulated by the improved model. As the dash line shows in Figure 6.12, only 20 hours is spend for the sample to reach 160°C from the same initial temperature.

Figure 6.12 Comparison of the simulation results between the previous model (solid line) and the improved model (dashed line)

To validate the model two cases were considered with the adiabatic testing data from experiments conducted by Beamish et al., 2012 and Kuchta et al., 1980 on the pyrite oxidation and moisture condensation, respectively.

Case I is used to investigate the effect of pyrite oxidation on coal self-heating rate. Coal samples with different pyrite contents, 4.93%, 8.10% and 19.53% (Coal A, B and C listed in Table 6.4), were selected representatively to perform the adiabatic tests starting at the ambient temperature around 25 °C (Beamish, et al., 2012).

Table 6.4 Coal quality analysis of the samples for modeling

Sample	Moisture (%)	Volatile Matter (%)	Fixed Carbon (%)	Ash (%)	Sulfur (%)
Coal A	12.7	38.0	41.4	7.9	4.93
Coal B	11.7	34.8	37.8	15.7	8.10
Coal C	10.3	25.1	35.3	29.3	19.53
Coal D	11.7	38.0	46.9	3.4	0.60

In the test, 200g samples of crushed coal (<212 µm) are placed in the reaction vessel and then oxidized in pure oxygen environment. Differing from the traditional R₇₀ test, in which, the samples are dried before oxidation, the coals were tested with its as-received moisture. In the modeling, it assumes the pyrite oxidation is chemical controlled without ash layer accumulated outside the particles. No moisture condensation is considered since the samples are not dried in this case. Coal quality analyses of the samples for modeling are listed in Table 6.4.

The effect of pyrite on the temperature history is shown in Figure 6.13. It can be seen from the plot that the temperature of the coal with highest pyrite content of 19.53% increased most rapidly to reach the thermal runaway which was considered to start at 100 °C. On the other hand, the temperatures increasing rates of the coal with pyrite content at 8.10% and 4.93% are smaller and smaller showing a slow temperature rise. In this case, the model results and experimental data show good agreement with each other between 25 °C and 100 °C and both of the temperature experienced a rapid rise. However, inconsistencies appear after the temperature reaches 100 °C. The experimental results show that all the samples' temperature followed by a gradual increase after 100 °C, and then grew very sharply again. This could be caused by the following reason: the samples used for the experiment are not dried before the tests are performed. Part of the heat generated by oxidation of pyrite and coal are consumed for

evaporating the moisture contained in the samples after 100 °C, which might be the case that retards the temperature rise slower than it should be.

Figure 6.13 Comparison between model results and experimental data for the self-heating rate of coal affected by different pyrite contents

Case II is used to validate the model on the effect of moisture condensation on the self-heating rate of coal. A sub-bituminous coal (Coal D in Table 6.4) of 100 g was first ground to the size of 100-200 mesh and then thoroughly dried to eliminate the inherent moisture content of 11.7%. After that the sample was cooled down to the ambient temperature around 30 °C and oxidized in saturated moist air and dry air respectively (Kuchta, et al., 1980). The comparison between model results and experimental data are shown in Figure 6.14. With 11.7% moisture condensed, the heat of wetting was apparently sufficient to promote self-heating of this coal in moist air and made the coal to reach the thermal run away only within 7 hours. The contribution to the heat release from 5% moisture condensation was only demonstrated by the modeling results as reference. The almost half less moisture condensation doubled the time (14h) to reach the

temperature of 100 °C. On the other hand, without the heat from moisture condensation, temperature of this sub-bituminous coal displayed no rise from beginning to the end within 18 hours indicating the heat generated was insufficient to produce a sustained reaction. The results follow the same trends determined by critical self-heating temperature (CSHT) method proposed by U.S. Bureau of Mines (USMB). In their empirical equation, the higher moisture content, the smaller self-heating temperature obtained and the greater the potential of spontaneous combustion to occur.

Figure 6.14 Comparison between model results and experimental data for the self-heating rate of coal affected by moisture condensation

This model was also allowed to study the effects of activation energy, relative humidity and initial temperature on the self-heating rate of the coal.

Activation energy as the reflection of the effect of volatile matter on coal's spontaneous combustion has significant influence on the temperature variation as shown in Figure 6.15. The less the activation needed in the process of volatile matter oxidation, the faster the temperature of the coal increases. The R_{70} self-heating rate for the first condition with activation energy of 50kJ/mol is 2.5°C/h and the time to reach thermal

runaway is 30 h. The R_{70s} for the coals with activation energies of 55 kJ/mol and 60 kJ/mol slowed down to 0.4 °C/h and 0.25 °C/h, respectively.

Figure.6.15 Effect of activation energy on the self-heating rate of coal

The dangerous scenario will appear when dry coal is exposed in an environment with high relative humidity. The coal is dried by a hot dry weather in summer would be subjected to self-heating after a light rain. If the coal partially dried during its mining, storage, or processing, with the potential to re-absorb moisture in a humid condition, the coal will produce heat. The impact of relative humidity is demonstrated in terms of self-heating curves as shown in Figure 6.16. As the relative humidity enhances from 40% to 100% at what temperature, the time spent for the temperature rise to thermal runaway at 100 °C is shortened for 30 h.

The effect of ambient temperature was also investigated using the model. As shown in Figure 6.17 the initial temperature contributes significantly to the coal self-heating. At the initial temperature of 70 °C, the modeled curve reach ignition portion within a very short period. For the cases with initial temperatures at 40 °C and 23 °C, the temperature developed nearly at a constant increasing rate before grew up sharply

to the ignition.

Figure 6.16 Effect of relative humidity on the self-heating rate of coal

Figure.6.17 Effect of initial temperature on the self-heating rate of coal

As the modeling results show, high pyrite, and moisture contents promote the temperature increasing rate. High relative humidity and initial temperature play an important role in shortening the time for temperature rise leading to ignition.

6.5 Summary

A mathematical model has been developed for R_{70} self-heating test for propensity of coal spontaneous combustion. The model can be used for various purposes such as to quantify the setup imperfections that may influence the accuracy of the testing results. The parameters reflecting the intrinsic property of coals such as specific heat capacity, heating value, activation energy and pre-exponential factor required as input data can be determined experimentally or by other empirical methods. The model shows a promising sign of being useful. The activation energy, an indicator of the propensity for spontaneous combustion, required for coal to continue its self-heating process is the most important input parameter. The model also shows that precise control of the oven temperature to equal that of the testing coal determines the accuracy of the testing results.

The mathematical model, which was developed based on the R_{70} self-heating test for studying the spontaneous combustion of coal, has been improved by quantifying the effects of pyrite and volatile matter oxidation, moisture condensation, and relative humidity variation on the process of coal self-ignition.

Heat release rates of pyrite oxidation and moisture condensation have been derived theoretically with shrinking core and mobile core models.

In the improved model, moisture content, volatile matter, fixed carbon, pyrite content in weight percent and total mass of the coal are independent variables and can be changed to perform the self-heating simulation. This model is thought to be the first theoretical description that facilitates adiabatic test to generate a complete self-heating curve using coal quality results as input parameters which is easy to be available through proximate analysis.

CHAPTER 7 CONCLUSIONS AND PROSPECTS FOR THE FUTURE RESEARCH

7.1 General Conclusions

Spontaneous combustion creates not only safety problems to surface and underground coal mines, but also causes problems in storage and transportation worldwide. Due to the complexity of chemical and physical properties of coal, spontaneous combustion is affected by many factors such as pyrites, moisture, volatile matter, coal rank, etc. Various methods for assessing the tendency of self-ignition of coal have been developed. Those factors and methods have been studied in this dissertation. In order for better understanding and reliable prediction of spontaneous combustion for further safety and health improvement, this dissertation dedicates to reveal the mechanism of this phenomenon and to facilitate risk assessment and hazard management. This research work draws the following conclusions:

- Evaluation facilities for propensity of spontaneous combustion have been established in mine ventilation lab. This testing platform has combined three widely used methods, R_{70} method, TGA method and USBM method for further improving the certainty and reliability of evaluation. Coal samples from a number of U.S. and Chinese coal fields have been collected and tested using these three methods.
- In the R_{70} method, the self-heating rate of the samples reacted with dry oxygen are far less than that of the samples oxidized in moist oxygen. Indiana sample appears the highest potential of self-ignition in dry oxygen conditions. However, in the moist oxidation environment, the low rank coals, PRB and BBCC, show extremely high tendency of self-ignition and reach thermal runaway only within several hours. For the higher rank coals, the propensity of spontaneous combustion determined by this method is low.
- In the TGA tests, Indiana sample has more significant weight gain stage and smallest activation energy than the other samples. The potential of self-ignition classified based on activation energy is: KM4 > KM3 > Suancigou No.6 > New Elk > Suancigou No.4 > Nanyangpo No.4 > Sewi WV > Sewi GM1012 > Pittsburgh > Xuandong No.3 > Nanyangpo No.3 >

Murray > WR > Sewi GM1013 > FR0913/14 > FR0804 > FR0809 > FR0803 > FR0910 > FR0801 > FR0802.

- In the USBM method, propensity of spontaneous combustion has been determined by proximate analysis results. The TGA setup can be used as an alternative method for proximate analysis for coal quality parameters which in turn can be used to determine critical self-heating temperature through an especially designed testing procedure. The original USBM method for prediction of SHT has been improved with testing results derived from two USBM technical reports.
- Quantified coal rank system has been developed for U.S. coals based on the Suggate ranking principle. The relationship of quantified coal rank and SHT could serve a quick estimate of the propensity of U.S. coals can be treated as a very cost effective way for initial risk assessment for any new mine development.
- A mathematical model has been developed for prediction of self-heating rate in an adiabatic environment for coal oxidation. Then the model is improved by quantifying the effects of pyrite and volatile matter oxidation, moisture condensation, and relative humidity variation on the process of self-ignition.

7.2 Recommendations for Future Research

Based on the research findings in the dissertation, the following work is recommended for the future studies:

- Experimental techniques and setups that take into account more relevant causative factors should be developed to assist testing of spontaneous combustion.
- More samples covered full range of ranks need to be tested with these three methods to establish a database for recording the spontaneous combustion properties for all kinds of coal.
- Correlate self-heating potentials of coal determined in the lab to self-heating time of coal in real mines to provide a reliable guidance and quick

estimate of propensity of self-ignition.

- Conduct the experiments on studying the effect of chemical retardant on inhibition of spontaneous combustion. Quantify the amount of retardant application for different kinds of coal.
- Develop retardant pumping techniques and field application for mitigation of spontaneous combustion in gob area and coal stockpile.

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