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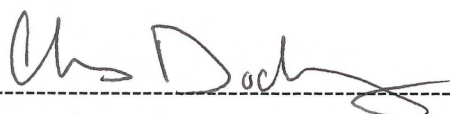
**INVESTIGATION OF SPONTANEOUS COMBUSTION INHIBITION OF COAL
FIRES UTILIZING DIFFERENTIAL SCANNING CALORIMETRY AND
THERMOGRAVIMETRIC ANALYSIS**

by

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B.S. Biochemistry
Kennesaw State University, 2013

Submitted in Partial Fulfillment of the Requirements
For the Degree of Master of Science in the
Department of Chemistry and Biochemistry
Kennesaw State University
May, 2015



Committee Chair



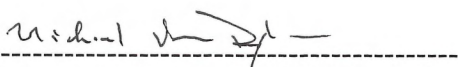
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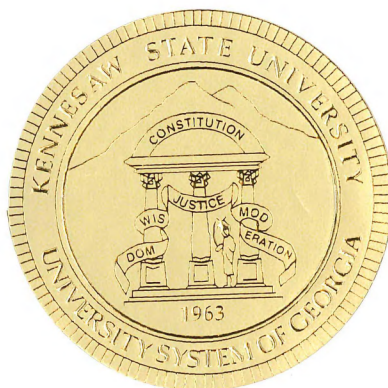
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ABSTRACT

Self-oxidation of coals can result in spontaneous combustion events at any time during mining, transporting, or processing, causing environmental, economical, and safety concerns. The total global primary coal production as of 2012 was 8.7 billion tons. Of that, 1.1 billion tons of coal was mined in the US, which accounts for 41% of the domestic electricity production. Spontaneous coal combustion, although dependent on coal rank, is a naturally occurring phenomenon that often causes damage to industrial and commercial facilities and freight, reduces the caloric value of coal, can release noxious gases and particulate matter, and increases CO₂ pollution levels locally and globally. Through the self-oxidation process, as heat accumulates, the internal temperature of the coal continues to rise over time and if left unaltered will lead to spontaneous coal fires. Thus there is a definite need for means to suppress this process. In this study, we investigated methods of spontaneous coal combustion inhibition. During experimentation, coal was ground into a fine dust (500 microns in diameter) and treated with inorganic phosphate and sulfonate salts combined with anionic and non-ionic surfactant blends. Each ingredient was applied to the surface of unreacted coal in combination, systematically varying the concentrations of each component, to reach a cost-effective and efficient formulation. Multiple approaches including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to analyze these effects. Results showed these novel formulations can reduce spontaneous combustion potential, making coal more thermally stable. Mechanisms by which these formulations inhibit coal spontaneous combustion are proposed.

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CHAPTER 1. INTRODUCTION

1.1 Coal Classification and Ranking

Coal is a substantial resource that has been exploited by for its uses as fuel and heat source. Coal consists of organic material that is remnants of organic life that has undergone millions of years of deposition and compaction. This matrix of carbonaceous material was subjected to increasing heat and pressure below the Earth's surface. This caused physical and chemical changes in the organic matter, transforming it into coal.¹ The quality of each coal deposit is determined by the amount of fixed carbon within the matrix and is dependent upon the depths of the burial, temperature and pressure at those depths, and the length of time the coal deposit has been forming. The degree of change over time undergone by a coal as it matures from lignite to anthracite is known as coalification.² Coalification has an important bearing on coal's physical and chemical properties and as a result is referred to as the rank of the coal.² Ranking is determined by the degree of transformation of the residual organic matter into carbon. The ranks of coals, from those with the least carbon to the most carbon, are lignite, sub-bituminous, bituminous and anthracite.

Early in the coalification process, lignite deposits are formed under the Earth's crusts at low depths. In comparison to other coals, lignite is quite soft and its color can range from dark black to various shades of brown. Since this coal type has undergone the

shortest amount of time during the formation process and has not been subjected to high heat and pressure as compared to higher ranked coals, it is thought to have low organic maturity.³

If coalification is allowed to progress over many more millions of years, the continuing effects of temperature and pressure produces further change in the lignite, progressively increasing its organic maturity and transforming it into the range known as 'sub-bituminous' coal. Further chemical and physical changes occur until these coals become harder and blacker, forming the bituminous type coals. Under the right conditions, the progressive increase in the organic maturity can continue, finally forming anthracite.²

In addition to carbon, coals contain hydrogen, oxygen, nitrogen and varying amounts of sulfur. High-rank coals are high in carbon but low in hydrogen and oxygen and therefore have a high heat content. Low-rank coals are low in carbon but are high in hydrogen and oxygen content therefore have a lower heat content. The heat content is measured in the number of British thermal units (Btu) per pound of coal. This value is particularly important for electricity and steel production. The heat content of coal is determine by the amount of energy generated through combustion to raise one pound of water one degree Fahrenheit known as one Btu.⁴ For example, one pound of coal that has a heat content of 8000 BTU can raise 8000 pounds (lbs) of water by 1 °F. The significance of the heat content of the coal is the amount of energy available per pound of coal. Energy is produced by coal combustion which generates steam that drives turbines that create mechanical energy in the form of electricity.

Low-rank coals, such as lignite and subbituminous coals, are typically softer, brittle materials with a dull, earthy appearance. They are characterized by high moisture levels and low carbon content, and therefore a low energy content. Higher rank coals are generally harder and stronger and often have a black luster. They contain more carbon, have lower moisture content, and produce more energy. Anthracite is at the top of the rank scale and has a correspondingly higher carbon and energy content and a lower level of moisture.²

Coal can be found throughout various regions of the country. Lignite, characterized by high moisture content and low carbon content, can be found in low-lying regions especially in coastal areas throughout the southern, gulf coast region of the contiguous states. Sub-bituminous coal is found primarily in the western parts of the country. Values of moisture, carbon, and heat content of sub-bituminous type coals fall between lignite and bituminous type coals but are still characterized by high moisture levels and low carbon content. The Powder River Basin (PRB) which comprises of northeast Wyoming and southeast Montana produced 407 million tons of sub-bituminous coal which equals 41.4% of total coal production in the U.S. in 2013.⁵ The demand for coal out of this region is high due to the low sulfur content and moderate heat content. Typical sulfur percentages range between 0.2%-0.6% for PRB coal. Burning coal with low amounts of sulfur reduces the amount of H₂S and SO₂ released into the atmosphere and reduces the costs associated with removing sulfur during the burning process. Bituminous type coals are typically found in interior regions of the U.S. where organic maturity is the greatest. Coal in these regions of bituminous deposits has been subjected

to long periods of heat and pressure compacting the organic material into a dense layer of carbon. These regions include Appalachian deposits and Interior Basin deposits.

1.2 Coal's Influence in Society

Coal has become a significant part of modern society. It is a substantial natural resource and is widely consumed for electricity, iron, steel, and concrete production as well as other industrial uses. In 2013, world coal production reached approximately 8.69 billion short tons (mass unit used by the coal industry equal to 2000 lbs) and generated 41.0% of the world's electricity needs. The U.S. produced nearly 11.7% of the world total at 1.02 billion short tons ranking them the second largest world coal producer. China ranks highest in total coal production at 4.02 billion short tons.⁶

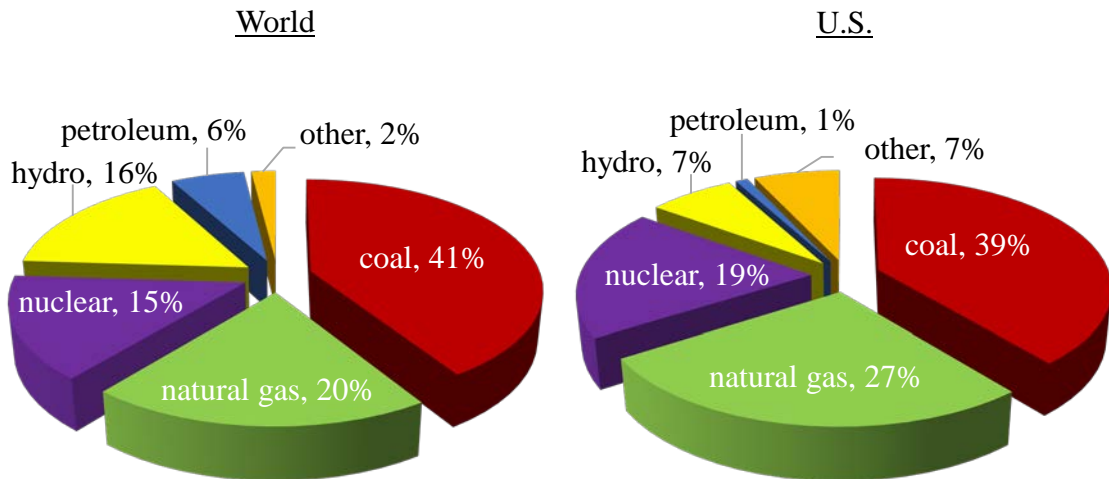


Figure 1. Total World and U.S. Electricity Generation by Fuel in 2013⁷

Coal is available in many regions across the world and is a relatively cheap form of energy. Coal is valuable commodity due to its higher energy density (8000 - 15000

Btu⁸) and low production cost (as of April 3, 2015, Powder River Basin Coal sells for \$11.55 per short ton and Northern Appalachian Coal is \$61.15 per short ton⁹). Not only is it cheap, coal can be easily transported and stored. Coal is expected to steadily increase in demand due to increasing world production of electricity and steel for years to come. Since 2008, world production has increased nearly 16.3% from 7.47 billion tons to 8.69 billion tons in 2013.⁶

Although coal has many beneficial uses, the U.S. Environmental Protection Agency (EPA) has stringent guidelines to help protect human health and prevent environmental damage. In the mining stages of production, workers are confined in spaces with increased carbon monoxide (CO) and methane (CH₄) concentrations and are exposed to heavy metals such as mercury and lead. There are numerous other concerns such as fire hazards and gas or dust explosion hazards, but over the last 40 years with help from the EPA and Mine Safety and Health Administration (MSHA), improvements in risk assessment and safety have been made. Stringent policies on waste disposal and air pollution have been implemented to reduce contamination of natural water resources and improve air quality. When coal has a high sulfur content, during the combustion process, large volumes of SO₂ (sulfur dioxide) are released and have to be filtered out of the exhaust to limit the release of pollutants. Large volumes of CO₂ (carbon dioxide) are released as a product of coal combustion and have contributed to the increase in global CO₂ concentration.¹⁰ Even with improvements in safety and risk assessment, a common problem with low grade coals such as lignite and especially sub-bituminous type coals is spontaneous fires.¹¹



Figure 2. Sub-bituminous Coal that has Spontaneously Combusted

Figure 2 shows an example of a spontaneous combustion event on a sub-bituminous coal bed. Through coal processing, the self-oxidation of coal, especially early in the production process, has created many naturally-occurring fires, some of which have been burning for over one hundred years.¹² In order to better understand this phenomenon, we must understand how spontaneous heating occurs.

CHAPTER 2. COAL OXIDATION AND SPONTANEOUS COMBUSTION INHIBITION

2.1 Concept of Spontaneous Heating

At ambient temperatures, the self-oxidation of coal is a thermodynamically spontaneous reaction, which means that it does not need an external source of energy to progress. Due to complex physical and chemical processes, the rise in internal coal temperature can take hours to days depending on the susceptibility of the coal to undergo oxidation and thermal decomposition at low temperatures (20°C – 150°C).¹³ These series of parallel reactions are mostly exothermic. The rate at which this occurs varies due to inherent properties of the coal such as moisture, fixed carbon, volatile matter, mineral content, and physical structures of the coal matrix such as porosity or available surface area.¹⁴ All of these factors are to be considered when determining the coals tendency to undergo a spontaneous heating event. If the heat is not dissipated, then the increasing temperature will lead to self-ignition, resulting in a spontaneous coal fire.

Due to the recent increased production of mid-grade sub-bituminous coal in the U.S., spontaneous coal fires have turned out to be a common phenomenon in mines, transport, and storage. This natural phenomenon is an under-estimated problem and in recent years has been studied to understand the mechanism¹⁵, degree of susceptibility¹⁶, and methods of inhibition¹⁷. The goals of this project are to understand the scope of

spontaneous heating, thereby allowing the prediction and control of this process to prevent coal fires in the mining, transport, and storage of coal. With this, appropriate inhibitors can be selected to slow the oxidative process physically and chemically. Physical inhibition generally involves limiting oxygen exposure and increasing the rate of heat loss. Chemical inhibitors are thought to be directly involved in the oxidation and combustion processes. The resulting additives have a wide range of use and potential for reducing the susceptibility of coal to self-igniting. Many methods including thermal analysis have been used to assess the success of inhibition spontaneous coal combustion.¹⁸

2.2 History of Spontaneous Combustion and Research

Most occurrences of spontaneous coal fires were recorded in the late 19th century with the coal industry boom, while many have been recently reported in mining sites¹², exposed coal seams¹¹, coal deposits, and power stations. Factors that affect the susceptibility of spontaneous coal combustion can be controlled during storage and transport but may not always be effective, resulting in large fires that are difficult to control. Sometimes these fires can take weeks to extinguish due to the amount of coal involved (millions of tons).¹⁹ This poses a safety concern and an economical concern. Large amounts of toxic gases and CO₂ are released into the atmosphere and the fire can spread easily if not contained. Additionally, there are significant losses in caloric value, a need for extra fire combatants, and in extreme cases coal fires can lead to human casualties. Thus early detection and prevention of spontaneous coal fires is of great value.

In 1908, Samuel Parr was one of the earliest researchers to study the initial stages of coal oxidation by quantifying volatile release and oxygen absorption using partial pressure and combustibility of gases.¹³ In a subsequent paper, Parr concluded that freshly mined coal absorbs oxygen in a rapid manner that does not result in the formation of CO₂ but rather leads to the incorporation of oxygen into the coal structure.¹⁴ His conclusions are still a part of the current understanding of the mechanisms of coal oxidation at low temperatures. He also was the first to heat coal at a constant rate under an oxidative atmosphere to measure temperature changes and was the first to develop a graphical representation of the oxidative process for coal.²⁰

In 1925, J. Davis quantified loss of caloric value using calorimetry, focusing on the propensity for spontaneous combustion rather than oxygen absorption.²¹ These studies identified several key parameters that influence the process such as coal rank, particle size, and surface area and showed the influence of moisture on spontaneous heating.²² It was concluded that coals with high moisture content have pores filled with water that cannot absorb oxygen; and dried coals will absorb moisture from the environment releasing the heat of condensation, which increases its critical temperature.²²

Over time, contributions from multiple disciplines have tried to understand the phenomenon of spontaneous heating with coal. Geologists have quantified mineral content and crystal structure²³, engineers measured bed temperature, caloric value, and fluid dynamics²⁴, while chemists introduced studies of reaction rates and mechanisms identifying components involved¹⁵. When these results are integrated, a clearer understanding of the spontaneous process can be considered.¹⁸

2.3 Understanding Self-Oxidation

Understanding the mechanism and kinetics of coal oxidation is fundamentally important when trying to understand the spontaneous combustion process. Several mechanisms have been postulated at different stages of the oxidation reaction that have been useful in kinetic modeling where rate of the reaction are calculated.¹⁵ These models have been useful to design storage and transport conditions in a variety of environmental conditions. However, due to the complexity of the coal matrix and the number of variables involved in determining reaction rate, mechanisms are only partially understood.

Coal oxidation is an exothermic process. The heat from oxidation can be either lost or retained. Coal will lose heat through three pathways: convection, conduction, or evaporation (see Figure 3). Heat lost to the surrounding atmosphere is known as convection. Conduction is heat lost to the minerals within coal. These minerals can act like a heat sink at levels as low as 5% by weight.²⁵ Heat transferred to the inherent moisture and volatile organic compounds within the coal matrix is lost through evaporation. If heat is not dissipated, then coal behaves as an insulator. When the heat is retained, the coal temperature will continue to rise, which also increases the rate of oxidation in a positive feedback mechanism.

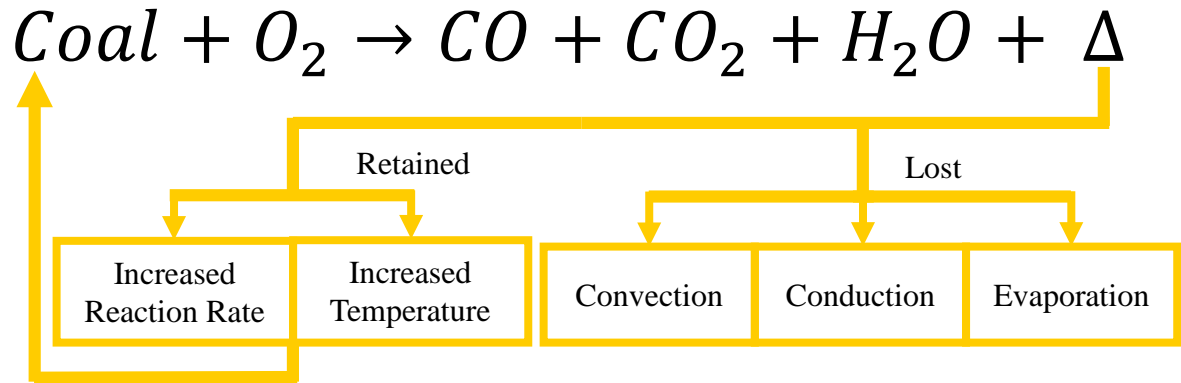


Figure 3. Heat Flow During Coal Oxidation

Coal oxidation at low temperatures follows a unique series of reactions when compared to the classical combustion reaction.¹⁵ These take place between 20 - 150°C without the presence of a flame in a very slow processes that continuously releases heat. When coal is stored in large stockpiles, the ability of the coal to transfer heat to the surrounding atmosphere is limited, creating localized pockets of heat. This heat accumulation will then accelerate the rate of the reaction until thermal runaway is reached, resulting in high temperature coal combustion and fire.¹

Previous research to establish mechanisms of oxygen absorption include early studies showing coal can absorb oxygen without releasing CO₂, but rather incorporating O₂ into the coal matrix.¹³ Oxygen is initially rapidly absorbed until all catalytic sites are occupied then the slow but extensive desorption of oxidation products can give way to the rise in water and CO₂ as well as an increase in coal bed temperature.¹⁶ However, this did not explain the mechanism leading to spontaneous combustion. Subsequent research was able to demonstrate the formation of normal gaseous oxidation products and the reaction rate could be estimated by measuring the heat release rate.^{18,21} Other researchers

were able to show that total weight of a coal sample could increase at low temperatures as a measure of oxygen absorption and therefore concluded that the speed of oxidation increases with increasing volatile matter.²⁶

With early successes in research, methods slowly improved. Studies included the effect of coal rank¹⁶ and temperature on the rate of oxygen consumption²⁷. Results supported the theory that the reaction is dependent upon temperature and could be modeled using the Arrhenius equation.²⁸ From this research the following mechanism was proposed. In the first stage, the external porous surface controls the rate of oxygen consumption which initially blocks all active sites, and creates new active sites due to the desorption of unstable coal by-products. In the second stage, the available surface increases through combined effects of absorption and desorption affecting the reaction rate by increasing the coal bed temperature. This is the rate-limiting step of the reaction. With increasing temperatures, the rate of oxygen consumption increases. The final stage is when the coal has reached a critical temperature and thermal runaway occurs. This means that the reaction is feed-forward and continues to release heat and increase the temperature in a destructive manner, past the point of no return.

Experimental work by Wang *et al.* proposed multi-step mechanisms including gas absorption, formation of gaseous and solid products, and thermal decomposition steps.¹⁵ The proposed mechanism starts with the chemisorption of oxygen molecules in the pores of the coal surface, forming a group of carbon-oxygen complexes at temperatures between ~20 to 70°C. Then, when a slightly higher temperature is reached (~50 to 70°C), these oxygenated complexes undergo a thermal decomposition which contributes to the emission of CO and CO₂. The reaction of the solid carbon-oxygen complexes also could

create new stable solid products, which can be decomposed at temperatures higher than 70°C, leaving available new active sites to be used by the reaction. This proposed sequence explains how the reaction regenerates the active sites, liberating carbon oxides.²⁹ Finally, Wang suggested that two parallel reactions sequences contributed to the emission of CO and CO₂ during oxidation.¹⁵

2.4 Role of Coal Rank on Spontaneous Combustion Potential

The spontaneous combustion of coal relies on many contributing factors: oxygen concentration, temperature, mineral content, inherent moisture, particle size, porosity, surface area, chemical composition, and coal rank. It has been determined that spontaneous combustion of coal occurs in the final phase of coal oxidation and each factor shares some level of contribution to the rate at which this occurs. Thus, the rate of oxidation and spontaneous combustion susceptibility vary with coal rank.

Initially physical interactions at ambient temperatures release heat. Physical interactions include coal-oxygen interaction³⁰, volatile organic desorption³¹, and water absorption/desorption³². With increasing temperatures, oxygen can be absorbed in two independent pathways proposed by Wang *et al.* releasing between 80-420 kJ/mol of heat.¹⁵ These reactions result in increasing coal temperatures leading to combustion reactions at high temperatures. The resulting heat release and internal coal temperature affects the rate of O₂ consumption. However, the structure of the coal matrix along with the porosity also directly impacts the rate of O₂ consumption. One study investigated the characteristics of oxygen consumption of different coal ranks at programmed temperatures to model spontaneous combustion susceptibility. Results show that at

ambient to low temperatures, oxygen consumption is measurable and trends can be made based on coal rank to determine spontaneous combustion susceptibility.¹⁶ Low rank coals such as lignite showed the highest rate of oxygen consumption which relates to a high probability that it will experience a spontaneous combustion event and rates of oxygen consumption slowed with increasing rank.¹⁶

Moisture content in the coal sample also has an influence during the oxidative process. For freshly mined coal, the inherent water content is proportional to the coal maturation reached during its geological formation and requires energy to be removed from the coal surface. The water content can produce a dual effect in the coal oxidation: A) inhibition by the obstruction of pores and active sites available for the oxidation reaction³³ or B) enhancing the oxidation process by acting as a catalyst producing heat from absorption³⁴. The competition between these phenomena will determine the net amount of heat released. When coal interacts with the atmosphere, water can be adsorbed or desorbed to reach equilibrium. The physical absorption of water in the coal particles is an exothermic process.³⁵ The ability for coal to absorb moisture depends on the porosity and internal surface area, which also depends on coal rank. It was found that physical absorption of water is much more significant with low rank coals such as lignite and sub-bituminous type coals due to their higher internal surface area.³³ When this absorption takes place and the evolved heat is not released, the temperature of the coal bed can rise and increase the oxidation rate. For this reason, the relative humidity of the air is a significant variable in the process.³⁴ Vapor absorption produces a considerable increase in the coal bed temperature, which is enough to start the spontaneous combustion chain reaction. This heat is released directly to the coal because the mass of water vapor

available to capture the heat is negligible compared to liquid water.³⁴ It means that the coal's capacity to adsorb water or moisture, and the heat released in this process are key variables when assessing a coal ability to self-heat.

Mineral content can have a dual effect in the self-heating phenomenon. With regard to self-oxidation, it has been found that some minerals can act as catalysts enhancing the reaction.^{36,37} Pyrites can release heat during oxidation, but some minerals such as calcium carbonate, sodium acetate, and potassium acetate can too³⁷. This can considerably reduce the activation energy barrier, even if their concentration is small (usually in the range of 1 to 5%)³⁷. Conversely, when the concentration of minerals in the coal matrix is higher, minerals can act as an inhibitor in the reaction, blocking the active sites and acting as a heat sink. This phenomenon usually occurs when the mineral content is above 5wt%³⁸, with the exception of some minerals that directly inhibit the reaction, such as potassium chloride, sodium chloride³⁷, calcium chloride, and magnesium acetate³⁸. The total mineral concentration is normally calculated as the residue remaining after burn out, and the inhibitor effect is independent on the chemical composition of the minerals when their concentration is higher than 10wt%³⁸.

The effect of particle size has been studied by several researchers^{39,40,41}. These studies have examined a range of sizes from pulverized coal particles to lumps of several centimeters. The smallest particle sizes produce the maximum external surface area producing an increase in the rate of oxygen consumption⁴¹. This increase in the external surface accompanying the reduction of particle size is of minor significance, compared to the increase in accessible internal surface, which is related directly to the self-oxidation

reaction.³² A maximum oxidation rate is reached when kinetic control is achieved, particularly for particle sizes in the range below 500 to 100 μm .⁴²

Surface area affects the rate of reaction through the internal porosity of the coal.² This porosity is usually a consequence of geological processes. For instance, it is understood that lignite and sub-bituminous coals have higher propensity for spontaneous combustion. This is explained mainly through the high surface area of this kind of coal, which provides a large number of active sites which can react with oxygen, and also because these sites are able to absorb moisture. Other contributing factors include the higher initial volatile and water content, compared to other types of coal.

Low coal rank such as lignite and sub-bituminous coals have a high degree of spontaneous combustion susceptibility. These two coal types also have greater reactivity than higher rank coals due to the composition, volatile content, high porosity and surface area, and high affinity to absorb water. This parameter is used by the coal industry as one of the main indicators of propensity to spontaneous combustion. Thus the aims of the project are to determine mechanisms of inhibition on sub-bituminous type coals due to the increased susceptibility to spontaneous combustion for factors previously mentioned.

2.5 Selecting Chemical Inhibitors to Prevent Spontaneous Coal Combustion

Coal is a complex, chemically reactive material which makes selecting chemical inhibitors rather challenging. Researchers have used a variety of inorganic compounds to investigate mechanisms spontaneous combustion inhibition as well as ways of preventing oxidation. One method in preventing self-heating of coals is creating an oxidative barrier

to the coal surface.⁴³ This showed to be the best method of prevention during storage having the lowest amount of total loss due to spontaneous combustion.

Other groups have considered the use of inorganic salts in decreasing spontaneous susceptibility. Some salts such as sodium acetate, potassium acetate³⁷ promote the oxidation reaction which increases the rate of spontaneous combustion while other salts like sodium chloride, calcium chloride^{17,44} calcium carbonate⁴⁵, sodium phosphate⁴⁶, sodium sulfite⁴⁷, and sodium sulfate⁴⁸ inhibit spontaneous combustion. These inhibitors improve the thermal stability of coal in three ways: adsorb water from the atmosphere which blocks active oxidation sites^{17,44}, promote polymerization and cross-linking through ester bond formation^{45,46,47}, or scavenger free radicals forming stable oxygenated complexes⁴⁸.

Another class of chemicals of interest in preventing spontaneous coal combustion are aromatic sulfonate salts. They have been shown as highly effective flame retardants in polymers and plastics such as polycarbonate at very low weight loads⁴⁵. They have been shown to slow thermal decomposition forming stable cross-linked solid oxygenate complexes. Sulfonates can also react with hydroxyl species to release sulfite in a direct substitution reaction⁴⁹. Sulfites act as radical scavengers reducing the number of free radicals in the coal structure, which inhibits further oxidation and decomposition of coal. Inorganic phosphate salts are also of interest for their use in preventing spontaneous combustion at low weight loading. With the addition of sodium phosphate, the rates of oxygen uptake by coal and formation of unstable solid oxygenated complexes slowed⁴⁶. For these reasons, sulfonate salts and phosphate salts are of high interest and have been incorporated into this study.

For the scope of the project, two non-ionic surfactants, tridecyl alcohol (TDA) and ethoxylated tallow amines (TAM), and one anionic surfactant, α -olefin sulfonate (AOS) were chosen to study the effects of an oxidative barrier on spontaneous combustion. Sodium xylene sulfonate (SXS) was chosen as the aromatic sulfonate salt and tetrapotassium pyrophosphate (TKPP) was chosen as the phosphate salt to be used in this study. Both are very soluble in water making them easy to use in industrial applications with water-based solutions and both promote the formation of stable cross-linked oxygenated carbon complexes and can scavenge free radicals during coal oxidation.

2.6 Thermal Analysis and Microscopy: Methods for Quantifying Spontaneous Combustion

A number of methods have been considered to measure the level of coal oxidation. Most approaches use thermal analysis, or the net heat release from the coal bed as a result of the dependence on oxygen absorption. Other methods such as microscopy can provide insight into the surface characteristics (Figure 4) of the coal matrix that can be associated with reactivity of the substrate. The primary techniques used in this study measure heat flow and/or thermal decomposition to estimate reactive coal properties. Such techniques include thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

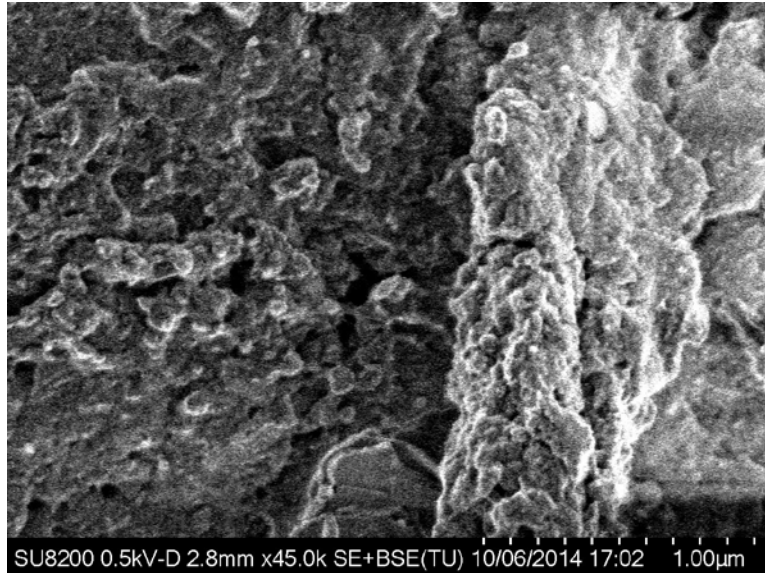


Figure 4. SEM Surface Image of PRB Coal

TGA is a standard technique used to characterize coal samples by the coal industry. This method has allowed investigators to measure parameters such as reactivity to air using different heating and atmospheric conditions as well as provide insights on a coal samples volatile content, mineral content, moisture content, and fixed carbon. There are only a few accounts of TGA being used to quantify the propensity of coal to spontaneously combust^{18,46}. Most studies to date have looked at low temperature studies to measure susceptibility (20 – 100°C) while others have looked at the overall heating characteristics of coals. DSC measures the difference in the amount of heat needed to raise the temperature of the sample versus the amount of heat needed to raise the temperature of a reference sample as a function of temperature. The difference is a physical or chemical transformation that is taking place within the sample.

While prior studies examined variables such as coal rank, temperature of the coal deposit, heat evolution of the stockpile, and oxygen concentration on the self-heating of

coal, they did not consider parameters such as changes in mass loss, change in petrology and chemical composition due to weathering. TGA measures the change in sample mass associated with changes in temperature. With this tool, it is possible to measure precise values for thermal runaway onset temperatures during the oxidation process, quantify absorption and desorption of oxygen, moisture, volatiles, and quantify reactive or unreactive components of the coal sample. These methods will serve as insight into the heating characteristics of the coal due to specific characteristics such as moisture and thermal runaway temperatures, but rates of oxidation are dependent upon a variety of contributing factors which have been discussed previously. By altering the heating characteristics of coal through mechanisms of inhibition, spontaneous combustion susceptibility can be reduced. TGA can be employed to observe changes in the coal's thermal profile as a result of adding chemical inhibitors to the coal bed and measuring mass loss over the same temperatures. The derivative of the weight loss can be associated with coal reactivity or increases in thermal stability with precise measurements of thermal events and reactivity to air. The addition of certain inhibitors can then be quantified to determine whether or not the susceptibility of coal to spontaneously combust has increased or decreased.

2.7 Thesis Overview

The work described in this thesis examines two key mechanisms to control spontaneous combustion: i) surfactant blends are employed to control low-temperature oxidation of coal by creating a physical barrier to the oxidative coal surface slowing the heat release rate; and ii) salts are used to increase the onset temperature and push the

thermal runaway temperature higher to prevent total loss due to spontaneous combustion. Chemical inhibitors chosen for this project include non-ionic and anionic surfactants including tridecyl alcohol (TDA), tallow amine ethoxylates (TAM), and α -olefin sulfonate (AOS), and two salts, sodium xylene sulfonate (SXS), and tetrapotassium pyrophosphate (TKPP).

CHAPTER 3. EXPERIMENTAL METHODS

3.1 Research Plan

Recent investigations into spontaneous coal combustion have made advancements in understanding the mechanism of low-temperature coal oxidation. As such, kinetic modelling and thermal analysis have shown to be effective techniques in the investigation of spontaneous combustion. The main focus of this study is to develop new materials as useful inhibitors to this natural phenomenon. Thermal analysis methods were chosen for experimental quantification of thermal runaway in coal. These techniques can provide insight into moisture content, runaway temperature, and reactivity to oxidation. With the application of inhibitors, we can achieve noticeable differences in the thermal characteristics of coal and make conclusions as to whether or not spontaneous combustion susceptibility has been reduced with the materials chosen.

3.2 Sample Preparation

Sub-bituminous coal was chosen due to its increased susceptibility to spontaneous combustion. In particular, Powder River Basin (PRB) coal was employed in this study due the rapid increase in market demand due to low sulfur content. This was compared with coal purchased from the National Institute of Standards and Technology, NIST 1635a. Samples were first ground into a fine powder and passed through a U.S.G.S. Tyler

mesh no. 35 sieve (equivalent to a 500 micron sieve mesh) to standardize the particle size. The resulting fine coal powders were used in the analysis of untreated and treated samples.

Formulation F101 mimics the potential use in industrial design formulations which is why materials were added in the following proportions: 74 % water, 10.5 % tetrapotassium pyrophosphate (TKPP), 5.5% tridecyl alcohol (TDA) and ethoxylated tallow amine (TAM) blend, 4% α -olefin sulfonate (AOS), 6% sodium xylene sulfonate (SXS). The resulting solution, Formulation F101, was applied to the coal with a misting sprayer at a 20wt% load. Once F101 was determined that can be used to prevent spontaneous combustion, each component of the formulation was investigated to determine its role in this process. Samples were treated with various concentrations from 1% - 40% of non-ionic and anionic surfactants, and phosphate and sulfonate salts which were sprayed onto the coal up to 20wt% loadings. These were allowed to air dry for 24 – 48 hours before thermal analysis using TGA and DSC.

To prepare for imaging under a scanning electron microscope (SEM), unreacted, untreated coal was placed in a vacuum oven for 6 hours at 130°C. Once removed, the coal was cooled to room temperature and an amount equal to 20% by weight of Formulation F101 was applied to the coal surface and allowed dry under vacuum conditions at room temperature. Once the samples were dried, portions of untreated and treated coal were burned for 30 minutes (refer to Section 3.5). Images were analyzed with a Hitachi SU8230 low-voltage SEM.

3.3 Thermal Analysis Equipment

Thermogravimetric analysis (TGA) was carried out using a TGA-50 (Shimadzu Scientific Instruments), with a gas flow of 40ml min^{-1} and a sample size of 5 – 15 mg. This instrument has one aluminum pan and a furnace which is controlled from a remote desktop that is also used to control the heating programs and record the weight of the sample as a function of time. A differential scanning calorimeter model DSC-60 (Shimadzu Scientific Instruments) was also used. The sample size range was 5 – 15 mg, and the gas flow was set at 40mL min^{-1} to have equivalence with the TGA analysis. In these instruments, the atmospheres used were nitrogen (N_2) and air (21% O_2 ; 79% N_2). A nitrogen atmosphere is used to study of the heat of volatilization of the sample and an air atmosphere is used to measure the heat of O_2 absorption. Please see Appendix A for Instrument Standard Operating Procedures.

3.4 Proximate Coal Analysis

PRB coal samples were sent to an outside lab to perform proximate analysis. Once proximate analysis was completed, coal from NIST was chosen to best match PRB coal resulting in the purchase of lot number 1635a as a control. Both results are listed in Table 1 for reference.

Table 1. Proximate Analysis – Sub-bituminous coal

PROXIMATE ANALYSIS	PRB	NIST 1635a
% Moisture	30.67	20.54
% Ash	4.80	6.29
% Volatile Matter	31.90	44.75
% Fixed Carbon	33.96	48.56
Btu/Lb	8,400	11,664
% Carbon	48.72	68.97
% Hydrogen	3.34	4.64
% Nitrogen	0.62	0.95
% Sulfur	0.32	0.29

3.5 Flammability Temperature Test

Coal was prepared according to sample preparations in Section 3.2. Two grams of untreated coal and two grams of coal treated with the combinatorial blend (F101) were placed into 30 cc crucibles over a lit Fisher burner under a vent hood. The samples were heated for 30 minutes and reached a minimum temperature of 750°F (400°C). As the coal burned, the temperature was monitored using an infrared laser thermometer. Under this method, the ignition temperature was determined and flammability of the coal could be seen.

3.6 Design Expert 9 (DX9) Experimental Design Analysis

Developers at Stat Ease, Inc have created modules within Design Expert 9 for making improvements to product formulations using statistical analysis and experimental design. The software screens vital response factors to locate ideal setting for top performance and optimization of product formulations which is advantageous for this research. Please refer to Appendix B for information on the DX9 software used in this work.

CHAPTER 4. RESULTS

4.1 Flammability Tests

The first step of the project was to determine whether or not coal treated with different inhibitors behaved differently than an untreated reference. Using the flammability temperature test method (Section 3.5), untreated coal ignited at 278°C within 3 minutes of heating. In the same amount of time, coal treated with F101 had not ignited even though the temperature of the sample was higher. As the untreated material continued to burn, the temperature of the sample continued to rise until a flame was no longer visible. The sample had burned within ten minutes after the test began. The coal sample treated with F101 did not ignite throughout the duration of the test. The only visible effects seen was white smoke coming off the sample which is most likely steam and products of incomplete combustion. The samples treated with F101 also had noticeably lower temperatures (over 100°C) under the same test conditions. Both untreated and treated samples remained over the heat source for 15 minutes. Once the test was complete and the samples were cooled, both samples were analyzed for color and weight (Figure 5). The untreated sample was a gray ash with residual approximately 10% of its original weight. The treated sample appeared unburned but with some char around the edge of the crucible. The residual weight was approximately 75% of the initial weight. The weight difference was due to moisture evaporation, volatile organic

compounds desorbing from the material and/or incomplete combustion products released from the coal. The results of the flammability temperature test provided preliminary confirmation of the effectiveness of a blend of salts and surfactants as a flame retardant material for coal combustion. Once the first formulation (F101) passed the flammability test, the samples were then analyzed under a scanning electron microscope (SEM).



Figure 5. Flammability Test of Untreated and Treated Coal

Scanning Electron Microscopy

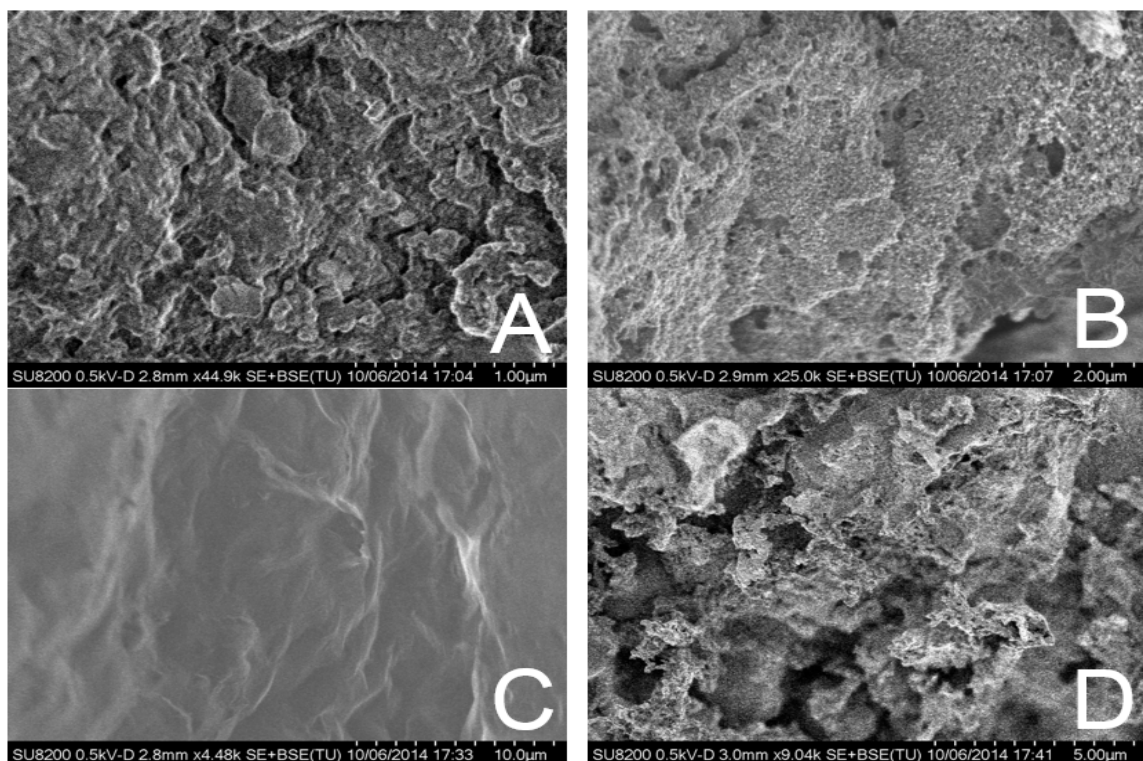


Figure 6. PRB SEM Images. **A.** Unreacted, untreated coal **B.** Burned, untreated coal
C. Unreacted coal treated 20wt% with F101 **D.** Burned, treated coal.

Imaging was performed using a low-voltage Hitachi SU8230 SEM. The surface characteristics of unreacted, untreated PRB coal in Figure 6A show the coal is a very uneven on the surface. The pockets within the surface features are where oxidation occurs. Heat cannot dissipate easily and as a result, the temperature of the coal increases.¹⁵ Once the untreated PRB coal was burned, the resulting ash was analyzed. The coal ash was a fine, flakey powder. The ash had lost many surface characteristics compared to those seen in Figure 6A. A drastic difference in the surface characteristics of unburned coal treated with F101 can be seen in Figure 6C. The surfactants have created a

smooth, visible film on the coal surface which creates a physical barrier to oxidation of the coal. Coal treated with F101 was then burned and analyzed under SEM shown in Figure 6D. Notice that the characteristics of the coal are similar to the features seen in Figure 6A which was the untreated, unburned coal sample. The visible surface features are only charred and most of the coal matrix appears the same as if it was unburned. Results from SEM supported the hypothesis that surfactants create a physical barrier to oxidation (Figure 6C) and the materials employed provide a retarding effect to coal combustion (Figure 6D).

4.2 Thermal Analysis Results: NIST and PRB Coal

NIST and PRB coals were added to the TGA to determine the reactivity of each sample as a function of temperature. As a result of the function of the instrument and the reactivity of the coal samples, once thermal runaway of the coal takes place, the temperature of the coal rapidly increases. The instrument attempts to correct the temperature increase and cools back down to maintain a constant heating ramp rate of 10°C (Figure 7). Therefore, for the remainder of the TGA analyses, % mass versus time will be used (Figure 8 for example). Thus, the derivative plot (dW/dT) gives a clear diagnostic variable (the onset temperature for thermal runaway) which can be used for analysis. The temperature of particular events of interest, especially thermal runaway temperature can be determined with precision.

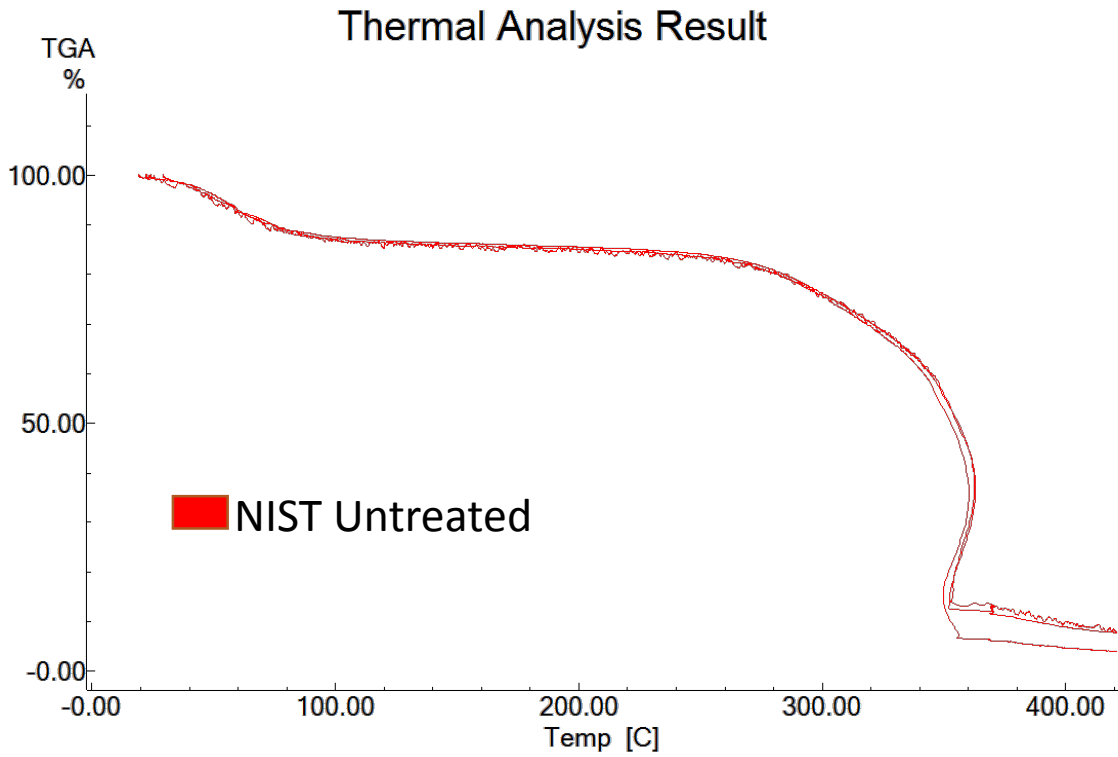


Figure 7. TGA Results of Untreated NIST Coal as a Function of Temperature

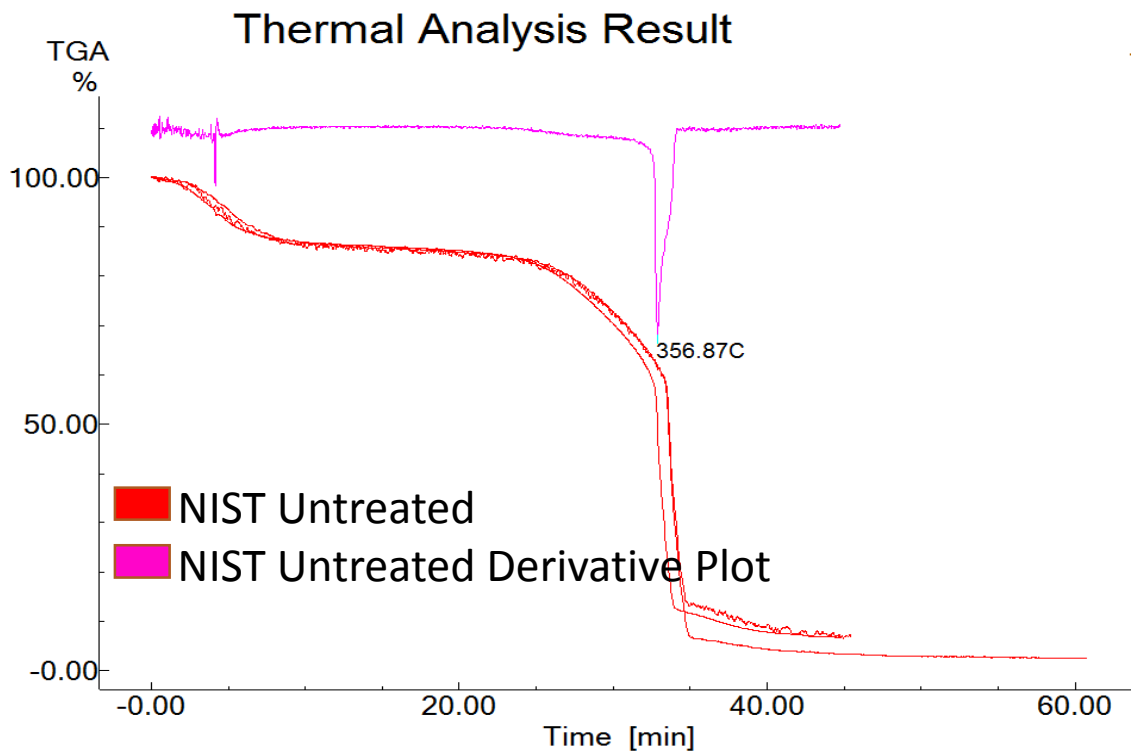


Figure 8. TGA Results of Untreated NIST Coal as a Function of Time

NIST and PRB coal were both treated with a 20wt% load of F101 and compared to an untreated coal sample. The thermal runaway temperature of untreated NIST coal was recorded at 362.3°C whereas the sample treated with F101 was 419.2°C (Figure 9). The thermal runaway temperature of untreated PRB coal was recorded at 364.9°C whereas the sample treated with F101 was 462.6°C (Figure 10). The temperature difference is significant and might explain why the treated PRB sample did not burn during flammability testing. In the untreated PRB sample, approximately 25.0% weight was lost initially whereas the treated PRB sample was only 12.9%. This could be explained by the surfactants creating an oxidative barrier during low temperature oxidation and preventing moisture and high volatile organics from escaping the internal coal surface.

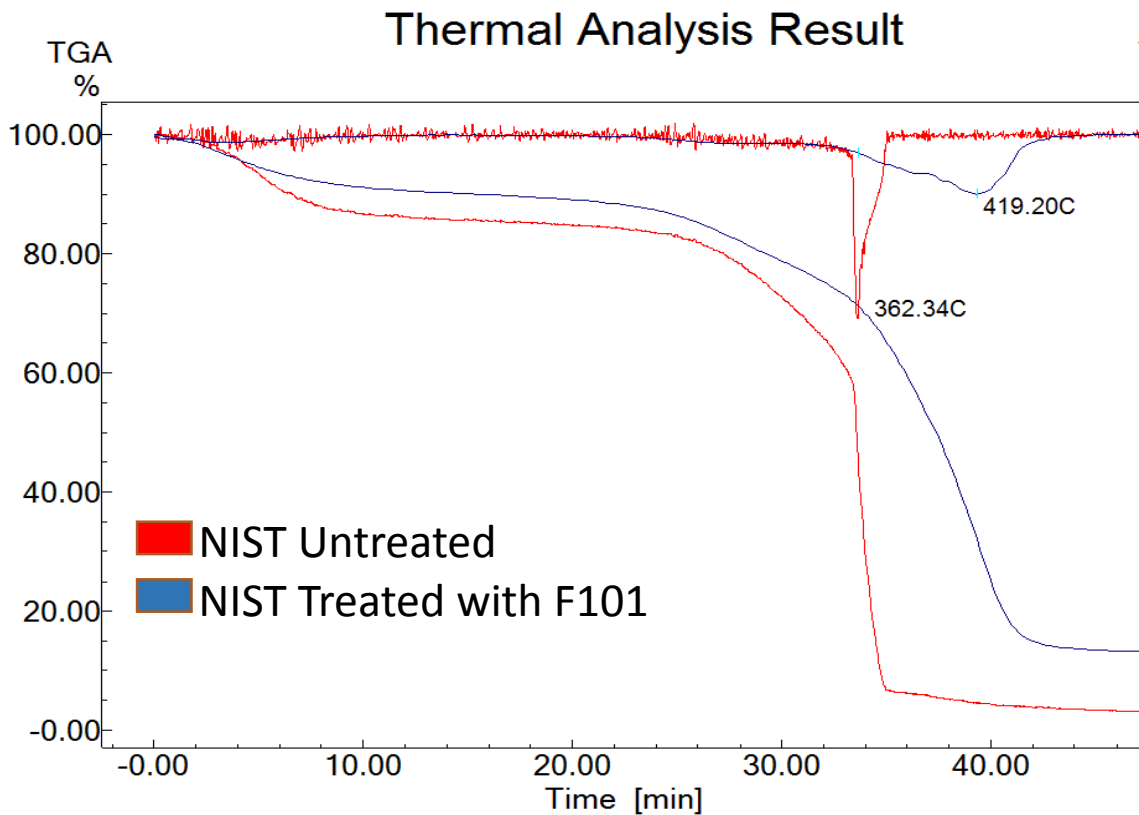


Figure 9. TGA: NIST Coal Untreated Versus Treated with 20wt% F101

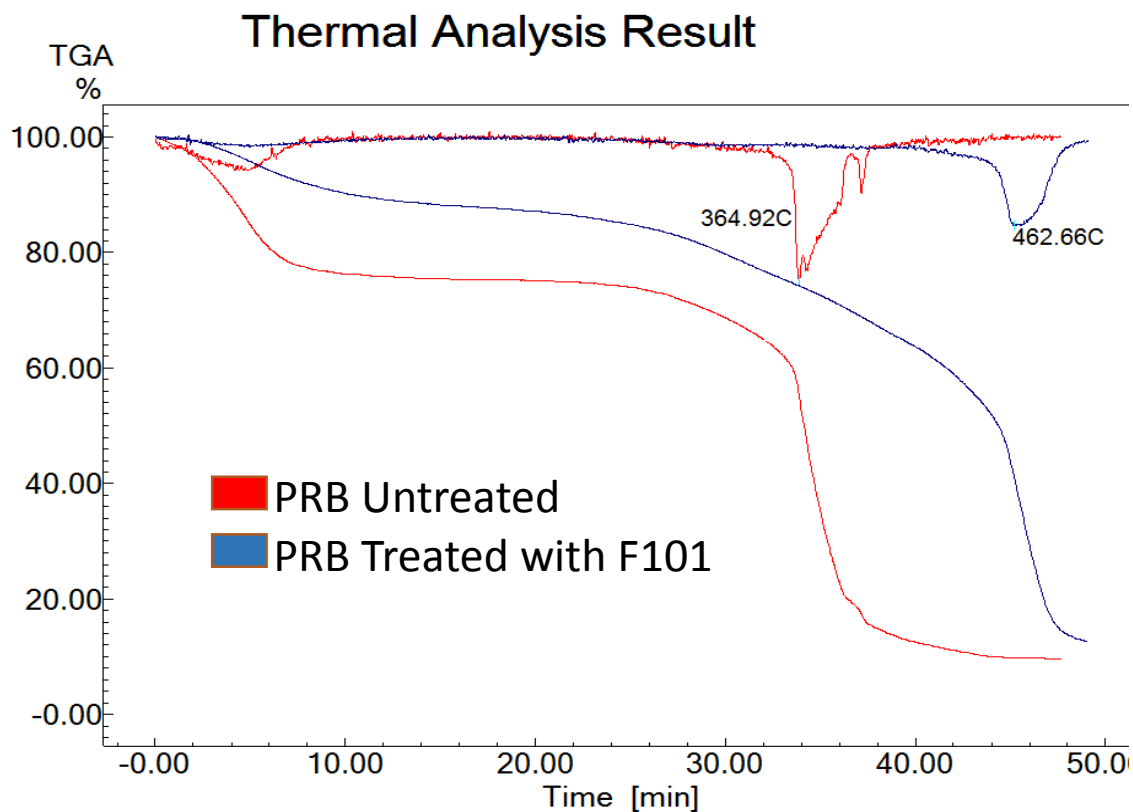


Figure 10. TGA: PRB Coal Untreated Versus Treated with 20wt% F101

Samples were also analyzed using DSC. This instrument measures the amount of energy required to heat a sample relative to the energy required to heat a reference material to the same temperature. If the recorded value is above 0.00 mW or a positive value, the events that are occurring at those temperatures are endothermic in nature. If the value is negative or below 0.00 mW, then the events occurring at those temperatures are exothermic. Heat of volatilization of an untreated coal sample initially is mostly an endothermic process as moisture is being driven out of the sample along with volatile organic compound. Once temperatures are high enough, coal combustion begins which is an exothermic process. Data supporting this can be seen in Figure 11. Once above 250°C, the process is mostly exothermic as combustion products are volatilized. As the

temperature continues to rise, more heat is being generated by the sample increasing the heat flow out of the sample.

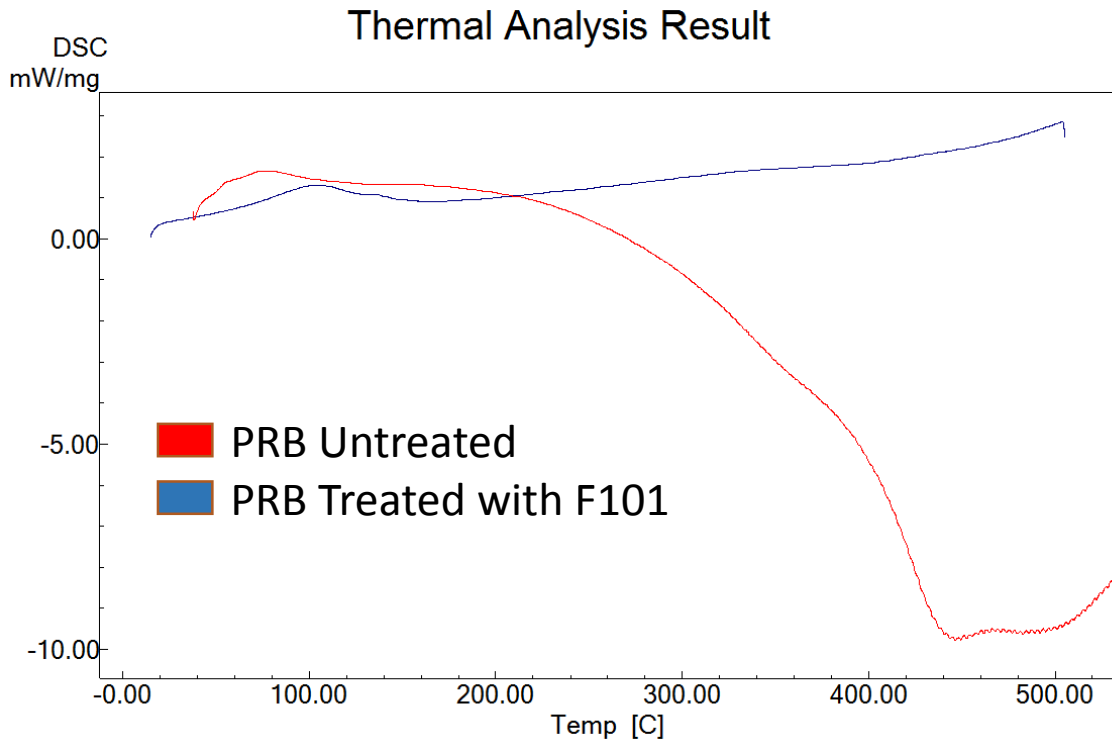


Figure 11. DSC: PRB Coal Untreated Versus Treated with 20wt% F101

When samples are treated with F101, the heat flow is endothermic from 20°C–500°C. As the temperature continues to rise, the heat flow is increasingly endothermic which shows the chemistries employed might be valuable in preventing spontaneous combustion. As the temperature continues to rise, the added salts and mineral act like a heat sink and continue to absorb as much of the energy surrounding the coal sample. It is also possible that decomposition of coal, when catalyzed by phosphoric acid formed by inorganic phosphate, is highly effective in an endothermic dehydration to yield char protecting the coal surface from further oxidation. Similar effects are seen in flame

retardant phosphorus compounds in cellulose.⁴⁶ Once it was shown that the formulation F101 was effective in increasing thermal runaway temperature and heat flow was mostly endothermic, each individual component of the formulation was tested on the coal sample to understand the influence of surfactants and salts on the spontaneous combustion of coal.

4.3 Thermal Analysis of Active Ingredients

Figure 12 shows coal was treated with a non-ionic surfactant blend of tridecyl alcohol (TDA) and ethoxylated tallow amine (TAM) in increasing weight loads from 1wt% - 40wt%. When compared to the untreated sample, there was not a significant difference in thermal runaway temperature, however with increasing weight loadings, the mass loss at lower temperatures had also decreased. This means that increasing the weight loading of the non-ionic surfactant blend reduces the amount of moisture lost from the sample and prevents oxidation of the coal from occurring which supports the hypothesis of a surfactant film barrier.

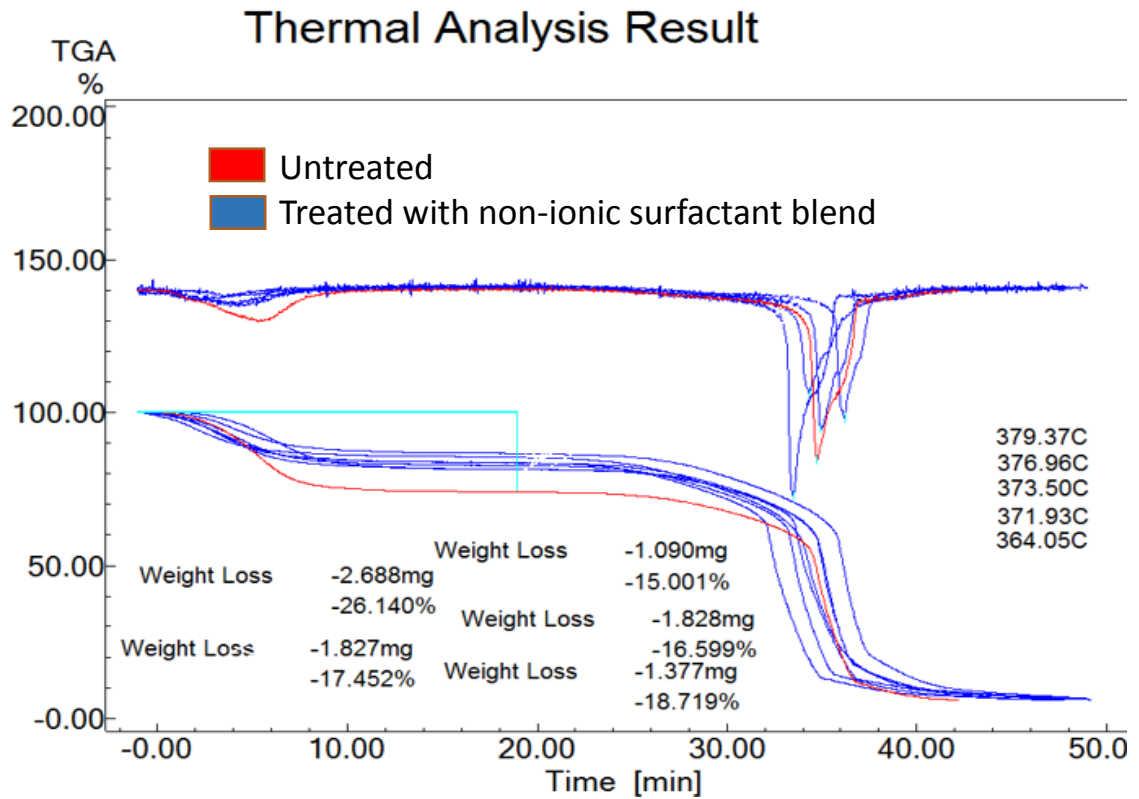


Figure 12. TGA: PRB Coal Untreated Versus Treated with Non-ionic Surfactant Blend with Increasing wt Loads

In Figure 13, coal was treated with α -olefin sulfonate and similar trends to the non-ionic surfactant were observed. As the weight loading of the surfactant was increased from 1wt% - 40wt%, the mass loss at lower temperatures decreased. Thus, one explanation for this behavior is that the surfactants added to the sample are creating a barrier to oxidation.

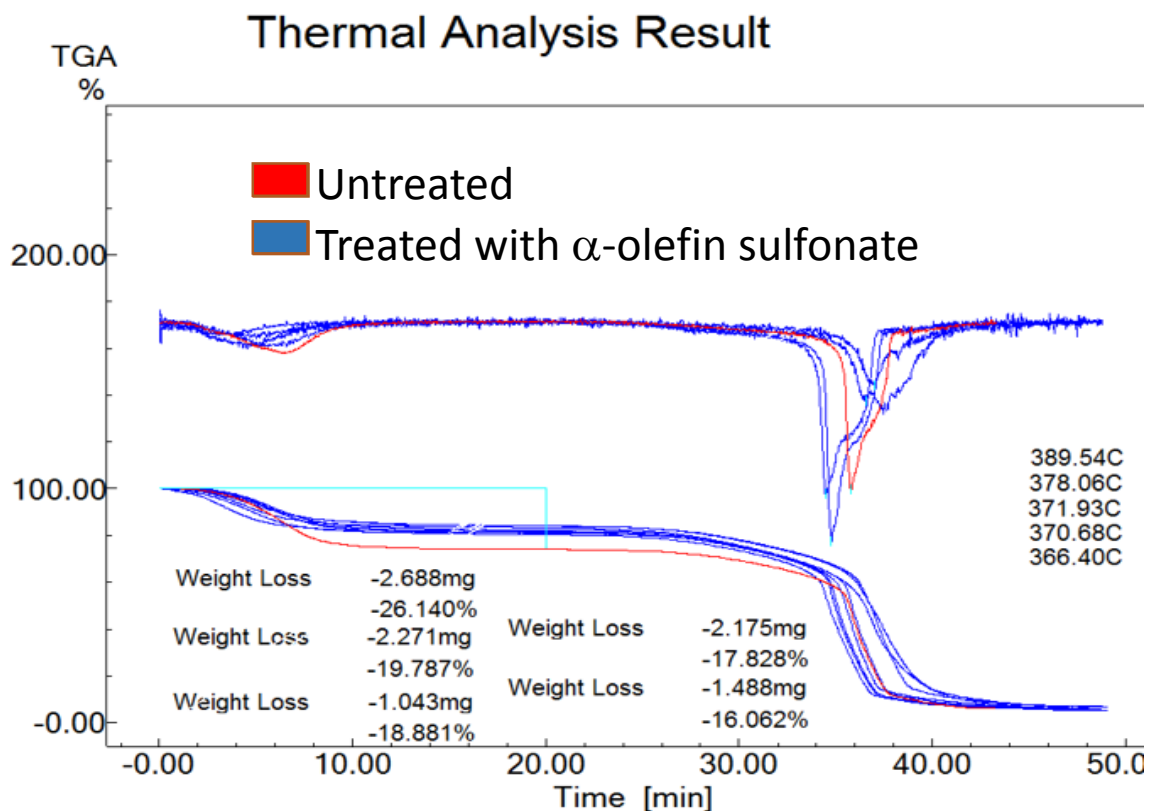


Figure 13. TGA: PRB Coal Untreated Versus Treated with AOS with increasing wt loads

Next, coal was treated with increasing amounts of tetrapotassium pyrophosphate (TKPP) from 1wt% - 40wt%. Figure 14 shows that weight loadings below 5%, the thermal runaway temperature was slightly lowered by 5 °C. Mineral content at this weight percent have been shown previously to catalytically enhance the reaction by lowering the activation energy.²⁵ Once the weight loading reached 5% or more, TKPP can act as an inhibitor to the reaction, acting as a heat sink or at elevated temperatures as a radical scavenger. The addition of TKPP also results in a reduction in the percentage of mass increase, indicating that the rates of oxygen uptake by coal and formation of unstable solid oxygenated complexes are slowed. The addition of inorganic phosphate to

the coal mainly influences the routes for the decomposition of hydroxyl by promoting its conversion into phosphate ester linkages.⁴⁶ The formation of ester bonds not only improves the thermal stability of the coal, but also reduces the number of free radicals in the coal structure, which allow an inhibition of further oxidation and decomposition of coal. With increasing weight loads above 5%, the thermal stability of the coal has increased which increases the thermal runaway temperature. At a 20wt% load of TKPP, the thermal runaway temperature was determined to be 425.0°C compared to that of untreated coal which was 371.9°C.

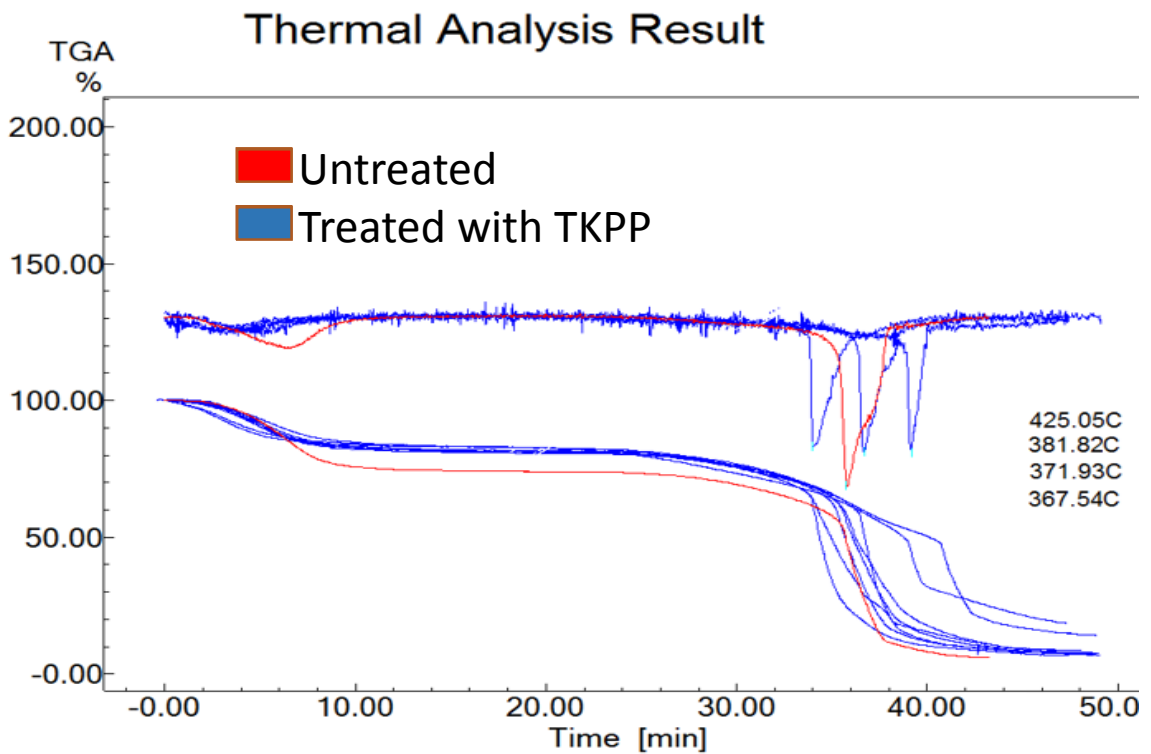


Figure 14. TGA: PRB Coal Untreated Versus Treated with TKPP with Increasing wt Loads

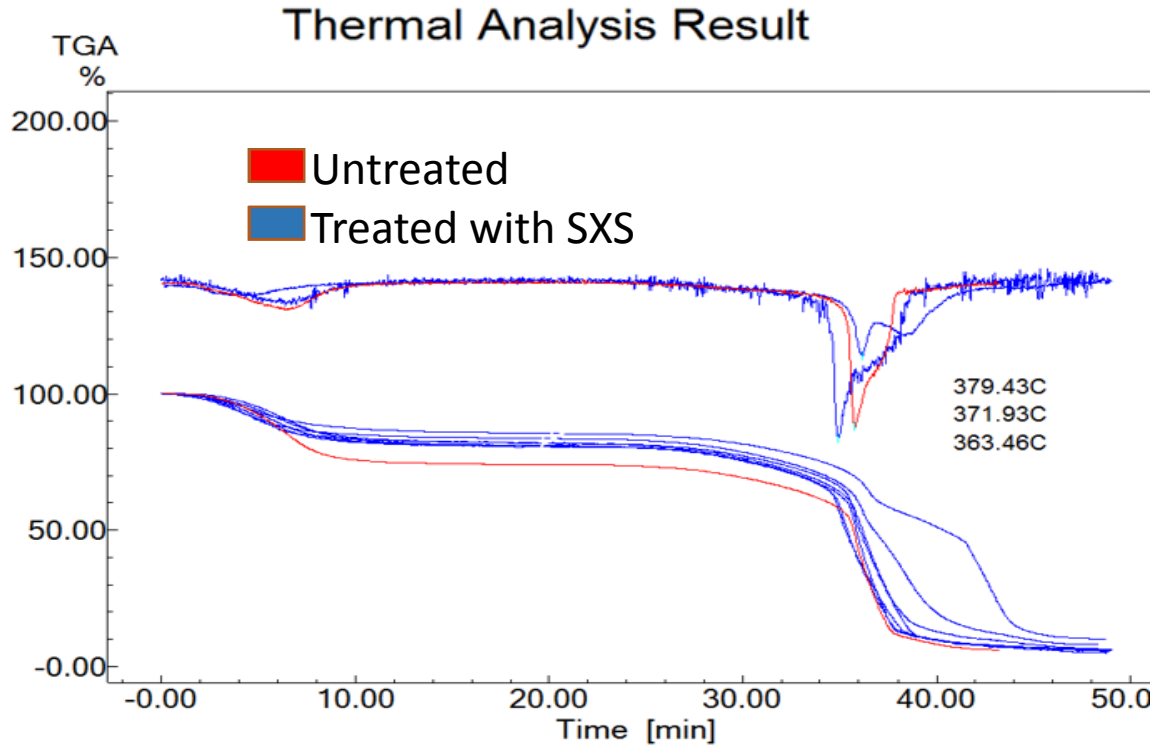


Figure 15. TGA: PRB Coal Untreated Versus Treated with SXS with Increasing wt Loads

The effects of sodium xylene sulfonate (SXS) are presented in Figure 15. There were no significant changes in thermal runaway temperature as the weight loading increases from 1wt% - 20wt%. However, SXS can react with hydroxyl species to release sulfite in a direct substitution reaction. Sulfites act as radical scavengers reducing the number of free radicals in the coal structure, which allow an inhibition of further oxidation and decomposition of coal. This could explain why retained mass at lower temperatures increases since these inhibitors promote char and cross-linking to reduce the number of active site but do not seem to have significant changes in thermal runaway temperature. However, Formulation F101 may still benefit from having SXS in the blended material. Sodium xylene sulfonate is a wetting agent that can help a formula

spread across a surface. It also acts a solubilizer that ensures even distribution of the other ingredients throughout the product.

4.4 Combinatorial Optimizations.

Experimental design software DX9 was used in an attempt to optimize the proportion of each material to maximize the synergistic effects of spontaneous combustion inhibition in combinatorial blends. Two variables were selected as the analytical response to optimize the formulations: onset temperature and foam height. Onset temperature is the temperature at which thermal runaway occurs. The goal is to maximize the onset temperature of treated coal versus untreated coal to make coal more thermally stable. Foam height was used as a measureable value which is comparable to ability of the surfactants to spread across the coal surface. For this study, a higher foam height is desirable for formulations to have industrial application and relevance.

The DX9 software designed experiments for a series of 25 formulations with 5 duplicate tests that were tested to determine responses in onset temperature and foam height. The formulations were programmed to have a total maximum concentration loading of 25% by weight. Concentrations of each component and results from testing are shown in Table 2.

Once values of onset temperature and foam height were entered into the software, some new formulations of interest were proposed and the concentrations of the new formulations are shown in Table 3. Formulation F103 was proposed, however, was discarded since it was not stable in solution to be a practical application.

Table 2. Formulations and Results for Optimization Experiments

Component 1 A:TDA/TAM %	Component 2 B:AOS	Component 3 C:SXS	Component 4 D:TKPP	Response 1 Onset Temp °C	Response 2 Foam Height mL
25	0	0	0	365.9	150
0	25	0	0	363.4	420
0	0	25	0	368.7	180
0	0	0	25	424.1	50
16.6667	8.33333	0	0	378	330
16.6667	0	8.33333	0	363.1	205
16.6667	0	0	8.33333	355.5	270
8.33333	16.6667	0	0	360	430
8.33333	8.33333	8.33333	0	357.2	430
8.33333	8.33333	0	8.33333	0	0
8.33333	0	16.6667	0	364.8	130
8.33333	0	8.33333	8.33333	365.5	120
8.33333	0	0	16.6667	0	0
0	16.6667	8.33333	0	364.5	380
0	16.6667	0	8.33333	367.8	380
0	8.33333	16.6667	0	360	430
0	8.33333	8.33333	8.33333	358.6	405
0	8.33333	0	16.6667	0	0
0	0	16.6667	8.33333	375.6	30
0	0	8.33333	16.6667	449	20
15.625	3.125	3.125	3.125	366.6	230
3.125	15.625	3.125	3.125	369.1	450
3.125	3.125	15.625	3.125	0	0
3.125	3.125	3.125	15.625	445	305
6.25	6.25	6.25	6.25	369.4	310
25	0	0	0	366.6	150
0	25	0	0	363.1	420
0	0	25	0	369.2	180
0	0	0	25	425.6	50
16.6667	8.33333	0	0	382	330

Table 3. New Optimized Formulations Determined by DX9 software

	F101	F102	F104	F105	F106	F107
Raw	% weight	% weight	% weight	% weight	% weight	% weight
WATER	74.00	40.17	33.60	65.00	30.00	30.00
TKPP	10.50	16.00	12.10	16.25	15.00	14.00
TDA/TAM blend	5.50	8.60	11.50	6.25	10.00	6.00
AOS	4.00	15.23	9.50	6.25	20.00	25.00
SXS	6.00	20.00	33.30	6.25	25.00	25.00

Each new formulation was then applied to coal at 20% weight loadings and tested using TGA and compared to untreated coal under air atmosphere. Results of the tests are shown in Figure 16. Each new formulation showed promise as each had a positive influence on spontaneous combustion inhibition. All showed a decrease in coal oxidation at low temperatures and an increase in thermal runaway temperature when compared to an untreated reference.

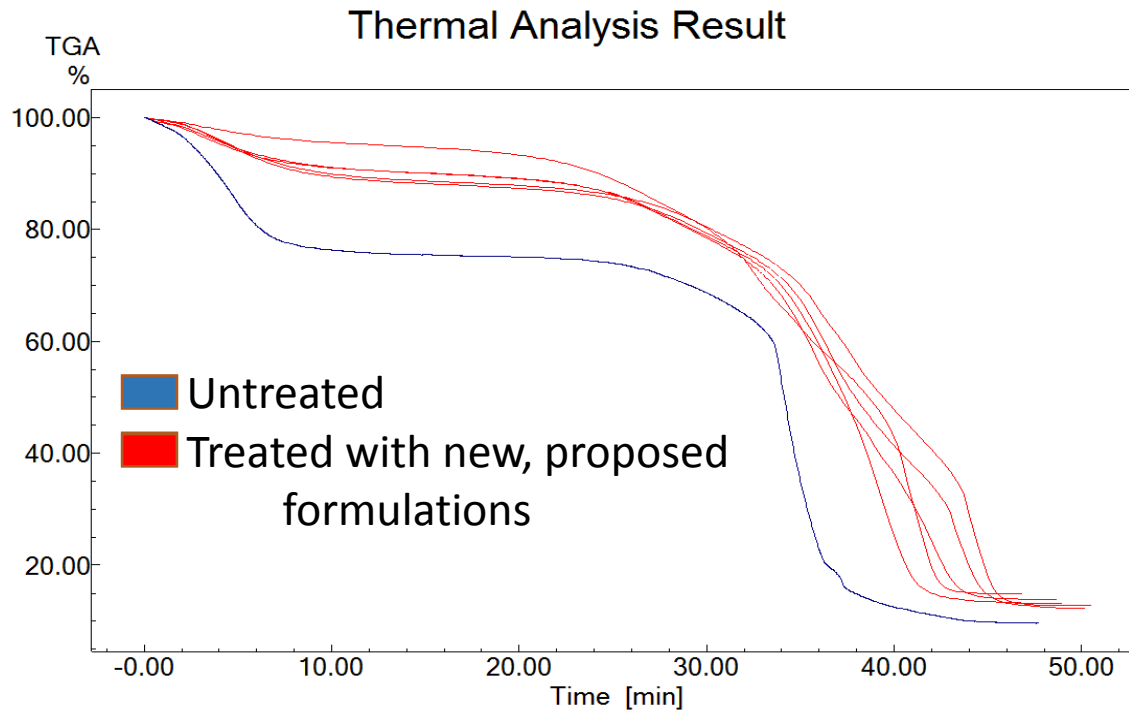


Figure 16. TGA Results of the New Proposed Formulations

Some key features of the results that were of interest include the mass loss at 200°C, temperature of surfactant degradation, and thermal runaway temperature. These values are summarized in Table 4.

4.5 Reformulation Successes - F104 Results

Formulation F104 shows the most promise since it had the highest thermal runaway temperature and only 6.70% mass loss at low temperatures (below 200°C) compared to the other proposed formulations (see Figure 17). Each formulation showed benefits of retained mass at low temperatures compared to untreated PRB coal indicating success in preventing coal oxidation with the use of surfactants.

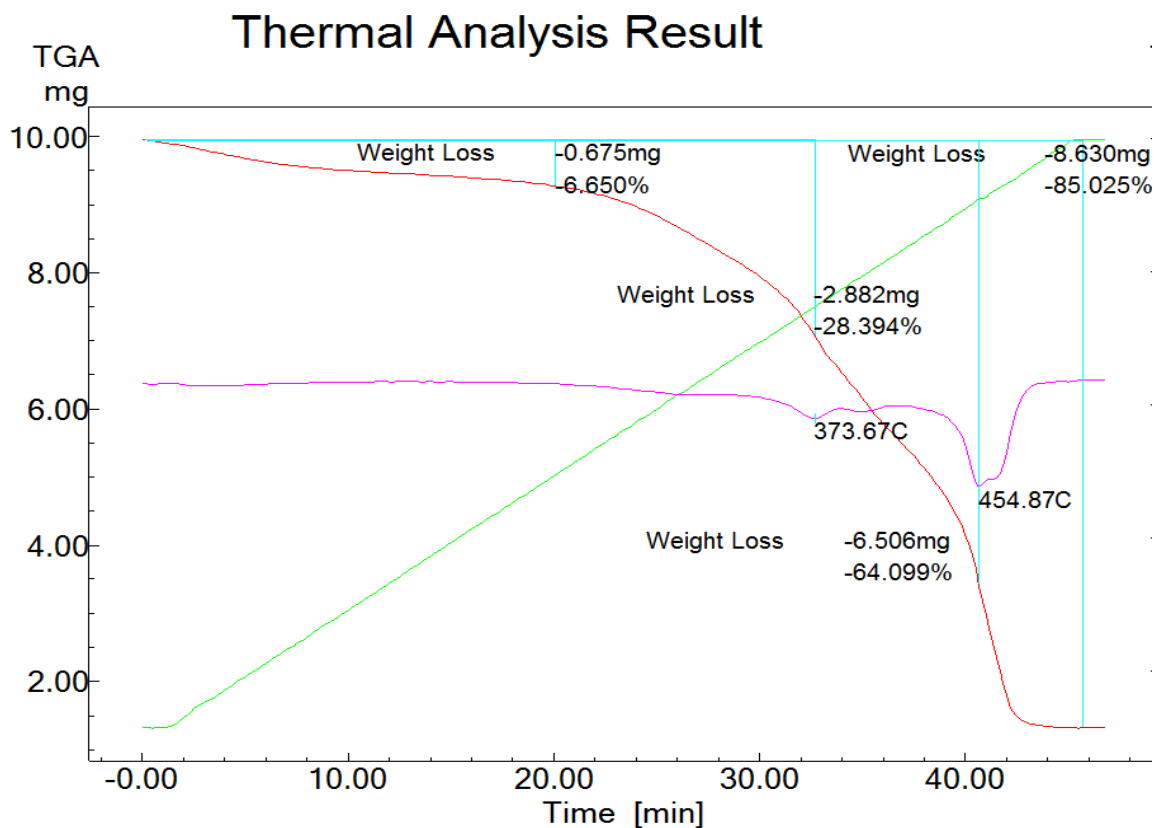


Figure 17. Key features: TGA Analysis of PRB Coal Treated with F104 in Air

Table 4. Summary of Results: Improved Formulations

Samples	%mass loss @ 200°C	Thermal Degradation: Surfactants	Coal Onset/Thermal Runaway Temp
Untreated PRB	24.6	---	354.8
F101	13.6	366.2	450.8
F102	12.0	370.3	452.4
F104	6.7	373.7	454.8
F105	12.0	380.8	448.5
F106	11.0	362.4	419.2
F107	10.1	373.0	450

However, F104 had the most SXS at 33.30%. This increased concentration of SXS compared to other formulations has slowed thermal decomposition forming stable cross-linking solid oxygenated complexes. The additional stable complexes slows down low temperature oxidation preventing the regeneration of new active sites. This increases the thermal stability which increases the thermal runaway temperature. The additional SXS generates excess radical scavenges slowing down coal combustion by reacting with coal, oxygen, and hydroxyl radicals. Through combined effects of SXS and TKPP promoting similar reactions, the total combined concentration of SXS and TKPP in formulation F104 is the greatest which could explain why it shows the lowest retained mass at 200°C and highest thermal runaway temperature. The addition of F104 increased the thermal runaway temperature of PRB coal 100.0°C from 354.8°C to 454.8°C at a 20wt% load and inhibits spontaneous coal combustion.

CHAPTER 5. CONCLUSIONS

5.1 Conclusion

Coal can be classified into four ranks depending the degree of change over time as it matures from lignite to anthracite. Coalification has an important bearing on coal's physical and chemical properties such as porosity, moisture content, fixed carbon, and mineral content. Each of these factors influence the susceptibility of coal to experience a spontaneous combustion event. Higher rank coals have been exposed to increased pressure and heat resulting in a compact matrix resulting in less available surface area and lower moisture content. Low rank coals such as lignite and sub-bituminous coal are the most susceptible to spontaneous combustion since they have a higher surface area and more porous structure. Low rank coals also absorb/desorb moisture easily increasing heat by heat of absorption and increasing available oxidative surface area.

PRB coal accounts for 46% of the total U.S. coal production due to its high demand as a low sulfur coal. Since it is a sub-bituminous type coal, PRB coal is susceptible and experiences spontaneous coal combustion. The resulting fire not only poses a safety hazard, but also a health hazard if it is not put out quickly. If the fire spreads, potentially hundreds to thousands of tons of coal could burn resulting in a significant loss and decrease in caloric value. Thus, a method of inhibition is of great importance.

Chemical additives such as inorganic phosphate and sulfonate salts can be used to prevent spontaneous combustion. Each promote cross-linking to form stable carbon oxygen complexes which increases thermal stability of coal and increase thermal runaway temperature. Both are also able to generate radical scavengers which can slow down the oxidative process. Surfactants can also be added creating a physical barrier to coal oxidative effectively slowing the heat release rate. Together, mixtures of non-ionic and anionic surfactants, and sulfonate and phosphate salts can be used to prevent spontaneous coal combustion.

The results of the flammability test provided preliminary confirmation of the feasibility of a blend of salts and surfactants to be used as a flame retardant material for coal combustion (Figure 5). Formulation F101 created a physical barrier to coal oxidation (Figure 6C) and as a result of the flammability test, showed only a charring characteristic leaving the coal surface primarily unburned (Figure 6D). Thermal analysis also supports the hypothesis that blends of these compounds reduce coal oxidation at low temperatures, promote cross-linking and char formation, and increases thermal runaway temperatures near 100°C (Figure 10).

The design phase of the experiment was used to maximize the effects of adding surfactants and phosphate and sulfonate salts to prevent spontaneous coal combustion. As a result, new and improved formulations were proposed. Formulation F104 showed to be the most promising as it had the highest retained mass at low temperatures and the highest thermal runaway temperature compared to untreated PRB coal. Thus, thermal analysis can be used to investigate spontaneous coal combustion and determine successful methods of inhibition which has been validated in this study. By altering the

heating characteristics of coal through the use of chemical additives, spontaneous combustion susceptibility can then be quantified to determine whether or not thermal stability has increased or decreased.

5.2 Future Research

The application of inhibitors to reduce spontaneous combustion susceptibility has a significant scope for future research. New formulations such as F104 should be tested on higher and lower rank coals such as lignite and bituminous coals to determine the effects it has on oxidation and thermal runaway temperature. Tests should also focus on optimizing percent weight loads on coal for the practical use in industry. The addition of these chemicals should have an insignificant effect on the loss of caloric value as coal is pulverized creating new available surface area upon utilization. Although laboratory testing can provide insight to certain industrial applications, testing on larger coal deposits should be considered to determine feasibility and longevity of these additives during storage and transport.

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APPENDIX A

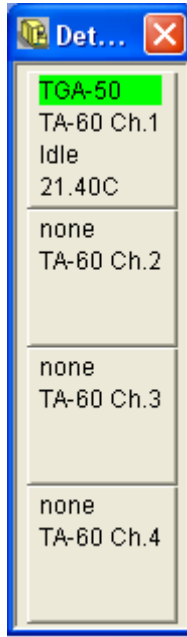
Standard Operating Procedures: Thermogravimetric Analyzer (TGA-50)

1. Open the gas valve on the N₂ or Air (79% N₂, 21% O₂) tank
2. Turn the valve on the regulator on (NOTE: Should be at ~35psi)
 - a. Boot up the computer. Turn software on by clicking “TA-60 workstation collection monitor” Icon on the desktop
3. Turn on the TA-60WS box (NOTE: The switch is on the back on the top.)
4. Turn on the TGA-50 (NOTE: The switch is on the right side of the instrument)
5. Click on “acquisition” and select “TGA: Channel 1 idle”
6. Software will automatically recognize the instrument
7. Remove the fan from below the furnace before dropping down.
8. Bring down the furnace by pushing the down arrow located on the front of the instrument.
9. Move suspended plate furnace cover to the left to cover the furnace hole.
10. DO NOT PROCEED UNTIL STEP 9 IS COMPLETE.
11. VERY carefully with tweezers (tweezers found in a drawer in the TGA/DSC tool box in a cabinet next to the computer) place an empty sample pan on the suspended balance hanging from the quartz hook on the TGA. (NOTE: Avoid touching pan with fingers).
12. Move the sliding plate back to the right and out of the way.
13. Close the furnace up by pushing the up arrow located on the front of the instrument.
14. Once the furnace is closed, allow the balance to reach equilibrium.
15. Zero balance:
 - a. Press “Auto zero” (NOTE: watch level indicator light). Press Enter.
 - b. Turn gray knob in either direction until level indicator lights are centered on zero.
 - c. Repeat a through c until the instrument reads zero.
16. Once zeroed, follow steps 8-9, remove empty sample pan from balance using tweezers and load a coal sample into pan. (Sample size should be in the range of 5-15 milligrams.)
17. Return the pan loaded with sample to the suspended balance (follow steps 11-14).
18. Place black fan, set to control, under furnace so that at the end of the run it will turn on automatically and increase the cooling rate.
19. Set mass limit
 - a. Press “Function” button. Use up and down arrows to find “Range.” Press Enter.

- b. There are three mass options: Auto, 20mg, and 200mg.
- c. Select 20mg and press Enter (counter balance is set at 20mg).

20. On software:

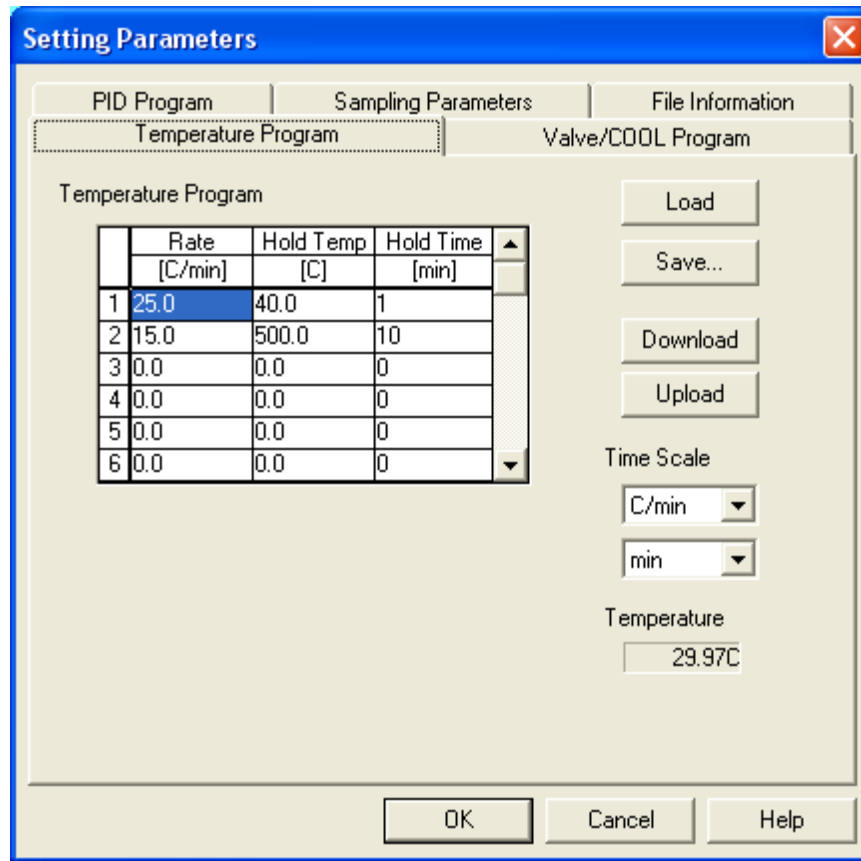
- a. Click on “TGA-50 / TA-60 Ch.1/ Idle” in detector window to bring up data acquisition screen.



- b. Click on “Measure” in the toolbar.

- c. From there click on “Measuring Parameters”
 - i. Click on “Temperature Program” tab to set temperature ramping program.
 - a. Row one column one is the rate at which the oven is going to heat the sample to the initial temperature.
 - b. Row one, column two is the initial temperature.
 - c. Row one, column three is the time that the furnace is going to hold at the initial temperature.
 - d. Row two, column one is the rate at which the oven is going to heat the sample to the final temperature
 - e. Row two, column two is the final temperature.
 - f. Row two, column three is the time that the furnace is going to hold at the final temperature once it is reached.
 - ii. The temperature program used in this project:
 - a. Rate: 10°C/ min
 - b. Hold Temp: 500°C
 - c. Hold Time: 5 min

EXAMPLE:



- d. Click on “File Information” tab.
 - i. Enter sample name.
 - ii. Input sample weight by selecting “Read Weight”
 - iii. Rate Flow has been set at 40mL/min and should be entered “40”
 - iv. Enter other relevant information
 - v. Click OK.

EXAMPLE:

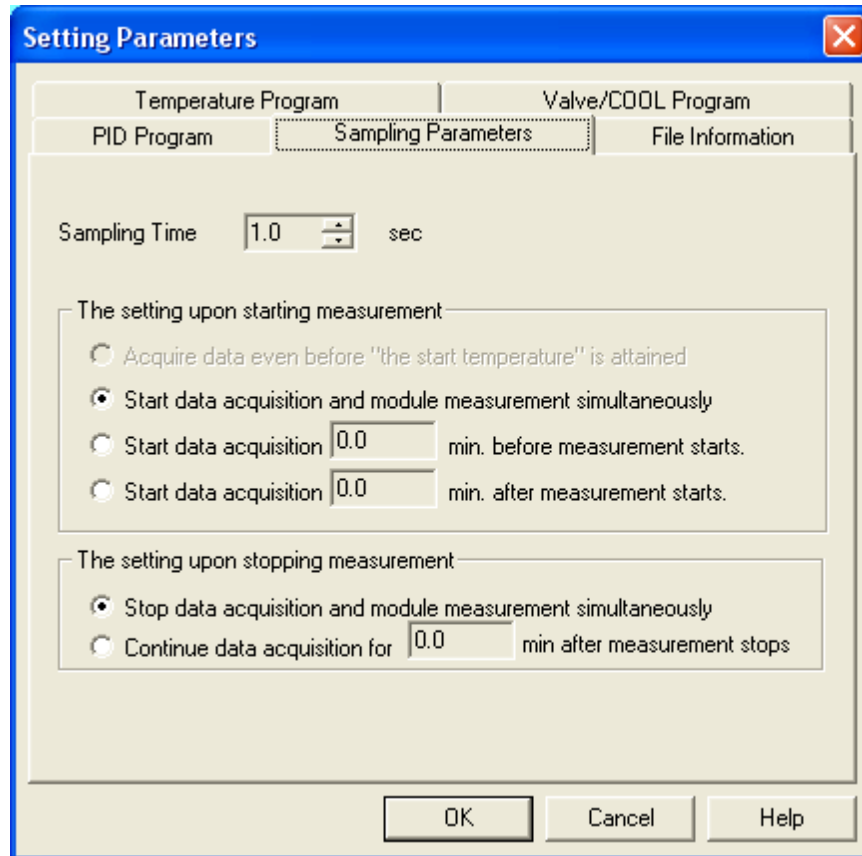
The image shows a software dialog box titled "Setting Parameters" with a close button (X) in the top right corner. The dialog is divided into two main sections: "Temperature Program" and "Valve/COOL Program". Under "Valve/COOL Program", there are three sub-tabs: "PID Program", "Sampling Parameters", and "File Information". The "File Information" tab is currently selected and highlighted with a dashed border. The "File Information" section contains the following fields:

- Lot No.:** A text input field.
- Sample Name:** A dropdown menu.
- Sample Weight:** A text input field followed by "[mg]" and a button labeled "Read Weight".
- Pan:** A dropdown menu.
- Atmosphere:** A dropdown menu.
- Rate flow:** A text input field followed by "[ml/min]".
- Operator:** A dropdown menu.
- Comment:** A multi-line text area with scroll bars.

At the bottom of the dialog, there are three buttons: "OK", "Cancel", and "Help".

- e. Click on “Sampling Parameters” tab to ensure that sampling time is 1.0s. Click OK.

EXAMPLE:



- f. Click “Measure” in toolbar:
 - i. Click “Start.” Confirm sample name and mass are correct. Click “Start.” NOTE: The acquisition analysis page background changed to a salmon color. The red curve is the Δ Temperature and the black curve is the Δ Mass.

21. While cooling, click “TA-60 Analysis” icon on desktop. Load data file.
 - a. Click “File”. Click “Open.”
 - b. Find filename in Open Dialog Window. NOTE: Date is inserted into beginning of filename.
 - c. Once file is opened, TGA Analysis can be performed.
22. Once the TGA has cooled below 40°C, follow steps 8-13 to remove the sample from the instrument.
23. Discard sample pan if you are finished with the experiment.

24. Repeat Steps 5 – 23 for the next experiment. If experiments are complete, follow steps 25 – 28.
25. Turn off TGA-50.
26. Turn off TGA-60 WS box.
27. Shutdown computer.
28. Turn off regulator and gas tank. *IMPORTANT*

Standard Operating Procedures: Differential Scanning Calorimeter (DSC-60)

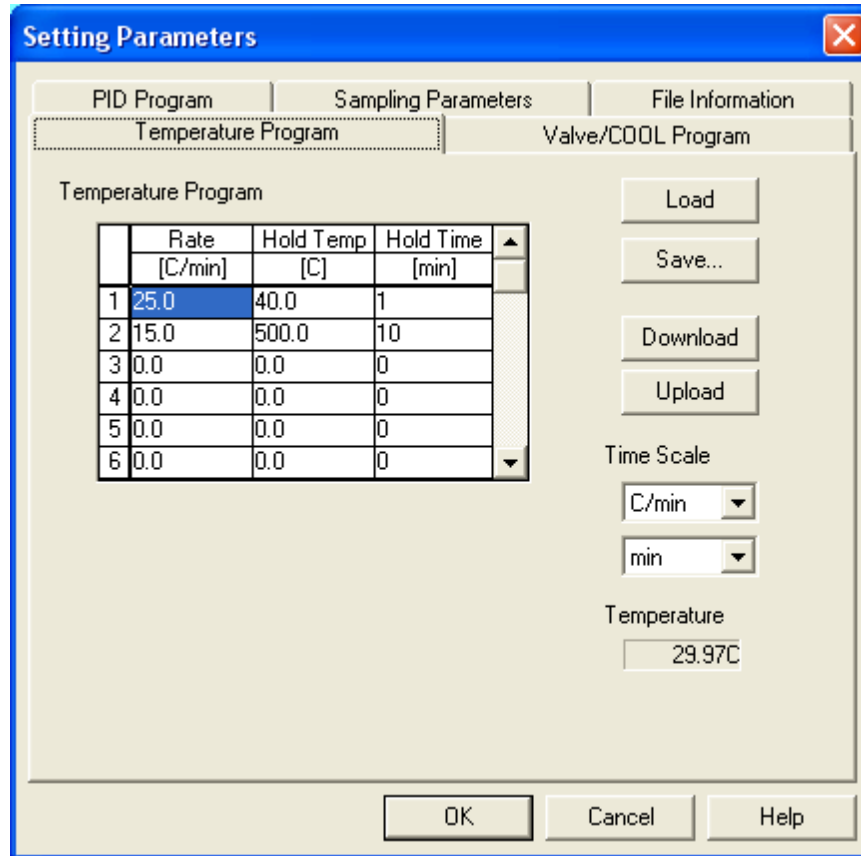
1. Open the gas valve on the N₂ or Air (79% N₂, 21% O₂) tank
2. Turn the valve on the regulator on (NOTE: Should be at ~35psi)
 - a. Boot up the computer. Turn software on by clicking “TA-60 workstation collection monitor” Icon on the desktop
3. Turn on the TA-60WS box (NOTE: The switch is on the back on the top.)
4. Turn on the DSC-60 (NOTE: The switch is on the backside of the instrument)
5. Click on “acquisition” and select “DSC: Channel 2 idle”
6. Software will automatically recognize the instrument
7. Remove outer cover on right hand side of the instrument below DSC-60 label.
 - a. Cover should slide off by pulling the cover toward users.
 - b. With tweezers, remove inner furnace cover.
 - c. Remove flat inner plate cover using tweezers
8. VERY carefully with tweezers (tweezers found in a drawer in the TGA/DSC tool box in a cabinet next to the computer) prepare a new coal sample in sample pan noting mass (5-15 milligrams) with an analytical balance. (NOTE: Avoid touching pan with fingers).
 - a. Using tweezers place pan on an analytical balance and push “0/T” button.
 - b. Remove sample pan from balance using tweezers and load sample into pan. (Sample size should be in the range of micrograms to milligrams.)
 - c. Return pan to analytical balance and record mass.
9. Remove the sample for the analytical balance and place a lid on the sample pan using tweezers.
10. Crimp sample using crimper.
 - a. Place sample pan with lid on center stage of the crimper
 - b. Turn the handle on the top of the crimper clockwise to lower the crimper press. (Note: Once the handle starts to resist, turn one full rotation further to seal the pan)
 - c. Turn the handle on the top of the crimper counterclockwise to raise the crimper.
 - d. Use a small rod to remove pan from crimper by positioning it into the hole located on top of the crimper shaft and push down until the sample is released.
 - e. Check to make sure the pan is sealed correctly. If the pan is NOT sealed, repeat steps 8 – 10. If sealed correctly, continue to step 11.
11. To prepare the reference pan, repeat step 10 with a new, empty sample pan and follow crimping procedures.

12. VERY carefully with tweezers (tweezers found in a drawer in the TGA/DSC tool box in a cabinet next to the computer) place the empty, crimped reference sample pan on the LEFT side of the sample holder (NOTE: Avoid touching pan with fingers).
13. VERY carefully with tweezers (tweezers found in a drawer in the TGA/DSC tool box in a cabinet next to the computer) place crimped sample pan on the RIGHT side of the sample holder (NOTE: Avoid touching pan with fingers).
14. Once both samples are loaded close the furnace by replacing all of the lids removed in step 7
 - a. Replace flat inner plate cover using tweezers
 - b. With tweezers, replace inner furnace cover.
 - c. Slide top cover back on the front of the instrument.

15. On software:
 - a. Click on “DSC-60 / TA-60 Ch.2/ Idle” in detector window to bring up data acquisition screen.
 - b. Click on “Measure” in the toolbar.
 - c. From there click on “Measuring Parameters”
 - i. Click on “Temperature Program” tab to set temperature ramping program.
 - a. Row one column one is the rate at which the oven is going to heat the sample to the initial temperature.
 - b. Row one, column two is the initial temperature.
 - c. Row one, column three is the time that the furnace is going to hold at the initial temperature.
 - d. Row two, column one is the rate at which the oven is going to heat the sample to the final temperature
 - e. Row two, column two is the final temperature.
 - f. Row two, column three is the time that the furnace is going to hold at the final temperature once it is reached.

- i. The temperature program used in this project:
 - a. Rate: 10°C/ min
 - b. Hold Temp: 500°C
 - c. Hold Time: 5 min

EXAMPLE:



- b. Click on “File Information” tab.
 - i. Enter sample name.
 - ii. Input sample weight recorded from the analytical balance.
 - iii. Rate Flow has been set at 40mL/min and should be entered “40”
 - iv. Enter other relevant information
 - v. Click OK.

EXAMPLE:

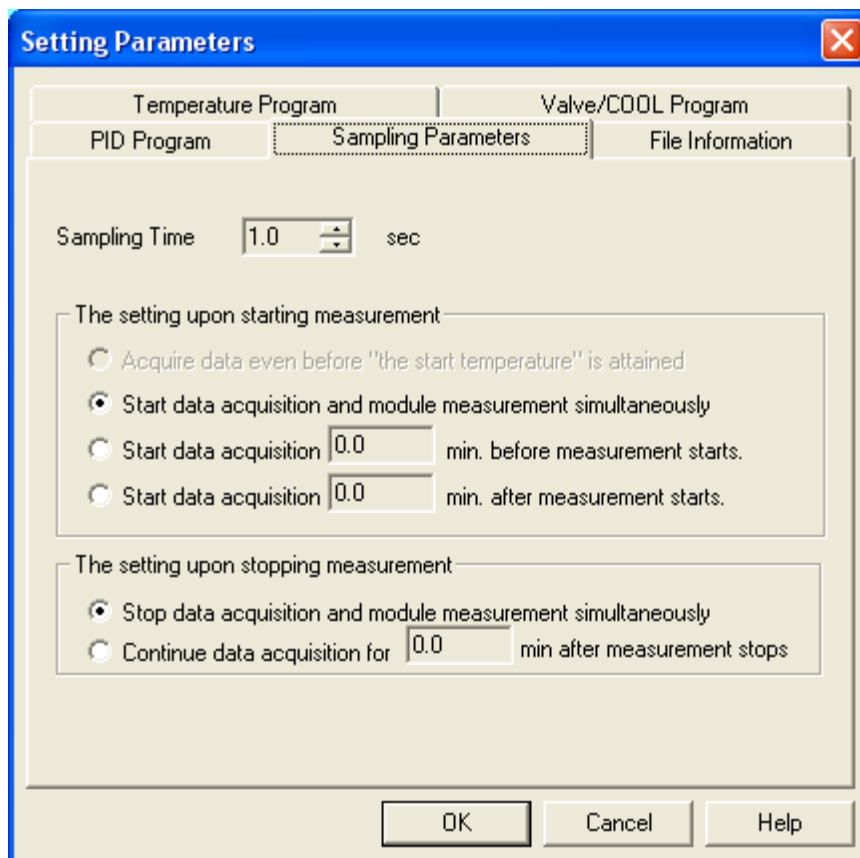
The image shows a software dialog box titled "Setting Parameters" with a close button (X) in the top right corner. The dialog is divided into two main sections: "Temperature Program" and "Valve/COOL Program". Under "Valve/COOL Program", there are three sub-tabs: "PID Program", "Sampling Parameters", and "File Information". The "File Information" tab is currently selected and highlighted with a dashed border. The "File Information" section contains the following fields:

- Lot No.: A text input field.
- Sample Name: A dropdown menu.
- Sample Weight: A text input field followed by "[mg]" and a "Read Weight" button.
- Pan: A dropdown menu.
- Atmosphere: A dropdown menu.
- Rate flow: A text input field followed by "[ml/min]".
- Operator: A dropdown menu.
- Comment: A multi-line text area with up/down arrow buttons on the right and left/right arrow buttons at the bottom.

At the bottom of the dialog, there are three buttons: "OK", "Cancel", and "Help".

- c. Click on “Sampling Parameters” tab to ensure that sampling time is 1.0s.
Click OK.

EXAMPLE:



- d. Click “Measure” in toolbar:
- Click “Start.” Confirm sample name and mass are correct. Click “Start.” NOTE: The acquisition analysis page background changed to a salmon color. The red curve is the Δ Temperature and the black curve is the Δ Mass.
17. While cooling, click “TA-60 Analysis” icon on desktop. Load data file.
- Click “File”. Click “Open.”
 - Find filename in Open Dialog Window. NOTE: Date is inserted into beginning of filename.
 - Once file is opened, DSC Analysis can be performed.
18. Once DSC has cooled below 40°C, follow steps 7, 12-14 to remove the sample from the instrument.
19. Discard sample pan if you are finished with the experiment.

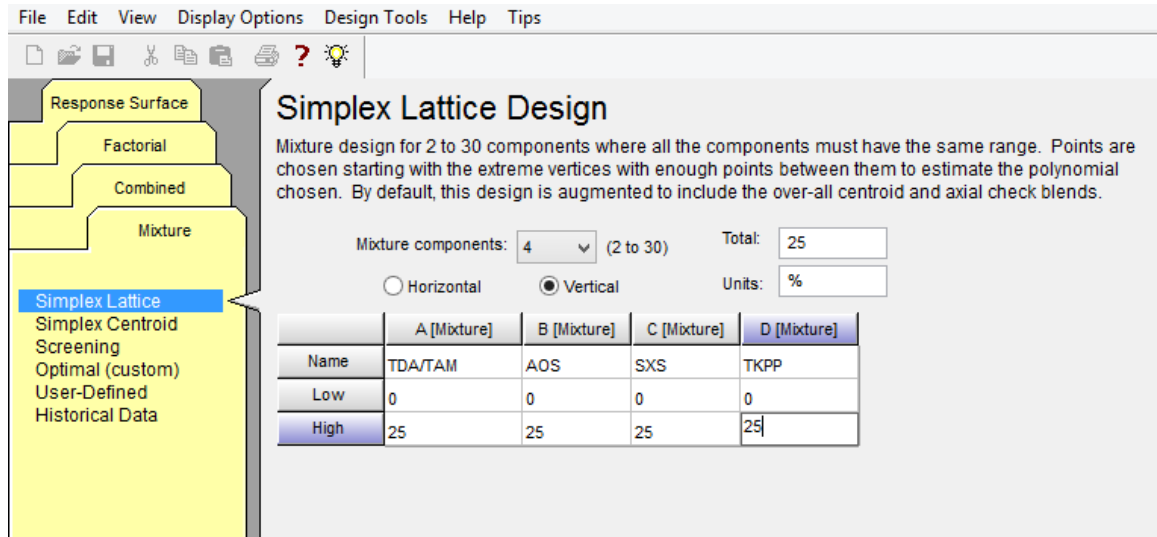
20. Repeat Steps 7 - 18 for the next experiment. If experiments are complete, follow steps 20 – 23.
21. Turn off TGA-50.
22. Turn off TGA-60 WS box.
23. Shutdown computer.
24. Turn off regulator and gas tank. *IMPORTANT*

APPENDIX B.

DESIGN EXPERT 9 (DX9) SOFTWARE

1. Open DX9 Software Program.
2. On the home page, click on “New Design.”
3. Click on the file folder labeled “Mixture”
4. Select “Simplex Lattice” Design
5. Change VARIABLES of the design to read:
 - a. Mixture Components: 4
 - b. Total: 25
 - c. Units: %
 - d. Edit name of 4 components to be used in mixture design
 - i. TDA/TAM, AOS, SXS, TKPP
 - e. Values for low and high for each component are to read 0 and 25 respectively.

EXAMPLE:



The screenshot shows the Design Expert 9 software interface. The menu bar includes File, Edit, View, Display Options, Design Tools, Help, and Tips. The left sidebar shows a tree view with categories: Response Surface, Factorial, Combined, Mixture, and Simplex Lattice (highlighted). The main window is titled "Simplex Lattice Design" and contains the following configuration options:

- Mixture components: 4 (2 to 30)
- Total: 25
- Units: %
- Orientation: Horizontal, Vertical

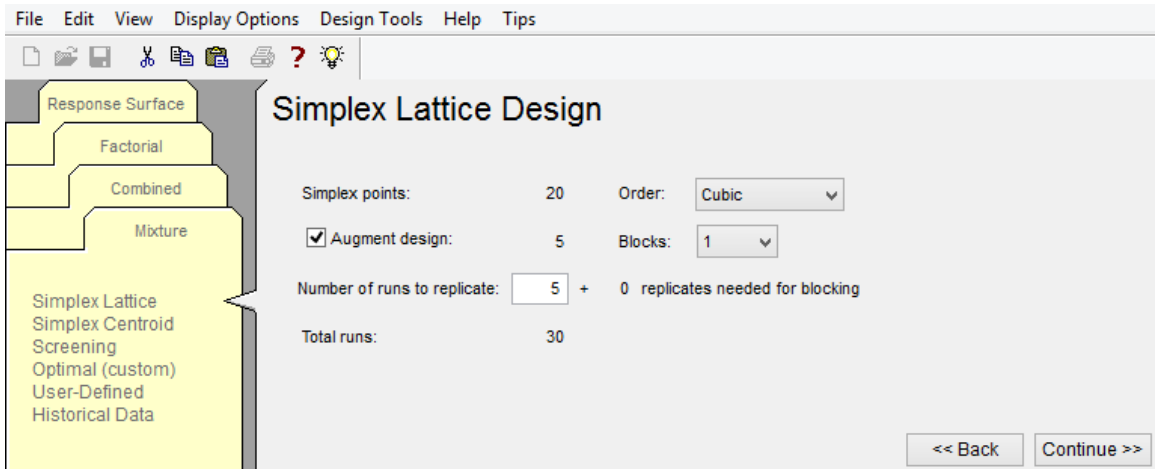
Below these options is a table with the following data:

	A [Mixture]	B [Mixture]	C [Mixture]	D [Mixture]
Name	TDA/TAM	AOS	SXS	TKPP
Low	0	0	0	0
High	25	25	25	25

6. Click “Continue” at the bottom of the page.
7. On the next screen, click the drop down menu next to ORDER and select “cubic”.
8. Make sure the augment design is “checked.”
9. Leave blocks as “1.”

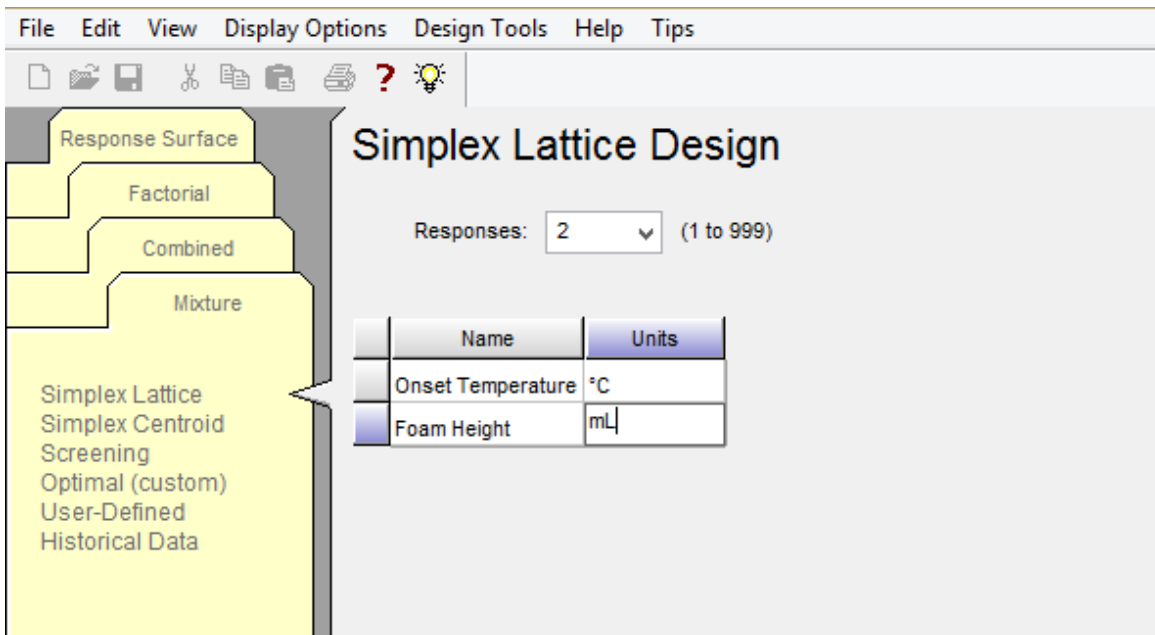
10. Number of run to replicate in this project was “5” which brought the total number of runs to equal 30.
11. Once complete, hit continue to move to the next screen.

EXAMPLE:



12. Change the number of responses from the drop down menu to “2.”
13. Enter the name of the response factor along with the associated units.
14. Click “Finish” to move to the next page

EXAMPLE:



15. Once the parameters of the experiment are entered into the software, wet formulations are batched in the lab using the concentrations listed in this chart:

Select	Std	Run	Component 1 A:TDA/TAM %	Component 2 B:AOS %	Component 3 C:SXS %	Component 4 D:TKPP %	Response 1 Onset/Therm... °C	Response 2 Foam Height mL
	1	7	25	0	0	0		
	2	13	0	25	0	0		
	3	30	0	0	25	0		
	4	16	0	0	0	25		
	5	15	16.6667	8.33333	0	0		
	6	19	16.6667	0	8.33333	0		
	7	22	16.6667	0	0	8.33333		
	8	6	8.33333	16.6667	0	0		
	9	8	8.33333	8.33333	8.33333	0		
	10	24	8.33333	8.33333	0	8.33333		
	11	29	8.33333	0	16.6667	0		
	12	4	8.33333	0	8.33333	8.33333		
	13	12	8.33333	0	0	16.6667		
	14	18	0	16.6667	8.33333	0		
	15	1	0	16.6667	0	8.33333		
	16	10	0	8.33333	16.6667	0		
	17	11	0	8.33333	8.33333	8.33333		
	18	21	0	8.33333	0	16.6667		
	19	26	0	0	16.6667	8.33333		
	20	3	0	0	8.33333	16.6667		
	21	27	15.625	3.125	3.125	3.125		
	22	20	3.125	15.625	3.125	3.125		
	23	25	3.125	3.125	15.625	3.125		
	24	9	3.125	3.125	3.125	15.625		
	25	17	6.25	6.25	6.25	6.25		
	26	28	25	0	0	0		
	27	2	0	25	0	0		
	28	23	0	0	25	0		
	29	14	0	0	0	25		
	30	5	16.6667	8.33333	0	0		

16. Once solutions are made, coal is treated with each design formulation to determine the onset temperature to thermal runaway.

17. Then data from foam height testing is also added into the design software.

18. Once response factor data is entered into the software, analysis of the results and formulation optimization can take place.

19. Results of these analyses are listed in Tables 2 and 3.