

# **SPONTANEOUS COMBUSTION OF COAL – A SOUTH AFRICAN PERSPECTIVE**

By

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I, Ofentse Marvin Moroeng declare that the thesis/dissertation, which I hereby submit for the degree Master of Science in Geology at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

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## ABSTRACT

Spontaneous combustion initiates as a result of low-temperature oxidation of organic coal components. The upper limit of the temperature range cited for oxidation is 70°C and the primary requirement is that combustion initiates without the use of external triggers. Oxidation results in the formation of oxygenated hydrocarbon complexes, decomposition of some of these complexes liberates a combination of heat and gaseous phases. In the instance where spontaneous combustion is triggered, this heat is insufficiently dissipated into the atmosphere such that the coal's temperature surpasses the so-called 'crossing point temperature'. The nature of the gases evolved is dependent on coal's overall composition, the ability of oxygen to flow through the coal-body and the maximum temperature of the body. CO<sub>2</sub> production requires that oxygen is able to circulate throughout the coal-body whereas CH<sub>4</sub> production requires that parts of the body reach high temperatures simultaneous with oxygen starvation.

Hydrocarbon complexes may be divided broadly into aromatic and aliphatic groups corresponding to benzene and related compounds, and alkanes (and alkenes and alkynes) respectively. The low-temperature oxidation of these two major groups is specific for the nature of the hydrocarbon involved. Oxidation of benzene and similar compounds require high temperature aqueous solutions as well as catalysation to progress. Conversely, aliphatic compounds readily oxidize liberating heat energy ultimately responsible for self-heating. Hydroxyls, carboxyls, carbonyls and inorganic carbonates thermally decompose at temperatures above those commonly accepted for low-temperature oxidation and subsequent spontaneous combustion. However, peroxides which are oxidation products of some ethers, decompose within the appropriate low-temperature range.

Inertinite has been largely taken to be the main maceral group in South African Coalfields and those of other Gondwana Provinces. However, this appears to be untrue for the Waterberg Coalfield in general and several other seams in some of the other coalfields. It is these vitrinite-dominated coals, that based on the knowledge of organic chemistry of vitrinite appear to be most risk of spontaneous combustion. The Highveld Coalfield and the No. 2 and 4 seams of the Witbank Coalfield as well as the Vryheid Formation in the Waterberg at least, are dominated by inertinite resulting in what has been interpreted to be similar organic chemical makeup. On the other hand, vitrinite is the principal maceral group of samples from the Waterberg specifically the Grootegeluk Formation and the No. 5 seam of

the Witbank. This study concludes that the Grootegeluk Formation of the Waterberg, No. 5 seam of the Witbank as well as the Ermelo Coalfield are dominated by aliphatic hydrocarbons and have an increased propensity towards to spontaneous combustion.

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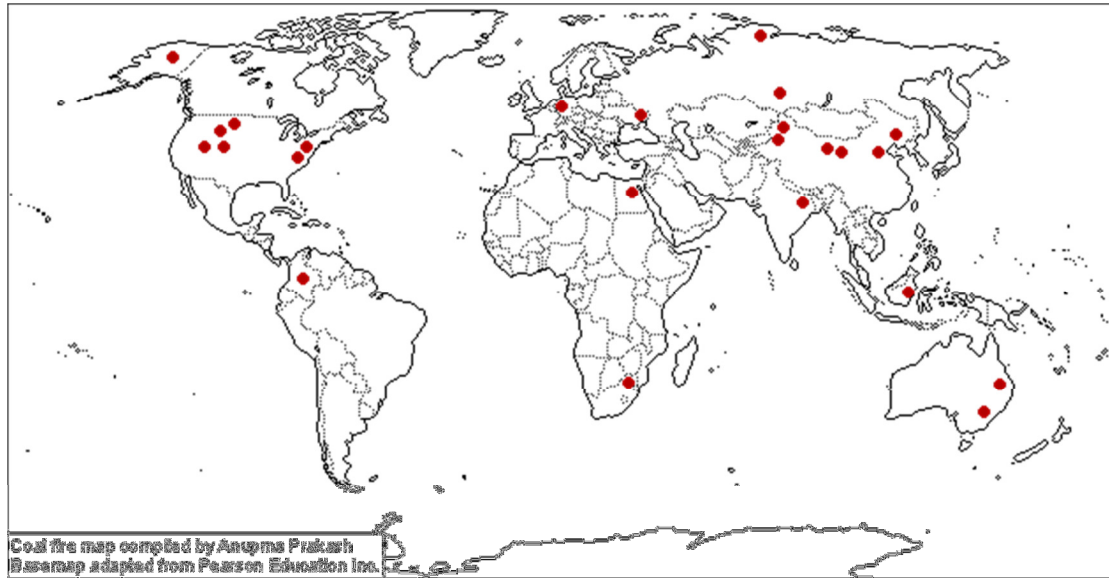
# **1 CHAPTER 1: INTRODUCTION**

In this chapter, a brief introduction to this study is presented. This includes the motivation as well as the aims and objectives of the study. A brief background and explanation of the topic of study will be provided together with a layout of the project in its entirety.

## **1.1 INTRODUCTION TO THE PROBLEM AND AIMS OF THE REVIEW**

Coal has and will continue to be, at least for the foreseeable future, a relatively cheap and due to its relative abundance over other energy sources, a major source of energy for both South Africa and other countries the world over. Coals that are prone to spontaneous combustion, either while *in-situ* or following extraction are a liability in terms of safety and revenue loss for producers, shippers (carriers) and consumers. Since coal combusts in a smoldering fashion (Ohlemiller, 1990; Rein, 2009), this means that combustion can initiate and continue for prolonged periods of time without detection rendering spontaneous combustion to be particularly dangerous. The gaseous phases liberated as combustion progresses also lead to atmospheric pollution (Pone *et al.*, 2007; Carras *et al.*, 2009) in addition to degrading the landscape and causing land subsidence in the case of spontaneously combusting coal seams (Keunzer *et al.*, 2007).

Incidences of spontaneous combustion have been reported and documented in almost all major coal producing and consuming regions of the world (Prakash, 2007) as depicted in Figure 1.1. As previously alluded to, coal may combust spontaneously before or following extraction in stock- and spoil-piles due to oxidation of organic components. The major requirement for combustion initiation is the availability of oxygen and its ability to flow unobstructed through a coal body. The exact nature of these organic compounds has remained largely unknown until recently to some extent, so that their reactivities can be investigated. Coal weathering may also alter the combustion properties of non-spontaneously igniting coals (Wang *et al.*, 2003) thus rendering the material unsuitable for the intended use.



**Figure 1.1:** World map of coal fire regions (Prakash, 2007).

The majority of studies regarding spontaneous combustion have focused primarily on detecting and predicting the susceptibility of coals to self-ignition by subjecting coal samples to varying experimental conditions and determining the physical response of the coal (e.g. Tarafdar & Guha, 1989; Clemens *et al.*, 1991; Martinez & Escobar, 1995; Avila *et al.*, 2014). Although such physical measurements have contributed and expanded our collective understanding of low-temperature oxidation, they are simply a manifestation of processes occurring at the molecular level. However, as any coal geologist or chemist can attest to, information regarding the organic chemistry of coal and its response to oxidation is sparse and far apart at best.

An attempt will be made to discuss low-temperature oxidation and spontaneous combustion in the context of South African coalfields. This discussion will be based chiefly on published ultimate analysis and petrographic data for the various coalfields. The hydrogen and carbon percentages from the elemental data will be used to calculate aromaticity based on the H/C ratio as suggested by other workers (e.g. Gerstein *et al.*, 1982). Petrographic information and coal rank will be used to supplement the aforementioned discussions based on aromaticity. Inertinite and vitrinite maceral groups are dominated by aromatic and aliphatic compounds respectively (Falcon, 1986). In addition, aliphatic compounds constitute the majority of low ranked coals whereas anthracitic coals are dominated by aromatic compounds (Mahajan, 1982).

## 1.2 BACKGROUND

The differences in the maturity (rank) of coals from northern and southern hemispheres, presumed to be a manifestation of the climatic conditions prevailing in the depositional environments on which the coals were deposited, is well documented in literature (e.g. Falcon & Ham, 1988). Gondwanian Provinces (including South Africa) are dominated by heterogeneous coals (ranging from lignite to anthracite), the majority of which are classified as 'low rank'. The effect of rank on coal's susceptibility to oxidation and subsequent self-heating has also been previously investigated (e.g. Wang *et al.*, 2003; Misra & Singh, 1994). The majority of investigations concluded that low rank coals are easily oxidized as opposed to their higher rank counterparts. As such and accepting the preceding reasoning, coal deposits and resources presently found in the former Gondwana Provinces (India, South Africa, Australia and South America) should be more prone to oxidation and the resultant self-heating. This observation necessitates a need to pay special attention to the coals of these regions so as to prevent potential self-ignition (or lowering of calorific value).

South African coal deposits are hosted within the widespread, Phanerozoic Karoo Supergroup. Numerous coalfields have been identified and continue to be exploited within this Supergroup, including Witbank, Springbok Flats, Highveld, Waterberg, Sasolburg-Vereeniging, Free State, Klip River, Soutpansberg, etc. (Jeffrey, 2005a; Hancox and Götz, 2014) with Ecca and Beaufort Groups together with Molteno Formation constituting the main coal-bearing sequences (Hancox and Götz, 2014). The variable nature of the coal rank in these coalfields is related to the intrusion of dolerites dykes (Du Toit, 1954) or more accurately, reflects varying degrees of burial metamorphism (Snyman & Barclay, 1989) coupled with hydrothermal metamorphism by circulating magmatic fluids sourced from dolerite intrusions (Bussio, 2012).

It is important to realize that the majority of research that has so far been conducted on spontaneous combustion has been concerned mainly with Northern Hemisphere coalfields. Thus Southern Hemisphere and South African coal deposits specifically, have as a result not been the main focus of such studies. The main aim of

this study then, is to review current knowledge on low-temperature oxidation and spontaneous combustion of coal and ultimately to attempt to put this in the context of South African coal deposits. However, it should be emphasized that it is neither the purpose nor the aim of this study to propose either a monitoring or detection technique for spontaneous combustion.

The effect of coal structure, referring specifically to the three dimensional arrangement of organic macromolecules, of South African coals in particular on low-temperature oxidation is yet to be investigated. This study will rely, even if only narrowly so, on molecular models found in literature to examine and make largely theoretical inferences about the possible effects of structure on coal oxidation and the resultant spontaneous combustion. Van Niekerk and Mathews (2010) constructed the molecular representations of two bituminous, Permian-aged, vitrinite-rich and inertinite-rich coals from the Waterberg and Highveld coalfields respectively. These representations will be discussed briefly in the context of spontaneous combustion.

Although it has been known for some time that oxidation of the organic constituents of coal is the main cause for self-heating, the exact mechanism of how the process progresses within a coal seam, lump or stockpile has remained largely illusive. This is likely because of the complex and highly varied, depositional environment-specific organic and inorganic constitution of coal. Due to this varied compositional makeup, it has proved rather difficult to correlate composition to behaviour before, during and following oxidation. This also raises other questions such as whether spontaneous combustion-prone coals perhaps contain a specific organic molecule which liberates a greater amount of heat upon oxidation and subsequent decomposition. Unfortunately, as has been found by previous authors, the answer to this question is not as simple as that because of other coal-intrinsic and physical parameters that must be accounted for.

The decomposition of oxygenated complexes referring to oxidation products, appears to impose important controls on spontaneous combustion initiation. First and most importantly, oxygenated complex decomposition controls the rate at which the coal temperature will increase by trapping heat and only releasing it upon break down. Secondly, liberation of heat is accompanied by emission of some greenhouse gases.

The nature of said gases and the rate at which they are liberated is dependent on the elemental composition of the coal as well as temperature and availability of oxygen (Carras *et al.*, 2009).

In the instance where coal that has previously been in contact with the atmosphere, therefore weathered or rather oxidized coal, fails to self-heat sufficiently so as to initiate spontaneous combustion, the increased oxygen concentration along with decreased carbon-hydrogen concentration tends to have a detrimental effect on the coal quality (Wang *et al.*, 2003). If a coal's combustion properties are negatively altered as a result of weathering and oxidation, such that it can no longer be employed for its originally intended use, both producers and consumers are penalized in terms of potential earnings.

## **2 CHAPTER 2: OXIDATION AND SPONTANEOUS COMBUSTION OF COAL**

### **2.1 INTRODUCTION**

The primary sources of spontaneously igniting coals may be subdivided widely into (after Carras *et al.*, 2009):

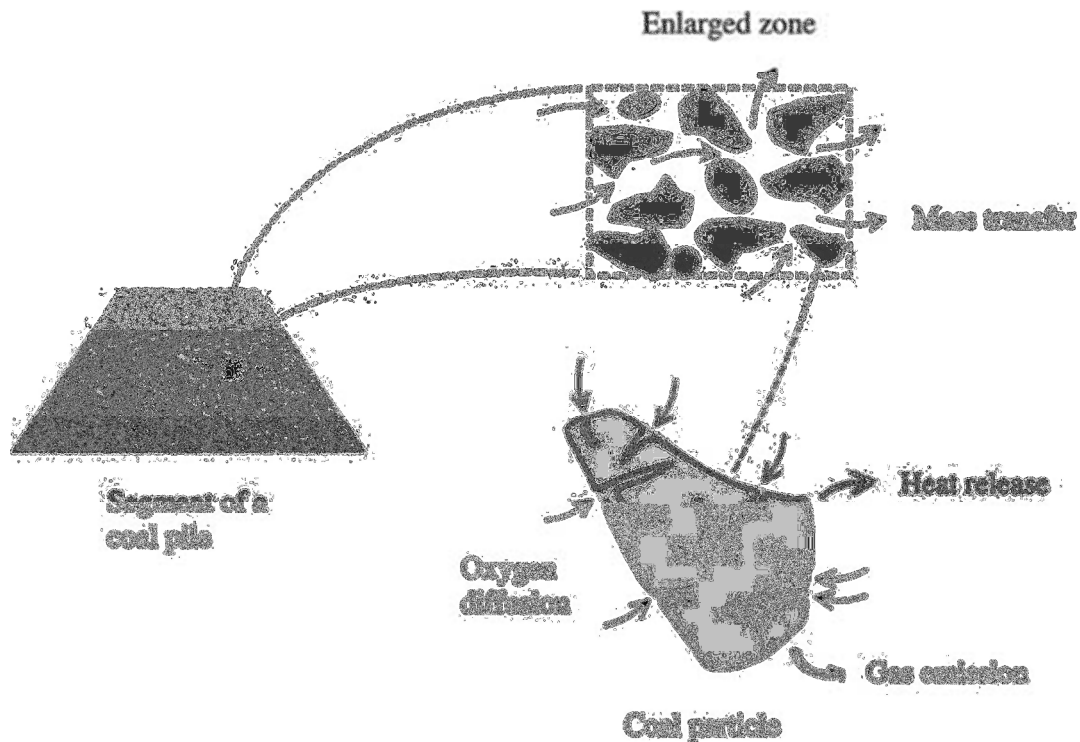
- 1) *in-situ* ore (Marchioni, 1983),
- 2) in stockpiles,
- 3) in spoils excluded from processing plants, and
- 4) any other materials containing significant amounts of hydrocarbon complexes.

When these materials come into contact with the atmosphere, either as a result of extraction related to mining activities, or because sufficient airflow is permitted due to the penetrability of the coal and overburden, oxidation will occur leading to self-heating and ultimately, should the conditions be favourable, spontaneous combustion. The main requirement for 'spontaneous combustion' is that ignition is initiated without the use of any external triggers. The potential losses for mining houses are somewhat obvious in terms of resource destruction or modification of properties thereof (Wang *et al.*, 2003). However, spontaneous combustion also releases significant amounts of greenhouse gasses into the atmosphere further contributing to the ever ensuing problem of climate change and its consequences (Pone *et al.*, 2007; Carras *et al.*, 2009).

Self-heating and the resultant spontaneous combustion of coal is a complicated and somewhat controversial process, but there is little disagreement, if any, that the low-temperature (20 to 70°C) oxidation of organic components in coal is vital to this process (Wang *et al.*, 2003). A coal's ability to oxidize is directly related to a coal's vulnerability to self-ignition. Following extraction, the sizes of the coal particles are inevitably reduced making the material more prone to oxidation due to the increased surface area. *In-situ*, low rank coals are also particularly susceptible to spontaneous combustion due to the increased porosity resulting in greater surface area available for reactions with oxygen. Most of the reactions between the various organic coal components and oxygen are exothermic in nature, and the energy (heat) given-off by each of the reactions during oxidation contributes to the net heat-gain should the heat



not be dissipated efficiently (Arisoy & Akgün, 1994; Clemens *et al.*, 1991). The consequence of an imbalance between the energy (heat) given-off by the oxidation reactions and heat released to the atmosphere is self-heating (Arisoy & Akgün, 1994; Wang *et al.*, 2003). The upper limit of the self-heating process is arbitrary and would be dependent on local climatic and atmospheric conditions together with the intrinsic properties of the specific coalfield.



**Figure 2.1:** An illustration of the fundamental phenomena occurring in the coal oxidation process (Wang *et al.*, 2003).

Oxidation is predominantly, a surface phenomenon and will follow cracks and cleats into the coal particle (pers. comm., N. Wagner). Since the internal surface area is greater than the outer surface area, largely due to fracturing and abundant porosity, airflow into the coal will be directed from the outside primarily through these openings allowing oxidation of surrounding coal material to occur (Wang *et al.*, 2003). The above illustration (Figure 2.1) depicts the process of oxidation as oxygen flows through grain boundaries and pores into a sample, ultimately diffusing through the fractures of a coal particle.

Oxidation of coal, recognized as the major chemical weathering process amongst other agents such CO<sub>2</sub>, water and biota (Martinez & Escobar, 1995), may



occur discreetly *in-situ* due to the limited oxygen availability, or more conspicuously, following extraction in stockpiles. It has long been recognized that coal oxidation leads to spontaneous combustion (e.g. van Krevelen, 1981; Chandra & Prasad, 1990). However, spontaneous combustion will only be initiated if the so-called ‘crossing-point temperature’ (CPT) is reached, that is, the temperature of the coal is sufficiently increased in comparison to that of its surroundings (Wang *et al.*, 2003). Nonetheless, oxidation of coal will occur immediately following exposure to free oxygen. The process proceeds at relatively low temperatures and the resulting reactions have been found to be specific for these temperature ranges (Attar & Hendrickson, 1982). These reactions proceed at temperatures ranging from about 20°C. The upper limit of this temperature range is found to vary greatly in literature but should be related to the complete decomposition of oxygenated complexes resulting from coal oxidation.

The rate at which the oxidation reactions proceed is in turn related to the temperature of the coal-body, with greater sized coal bodies (i.e. stock- or spoil-pile) increasing the oxidation rate. Coals exposed to oxygen but not spontaneously igniting have been found to have lost some of their combustion properties due to increased oxygen content and the resulting oxygenated complexes, as well as the destruction of carbon-hydrogen bonds (Martinez & Escobar, 1995; Wang *et al.*, 2003).

In addition to coal rank, spontaneous combustion and/or self-ignition depends on moisture and volatile matter content, particle size and surface area, mineral matter and pyrite content, and the petrographic composition (Wang *et al.*, 2003; Mastalerz *et al.*, 2011). A brief discussion of each of the different factors affecting spontaneous combustion of coal is given below:

### **2.1.1 Coal rank**

Low rank coals are more susceptible to low-temperature oxidation and spontaneous combustion than higher ranked counterparts (Wang *et al.*, 2003). This is partly related to the high porosity and moisture content (both to be discussed below) of low rank coals, but is also related to the chemical composition of these coals. Low rank coals contain a higher concentration of a variety of mineral phases (Ward, 2002), which could potentially accelerate the rate at which oxidation takes place.

Furthermore, low rank coals are dominated by so-called aliphatic compounds (Mahajan, 1992) which are known to react exothermically with oxygen releasing a substantial amount heat to the surroundings (McMurry, 1995). Anthracitic coals on the other hand, are dominated by the more stable aromatic compounds which do not oxidize as readily (Mahajan, 1992).

Coal maturity also has a direct influence on the thermal properties, of specific interest the thermal conductivity thereof (Speight, 2005). Mature (high ranked) coals generally have high thermal conductivities in comparison to lower ranked counterparts suggesting that heat can potentially be distributed with more ease throughout the coal body.

### **2.1.2 Moisture and volatile matter content**

Inherent water in coals may be divided into two types, chemically and physically bound water (Wang *et al.*, 2003) corresponding to hydrated organic species and water physically held in pores respectively. Some disagreement continues to exist as to whether water plays an inhibiting or promoting role with regards to low-temperature oxidation. However, there seems to be a ‘critical moisture content’ below which oxidation is promoted due to the role it plays in formation of peroxide species and above which it is inhibited because it becomes necessary for oxygen molecules to diffuse through the water layer (Xu *et al.*, 2013). The critical moisture content at which low-temperature oxidation is at its peak was determined to be 25% and 20% for lignitic and anthracitic coals respectively. Lower ranked coals generally have higher moisture content (Clemens *et al.*, 1991) in comparison to higher ranked counterparts.

### **2.1.3 Particle size and surface area**

The internal surface of coal, i.e. the surface area associated with pores, is much larger than the external surface area, thus low temperature oxidation is considered to be a primarily internal process (Wang *et al.*, 2003). Lignites are more prone to self-oxidation than anthracitic coals reflecting low and high degrees of burial metamorphism respectively (Xu *et al.*, 2013). The effect of low degrees of metamorphism (limited coalification) is to conserve a relatively high porosity within the resulting coal layer. The increased void space increases the surface area available for reactions with gaseous phases. This in turn, increases the rate at which the coal

consumes oxygen. Two major processes by which oxygen consumption is achieved are recognized in literature, namely, adsorption and chemisorption corresponding to physically and chemically adsorbed oxygen respectively (Wang *et al.*, 2003).

Higher oxidation rates imply higher coal weathering rates with corresponding higher rates of heat energy liberated by the exothermic reactions. Extraction inevitably causes pulverization (reduction in the size of coal clasts) ultimately increasing the available surface area for reaction. Subsequent processing of the coal through crushing results in finer coal fragments, further increasing the total surface area. Thus, continued reduction in the size of the coal fragments increases the area available for reactions with the atmosphere (Wang *et al.*, 2003).

It has also been previously documented that fresh coal surfaces (recently exposed) consume oxygen at a rate far greater than coal surfaces that have been exposed for longer periods (Wang *et al.*, 2003). Therefore, a recently exposed coal surface would be subjected to a greater degree of oxidation, at least initially, compared with surfaces that have long been exposed and have thus previously been oxidized. Continued size reduction of coal particles increases not only the surface available for oxidation but the heat liberated by the reactions on the now increased surface area would also increase accordingly and significantly contribute the net heat gain by the coal-body. Thus, the temperature of the body will rise exponentially in a shorter time period, increasing the likelihood of self-ignition.

#### **2.1.4 Mineral matter and pyrite content**

The mineralogical composition of coals, though limited in composition, is varied and complex, with several discrete inorganic portions possibly present. Mineral matter in coal can be subdivided broadly into salts dissolved in pore water, and inorganic elements and crystalline mineral lenses dispersed in the organic matrix (Ward, 2002). Dissolved salts and inorganic materials are both commonly found in lower rank coals and less so in higher ranked counterparts (Ward, 2002). During coalification, elimination of water typically occurs in parallel with chemical and structural re-arrangements as well as removal of inorganic materials. Inorganic materials represent the ash content in coals, and the diminished ash content of

anthracitic coals results directly from expulsion of inorganic substances as coalification progresses (Ward, 2002).

Although pyrite reacts exothermically with oxygen to liberate heat and is one of the major inorganic constituents of coal, it typically constitutes less than 1% of any given coal and therefore adds negligible heat to the total budget available for self-heating (Wang *et al.*, 2003). However, pyrite oxidizes to form sulphuric acid which is known to drastically increase the rate at which low-temperature oxidation occurs (e.g. Sujanti & Zhang, 1999; Wang *et al.*, 2003). Calcium carbonate, sodium acetate and potassium acetate have also been found to promote low-temperature coal oxidation and spontaneous combustion (Sujanti & Zhang, 1999). Conversely, potassium chloride, and sodium chloride were found to most effectively impede oxidation, and sodium nitrate and ammonium chloride neither promoted nor obstructed oxidation (Sunjati & Zhang, 1999).

#### **2.1.5 Petrographic composition**

Petrographically, coal is composed of assemblages of macerals called litho-types (Meyer, 1982). The litho-types, together with inorganic mineral lenses, are dispersed and suspended within the organic matrix. The porosity is largely due to the imperfect manner in which the organic matrix is assembled whereas fissures and fractures result primarily from tectonic processes related to diagenesis and coalification (Meyer, 1982). Since the composition and structure of macerals vary widely amongst the three main groups, the response to low-temperature oxidation thereof is also variable. Coal oxidation results in the formation of oxidized rims adjacent to grain-boundaries and micro-fractures, and increases overall porosity and the degree of fissuring (Marchioni, 1983). Low temperature oxidation will also increase relief and affects vitrinite reflectance (Ingram & Rimstidt, 1984).

## 2.2 DISCUSSION

Wang *et al.* (2003) refers to the oxidation history of the coal as playing an important role in a coal's ability to continue to consume oxygen. This is directly related to the fact that fresh, recently exposed coal surfaces will consume oxygen at a rate far greater than the surfaces that have been exposed for longer periods of time. This is in turn related to and has been attributed to, in part, the formation of oxygenated complexes on the coal surface as oxidation progresses. The oxygenated complexes have a lower affinity for reactions with oxygen while simultaneously forming a barrier on the surfaces thus inhibiting the inwards diffusion of oxygen. These complexes form not only on the surface but also along pores and fractures thus further decreasing the total surface area available for oxidation (Marchioni, 1983). Various workers have attempted to derive mathematical equations to aid computing the rate of oxygen consumption as cited in Wang *et al.*, (2003), but consensus on how this computation can accurately be derived is yet to be reached. One of the major sources of contention is fundamental and is related to primary factors influencing oxygen consumption rate and the empirical manner in which the constants employed by most of these computations are determined.

An important distinction is made between physically adsorbed and chemisorbed oxygen using the strength of the chemical bonds operating in each case to differentiate between the two (Wang *et al.*, 2003). Chemisorbed oxygen is bound more strongly than physically adsorbed oxygen making recovery of the former more difficult or rather, impossible (Wang *et al.*, 2003). Physically adsorbed oxygen is held within coal pores and is therefore not currently participating in the oxidation process whereas chemisorbed oxygen is actively involved in the process. Chemically adsorbed oxygen is thus of major interest in study of spontaneous combustion as it is directly responsible for the formation of oxygenated complexes on the coal surface and within pores and fractures (Avila *et al.*, 2014).

Oxygenated complexes in coals most susceptible to self-heating break down as oxidation progresses, and are more stable in those coals least likely to self-heat (Avila *et al.*, 2014). Decomposition of the oxygenated complexes liberates heat which may raise the coal temperature causing self-heating. The formation of oxygenated

complexes typically manifests as a mass increase during oxidation (Avila *et al.*, 2014). Subsequent decomposition of the complex (provided conditions allow) returns the coal mass to its original value while simultaneously releasing heat. Following oxidation, increased coal mass points toward the presence of oxygenated compounds, thus coal least prone to self-heating. The stability of oxygenated complexes is itself dependent on the overall temperature of the coal, thus previously ‘stable complexes’ may break down at higher temperatures (Clemens *et al.*, 1991).

In addition to releasing significant amounts of heat energy, the decomposition of oxygenated complexes releases water, carbon dioxide and potentially, other greenhouse gases to the atmosphere. The exact nature of the gases produced and liberated would depend on the elemental (ultimate analysis) composition of the coal being oxidized. It follows that coals with significant amounts of sulphur are most likely to produce sulphur dioxide and monoxide. The production of carbon-hydrogen gasses such as methane is stimulated by the inability of oxygen to penetrate and circulate unhindered, thus unable to reach the coalfield in its entirety (Carras *et al.*, 2009).

Although J. Bussio (thesis under examination) determined the organic constitution of coal, the quantity of each individual molecule in a given volume of coal is yet to be determined. It is more than likely that the concentration of organic constituents is a function of coalification and maturity. The susceptibility of lignite ranked coals to self-heating is typically attributed to the higher porosity of these coal types (e.g. Xu *et al.*, 2013) in addition to abundant aliphatic hydrocarbons (Mahajan, 1982). However, it is also possible that in addition to higher porosity, low rank coals also have the greatest concentration of a specific hydrocarbon that upon oxidation forms oxygenated complexes that decompose more easily at low temperatures. If the concentration of starting hydrocarbons is similar across all coal ranks, the decomposition temperature requirements of oxidation products may differ based on degree of coalification of the starting coal material. The formation of heat-liberating oxygenated complexes depends on the availability of appropriate hydrocarbon precursors. A greater concentration of appropriate, primary hydrocarbons increases the area of active surface reaction sites, increasing the number of sites on which potential oxygenated complexes can form.

The crossing point temperature is that temperature at which the temperature of the coal increases at a rate far greater than that of the surroundings. Higher ranked coals have been found to have a higher crossing point temperature than lower ranked coals (Xuyao *et al.*, 2011). The implication is that high ranked coals potentially take longer to raise the temperature thereof sufficiently in comparison to the surroundings. This is likely related to abundance of stable aromatic compounds instead of aliphatic compounds in higher ranked coals, in addition to the decreased porosity. The delay reaching an appropriate CPT in anthracitic coals is probably one of the major reasons why, generally speaking, high ranked coals are found to be less susceptible to spontaneous combustion. The term ‘generally’ is used because there are situations where even high rank coals have been found to self-ignite (e.g. Chen *et al.*, 1996), as a result of what Chen *et al.* (1996) term heterogeneous ignition at high ignition temperatures. Again, this deviation in behaviour is attributable to the complex and often unpredictable organic chemistry of coal, and the response thereof to oxidation.

### 2.3 SMOLDERING COMBUSTION

Smoldering as opposed to flaming combustion is an extremely slow, low-temperature phenomenon typically observed in condensed fuels (Rein, 2009), thus it is the dominant combustion process in the spontaneous combustion of coal. In addition to coal, some materials such as cotton, dusts, paper, polyurethane foams and wood are also susceptible to this type of combustion mechanism (Sudip *et al.*, 1987). Smoldering as a combustion mechanism poses a particularly serious environmental hazard due to its ability to evolve undetected for prolonged periods of time. The major difference between smoldering and flaming combustion is that in flaming combustion oxidation reactions occur in the gaseous phases around the fuel source, whereas in smoldering combustion, the reactions resulting in heat liberation occur directly on the surfaces of the fuel source (Rein, 2009). Materials that are susceptible to this combustion mechanism contain interconnected pores through which gaseous phases, oxygen in particular, is able to flow unobstructed (i.e. with relative ease) as opposed to densely packed (compacted) materials that would otherwise hinder airflow (Ohlemiller, 1990). In the case where coal is the fuel source, low-ranked coals (high primary porosity), coals with a high tertiary porosity (due to size reduction during

processing), and underground coal seams made susceptible to oxidation due to mining should thus be more inclined to smoldering combustion.

As previously mentioned, smoldering combustion progresses at extremely slow rates. The burial depth of the combustible material is important as pressure directly influences the rate at which combustion takes place (Ohlemiller, 1990). Shallow materials or rather, in the context of this study, shallow lying coal beds (seams) should be more likely to combust in a smoldering fashion in comparison to deeper beds. In a study conducted by Ohlemiller (1990), shallow materials reached peak temperatures at faster rates than deeper buried material, which, in addition to taking longer to reach peak temperatures, also have a higher 'peak temperature'. The reason for the differing rates of heating (for similar materials) at different depths is likely related to decreased porosity primarily as a result of the increased pressure from the overlying rock column.

#### **2.4 THE STABILITY OF COMPLEXES RESULTING FROM PROGRESSIVE OXIDATION OF DIFFERENT ORGANIC COAL COMPONENTS**

Low-temperature coal oxidation results in the formation of various oxygenated hydrocarbon-complexes subdivided broadly into stable, unstable and/or unreactive (Avila *et al.*, 2014). The peroxygen, hydroperoxide and hydroxyl group of complexes constitutes unstable complexes whereas the carbonyl- or carboxyl-containing complexes and humic acid groups constitute stable and unreactive complexes respectively (Avila *et al.*, 2014). Thus, the ability of a reaction site to remain active, therefore available for further reactions following the initial oxidation event, is dependent mainly on the nature of the complex that forms and its ability to decompose at low relatively low temperatures.

A reaction site will remain active provided unstable products (i.e. complexes still able to oxidize beyond their current state) continuing to form at the prevailing temperature condition as oxidation progresses. These sites together with the resulting complexes are important for the process of coal self-heating. Early formation of a so-called unreactive complex will render a specific site redundant and unavailable for further oxidation, thus unable to contribute to the heat-gain of a system (referring to a coal lump) at present. However, a previously inactive site may reactivate as heat



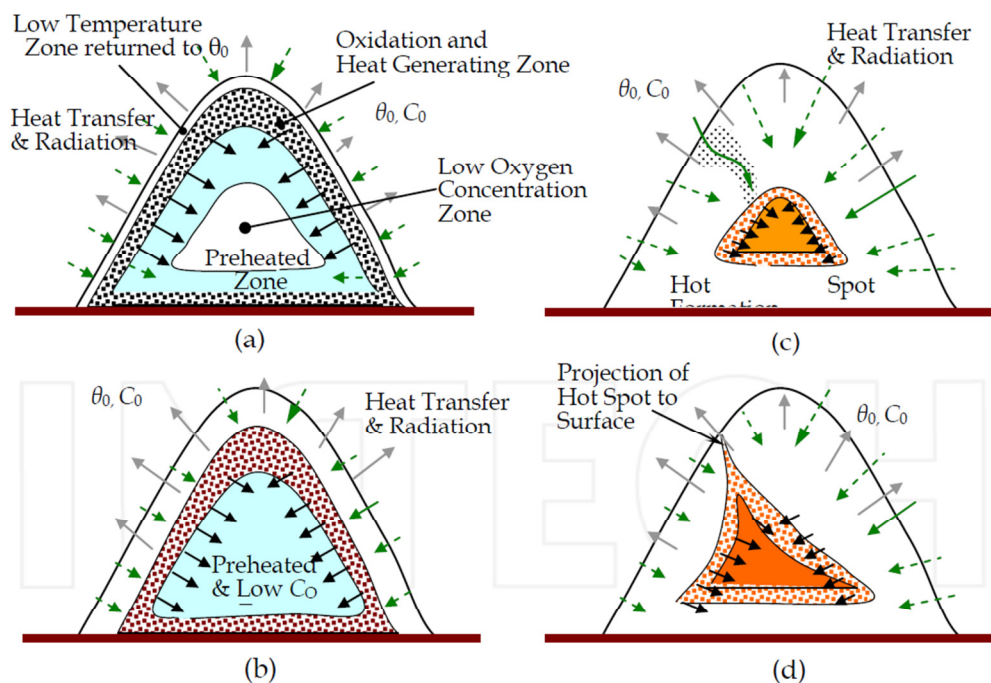
evolved from other sites adds to the net heat budget of the system as a whole, thus the unreactive or stable complex is essentially destabilised by the increasing temperature. The dependence of catalysis on temperature is well documented in literature and has been cited (e.g. Kötzt *et al.*, 2009).

The presumption of the dependence of coal oxidation on temperature is consistent with the findings of Clemens *et al.* (1991). Clemens *et al.* (1991) found that when coals that have previously been oxidized come into contact with oxygen again ('re-oxidized') at a similar temperature condition, no heat-liberating complexes form implying that 'all' the inactive reaction sites remain largely inactive. However, if the second oxidation event takes place at a temperature higher than that of the first event, heat-liberating complexes are created (Clemens *et al.*, 1991). Although the current study proposes a much smaller system (a stockpile vs. a coal lump), the principle of re-oxidation at higher temperatures remains valid. There is no reason to assume that all reaction sites on the surface of a coal lump can be collectively categorized as either 'active' or 'inactive', corresponding to reactive and unreactive coals respectively as has previously been proposed (e.g. Avila *et al.*, 2014), especially when the varied and complex organic chemistry of coal is taken into account.

Such a classification scheme is likely too broad and simplistic as inactive sites may reactivate with increasing temperature. Therefore, what is more likely is that sites active at the current temperature are able to raise the overall temperature of the 'system' sufficiently so as to allow oxidation of previously inactive sites, or decomposition of oxygenated complexes such that new reaction sites are created. In this context, the reactivity of coal is temperature-dependent and is based on the total area of active sites at a given temperature. The formerly inactive sites are thus able to contribute to the heat evolution of the system in the long-term. Reactivation of inactive sites operating simultaneously with reactions on active sites will increase the rate at which the temperature rise of the system takes place.

In the model put forward by Sasaki and Sugai (2011), where heat from individual sites diffuse inwards and concentrate at the centre of a circular coal lump to form a hotspot (Figure 2.2), the number and area of active reaction sites from which heat can potentially be drawn to ultimately form the hotspot is thus drastically

increased by reactivation of inactive sites. The total surface area of active reaction sites is directly proportional to the rate of oxidation (Karsner & Perlmutter, 1982), thus the number of active sites directly determines the time-elapsd prior to hotspot formation with fewer sites leading to delays and increased sites leading to rapid hotspot formation. The size and maximum temperature of the hotspot will also be directly proportional to the number of reaction sites contributing heat. This is supported by the findings of Clemens *et al.* (1991) who found that the number of heat-liberating complexes increases with rising temperature. This will in turn determine the amount of time a coal lump will require for self-heating and the subsequent spontaneous combustion.



**Figure 2.2:** Schematic showing spontaneous combustion of large amount of coal stock, (a), (b) and (c): Hot spot forming process with accumulating heat and shrinking zone of oxidation and preheating zone, (d): Projection growth of hot spot toward to stock surface through high permeable path (Sasaki & Sugai, 2011).

The concurrent destruction of old and construction of new complexes on coal surfaces during the oxidation process as a function of multiple, succeeding ‘oxidation events’, governs the varying behaviour of the resulting reaction site with increasing temperature. However, understanding and information on the nature of such complexes is currently lacking, together with information on the supposed varying

oxidizability thereof, especially oxidizability of coal components with increasing temperature. Determination of oxidation potentials of different organic compounds found in coal would go a long way in investigating this phenomenon. Since coal oxidation is currently the most accepted mechanism by which spontaneous combustion is initiated (e.g. van Krevelen, 1981; Falcon, 1986; Sasaki & Sugai, 2011; Avila *et al.*, 2014), the findings of such a study should increase our collective understanding of this phenomenon.

Thermodynamic principles readily explain the temperature change resulting from heat liberated by exothermic reactions or conversely, heat taken-up by endothermic reactions as per the following mathematical equation (Kötz *et al.*, 2009):

$$C = \frac{q}{m\Delta T}$$

If the amount of energy liberated during an exothermic reaction is known, the temperature change ( $\Delta T$  in  $^{\circ}\text{C}$ ) caused by the heat-gain can be calculated using the above equation where  $C$ = specific heat in  $\text{cal/g.}^{\circ}\text{C}$  or  $\text{kJ/mol.g.}^{\circ}\text{C}$ ,  $q$ = heat added in calories or  $\text{kJ/mol}$ , and  $m$ = mass in grams (Kötz *et al.*, 2009). Correspondingly, if the energy (calories or  $\text{kJ/mol}$ ) needed to initiate an endothermic reaction is known, the corresponding requisite temperature change for reaction progression can be readily computed. Essentially, since the energy required by the endothermic reaction to initiate can be taken as, in this context, the energy required by an inactive site to reactivate, the reactivation temperature can also be determined provided that all other variables in above equation are known.

## 2.5 GREENHOUSE EMISSIONS RESULTING FROM SPONTANEOUS COMBUSTION

The other, potentially more disturbing consequence of spontaneous combustion and low temperature oxidation of coal is the emission of greenhouse gases (Carras *et al.*, 2009). The emission of these gaseous phases is temperature-dependent. Carbon dioxide is the dominant phase released at ambient temperature whereas methane production occurs at elevated temperatures when oxygen supply to portions of the coal-body may be sufficiently reduced (Carras *et al.*, 2009). An important distinction

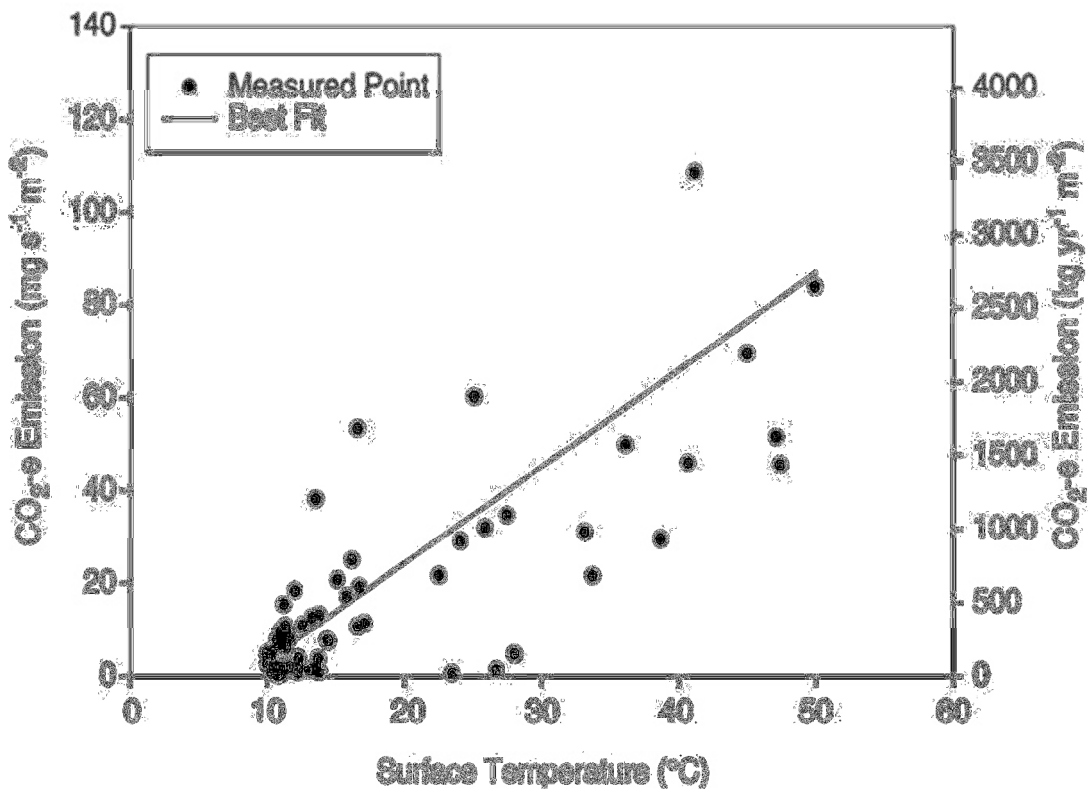
between the aforementioned methane production at high temperatures and the portion that is “seam trapped” must be made. The ability of oxygen to reach an entire coal-body will directly determine the ratio of CO<sub>2</sub> to CH<sub>4</sub> produced by the pile. This ratio is dependent on the rate of oxygen supply, as diffusion through pores of a coal-body will limit the amount of oxygen able to reach the inside thereof as opposed to relatively free-flowing air in stockpile (Carras *et al.*, 2009).

Carras *et al.* (2009) measured the emission rates of CO<sub>2</sub> and CH<sub>4</sub> produced by low-temperature oxidation and spontaneous combustion in the spoil-piles of five open-cut mines in Hunter Valley and six in the Bowen Basin, both localities found in Australia. Both piles with obvious signs of spontaneous combustion and those without were deliberately included in the study. The surface temperature of some of the spoil-piles was found to be significantly higher than of the atmosphere at 100°C. Emissions from spoil-piles with noticeable indications of low-temperature oxidation were found to be a lot higher than those from piles without conspicuous signs of spontaneous combustion. The gas emission results from rejects and tailings in the study by Carras *et al.* (2009) are summarized in Table 2.1. The data was classified into three broad groups, namely, 1) intense spontaneous combustion areas characterised by high emissions, 2) areas with less obvious signs of spontaneous combustion characterised by moderate emissions and lastly, 3) areas with no signs of spontaneous combustion characterised by low emissions (Carras *et al.*, 2009).

**Table 2.1:** Emission from coal rejects (Carras *et al.*, 2009).

	CO <sub>2</sub> (mg s <sup>-1</sup> m <sup>-2</sup> )	CH <sub>4</sub> (mg s <sup>-1</sup> m <sup>-2</sup> )	CO <sub>2</sub> -e (mg s <sup>-1</sup> m <sup>-2</sup> )
<i>Category 1 – high emissions</i>			
Number of measurements=9			
Minimum	23	0.0	23
Maximum	264	4.7	287
Average	95	0.8	111
RMS deviation	69	1.4	92
<i>Category 2 – moderate emissions</i>			
Number of measurements=15			
Minimum	0.1	0.0	0.1
Maximum	8.5	0.2	9.4
Average	3.1	0.03	3.8
RMS deviation	2.5	0.1	3.2
<i>Category 3 – low emissions</i>			
Number of measurements=47			
Minimum	0.0	0.0	0.0
Maximum	11.0	0.0	11.0
Average	1.5	0.0	1.5
RMS deviation	2.8	0.0	2.8

Note that the CO<sub>2</sub> and CH<sub>4</sub> values do not necessarily correspond; hence the CO<sub>2</sub>-e may not be the sum of the CO<sub>2</sub> and CH<sub>4</sub> shown.



**Figure 2.3:** Measured average emission rates (as CO<sub>2</sub>-e) as a function of average surface temperature (Carras *et al.*, 2009).

Carras *et al.* (2009) also determined the dependence of emission rate on spoil surface temperature. The temperature measurements were taken on spoils in winter and in the early hours of the morning to minimize the contribution of solar radiation. The results clearly indicate the association of high emission rates with high surface temperatures (Figure 2.3). The lowest surface temperature was 10°C, corresponding to virtually no emissions.

## 2.6 SPONTANEOUS COMBUSTION MODELS

### 2.6.1 Tarafdar and Guha (1989) Model

Tarafdar and Guha (1989) performed a wet oxidation experiment on coal using an alkaline permanganate solution. The analytical characteristics, including crossing point temperature (which is the temperature at which the coal temperature begins to exceed that of the surroundings (Xuyao *et al.*, 2011) of seven samples from different collieries were determined. The samples were crushed to 212µm, following which the wet oxidation experiment was performed using the potassium permanganate solution. Potential difference measurements were taken between a saturated calomel and carbon electrode. Readings were taken at the beginning and the end of the experiment and the difference between the readings determined. Crossing point temperature of the samples was found to correlate with the change in electromotive force (emf). The increase in base temperature is attributed to the contribution of heat liberated by exothermic reactions (Tarafdar & Guha, 1989). A plot of the increase in temperature (differential temperature) vs. the base temperature was constructed, where the peak temperatures are related the ease of oxidation of the specific sample. The area under a curve reflects the total heat given-off by the individual sample provided all other factors are true. The similarity of the curves is indicative of the similarity of the coals and more importantly, the concentration of heat-liberating complexes on the coal surfaces.

### 2.6.2 Clemens *et al.* (1991) Model

Isothermal Differential Thermal Analysis (DTA) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) were used by Clemens *et al.* (1991) to investigate the response of six dried coals following exposure to oxygen. The coals used in the study varied in rank from lignite through sub-bituminous to bituminous. Following collection, the fresh samples were submerged and stored in

water, after crushing. Coal samples were then placed in a nitrogen-filled bag for further grinding and sieving to a size of more than 76 $\mu$ m. For thermal analysis (DTA) experiments, the samples were dried at a temperature of 105°C under nitrogen. Once the moisture content was sufficiently decreased, the samples were allowed to 'stabilize' at temperature ranges between 30 to 180°C. The experiment was then performed for a one hour period while the necessary parameters were measured. Complexes liberating heat were detected at temperatures as low as 30°C, and the amount of heat-liberating complexes increased with increasing temperatures. Heat-liberating complexes peaked at 90°C and lower, between 1050 and 1600 seconds into the experiment.

In the temperature-programmed DRIFTS experiment, samples weighing 10mg with sizes lower than 76 $\mu$ m were used. Following additional sample preparation, the samples were dried at the same 105°C temperature under nitrogen for 18 hours. Similar temperature ranges as with the DTA experiment were used to allow the samples to 'stabilize' and dry air with a flow rate 2cm/min was used. This continued for about 5 hours to allow the formation of products, more time (days) was required for when the experiment was performed at lower temperatures. The DRIFTS identified a carbonyl of either carboxylic/aldehyde functionality, this carbonyl-containing complex is supposed to result from the breakdown of peroxygen and hydroperoxide complexes. The exothermic decomposition of the peroxy-species occurs at temperatures in the range 30-180°C, which is well above the temperatures typically cited for spontaneous combustion for coal. At higher temperatures, coals of various ranks, including anthracitic types, signalled the formation of the heat-liberating complexes demonstrating that all coal types can spontaneously combust provided the conditions for the formation of the necessary complexes allow. The major factor responsible for the formation of these complexes appears to be related temperature increases, with the appropriate heat-liberating complexes forming at higher temperatures in high ranked coals.

### **2.6.3 Martinez and Escobar (1995) Model**

Martinez and Escobar (1995) investigated the effects of oxidation on coal properties. The study makes use of fourteen fresh and weathered coal samples from Venezuela, ranging in rank from sub-bituminous to high-volatile bituminous. The



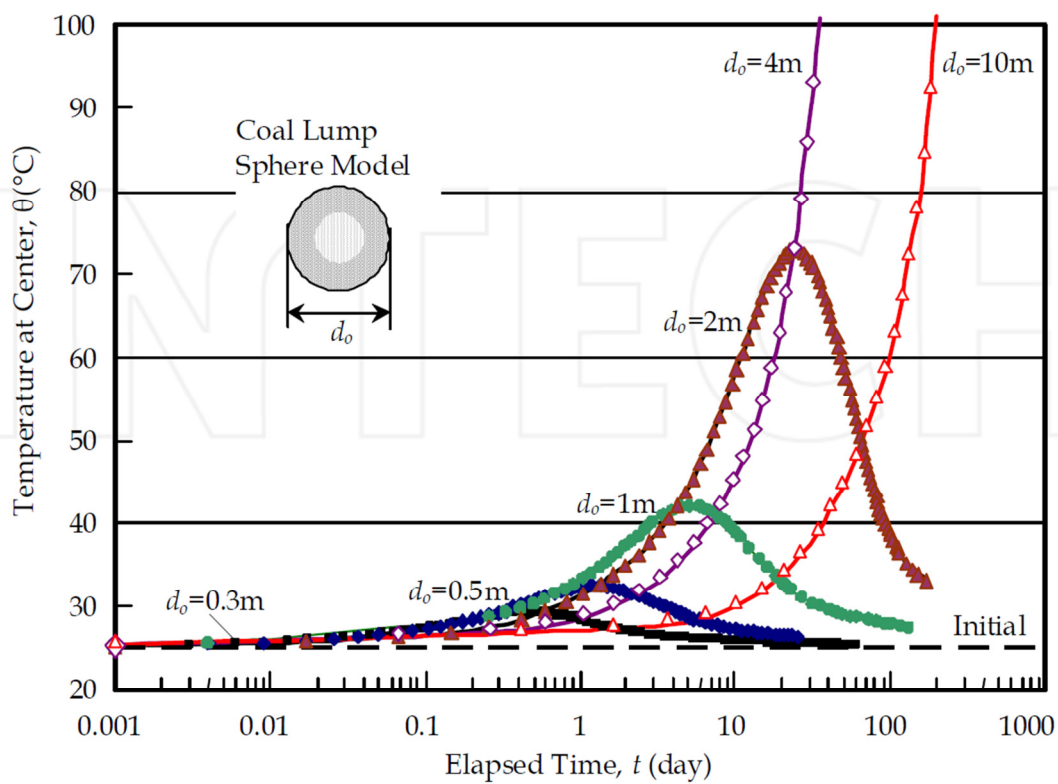
fresh samples were collected from active mining exposures while the weathered samples were collected from outcrops. Two peat samples were also include in the study. The floatability of the fresh samples was found to be generally high with the exception of one sub-bituminous sample and both peat samples. In contrast, the floatability of the weathered samples was found to always be lower than that of the corresponding fresh sample. Martinez and Escobar (1995) postulated that this was directly related to the degree of weathering. The floatability index ( $N_f$ ) was then described in the paper. Fourier transform infrared spectroscopy was then used to identify different organic functional groups present in each of the samples. The infrared spectra of the fresh samples peaked at 2900/cm signalling the presence of carbon-hydrogen bonds. In contrast, the weathered samples peaked at 3390/cm and 1710/cm signalling the presence oxygen-hydrogen bonds and carboxylic acids respectively. Based on the information gathered from infrared spectra, it was concluded that weathering increases the concentration of carboxylic, phenolic, ether and hydroxylic groups at the expense of the coal's natural aliphatic structure. The moisture content of the weathered samples was found to be significantly higher than that of the corresponding fresh sample, however a relationship between moisture and the floatability index ( $N_f$ ) could not described. Coal oxidation was found to significantly increase the carboxylic acid content (Martinez & Escobar, 1995).

#### **2.6.4 Sasaki and Sugai (2011) Model**

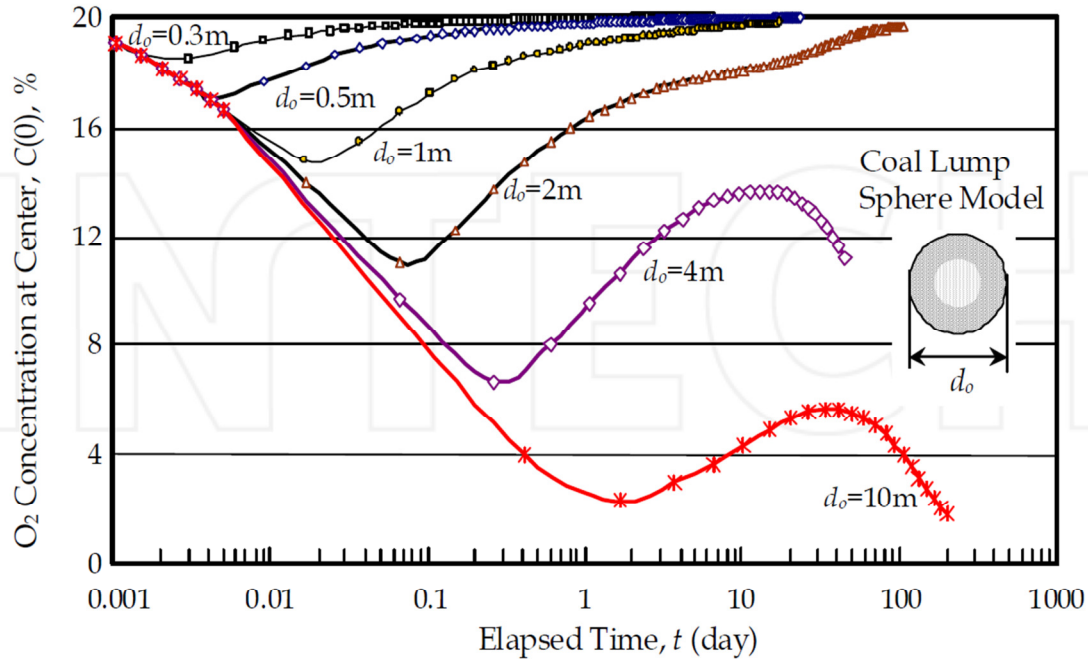
Sasaki and Sugai (2011) report the temperature range for initiation (what they term 'pre-stage') of spontaneous combustion to be in the range of 50 to 55°C with the corresponding carbon monoxide concentration in the air (in the immediate vicinity of the coal) to be between 100 and 200ppm. However, the concentrations of other constituents of this 'air' are neither quantified nor discussed along with other factors that supposedly influence coal combustion. As with most self-ignition models proposed in literature, oxidation of the coal surfaces resulting in the production of heat energy is the major process in Sasaki and Sugai's spontaneous combustion model. In this model, the heat given-off by the oxidation reactions is not efficiently dissipated onto the surroundings. Thus, the excess heat remains on the coal surfaces and has no recourse but to diffuse inwards while simultaneously allowing the coal surfaces to return to their initial temperature state. It is worth noting that by this stage



(leading to spontaneous combustion), the coal surfaces are not as prone to oxidation as they originally were due to the formation of oxygenated complexes, provided the temperature of the coal body has remained largely constant. Heat diffusing from the various reaction sites located on the coal surfaces merge and concentrate the heat within the coal body. A 'high temperature spot' is formed inside the coal body, sustained partly by the limited amount of oxygen diffusing from the atmosphere into the coal body. Temperatures and oxygen concentrations as a function of time at the centre of different sized coal spheres are shown in Figure 2.4 and 2.5.



**Figure 2.4:** Temperature at sphere centre vs. elapsed time for different diameter (Sasaki & Sugai, 2011).



**Figure 2.5:** Oxygen concentration at sphere centre vs. elapsed time for different diameter (Sasaki & Sugai, 2011).

The high temperature spot will be located at the centre of the coal body if we assume, (a) a homogenous coal body resulting with similar diffusion rates for heat from each site towards the hotspot, and (b) identical travel distances from the various reaction sites. Temperature of the spot increases whilst the size of the heat spot is reduced, this results in the formation of what Sasaki and Sugai (2011) call a ‘hotspot’. Following hotspot formation, the coal body gradually burns outwards towards the surfaces. These hotspots have temperatures in the region of 400-600°C, and the lack or rather limited amount of oxygen available for consumption by the hotspot due to low diffusion rates results in smoldering as opposed to flaming combustion. Upon arrival on the coal surface, spontaneous combustion is triggered supposedly when the necessary carbon monoxide concentration is reached. The contemporaneous surface arrival of multiple hotspots, in numerous coal particles will lead to a sudden temperature increase immediately triggering spontaneous combustion. The formation and continued growth of the hotspot inside the particle is particularly problematic since without close inspection and monitoring, the hotspot will form and burn undetected.

Sasaki and Sugai (2011) also introduce the concept of ‘equivalent oxidation exposure time’ (EOE time). Prior to formation of the actual hotspot but following surface oxidation, heat diffusion is the dominant process as opposed oxygen diffusion. A coal body with a large diameter will take longer periods of time for heat to concentrate and for the resulting hotspot to eventually form. Essentially, equivalent oxidation exposure time is the time it takes for oxygen diffusing from the atmosphere to reach the newly formed hotspot and this delay increases linearly with increasing coal size. The heat generating rate decreases, almost exponentially with increasing EOE time thus the consequence of a larger EOE time is to. A large EOE time would be induced by heat loss to the atmosphere before hotspot formation.

### **2.6.5 Avila *et al.* (2014) Model**

Avila *et al.* (2014) employed thermogravimetric analysis to assess and predict the susceptibility of coals to spontaneous combustion. A variety of coals (based largely on rank), from various coal regions of the world were used in the study. Preparation of the coal samples included crushing (to less than 106 $\mu$ m) so as determine intrinsic oxidation rates while simultaneously maintaining low mass- and heat-transfer rates. A thermogravimetric analyser (TGA) with a set sample size and gas flow was used. Accuracy of the apparatus was found to be around 0.5 wt%. When testing for oxygen adsorption (therefore chemically adsorbed oxygen), Avila *et al.* (2014) records a weight gain in the coal samples upon being placed in the TGA at temperatures between 20 and 300°C, presumably resulting from oxygen adsorption. However, it is unclear how a distinction between chemisorbed (reacting to form complexes) and adsorbed oxygen (physically held in pores) was made in the study. Nonetheless, for samples showing an increase in weight, a ‘start temperature’ ( $T_{\text{start}}$ ) and a ‘peak temperature’ ( $T_{\text{peak}}$ ) were determined at heating rates of 3 and 5°C/min. The lowest  $T_{\text{start}}$  and  $T_{\text{peak}}$  for all samples in the study corresponded to low heating rates. Weight gain ranged between 0.0% and 4.37% for the 3°C/min heating rate with this heating rate resulting in the most weight gain. The increased weight gain at low heating rates was supposedly due to higher ‘contact times’ with oxygen adsorption increasing to 80% for samples subjected to this low the heating rate. Extrapolation of these results in an attempt to determine ‘actual heating rates’ in a spontaneous combustion event yields a much lower value at 0.02% °C/min (70°C increase over

two days). The total weight gain is difference between oxygen adsorbed and desorbed during the heating process which is related to the 'net adsorption temperature range' ( $\Delta T$ ). Determination of the individual contributions of adsorption and desorption processes to the total weight gain proved, for obvious reasons, to be problematic. Samples for which no weight gain was recorded were either known to be prone to spontaneous combustion or highly reactive; either way, it was concluded that oxygenated complexes in these samples had broken down along with the corresponding heat release. In contrast, coals that experienced the greatest weight gain, recording the highest peak temperatures were also found to form surface complexes that were stable over wider temperature ranges. Heat liberation by oxygenated complexes and the subsequent temperature rise is thus dependent on the stability of organic complexes forming on the coal surface. Reactive coals, susceptible to spontaneous combustion form unstable complexes on the surfaces during oxidation, these complexes thermally decompose and liberate heat at the lower temperatures without increasing in weight. Conversely, unreactive coals were found to form stable complexes which decompose at elevated temperatures with conspicuous weight changes.

## **2.7 EFFECTS OF LOW-TEMPERATURE OXIDATION AND SPONTANEOUS COMBUSTION ON COAL STOCK- OR SPOIL-PILES**

Stockpiled coal in direct contact with the atmosphere should be more susceptible to oxidation due to the reduced particle sizes. The ability of air to flow with relative ease through the stockpile, relative to particle size distribution, is two-fold. In the first instance, if air is able to flow freely, the majority of particles should come into contact with oxygen at some point due to this uninhibited flow. Secondly, the heat released by the exothermic oxidation reactions should be dissipated onto the atmosphere more efficiently implying negligible heat-gain by the pile. This may also explain why the temperature of some stockpiles never exceeds that of the ambient atmosphere, that is, the coal temperature stays below the CPT and self-heating is essentially halted. Such coals are likely to experience a decrease of calorific value (Wang *et al.*, 2003) owing to the increased oxygen content (Martinez & Escobar, 1995).

Carras *et al.*, 2009 lists the following factors as affecting spontaneous combustion of coal in stock or spoil-piles:

- Location of the coal and carbonaceous waste.
- The particle size distribution of the pile, directly determines the diffusion and permeability characteristics of the pile.
- The ease with which air is able to flow unhindered, directly determining the ratio of CO<sub>2</sub> and CH<sub>4</sub> released by the pile at any given time
- Fractures or cracks in the pile serve as pathways for the gaseous spontaneous combustion products, releasing them to the atmosphere.

In the instance where the size distribution within the pile is sufficiently reduced, the outermost coal fragments will be oxidized whereas the innermost fragments remain largely unoxidized (Carras *et al.*, 2009). During the initial period of oxidation and combustion of coal in direct contact with the atmosphere, CO<sub>2</sub> will be the dominant gas produced. The amount of carbon dioxide will then decrease linearly until methane production predominates due to the inability of airflow to reach centre of the pile (Carras *et al.*, 2009).

Various measures have been proposed to minimize if not completely eliminate low-temperature oxidation and subsequent spontaneous combustion of coal in stockpiles. Fierro *et al.* (1999) recommends repetitive compaction of coal stockpiles as a means ensuring that airflow is eliminated, covering the coal stockpile with either an 'artificial barrier' or ash-water slurry both of which will also ensure oxygen flow into the pile is drastically reduced.

### **3 CHAPTER 3: THE STRUCTURE AND REACTIVITY OF AROMATIC AND ALIPHATIC COMPOUNDS OF COAL AND THE INFLUENCE THEREOF ON SPONTANEOUS COMBUSTION**

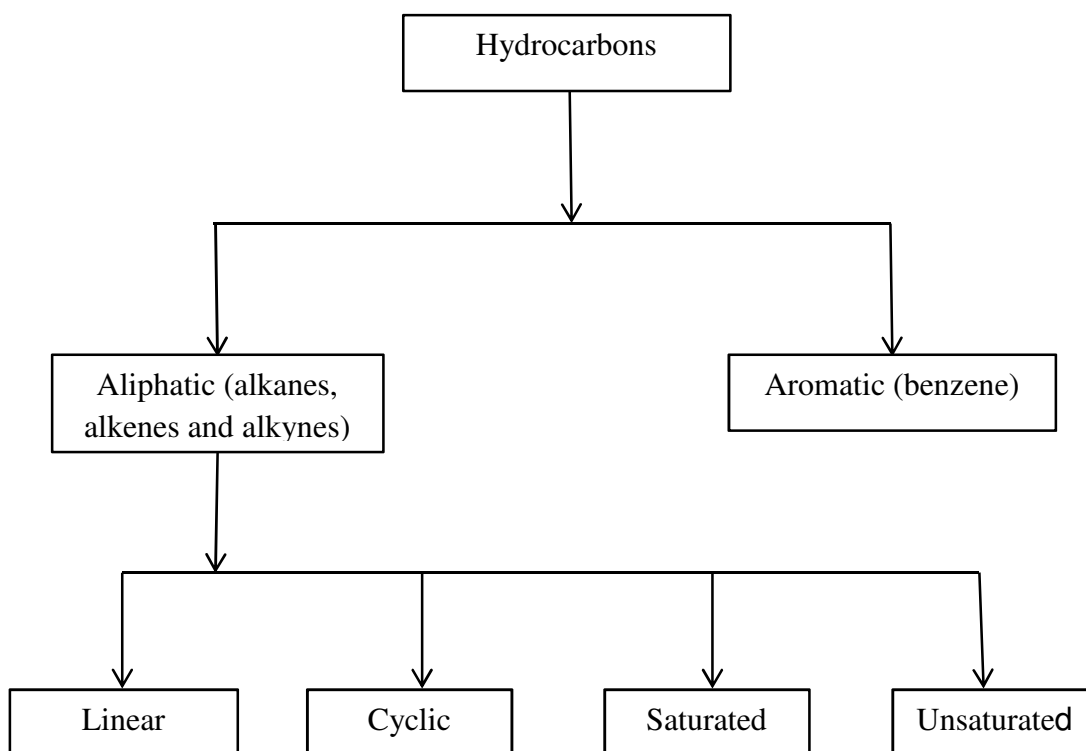
#### **3.1 INTRODUCTION**

Coal is an assemblage of organic hydrocarbons, mineral species with densities higher than the organic portions, microscopically homogenous sections with evidence of ancient precursor plant material called macerals, pores within the organic matrix and salts dissolved in water held within pores (Meyer, 1982). The matrix is an assemblage of organic molecules of various sizes chemically bonded to form a polymer-like structure. The organic matrix is derived primarily from decomposition of plant material that has subsequently been subjected to varying degrees of decay as a function of pressure, temperature and time. Coalification is the process of converting this plant material into coal and directly determines the rank (maturity) of the resultant coal (Mastalerz *et al.*, 2011). Mineral species are embedded within the matrix, while pores form from the spaces created by the imperfect linking of the organic molecules (Meyer, 1982).

**Table 3.1:** Coal structure (modified from Meyer, 1982).

<b>Structure Class</b>	<b>Description</b>	<b>Size (m)</b>
<b>Primary</b>	Organic and inorganic molecules aggregated as polymers and crystalline zones (condensed aromatic rings) and individual crystals (inorganic molecules)	$10^{-9} - 10^{-8}$
<b>Secondary</b>	Pore system and fractures	$10^{-9} - 10^{-5}$
<b>Tertiary</b>	Fossil plant material termed macerals. Aggregates of macerals termed lithotypes. Mineral lenses and nodules and deposits in cleats	$10^{-5} - 10^{-1}$

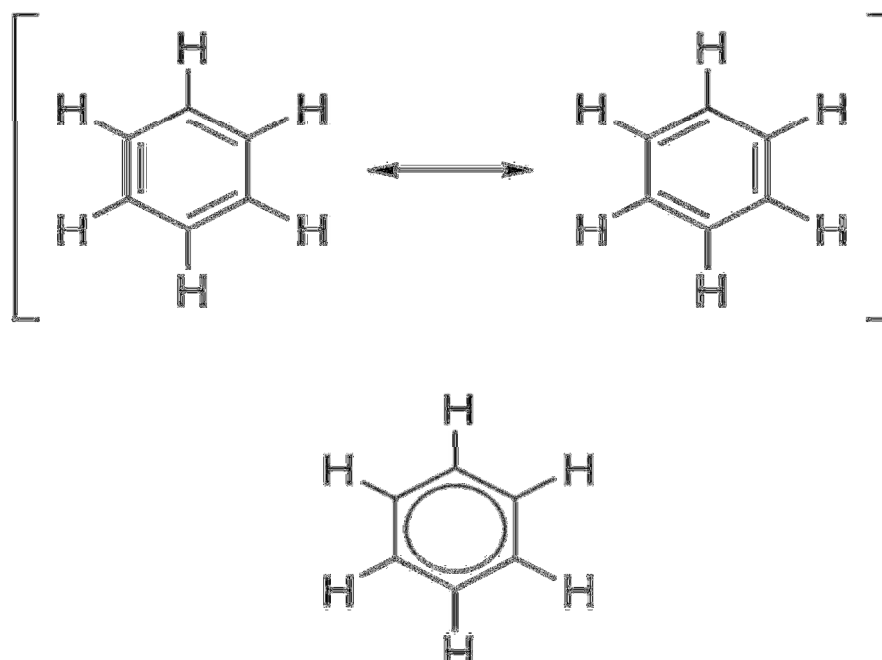
Coal macerals are the organic equivalent of minerals in rocks (Ting, 1982). These macerals bear features diagnostic of the paleo, predecessor plant material. Three major categories of macerals are recognized in literature, namely, vitrinite, liptinite (exinite) and inertinite (Ting, 1982). The inorganic component of coal ranges from a few percent to more 50%, if the organic component is more than 50% the rock is called carbonaceous shale. The process of coalification progresses through selective destruction of plant material from which coal ultimately forms (Hatcher & Clifford, 1997), with preserved portions transforming into what we recognize to be macerals. Thus, macerals are named from the plant tissues from which they are derived (Ting, 1982). Vitrinites are derived from woody tissues whereas liptinites are derived from spore and pollen coats, cuticles and resins and the carbonization of different plant tissues by fire forms the inertinite group of macerals. The mineral matter component of coal is represented mainly by clay minerals, quartz, carbonates, sulphides, sulphates and other inorganic species in minute concentrations (Ting, 1982).



**Figure 3.1:** Classification scheme for hydrocarbons (McMurry, 1996).

### 3.2 STRUCTURE OF COAL

The main organic building blocks of coal have been recognized to be aromatic and hydroaromatic compounds for a number of decades now (Mahajan, 1982). The so-called aromatic compounds are primarily benzene and compounds with benzene-like structures (the structure of benzene and related compounds to be discussed below) (McMurry, 1996). Coal is composed of a network of aromatic, hydroaromatic (benzene-like rings) and aliphatic (CH, CH<sub>2</sub>, CH<sub>3</sub>) macromolecules that are bonded/interconnected in the three dimensional space by cross-links/bridges of methylene, oxygen and sulphur (Mahajan, 1982). The organic macromolecules are two dimensional, planar discs with carbon at their centres. Free carbon can only be found in coal that has previously been intensely metamorphosed (Bouška, 1981).

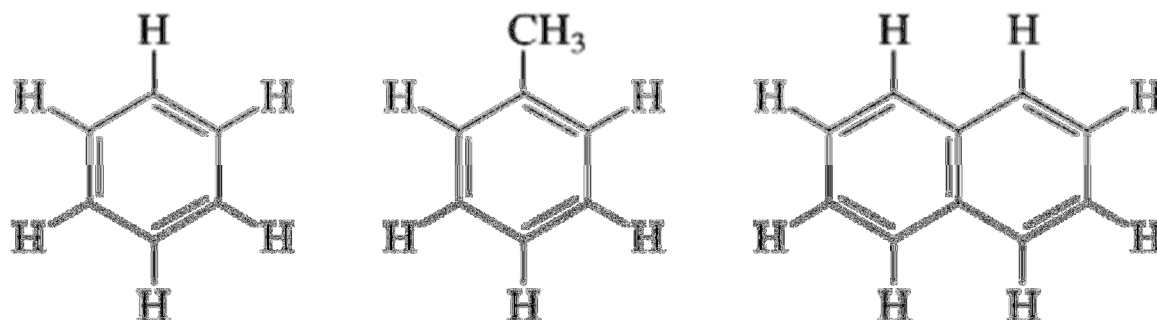


**Figure 3.2:** Benzene resonance structures (McMurry, 1996).

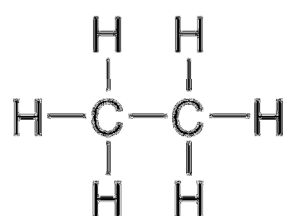
Benzene is a saturated hydrocarbon since all previously unpaired electrons in the outer-shells of the carbon atoms have now been paired due to single and double bonds with other carbon atoms, and the bonds with the hydrogen atoms. The idea of ‘resonance’ (Figure 3.2), is that the actual molecule is a hybrid of two, theoretical structures. This follows from the fact that benzene does not actually possess double or single bonds but rather, all carbon-carbon bonds have lengths intermediate between C-C and C=C typically observed in other hydrocarbons (McMurry, 1996). The bottom structure is thus a combination of the two, top structures, such that it represents the



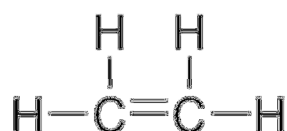
actual benzene structure. Toluene and naphthalene (Figure 3.3) represent some of the compounds with benzene-like structures (McMurry, 1996).



**Figure 3.3:** Benzene and related structures, toluene (methylbenzene) and naphthalene (McMurry, 1996).



**ethane**  
(an alkane)



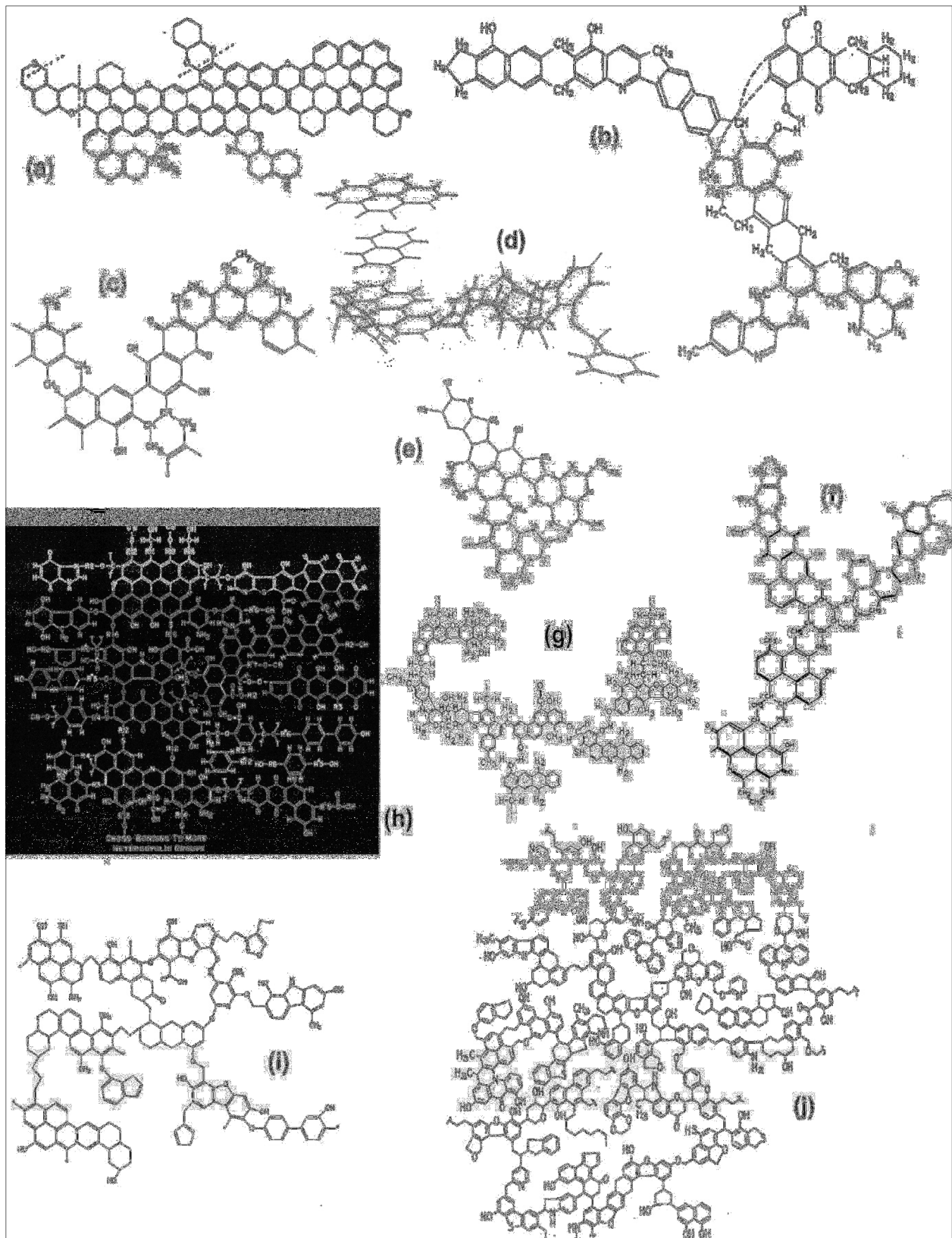
**ethene**  
(an alkene)



**ethyne**  
(an alkyne)

**Figure 3.4:** Aliphatic hydrocarbons, ethane (left), ethene (middle) and ethyne (right) (McMurry, 1996).

A plethora of structural representations of coal, bituminous ranked coals in particular, have come to light since the 1940's, probably due to the continued recognition of the importance of coal as a relatively cheap and abundant energy source. Mathews and Chaffee (2012) provide an excellent summary of most these illustrations, Figure 3.5 is an example. However, most workers recognize the coal structure to be a three dimensional macromolecular network structure (polymer-like) citing the swelling and elastic nature of the material to support the existence of such a structure (Mahajan, 1982; van Niekerk & Mathews, 2010). The three dimensional network structure is in turn produced by stacking the aforementioned two dimensional, macromolecular discs (Bouška, 1981).

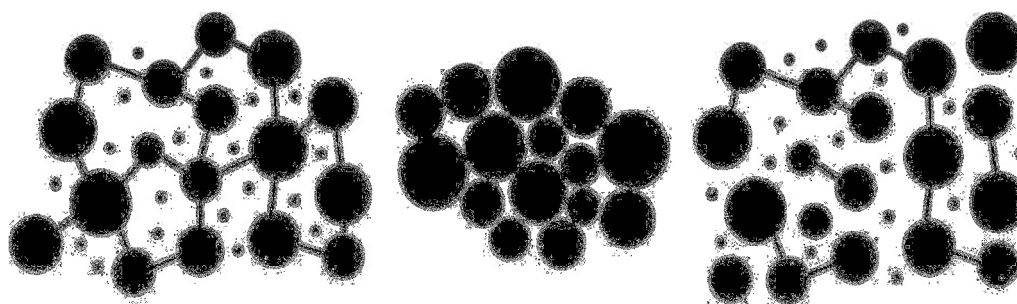


**Figure 3.5:** An example of the numerous structural representations of bituminous ranked coals (a) Fuchs and Sandoff structure, (b) Given, (c) adapted from Given, (d) Meyers, (e) Cartz and Hirsch, (f) Ladner (as printed in Gibson), (g) Solomon, (h) Hill and Lyon, (i) adapted from Wisner, (j) Shinn . As cited in Mathews and Chaffee (2012).

The variable solubility of coal, specifically that of lower ranked coals, in different solvents has led to some difference of opinions with regards to how the ‘3D network’ is assembled. This disagreement is concerned with the exact character of chemical bonds between and linking the numerous building blocks to ultimately form the macromolecular network structure. Two types of structures based on the nature of the bonds between the various macromolecules are recognized in literature (van Niekerk & Mathews, 2010), these are associative (non-covalently bonded macromolecules) and non-associative (covalently bonded macromolecules) network structures. Different but nevertheless valid lines of reasoning have been evoked in support for either of the two structures, such as the insolubility of coal for the non-associative and the low extraction yields for the associative structure (van Niekerk & Mathews, 2010). However, there is no reason to assume that the two structures are mutually exclusive and cannot co-exist especially considering the varied and complex chemical constitution of coal.

What is likely is that the three dimensional macromolecular network structure of coal possesses both associative and non-associative features such that both covalent and non-covalent bonds can be found within the network (van Niekerk & Mathews, 2010). The nature of each bond in such a hybrid network structure would then be dependent on the nature of the adjoining macromolecules, or rather, on the nature of the functional groups or atoms responsible for bonding, thus likely located at the periphery of each of the individual macromolecules. The idea of a hybrid (combined) model is further strengthened by the fact that with the exception of anthracites (Gerstein *et al.*, 1982), other coal types appear to be at least partially soluble in a variety of solvents. Such selective destruction with the simultaneous preservation of other chemical bonds by different solvents can probably be justified by the existence of a variety of bond types with differing strengths so that covalent, van der Waals, electrostatic, hydrogen and  $\pi - \pi$  bonds can all be found within the network structures of bituminous and lower rank coals (van Niekerk & Mathews, 2010). The solubility of coal has been found to increase substantially when a ‘mixture’ of solvents is used rather than when one pure solvent is employed (Gerstein *et al.*, 1982). This implies that the individual solvents are then able to selectively and appropriately disrupt the different chemical bonds.

The hybrid model is a combination of different sized macromolecules held together by the various, previously mentioned chemical bonds (Figure 3.6). The bond distribution and strength thereof in high ranked coals (e.g. anthracites) is likely more uniform and dominated by non-associate (e.g. covalent) bonding so that the insolubility of these coal types is more pronounced and consistent regardless of the solvent being employed. Whether a structure is associative or non-associative, will also directly determine the density of the of the resulting coal structure. This is in-line with the observation that coal density increases with maturity (Speight, 2005), presumably due to the increase in non-associative with the corresponding decrease in associative bonding mechanisms.



**Figure 3.6:** Non-associated (left) and associated (middle) and combined (right) molecular network coal structures (van Niekerk & Mathews, 2010).

Figure 3.6 is a two dimensional representation of the aromatic layers, the mode of stacking and subsequent alignment or lack thereof, coupled with bond lengths and strengths will be dependent on the coal rank being constructed. During coal deposition, the aromatic layers form roughly parallel to the bedding plane (Mahajan, 1982). The degree of coalification will then determine the degree to which the macromolecular layers are aligned as well the distance between the layers, which essentially constitutes porosity. The vertical stacking of macromolecular discs is responsible for macromolecular network structure of coal. The macromolecular network floats in a disordered gel-like material (Bouška, 1981).

Hirsch (1954) proposed the occurrence of three structural changes as coalification progresses and the carbon content of the material increases (Figure 3.7). He proposed that coal with less than 85% carbon has the so-called open structure. The lamellae in this open structure are poorly aligned and connected by crosslinks.

Secondly, coal with carbon content in the range 85% to 91% has a liquid structure. The lamella in this structure shows some alignment. Lastly, coal with a carbon content of 90% has an anthracitic structure such that both lamellae and pores are in alignment. The alignment or lack thereof of pores and lamellae in the various structural stages in this model must be related to the strengths and possibly lengths of the cross-links connecting the macromolecules. The lengths of the cross-links are important because shorter cross-links, likely found in high ranked coals, are likely more rigid resulting in mechanically more stable structural arrangements.

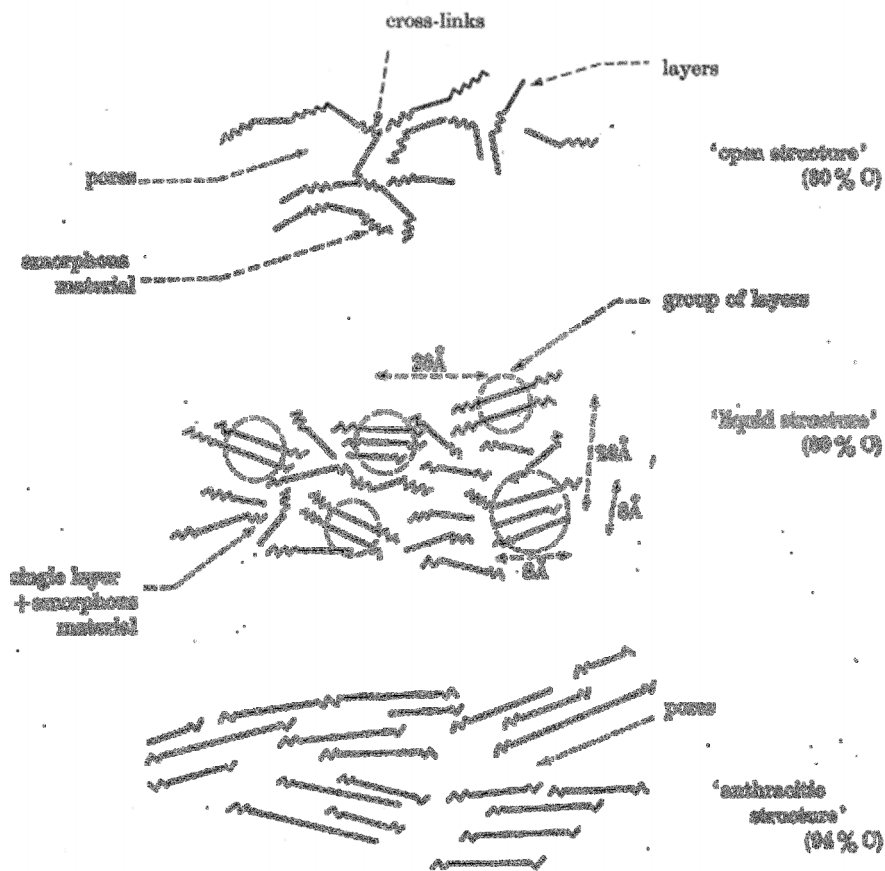
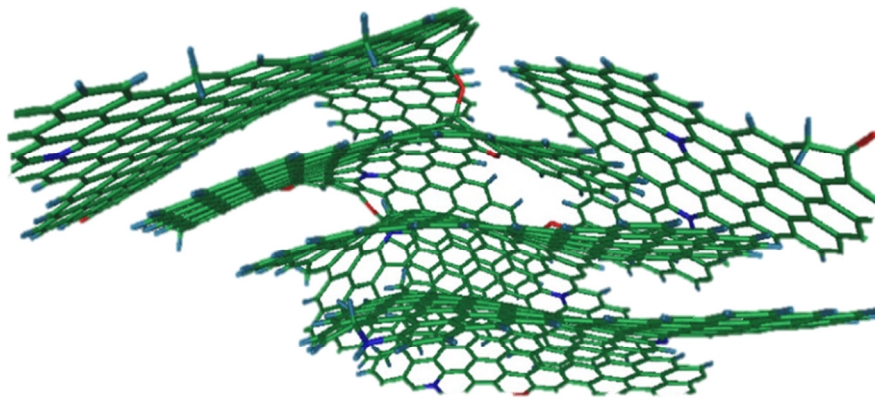


Figure 3.7: Changes of stacking order with rank (Hirsch, 1954).

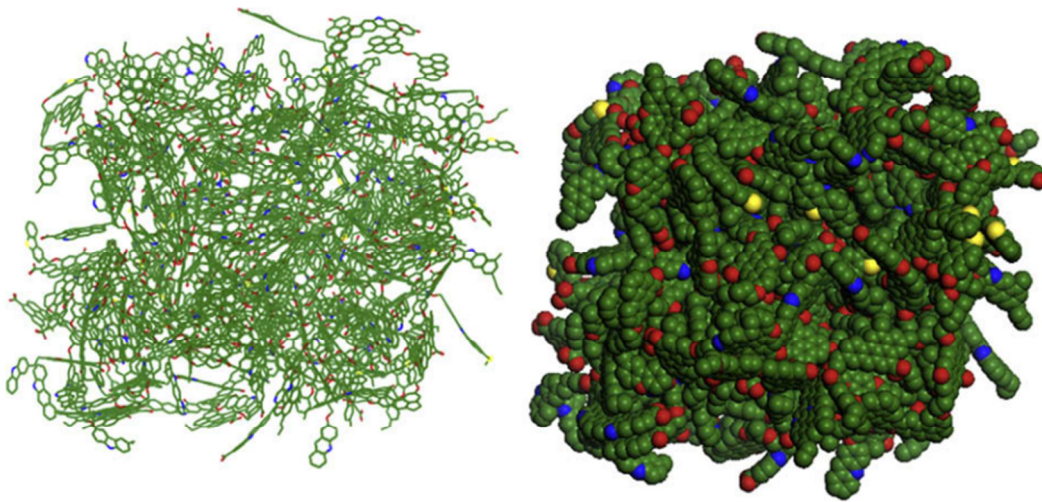




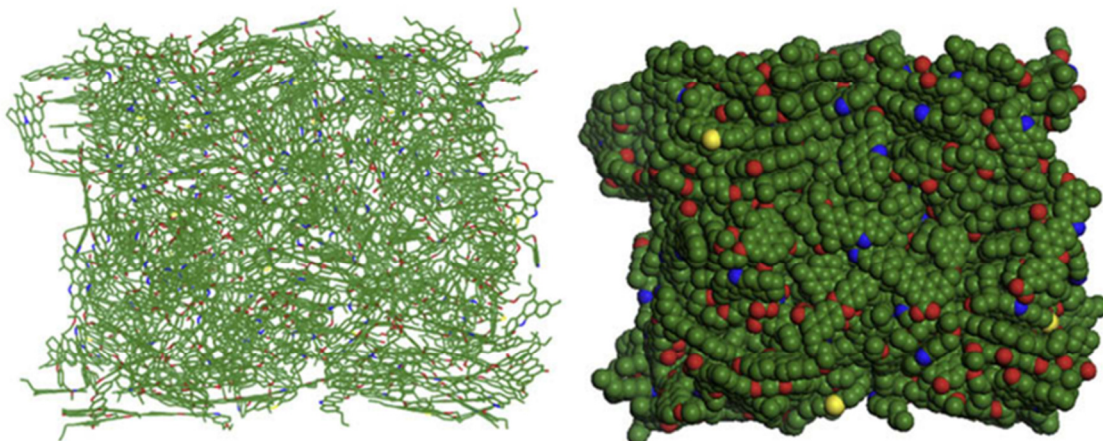
**Figure 3.8:** Representation of Jeddite anthracite (Mathews & Chaffee, 2012).

The degree of cross-linkages and the bond lengths are expected to change significantly and continuously with increasing degree of coalification (Hirsch, 1954), such that macromolecules in higher ranked coals exhibit a higher degree of interconnectedness with corresponding shorter bond lengths than lower ranked counterparts as depicted in Figure 3.8 for anthracitic coals. Higher ranked coals are thus, structurally more well-organized and consistent than low rank coals. This will directly affect both the porosity and the density of the resulting coal so that shorter bond lengths mean smaller pores and higher densities as is found in higher ranked coals.

A substance composed of macromolecules will behave differently in comparison to a substance composed of ‘molecules’, this is primarily due to the differences in the size of the building blocks in each case. The greater size of macromolecules means that the resulting substances are more flexible in contrast to the smaller and more rigid molecule (Green *et al.*, 1982). Coal therefore, being composed of macromolecules, will have mechanical properties similar to those found in polymeric materials as opposed to crystalline ones. It follows then that coal should exhibit viscoelastic behaviour. The excessive porosity of coal especially that found in low ranked coals, can be attributed to the poor, three dimensional alignment of these macromolecules (Mahajan, 1982). The progressive alignment of macromolecules with increasing coal maturity leads to progressive reduction of pore spaces in-between the macromolecule layers.



**Figure 3.9:** Molecular model for inertinite-rich Highveld coal in line and van der Waals radii rendering (green represents carbon, red = oxygen, blue = nitrogen, yellow =sulphur, hydrogen not shown) (van Niekerk & Mathews, 2010).



**Figure 3.10:** Molecular model for vitrinite-rich Waterberg coal in line and van der Waals radii rendering (green represents carbon, red = oxygen, blue = nitrogen, yellow =sulphur, hydrogen not shown) (van Niekerk & Mathews, 2010).

In the context of South African coals, molecular models for an inertinite- and a vitrinite-rich coal of similar rank from the Highveld and Waterberg coalfields were constructed by van Niekerk and Mathews (2010). For the purposes of the present study (i.e. spontaneous combustion), it is important to recognize the open (porous) molecular structures of these coals with the inertinite-rich coal possessing a higher porosity apparently due to the higher degree of aromaticity and the non-associative network structure (Figures 3.9 & 3.10). Owing to the ring structure of benzene and other aromatic compounds, coals in which they dominate should possess relatively

high macro-porosity. This porosity could potentially permit the inwards diffusion of air bringing molecules that surround pores into direct contact with oxygen. Consistent with this premise is the higher oxygen content of the more porous inertinite-rich coal.

Furthermore, the authors found that the network structures were dominated by associative as opposed to non-associative bonding types. Although the moisture content was not quantified in the study by van Niekerk and Mathews (2010), in a different study, Unsworth *et al.* (1989) found that inertinite-rich coals were generally more abundant in macro-pores than vitrinite-rich counterparts. The conflicting, two-fold ability of water to either promote or retard oxidation has previously been investigated by others (e.g. Xu *et al.*, 2013) and depends on the thickness of the water layer lining the surface and pores of the coal sample. However, since the inertinite-rich sample studied by van Niekerk and Mathews (2010) was found to have higher oxygen content than the vitrinite sample, it follows that oxygen molecules were possibly able to diffuse through the water film in the inertinite sample. The higher porosity and oxygen content of the inertinite-rich sample is important for studying spontaneous combustion since inertinite is the dominant maceral group in South African Permian-aged coals.

### 3.3 THE AROMATICITY OF COAL

The aromaticity of coals increase with increasing rank, thus lignites are less aromatic than bituminous coals (Mahajan, 1982). The molecular makeup of lignites is similar to that of precursor plant material owing to the limited coalification that these coals have been subjected to. Lignite is composed of single aromatic structures connected by long aliphatic side chains, cations also act as bridges between phenols and carboxylic acids functional groups. Oxygen bearing functional groups such as carboxylic acids, ketones, phenols, alcohols, ethers, and furan are abundant within lignite ranked coals (Mathews & Chaffee, 2012), as are compounds typically associated with lignin such as aryl-methoxy and C<sub>3</sub>-aliphatic chains.

Ultimate analysis is related to the elemental composition of coal. Carbon and hydrogen by-far constitute the major elements in coal at a maximum of 95% and 6% respectively (Speight, 2005). Nitrogen and sulphur occur in relatively minor proportions with other elements occurring in minute concentrations, together all these



minor elemental coal constituents are termed heteroatoms. Heteroatoms such as N (occur as indole, amide, amine or hydrolamine) and S (occurs as thiol, thiophene or thioether) are typically 'abundant' in low ranked coals together with a significant amount of water (Mathews & Chaffee, 2012).

Sub-bituminous coals also contain lignin structure with appropriate coalification transitions along with ring and limited hydroaromatic structures (Mathews & Chaffee, 2012). Bituminous coals on the other hand are composed of multiple aromatic structures that are highly substituted by aliphatic types. Oxygen functional groups are less diverse in bituminous coals (Mathews & Chaffee, 2012) due to the decreased porosity obstructing oxygen flow and the expulsion of hydroxyls as moisture with progressing coalification. Anthracitic coals are composed of highly aromatic functionalities with little maceral structural diversity (Mathews & Chaffee, 2012). Properties of the different coal types are summarised in Tables 3.2 and 3.3.

**Table 3.2:** Relationship between rank coal (lignite and subbituminous), chemistry and porosity (extracted from Mathews and Chaffee, 2012).

<b>Coal Rank</b>	<b>Precursor Material</b>	<b>Porosity</b>	<b>Aromatic/ Aliphatic Macromolecules</b>	<b>Oxygen-bearing Functional Groups</b>	<b>Heteroatoms</b>
<b>Lignite</b>	Lignite through brown coal to form lignite.	Porous with significant water held within pores	Both, dominated by aliphatic functional groups. Cations act as bridges between the macromolecules	Carboxylic acids, ketones, phenols, alcohols, ethers, and furan	N (as indole, amide, amine or hydrolamine) and S (as thiol, thiophene or thioether)
<b>Subbituminous</b>	Lignite to subbituminous coal. Lignite structure with appropriate coalification transitions.	Porous	Lignite structure with coalification transitions, Small ring structures with limited hydroaromatic structures		

**Table 3.3:** Relationship between rank coal (bituminous and anthracite), chemistry and porosity (extracted from Mathews and Chaffee, 2012).

<b>Coal Rank</b>	<b>Precursor Material</b>	<b>Porosity</b>	<b>Aromatic/ Aliphatic Macromolecules</b>	<b>Oxygen-bearing Functional Groups</b>	<b>Heteroatoms</b>
<b>Bituminous</b>	Subbituminous	Less porous	Small, numerous aromatic rings (benzene), highly substituted by aliphatic groups. Conjugated aromatic rings interconnected with hydroaromatic (dihydro-9,10-phenanthracene), cyclopentane ethers.	Oxygen functionalities less complex, as expected with higher ranked coals. These include phenolic functional groups.	N (amines, pyridine, pyrrole and aniline) and S (thiol, thiophene)
<b>Anthracite</b>	Bituminous		Very little maceral structural divergence. Highly aromatic functionalities	Very little oxygen	

In organic chemistry, the term aromaticity is primarily used to describe benzene and other compounds with similar structure (McMurry, 1996). These naturally occurring compounds are benzene, benzaldehyde and toluene (referring to a specific type of methylbenzene) and others such as estrone and morphine which are of no consequence to the present study. Other synthetic drugs such as diazepam are also aromatic. Of particular interest to the current study, the main source of naturally occurring aromatic compounds is coal and petroleum (McMurry, 1996). The main constituent of coal is a complex mixture of large arrays of benzene-like rings cross-linked together by other atoms acting as bridges. On the other hand, petroleum consists primarily of alkanes with negligible aromatic compounds. Benzene has the molecular formula  $C_6H_6$  and has been found to be unusually stable in comparison to other alkenes or alkynes. The puzzling nature of benzene does not end there, the carbon-carbon bonds in the compound have been found to have the same length. This length is intermediate between the lengths of single and double C-C bonds found in other organic molecules.

The main requirements for a compound to be classified as aromatic is that it must have ring structure and be conjugated (McMurry, 1996). This accounts for the relative stability of these compounds. On the other hand, aliphatic compounds have both open and ring structures, can be either saturated or unsaturated so that their reactivity is more variable. Aromatic compounds have been found to oxidize more readily in aqueous solutions in the presence of a variety of catalysts such as iron and copper ions, liquid hydrofluoric acid and a mixture of hydrogen fluoride-boron trifluoride to mention a few (Enisov & Metelitsa, 1968). Conversely, aliphatic compounds oxidize with ease, releasing heat energy to the surroundings (McMurry, 1996).

One of the more accepted indicators of aromaticity in coal is the atomic ratio of hydrogen to carbon (H/C), determined on the 'dry mineral-free' portion of a sample (Gerstein *et al.*, 1982). The ratio ranges from 1 in low rank to 0.3 in anthracitic coals. Clearly, aromaticity increases as a function of increasing carbon content in parallel with decreasing hydrogen content. Gerstein *et al.* (1982) also points out that aromaticity, in the context of coal at least, might mean "interatomic and interlayer distances similar to graphite". van Krevelen (1981) was able to develop a technique to determine the 'carbon aromaticity' of different macerals.

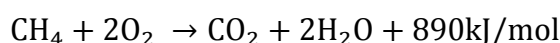
**Table 3.4:** Aromaticities of coal of different ranks inferred from X-ray diffraction (Kwan and Yen (1976) as cited in Gerstein *et al.*, 1982).

Coal Rank	Source	Carbon Aromaticity
<b>Anthracite</b>	Pennylvanian	0.86
<b>Low volatile bituminous</b>	West Virginian	0.83
<b>High volatile bituminous</b>	Dorchester Wise Co., VA	0.64
<b>Lignite</b>	MT	0.60

The aromaticity of variously ranked coals from several locations in the United States have been determined (Table 3.4) by Kwan and Yen (1976) as cited in Gerstein *et al.* (1982) using X-ray diffraction. These results indicate a general increase in aromaticity with increasing degree of coalification which is in agreement with other sources. However, another striking feature of the results is the near equivalent aromaticity values of anthracite and low volatile bituminous with a difference of only 0.03. The difference in aromatic value for high volatile bituminous and lignite also stands at a mere 0.04. Aromaticity increases by 0.19 between the low and high volatile bituminous coals which in this context, is quite substantial. If these results are anything to go by, aromaticity increases significantly during the coalification process especially through the progression from high to low volatile bituminous coal.

### 3.4 OXIDATION OF AROMATIC AND ALIPHATIC COMPOUNDS

Alkanes are sometimes also referred to as aliphatic compounds (McMurry, 1996), this is the other major group of compounds typically found in coals, lower ranked coals in particular. These so-called aliphatic compounds (alkanes) can sometimes occur as alkyl functional groups in coals, signalling the removal of a hydrogen atom (McMurry, 1996). Alkanes are known for their highly exothermic reactions with oxygen and other substances provided the necessary conditions are met. During oxidation, carbon dioxide and water form as by-products along with the liberation of a significant amount heat (McMurry, 1996). A notable example of this is the oxidation of methane (from McMurry, 1996):



The oxidation of these aliphatic compounds is of special interest with regards to the current question of spontaneous combustion of coal, since the liberation of heat is directly

related to the ability of a coal to raise its temperature. Alkanes themselves are held together by weak van der Waals forces, which result from induced polarization of the electron clouds in the molecules (McMurry, 1996). This is consistent with the observation that the structural integrity of coals increase as a function of maturity. Therefore, it is possible that low and high ranked coals are dominated by the so-called associative and non-associative molecular network structures respectively, with intermediate ranked coals having the previously discussed hybrid (combined) structures. Heat released by the exothermic oxidation of the aliphatic portion of coal composition is essential to the coal's ability to self-heat.

It has been argued and proved that aromaticity of coal increase with increasing rank, thus bituminous and anthracitic coals are more aromatic than lignites (Mahajan, 1982). It follows that low ranked coals are dominated by aliphatic compounds which release a substantial amount of heat upon oxidation leading to the spontaneous combustion of these coals. Following and accepting the preceding logic, the observation that high ranked coals are less likely to spontaneously combust may also be related to the increased concentration of more stable aromatic compounds (at the expense of aliphatic) in addition to the reduced porosity.

### **3.5 HEAT-LIBERATING COMPLEXES DURING LOW-TEMPERATURE OXIDATION**

Oxygen functional groups in run-of-mine coal are related to and are the direct result of oxygen functionalities in ancient plant matter (Attar & Hendrickson, 1982). Coal will weather when brought into contact with the atmosphere, increasing its oxygen content (Wang *et al.*, 2003). Decomposition of oxygen functionalities, which is temperature-dependent, leads to liberation of heat. Thermal decomposition of ethers, carbonyls and phenols takes place through “free radical mechanisms” (Attar & Hendrickson, 1982). A free radical is particularly reactive since it contains an atom with an odd number of electrons in its outermost shell, as opposed to the eight typically found in stable noble-gas octets (McMurry, 1996). The noble-gas octet is then achieved by substitution with other atoms or addition reactions with alkenes, creating new radicals in the process. A self-sustaining chain of reactions with repetitious cycles is thus started (McMurry, 1996). On the other hand, carboxylic acids decompose through hydrogen transfer or radical ion mechanism (McMurry, 1996).

Examination of two gaseous, oxidation products evolved during pyrolysis show the following trends, 1) CO<sub>2</sub> peaks at 360°C and around 750 – 800°C, 2) CO peaks at 420°C and 670°C (Attar & Hendrickson, 1982). The first and second CO<sub>2</sub> peaks are attributable to decomposition of carboxylic acids and inorganic carbonates respectively (Attar & Hendrickson, 1982). The first CO peak results from the decomposition of quinones and second from decomposition heterocyclic ethers (Attar & Hendrickson, 1982). These temperature peaks are too high for spontaneous combustion initiation, as decomposition of the relevant oxygenated complexes is believed to occur below 70°C (Wang *et al.*, 2003). Therefore the decomposition of carboxyls, carbonyls, quinones, heterocyclic ethers and inorganic carbonates occurs at temperatures too elevated in the context of spontaneous combustion and is thus immaterial to this study. However, according to Attar and Hendrickson (1982) substantial amounts of peroxides may be found in weathered (i.e. oxidized) coals and these decompose at temperatures well below 200°C. Avila *et al.* (2014) classifies peroxides and related compounds as ‘unstable complexes’, these are responsible for self-heating in coal ultimately resulting in self-ignition.

Peroxides (compounds with O-O bonds) can result from slow reactions between air and some ethers (McMurry, 1996). Low molecular weight ethers produce predominantly explosive peroxides even in minute quantities. Ethers are essentially organic derivatives of water where the two hydrogen atoms have been substituted by organic functionalities, R-O-R as opposed to H-O-H. Organic functional groups can be alkyl (aliphatic), aryl or vinylic and the oxygen atom may be in either an open-chain or ring structure. Peroxygen functionalities are stable until a temperature of 70°C is reached (Jones & Townsend, 1949). However, exothermic decomposition of peroxide species has been found to occur at temperatures between 30-180°C (Clemens *et al.*, 1991), well within the temperature range typically cited for spontaneous combustion initiation in coal.

## **4 CHAPTER 4: MAJOR COALFIELDS OF SOUTH AFRICA AND THE POTENTIAL FOR SPONTANEOUS COMBUSTION**

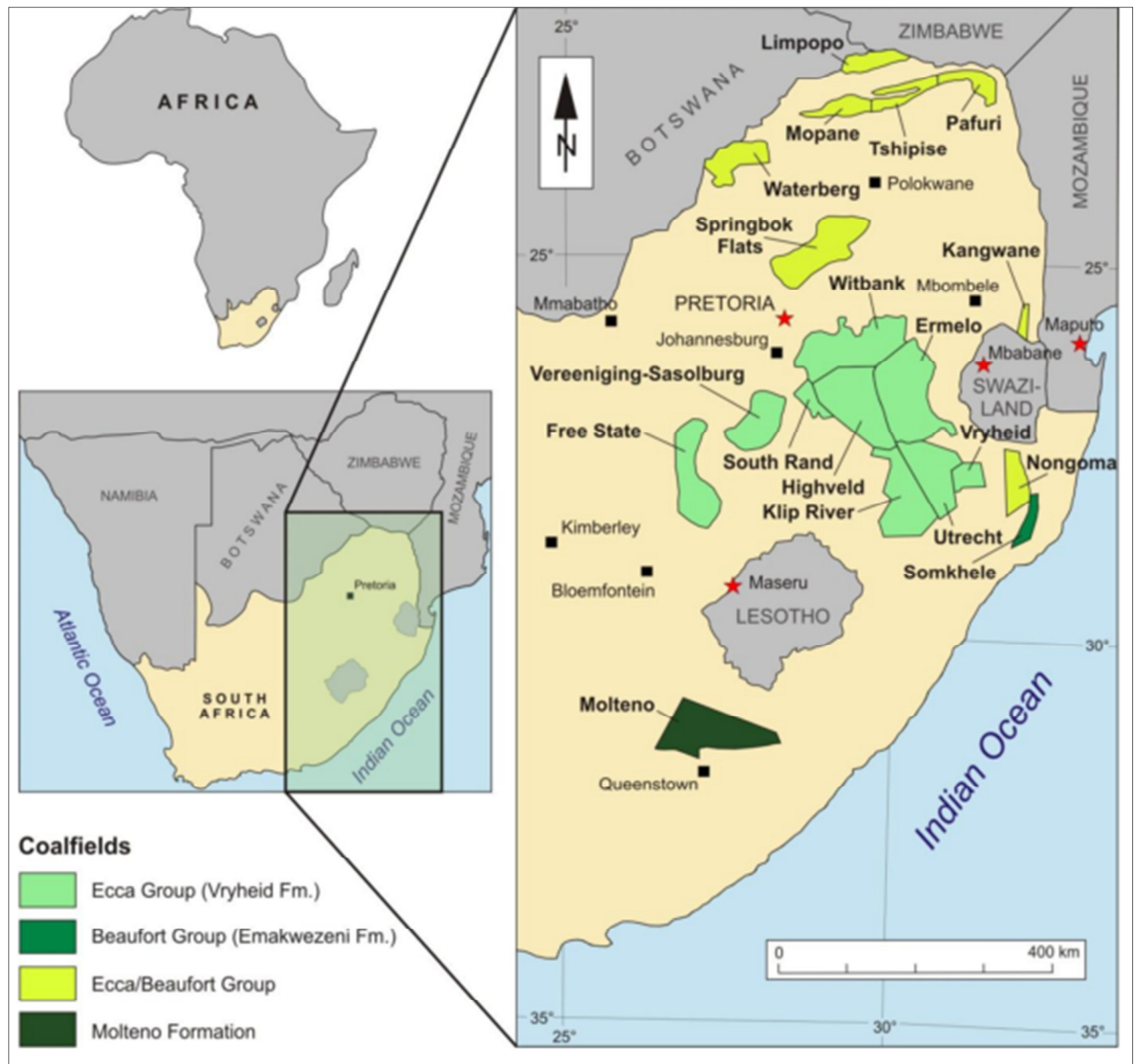
### **4.1 INTRODUCTION**

This chapter is a reconnaissance study in which data relevant to coal oxidation in South African coals, specifically ultimate and infrared spectroscopy analysis, together with petrographic and coal quality information will be sourced from literature as a preparatory step to designing a comprehensive analytical programme for a PhD study. To the author's knowledge, South African studies that contain the required information exist, but these studies had their own objectives and low-temperature oxidation or spontaneous combustion is not the main focus of this previous work.

Therefore, existing data needs to be reanalyzed for use in coal oxidation studies. In particular, ultimate analysis can be used to calculate the aromaticity value of a coal sample based on the atomic ratio of hydrogen to carbon (Gerstein *et al.*, 1982). This ratio is indicative of coal rank and can be used to infer the organic chemistry of a coal sample such that the dominance of either aliphatic or aromatic hydrocarbons can be estimated. On the other hand, FT-IR and other methods such as gas chromatography – mass spectroscopy can be used to directly determine the nature of organic compounds in coal or other substances. However, both FT-IR and GC-MS determine only the occurrence of a compound and not the concentration thereof. Such studies are lacking with regards to South African coals or if they do exist, remain largely unpublished. If low-temperature oxidation and spontaneous combustion are to be comprehensively studied in terms of the organic chemistry, it is necessary to determine not only the occurrence of an organic compound but also its concentration. The concentrations will enable direct comparison of the organic constitution of different coal samples so that in the end, the effect of chemistry on spontaneous combustion can be evaluated. Petrographic and coal rank data can then be used to supplement the discussions based on aromaticity and FI-IR.



## 4.2 BACKGROUND



**Figure 4.1:** Coalfields of South Africa (variously modified after Snyman, 1998). The Mopane, Tshipise and Pafuri coalfields collectively form the Soutpansberg Coalfield. Fm. = Formation. (Hancox & Götz, 2014).

A total of 19 coalfields (Figure 4.1) with variable combustion properties are recognized within the borders of South Africa (Jeffrey, 2005a; Hancox & Götz, 2014). The 19 coalfields are spread across multiple provinces including KwaZulu-Natal, Mpumalanga, Limpopo, Free State, Gauteng and the North West (Jeffrey, 2005a), and have been subdivided based on geographical concerns as well as the style of sedimentation, origin, formation, distribution and quality of the coal deposits (Hancox & Götz, 2014). However, current resource exploitation is restricted primarily to the Mpumalanga and Free State Provinces with smaller operations in the KwaZulu-Natal Province (Jeffrey, 2005a).

The age, rank and maceral composition of the coal deposits have been found to be variable and coalfield-specific, likely reflecting certain depositional environments. The Main Karoo Basin and its sub-basins host all of the 19 coalfields. The main Karoo Basin, the Parana Basin of South America, the Beacon Basin of Antarctica and the Bowen Basin of Australia are fragments of a larger, Phanerozoic basin that formed along the southern margin of the Gondwana Supercontinent, and the depositional sequences contained within the basins were laid-down between the Late Carboniferous and the Middle Jurassic (Hancox & Götz, 2014).

Coal production in South Africa stood at 280 million tons in 2010 with open-cast and underground mining accounting for roughly 50% of total production each (Stracher et al., 2013). Surface mining methods are typically employed for Mid-to-Late Permian deposits which are shallow lying and fairly thick. Approximately 75% of bituminous ranked coals lie at a depth ranging between 50 and 200 meters with the other 25% lying above 50 meters (Stracher et al., 2013). The Vryheid Formation of the Ecca Group (Karoo) is the main coal-bearing sequence where the bulk of mining operations has and continues to take place. The sequence ranges in thickness from less than 50 meters near the town of Bloemfontein to over 500 meters near Newcastle and Vryheid (Hancox & Götz, 2014).

The Waterberg, Highveld and Witbank Coalfields together host more than 70% of South Africa's coal resources. However, as stated by Jeffrey (2005a), the Witbank Coalfield is almost exhausted, whereas the Waterberg Coalfield is likely to have considerable coal deposits which can be exploited for benzene, toluene and xylene (BTX), provided the sulphur therein can be economically removed. These aromatic compounds are important industrial chemicals typically used in the production of a wide range polymers, polystyrenes and polyamides. Mineral matter as represented by the ash content within coals of the Waterberg varies significantly and can be as high as 65% (Stracher et al., 2013) necessitating major beneficiation before the coal can be profitably traded and suitably utilized (Jeffrey, 2005b). The Highveld together with the Sasolburg-Vereeniging Coalfields serve as the main feedstocks for both Sasol Synthetic Fuels and Sasol Chemical Industries (Jeffrey, 2005a).

The four most important coalfields based on economic considerations as well as historical, current and potential future exploitation are the Witbank, Highveld, Sasolburg-Vereeniging and Waterberg Coalfields. In this section, a review of available literature on these coalfields is presented, after which an attempt will be made to discuss the coalfields in

the context of low-temperature oxidation and spontaneous combustion based on the limited organic chemistry information available.

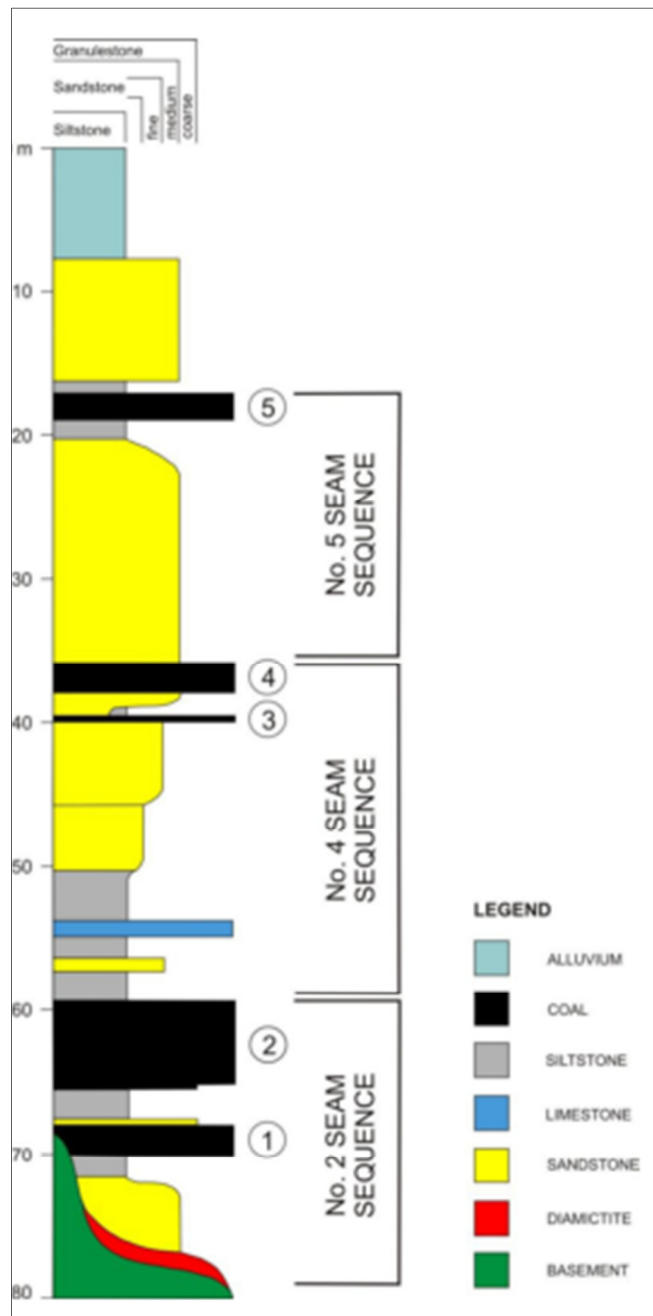
Following a study on the Witbank Coalfield, Holland *et al.* (1989) concluded that thick, continuous coal seams are enriched in the inertinite maceral group. Conversely, laterally discontinuous and thin seams are associated with high vitrinite contents. The differences in petrographic composition is attributed to varying depositional environments with the inertinite-rich seams corresponding to glacio-fluvial and upper delta settings whereas high vitrinite contents are related to lower delta settings (Holland *et al.*, 1989). Liptinite (exinite) only reaches a maximum of 15% in South African Coalfields (Holland *et al.*, 1989), thus evidently, both depositional settings did not favour formation of significant amounts of this maceral group.

Coal quality data (Table 4.1) and the response of different macerals to oxidation (Table 4.2) are used to infer the oxidation properties of selected South African Coalfields.

**Table 4.1:** Aromaticity and the response of the three main maceral groups to oxidation (extracted from Falcon, 1986).

<b>Maceral Group</b>	<b>Response to oxidation</b>
<b>Vitrinite</b>	<ul style="list-style-type: none"> <li>- More non-aromatic groups (i.e. possibly dominated by aliphatic groups) than inertinite.</li> <li>- Likely more susceptible to low-temperature oxidation than inertinite-rich coals of the same rank owing to its ability to absorb more oxygen its structure per unit area.</li> </ul>
<b>Inertinite</b>	<ul style="list-style-type: none"> <li>- Oxygen absorption requires high activation energies due to the compacted nature of aromatic in its structure.</li> <li>- Increased macro-porosity owing to the ‘ring’ structure of aromatic compounds means more oxygen can pass-through or be stored in comparison to vitrinite.</li> </ul>
<b>Exinite (Liptinite)</b>	<ul style="list-style-type: none"> <li>- Very little porosity, however reactive to the adsorption of oxygen.</li> <li>- In general, not a serious concern in Southern Hemisphere coals because the low contents.</li> </ul>

#### 4.2.1 Witbank Coalfield

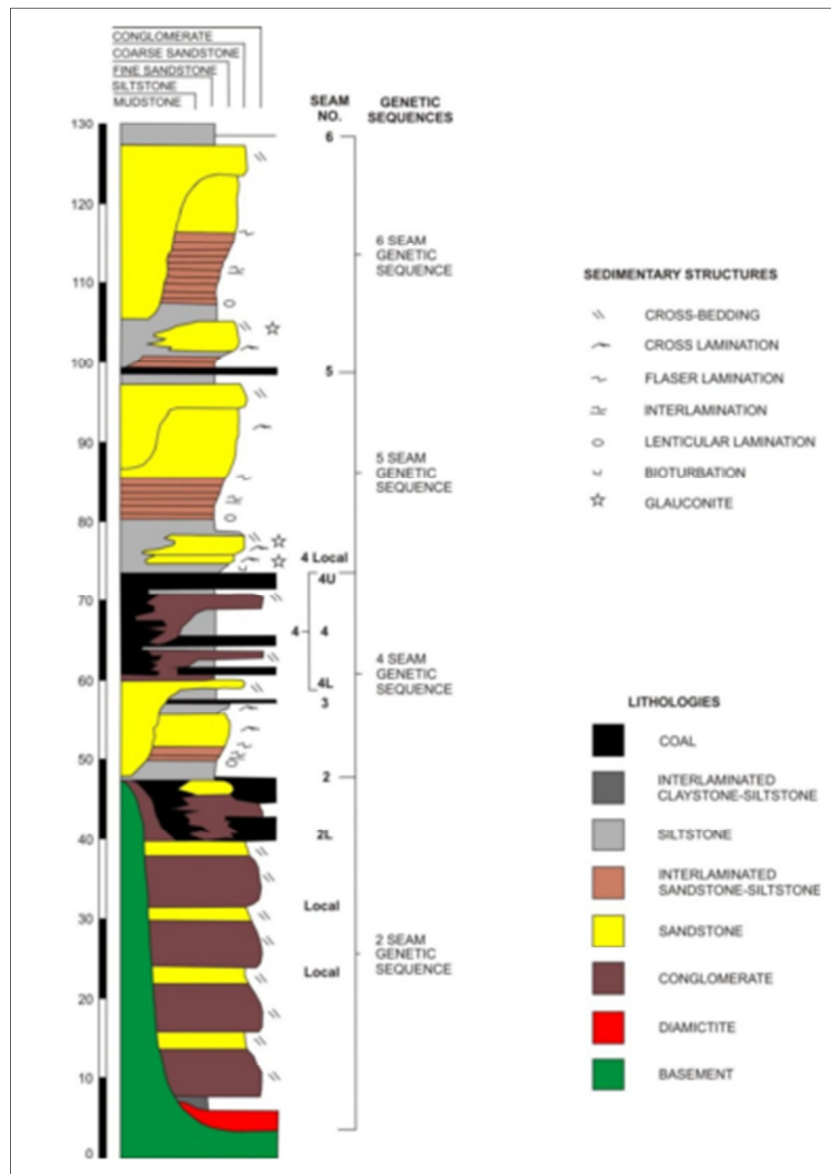


**Figure 4.2:** Stratigraphic column for the Vryheid Formation in the Witbank Coalfield (redrawn from Cairncross and Cadle, 1988). Individual coal seams are numbered from No. 1 at the base to No.5 at the top (Hancox & Götz, 2014).

The Witbank Coalfield is bordered by the towns of Belfast and Springs in the east-west and Middelburg and Rietspruit in north-south directions attaining a total area of approximately 568 000 hectares (Hancox & Götz, 2014). It extends over a distance of 180km in the east-west direction where the basement consists of a combination of the older Karoo, Transvaal, and Waterberg sequences, as well as the Bushveld Igneous Complex.

A total of five coal sequences are recognized within the Witbank Coalfield as depicted in Figure 4.2 (Jeffrey, 2005a). The Volksrust Formation, also known as the No. 1 seam, is the lowermost unit. This unit is irregular due to the nature of the underlying strata and has a maximum thickness of 3 meters. The No. 2 seam is the most economically important, ranging from 20 meters in thickness to 4.5 meters. The No. 3 seam attains a maximum thickness of 0.5 meters and is reportedly uneconomic despite its high quality. The No. 4 seam is divided into two zones, namely the 4 Upper and 4 Lower, by fine-grained sedimentary strata, and is economically important although it is of lower quality than the No. 2 seam. The No. 5 seam ranges in thickness from 0 to 5 meters and is interpreted to represent an erosional surface (Jeffrey, 2005a).

## 4.2.2 Highveld Coalfield



**Figure 4.3:** The generalised stratigraphy and depositional sequence of the Highveld Coalfield (from Winter, 1985 as cited in Hancox & Götz, 2014).

The Highveld Coalfield extends through the Gauteng and Mpumalanga Provinces with a total area of 700 000 hectares (Hancox & Götz, 2014). The Witbank Coalfield lies north of the Highveld with the Smithfield Ridge forming the boundary between the two. Although the two coalfields contain similar depositional sequences, they are recognized as separate entities. The basement granite forms the lowermost stratigraphic unit in the area of the Highveld Coalfield, followed by igneous rocks of the Bushveld Igneous Complex and then the sedimentary deposits of the Witwatersrand Supergroup and finally by the Transvaal sequences as depicted in Figure 4.3 (Hancox & Götz, 2014). Stratigraphic units of the Karoo

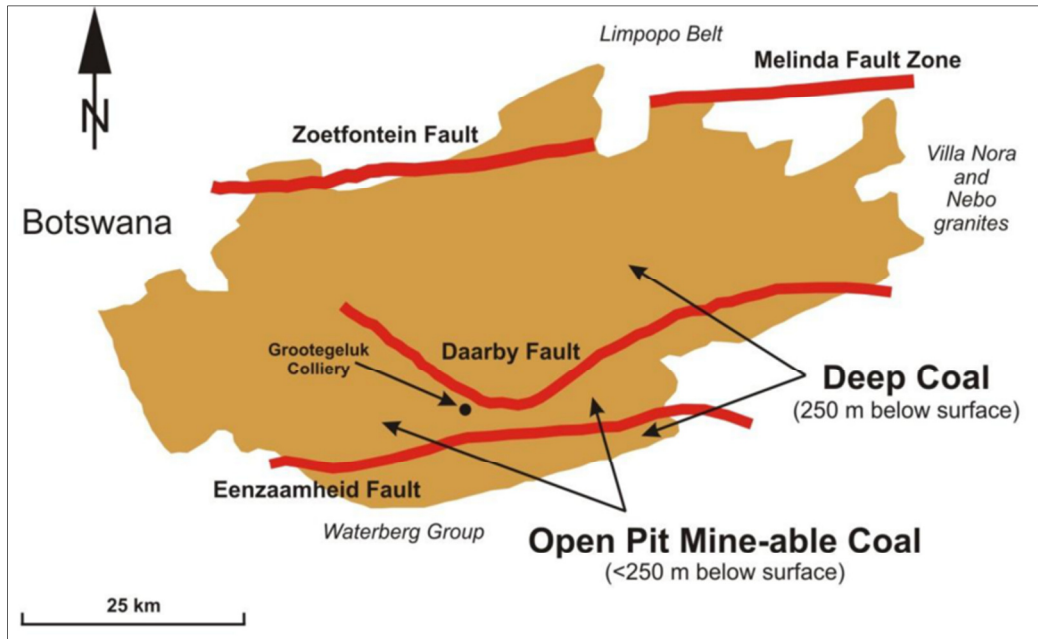
Supergroup have been found to vary greatly in thickness throughout the Highveld Coalfield presumably due to the irregular nature of the sequences on which they were deposited.

#### **4.2.3 Sasolburg-Vereeniging Coalfield**

The Sasolburg-Vereeniging together with the Free State Coalfield are located in the Free State Province but are recognized as separate entities (Hancox & Götz, 2014). Three sub-basins are distinguished within the Sasolburg-Vereeniging Coalfield, namely Sigma, Cornelia and Coalbrook. The Sigma sub-basin is located south of the town of Sasolburg, where the Ventersdorp and Transvaal Supergroups form the basement for Karoo sequences in this sub-basin. Roughly horizontal coal seams resulted from the flat topography of the Ventersdorp lavas. The 'coal zone' in this sub-basin ranges in thickness between 30 and 40 km and contains four seams termed C1, C2A, C2B and C3. The Cornelia sub-basin contains three coal seams known as bottom, middle and top, and the Coalbrook sub-basin is an extension of the two other sub-basins and contains three coal seams known as No. 1, 2 and 3 (Hancox & Götz, 2014).

#### **4.2.4 Waterberg Coalfield**

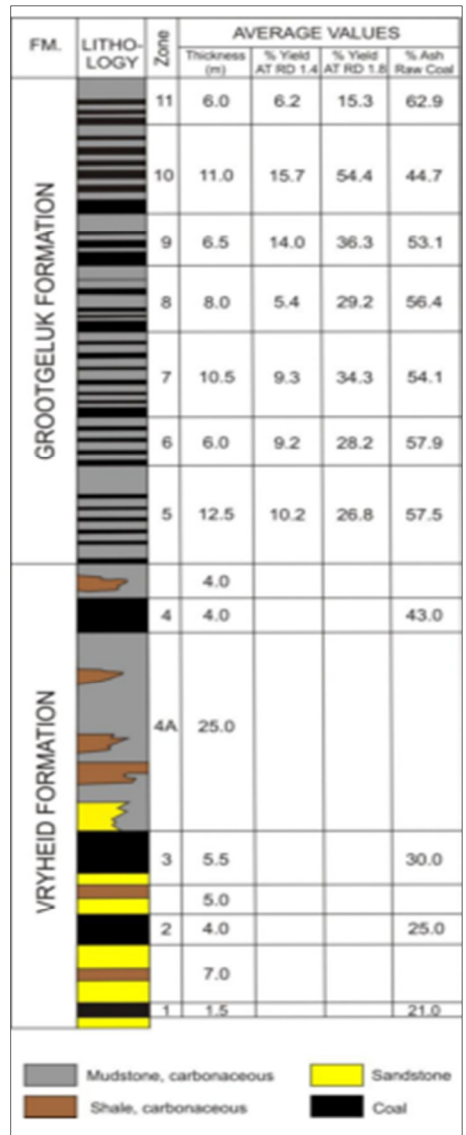
The Waterberg Coalfield is located in the Limpopo Province, approximately 400km north-west of Johannesburg. It lies between the Palala Shear Zone in the east and Botswanan border in the west, and the Melinda and Eenzaamheid Fault Zones in north and south respectively. The Daarby Fault divides the coalfield into two, corresponding to deep and shallow lying deposits as per Figure 4.4 (Jeffrey, 2005b; Hancox & Götz, 2014).



**Figure 4.4:** Schematic overview of the extent of the Waterberg Coalfield showing areas of shallow and deep coal and the main faults (after Jeffrey, 2005b).

The Waterberg Coalfield is hosted within the Ellisras sub-basin of the Kalahari Basin of Botswana. The Waterberg Coalfield was deposited on a basement of Beit Bridge Complex and earlier Waterberg rocks to the north and south respectively. The sedimentary Dwyka, Ecca, Beaufort and Stormberg rocks are thus underlain by earlier Waterberg rocks as well as the Bushveld Complex. Coal seams in this coalfield are named 1, 2, 3, 4A and 4 in the Vryheid Formation and 5-11 in the Grootegeluk Formation (Hancox & Götz, 2014).





**Figure 4.5:** Stratigraphic column of the geology of the coal-bearing sequences of the Waterberg Coalfield showing the nature and coal qualities of the 11 coal zones (Hancox & Götz, 2014).

**Table 4.2:** Coal quality of selected South African coalfields (modified from Jeffrey, 2005a).

Coalfield	Coal Quality
<b>Witbank</b>	<ul style="list-style-type: none"> <li>- No. 1 Seam is a source of high-grade steam coal. The No. 1 Seam often has very low phosphorus content and in such cases it is usually mined separately as metallurgical feedstock.</li> <li>- The No. 2 Seam contains some of the best quality coal. It generally displays a well-defined zoning with up to seven (five in some areas) distinct coal zones of different coal quality. The upper part of the seam is generally shaly and unmineable.</li> <li>- The No. 4 Seam is generally of poor quality and consists of predominantly dull to dull lustrous coal with the upper portion being of poor quality, Thus mining is restricted to the lower 3.5 m portion of the coal-seam.</li> <li>- The No. 5 Seam has been mined as a source of blend coking coal and for metallurgical uses especially in the central Witbank area where it is of higher quality.</li> </ul>
<b>Highveld</b>	<ul style="list-style-type: none"> <li>- No. 2 Seam contains low-grade bituminous coal with an ash content of 22–35%. In areas where the No. 2 Seam is of better quality and has good washability characteristics, like in Leandra, a coal product of 27 MJ/kg at yields of greater than 70% can be produced.</li> <li>- The No. 4 Seam generally contains mainly low-grade bituminous coal with an ash content of 20–35%. However, the ash content can increase to 40% in the upper one to two metres. The No. 4 Upper Seam quality is extremely variable but the seam generally contains low-grade bituminous coal with approximately 25% ash content.</li> <li>- The No. 5 Seam has better quality coal than the other seams, ash and volatile matter contents of 19% and 32% respectively.</li> </ul>
<b>Waterberg</b>	<ul style="list-style-type: none"> <li>- Coal rank increases steadily from west to east. It must be assumed that qualities observed at GCM are potentially representative of the entire coalfield.</li> </ul>

### 4.3 CALCULATION OF AROMATICITY FROM PUBLISHED DATA

In South Africa, the data required to quantitatively assess coal oxidation potential has been found to be terribly lacking such that, in the end, the results of the current study can only be considered semi-qualitative than quantitative. As an example, one of the more ‘comprehensive’ studies, in terms of what this study is attempting to achieve, has analysed a maximum of six coal samples. Although this may arguably have been sufficient for the

specific study, it is in the whole statistically unrepresentative in terms of studying the oxidation properties of the coalfield. Only once statistically representative samples are obtained and analysed can the oxidation properties of the coalfields and the seams therein be fully studied, and spontaneous combustion better predicted and controlled. This study is expectedly only a first step, although an important one in the study of the chemistry and oxidation properties of the various coalfields.

The lack of chemical data with regards to the coalfields is partially attributed to the unwillingness of mining companies operating in the specific coalfields to bring this information into the public domain. Thus, in the future, it might be necessary to persuade the respective miners that it is economically more important for them to make the samples available and that the information gathered by such studies would in the long run be in their interests. It will, for the mining companies, mean expenses related with mine closure can be minimized if the coal oxidation properties are better understood and the threat of fires in abandoned mines be eliminated, thus also preventing potential litigation in terms of civil claims by communities in these mining areas. Measures to reduce the threat of resource destruction with regards to spontaneously combusting seams or coal in stockpiles can also be developed. The lack of research regarding coal is seemingly a world-wide shortcoming, but, the problem is perhaps exacerbated in South Africa by the lack of resources in terms of expertise, financial support and access to the required specialised equipment.

As previously mentioned, coal aromaticity can be calculated based on the atomic ratio of hydrogen to carbon (Gerstein *et al.*, 1982). For the computation, the percentages of hydrogen and carbon as determined through ultimate analysis are normalised with their respective atomic weights. The resulting ratio, called carbon aromaticity ranges from 1 for low rank lignitic coals to 0.3 for high rank anthracitic ones. The organic chemical constitution of the low and high coal ranks is specific corresponding largely aliphatic and aromatic hydrocarbons respectively.

$$\text{Carbon Aromaticity (C}_{ar}\text{)} = \frac{\frac{\% \text{ H}}{\text{H atomic weight}}}{\frac{\% \text{ C}}{\text{C atomic weight}}}$$

#### 4.3.1 Highveld and Waterberg Coalfields

In one of the few studies of coal chemistry in South Africa, van Niekerk *et al.* (2008) used two coal samples, one run-of-mine coal from the Highveld and the other, a

commercially cleaned Waterberg coal, corresponding to an inertinite- and a vitrinite-rich coal respectively. Ultimate analysis of the Waterberg coal revealed 6.23% hydrogen and 84.07% carbon, compared with 4.53% hydrogen and 83.72% carbon for the Highveld sample. From this, it is possible to calculate the aromaticity of the two coal samples based on a method similar to that proposed by Gerstein *et al.* (1982), and therefore the atomic ratio of hydrogen to carbon (H/C). The results of this calculation are shown in Table 4.3.

**Table 4.3:** Maceral composition, selected elemental analysis and aromaticity of coal samples from the Waterberg and Highveld coalfields (modified after van Niekerk *et al.*, 2008). Aromaticity calculated for this study using Gerstein's (1982) formula.

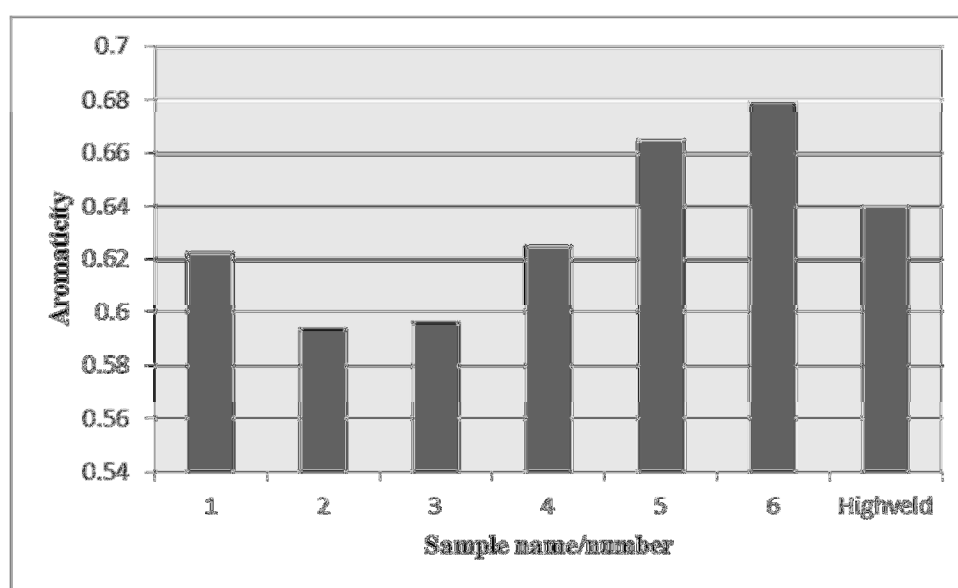
Coal Samples	Maceral Composition (%)			Elemental Analysis		Aromaticity (H/C)
	Vitrinite	Inertinite	Liptinite	Carbon	Hydrogen	
<b>Waterberg</b>	91.8	5.8	2.4	84.07	6.23	0.88
<b>Highveld</b>	11.2	87.7	1.1	83.72	4.53	0.64

It is necessary to mention that the above two samples from the van Niekerk *et al.* (2008) study were used to study coal structure and other similar properties. It is debatable whether two samples would be considered sufficient and representative for any study. However, it is safe to assume that the lack of information regarding coal structure and chemistry inevitably renders the van Niekerk study a major contribution. In terms of the objectives of this study, two samples are without a doubt inadequate and allow for very narrow interpretations to be made in terms of organic composition and oxidation properties of the various coalfields.

In a different study, Wagner and Hlatswayo (2005) also report typical proximate, ultimate and petrographic values for Highveld coals. The carbon contents in this study are markedly lower than those reported by van Niekerk *et al.* (2008). The aromaticities of six Highveld samples were calculated using the ultimate analyses published by Wagner and Hlatswayo (2005), and shown in Table 4.4 and Figure 4.7. Although the carbon contents in these Highveld coals are generally lower than the sample in the van Niekerk *et al.* (2008) study, the aromaticities are similar to some degree, ranging between 0.59 and 0.68. Based on these two studies, the organic constitution of the Highveld Coalfield appears consistent, with an average over 7 samples of 0.63 (RSD= 0.63). Inertinite is the dominant maceral group in these samples with the sample with lowest aromaticity value also containing the lowest amount of this maceral. The highest vitrinite volume percentage is 30.

**Table 4.4:** Typical petrographic and selected ultimate analyses values as well as aromaticities for selected Highveld coals (modified after Wagner and Hlatswayo, 2005). Aromaticity calculated for this study using Gerstein's (1982) formula.

Sample	Petrographic data (vol. %)			Ultimate analyses (% air-dried)		Aromaticity (H/C)
	Vitrinite	Liptinite	Inertinite	Carbon	Hydrogen	
1	22	4	74	58.23	3.04	0.62
2	33	5	62	52.22	2.6	0.59
3	17	3	80	54.81	2.74	0.60
4	30	4	66	58.19	3.05	0.62
5	24	3	73	56.11	3.13	0.66
6	20	4	76	49.7	2.83	0.68



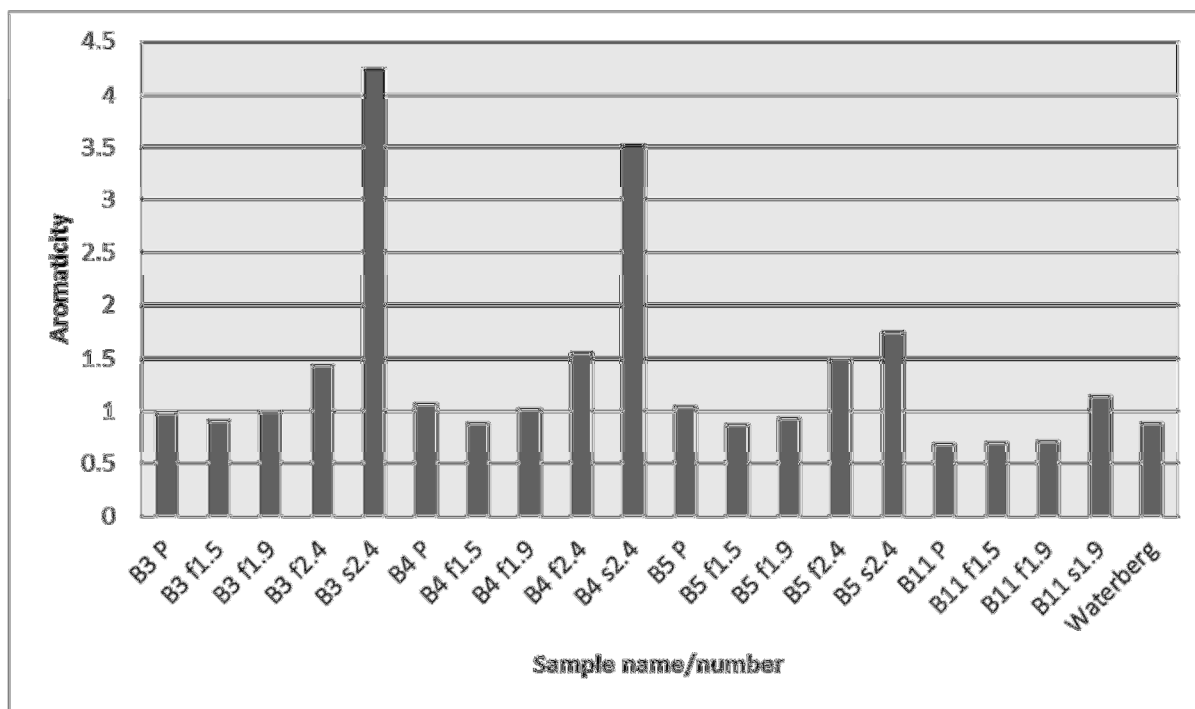
**Figure 4.6:** Histogram depicting the aromaticities of coal samples from the Highveld Coalfield. Samples numbered 1-6 are from Wagner and Hlatswayo (2005), as well as one sample from Van Niekerk *et al.* (2008) named 'Highveld'.

Wagner and Tlotleng (2012) determined ultimate analysis for Waterberg 'parent coals' and their 'density fractions'. This data has been used to calculate the aromaticities for the samples, as per previous examples. The ultimate analysis of the Waterberg coal sample used in the study by van Niekerk *et al.* (2008) differs substantially from the ones used by Wagner and Tlotleng (2012; Table 4.5). This is ascribed to the fact that the sample in the van Niekerk *et al.* (2008) was 'commercially cleaned' whereas the coal samples in the other study were simply run-of-mine samples, as there were vast differences in the objectives in each study. The samples in the Wagner and Tlotleng (2012) study thus contain significant inorganic matter as represented by the ash content in the range of 10.7% and 53.7% for the parent coals. Stracher *et al.* (2013) and Jeffrey (2005b) attest to the above typically accepted

mineral matter content of the Waterberg Coalfield. Based on the high inorganic component of some of the samples, the rocks are better classified as carbonaceous shales (or such an equivalent) as suggested by Ting (1982).

**Table 4.5:** Petrographic data, pyritic sulphur and selected ultimate analyses values as well as aromaticities for selected Waterberg coals, GF= Grootegeluk Formation; VF= Vryheid Formation (modified after Wagner and Tlotleng, 2012). Aromaticities calculated using Gerstein's (1982) formula.

Sample		Petrographic data (vol. %)			Pyritic S (% of total S form)	Ultimate analysis (% a.r.)		Aromaticity (H/C)
		Vitrinite	Liptinite	Inertinite		Carbon	Hydrogen	
<b>GF</b>	<b>B3 P</b>	40.5	9.3	11.3	0.7	46.2	3.79	0.98
	<b>B3 f1.5</b>	80.5	4.8	7.8	0.16	69.2	5.23	0.90
	<b>B3 f1.9</b>	52	11.1	19.2	0.62	46.2	3.85	0.99
	<b>B3 f2.4</b>	9.6	7.9	22	0.41	16.5	1.97	1.42
	<b>B3 s2.4</b>	2.6	1	4	1.96	4.24	1.51	4.24
	<b>B4 P</b>	28.5	16.1	17.8	0.68	37.6	3.36	1.06
	<b>B4 f1.5</b>	81.1	7.5	90.8	0.08	71.2	5.23	0.88
	<b>B4 f1.9</b>	29.5	20.2	30.6	0.24	43	3.67	1.02
	<b>B4 f2.4</b>	3.8	14	27.2	0.12	16.2	2.11	1.55
	<b>B4 s2.4</b>	1.6	0.4	2.4	2.87	5.46	1.61	3.51
	<b>B5 P</b>	16.2	9.8	28.2	0.87	35.5	3.1	1.04
	<b>B5 f1.5</b>	71.4	9.7	14.7	0.07	70	5.09	0.87
	<b>B5 f1.9</b>	25	19.5	44.6	0.12	46.7	3.64	0.93
	<b>B5 f2.4</b>	2.8	7.4	30.9	0.1	16.8	2.1	1.49
	<b>B5 s2.4</b>	4	0.6	6	24.9	10.6	1.55	1.74
<b>VF</b>	<b>B11 P</b>	12.7	6.1	74.7	0.4	69.7	4.01	0.69
	<b>B11 f1.5</b>				0.01	75	4.37	0.69
	<b>B11 f1.9</b>				0.01	60.3	3.59	0.71
	<b>B11 s1.9</b>				16.5	20.3	1.94	1.14



**Figure 4.7:** Histogram depicting aromaticities four parent coal samples and their density fractions from the Waterberg Coalfield. Samples B3P to B11s1.9 are from Wagner and Tlotleng (2012) as well as one sample from van Niekerk *et al.* (2008) named ‘Waterberg’.

The aromaticities of the samples from the study by Wagner and Tlotleng (2012) as determined based on the H/C atomic ratio are quite high with an average of 1.14 for the 4 ‘parent coals’ and the sample from van Niekerk *et al.* (2008). The aromaticities of the density fractions are even higher, perhaps expectedly so, at an average of 1.47. Based on the aromaticity of the parent coals, the sample from the Vryheid Formation is of higher rank and dominated by aromatic compounds. Samples from the Grootegeluk Formation on the other hand, are low rank and dominated by aliphatic compounds. Pyritic sulphur, calculated as percentage of total sulphur was found to range between 0.4% and 0.87% for the parent samples in the Waterberg coals of the Wagner and Tlotleng (2012) study. Pyrite content was a lot higher in the higher density fractions (RD = 2.9) as may be expected from the density of pyrite.

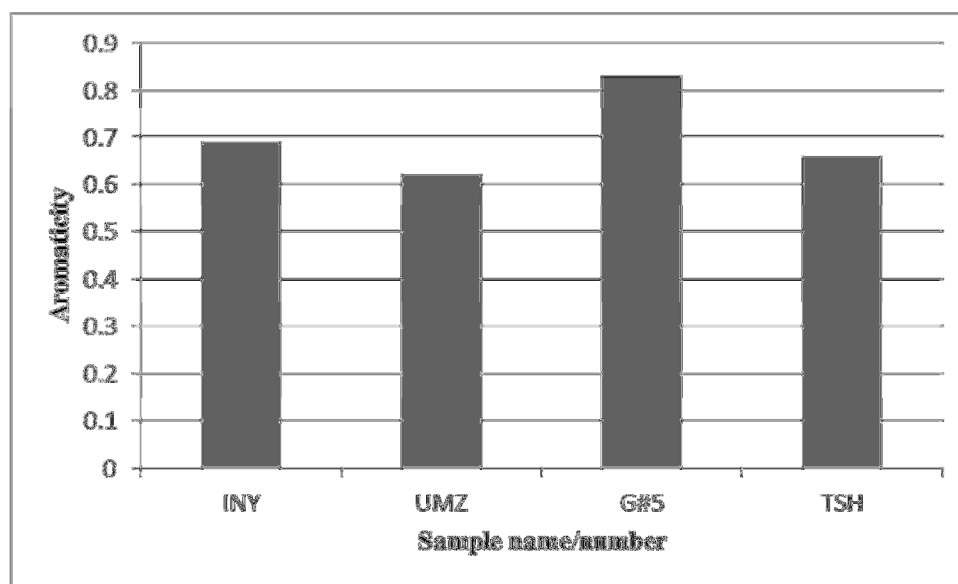
#### 4.3.2 Witbank, Sasolburg-Vereeniging and other Coalfields

Hattingh *et al.* (2013) report petrographic, ultimate and aromaticity values for three non-coking coals from the Witbank (samples INY, UMZ and G#5 corresponding to the No. 2, 4 and 5 seams respectively) and one coking coal from the Venda-Pafuri deposit of the Soutpansberg Coalfield (sample TSH). Two of the coals from the Witbank are inertinite-rich whereas the other (G#5) along with the Soutpansberg coal sample are vitrinite rich. The

vitronite-rich Witbank sample has the highest aromaticity value of all four samples, this is in agreement that with the observation that vitronite consists mostly of aliphatic hydrocarbons. However, although the Soutpansberg sample has the highest proportion of vitronite, the aromaticity value for this is much lower than that of vitronite-rich Witbank sample.

**Table 4.6:** Petrographic data, selected ultimate analysis and aromaticity values for samples from the Witbank and one from the Venda-Pafuri deposit of the Soutpansberg Coalfields (modified after Hattingh *et al.*, 2013). Aromaticities calculated using Gerstein’s (1982) formula.

Sample	Petrographic data (vol. %)			Ultimate analyses (% air-dried)		Aromaticity (H/C)
	Vitronite	Liptinite	Inertinite	Carbon	Hydrogen	
INY	36.7	3.3	60	81.2	4.7	0.69
UMZ	24.4	3.3	72.2	83.8	4.3	0.62
G#5	59.1	9.7	30.1	79.2	5.5	0.83
TSH	65.9	1.1	29.7	90.8	5	0.66



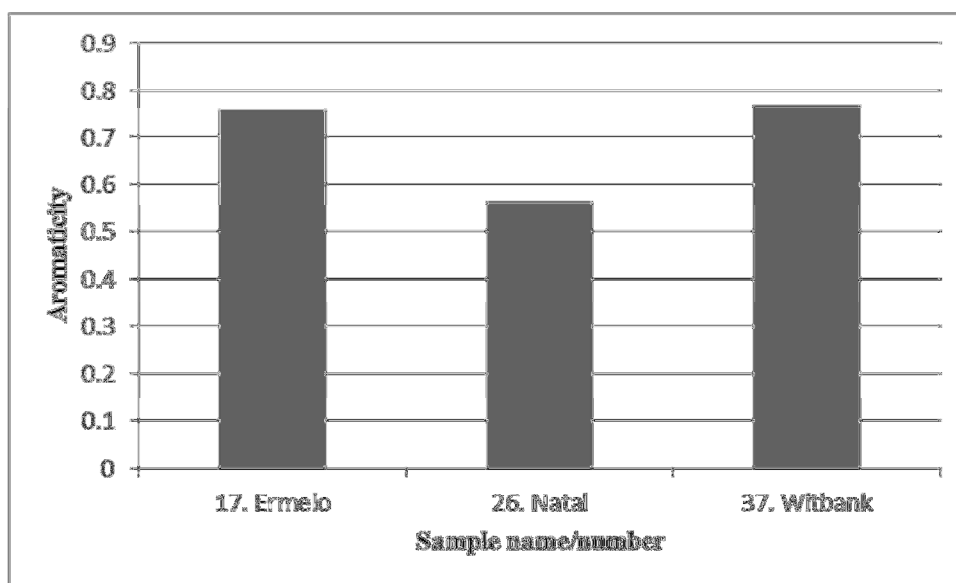
**Figure 4.8:** Histogram depicting aromaticities of coal samples from the Witbank and one from the Venda-Pafuri deposit of the Soutpansberg Coalfields.

Ultimate analyses data from Vassilev *et al.* (2010) is used to calculate aromaticity values of coal samples from the Ermelo, so-called Natal and Witbank coalfields. Vassilev *et al.* (2010) classified both the Ermelo and Witbank samples as ‘bituminous (medium ash)’ whereas the Natal sample is classified ‘bituminous, semi-anthracite’. The former bituminous coal samples have similar aromaticities as calculated based on the H/C atomic ratio at 0.76 and 0.77 whereas the aromaticity of the latter sample is 0.56. This is in line with observations that aromaticity increases as a function of increasing coal maturity.



**Table 4.7:** Selected ultimate analysis and aromaticity values for samples from the Ermelo, Natal and Witbank Coalfields (modified after Vassilev *et al.*, 2010). Aromaticities calculated using Gerstein's (1982) formula.

Sample	Ultimate analyses (wt. % dry, ash free basis)		Aromaticity (H/C)
	Carbon	Hydrogen	
17. Ermelo	78.8	5	0.76
26. Natal	86.5	4.1	0.56
37. Witbank	82.3	5.3	0.77



**Figure 4.9:** Histogram depicting the aromaticities of a coal samples from the Ermelo, Natal and Witbank Coalfields.

#### 4.4 GREENHOUSE EMISSIONS RELATED SPONTANEOUS COMBUSTION IN SOUTH AFRICA

Although spontaneously combusting coals in the Witbank and the Sasolburg-Vereeniging Coalfields have previously been identified (e.g. Bell *et al.*, 2001; Pone *et al.*, 2007), ultimate analysis and petrographic composition data have been found to be lacking particularly for the Sasolburg-Vereeniging Coalfield, preventing the application of Gerstein's (1982) formulas for aromaticity. The studies by Bell *et al.* (2001) and Pone *et al.* (2007) focused primarily on by-products, gas emissions and the environmental impacts of spontaneous combustion rather than its initiation. Among the other numerous analysis carried out by Pone *et al.* (2007) , the greenhouse gas emissions resulting from spontaneous combustion in the Witbank and Sasolburg coalfields of South Africa were determined. The carbon dioxide concentration was found to be the highest in both coalfields with Sasolburg recording the highest at 89 612ppm. Methane production was the second highest at 1793 and

11 710ppm at Witbank and Sasolburg respectively. This was followed by the concentration of carbon monoxide at 641ppm in Witbank and 27 500ppm in Sasolburg.

**Table 4.8:** Greenhouse and other gases from Witbank and Sasolburg coalfields, South Africa (Pone *et al.*, 2007).

Greenhouse gases and others		
Compounds	Witbank (ppm)	Sasolburg (ppm)
Methane	1793.0	11710.0
Carbon monoxide	641.0	27500.0
Carbon dioxide	31925.0	89612.0
Cysteinesulfonic acid	6.3	6.1
Dimethyl sulfoxide	0.0	0.0
Carbon bisulfide	0.4	2.2
Methyl nitrate	0.0	0.0
Ethyl nitrate	0.0	0.0
Alkyl nitrate ( <i>i</i> -PrONO <sub>2</sub> )	0.0	0.0
Alkyl nitrate ( <i>n</i> -PrONO <sub>2</sub> )	0.0	0.0
Alkyl nitrate (2-BuONO <sub>2</sub> )	0.0	0.0

#### 4.5 DISCUSSION

The inertinite-rich, Highveld coal samples from the both van Niekerk *et al.* (2008) and Wagner and Hlatswayo (2005) have an average aromaticity value of 0.63. This is consistent with previous findings that aromatic compounds are the principal components of the inertinite maceral group. Coals composed largely of the inertinite maceral, corresponding to coals with a higher proportion of aromatic hydrocarbons are expected to remain largely unoxidized at temperatures between 20 to 70°C at which low-temperature oxidation is expected to occur. Although aromatic hydrocarbons may oxidize at increased temperatures in the presence of a variety of catalysts, they are unable, by themselves to initiate spontaneous combustion primarily due to their inability to oxidize at the previously mentioned temperatures. Coalfields and coal seams in which inertinite and, correspondingly, aromatic hydrocarbons are the main constituents are unlikely spontaneously combust, and the Highveld Coalfield appears to be such an example, presupposing the absence of catalysts as discussed in previous sections, and a low coal temperature.

In contrast, coalfields in which vitrinite is the main maceral group have an increased propensity towards spontaneous combustion. Petrographic and ultimate analysis of five coal samples from the Waterberg were obtained from van Niekerk *et al.* (2008) and Wagner and Tlotleng (2012). As opposed to the Highveld samples, these samples are predominantly vitrinite-rich with correspondingly higher aromaticities. A higher aromaticity value is indicative of coals dominated by aliphatic hydrocarbons. This group of hydrocarbons undergoes low-temperature oxidation resulting in the formation of oxygenated hydrocarbon complexes. Upon thermal decomposition, the oxygenated hydrocarbon complexes release a combination of greenhouse gases, water and heat energy. It is this energy that leads self-heating and should the crossing point temperature be exceeded, initiation of spontaneous combustion.

Samples from the Wagner and Tlotleng (2012) study were not cleaned resulting in a greater amount of inorganic matter whereas the sample from van Niekerk *et al.* (2008) was cleaned. As a result, the aromaticity values of the Waterberg samples from Wagner and Tlotleng (2012) differ somewhat with the sample from van Niekerk *et al.* (2008), likely because the sample from the latter study was commercially cleaned whereas samples from the former were not cleaned. The aromaticity of some of the inorganic matter-rich samples may be masked by the presence of silicate impurities, implying a requirement for sample cleaning prior to ultimate (elemental) analysis if the ‘true’ aromaticity of the Waterberg Coalfield is to be accurately computed. Aromaticity based on the H/C atomic ratio presupposes that the hydrogen and carbon quantities are solely from hydrocarbons i.e. the organic coal portions (Mazumdar, 1999). Contributions to the total hydrogen and carbon quantities by mineral species are thus not accounted for

Nonetheless, aromaticity values calculated using data from both studies are in agreement pointing to the predominance of aliphatic hydrocarbons. The dominance of vitrinite, which is the main maceral group in most of the Waterberg samples is consistent with the dominance of aliphatic hydrocarbons. Based on this, the Waterberg Coalfield and specifically coals from Grootegeluk Formation are more susceptible to low-temperature oxidation and spontaneous combustion. The sample from the Vryheid Formation is inertinite-rich, so coals from this seam will have oxidation properties similar to those discussed above for the Highveld Coalfield. The presence of high values of pyrite is of further concern. Pyrite is known to drastically increase the rate at which low-temperature oxidation of hydrocarbons

in coal takes place. Although the pyrite contents of <1% in the parent coals is sufficiently low such that negligible heat is available for coal self-heating through pyrite oxidation, the resultant formation of sulphuric acid will increase the oxidation rates of hydrocarbons within the coal.

The difficulty in correlating aromaticity based on the H/C atomic ratios with aromaticity determined using nuclear magnetic resonance especially in anthracitic coals has previously been discussed (Mazumdar, 1999). In their study, Hattingh *et al.* (2013) utilise the H/C atomic ratio as well as solid state nuclear magnetic resonance to determine aromaticity. The NMR results indicate that the Soutpansberg sample has the greatest amount of aromatic hydrocarbons with the vitrinite-rich, Witbank No. 5 seam sample containing the smallest amount of aromatic hydrocarbons. The inertinite-rich Witbank coal samples have aromaticities consistent with the petrographic composition thereof, suggesting relatively high aromatic hydrocarbon contents which fail to oxidize at the temperatures commonly suggested for spontaneous combustion initiation. Therefore, the No. 2 and 4 coal seams of the Witbank Coalfield possibly have lower propensity to spontaneous combustion. On the other hand, coals from the No. 5 seam appear to be more susceptible to this phenomenon. The Soutpansberg Coalfield, although seemingly enriched in vitrinite, appears to contain an increased amount of aromatic hydrocarbons thus may likely be almost immune to spontaneous combustion. The Witbank and Ermelo samples from Vassilev *et al.* (2010) have similar aromaticity values and are classified as 'bituminous (medium ash)' implying these coalfields have a higher propensity towards spontaneous combustion in comparison to what Vassilev *et al.* (2010) terms the Natal Coalfield.

Unsworth *et al.* (1989) and van Niekerk and Mathews (2010) found that inertinite-rich coals generally had higher macro-porosity than vitrinite-rich counterparts at same rank. Owing to the dominance of aromatic compounds in inertinite coals, the increased void-space which may accommodate greater oxygen contents means that although these coals may be oxygen-rich, they remain largely un-oxidized at low temperatures. The lower macro-porosity of vitrinite coals means these have less space to accommodate oxygen-flow and storage. However, in South Africa, at least in the coalfields discussed, significant amounts of both vitrinite and inertinite may sometimes be found within a single coalfield. It therefore becomes necessary to investigate the combined structure of these coals so that macro-porosity and its influence on low-temperature oxidation may be investigated. In coals with inertinite- and

vitritine-rich portions, initial oxidation of vitritine-rich portions may raise the overall temperature of the coal such that the inertinite portions oxidize at higher temperatures. Failure of an inertinite-rich coal to self-ignite following prolonged exposure to the atmosphere likely means the coal contains significant amounts of oxygen such that its combustion properties are adversely altered.

#### 4.6 CONCLUSION

In conclusion, the lack of published results on South African coal prevents the author from obtaining statistically representative data for the oxidation potential of South African coals. However, since this study aims to attempt to interpret aromaticity in the context of low-temperature oxidation and spontaneous combustion specifically in South Africa, the conclusions herein will either be validated or disputed once more samples are obtained and analyzed. This study interprets the aromaticity calculated based on the hydrogen-carbon ratios obtained from two different studies for the Highveld to be consistent indicative of predominance of the aromatic compounds. However, the aromaticity of samples from the Waterberg Coalfield is more varied even though the data is also sourced from two different sources. The varying aromaticity is attributed to fact that one of the studies utilizes a commercially cleaned sample while the four parent samples from another study were not. The cleaned Waterberg sample has an aromaticity value higher than the Highveld sample in the same study. Furthermore, four parent samples from the Waterberg in another study also have aromaticity values higher than 1. Although these very high aromaticities herein are interpreted to be indicative of contributions to the total hydrogen and carbon contents by inorganic portions, they nonetheless show that the organic chemistry of coals from Waterberg is more aliphatic in comparison to Highveld coals. The dominance of aliphatic hydrocarbons in the Waterberg suggests that this coalfield has a higher propensity to spontaneous combustion in comparison to the Highveld Coalfield.

In another study, three samples corresponding to the number 2, 4 and 5 seams of the Witbank Coalfield together with a sample from the Venda-Pafuri deposit of the Soutpansberg Coalfields are reported. The aromaticity values for the three Witbank samples indicate that organic chemistry of a coalfield can be varied, since a single coalfield typically hosts a number of seams. The sample from the No. 5 has a higher aromaticity value in comparison to samples from the same coalfield but from different seams. Notwithstanding the absence of sufficient samples, the organic chemistry of the No. 5 coal seam is dominated by oxidation

prone aliphatic hydrocarbons followed by the No. 2 and then lastly the by the No. 4 seam. The Venda-Pafuri sample has an aromaticity value intermediate between the No. 2 and 5 seams.

Data from another study indicates that the Ermelo and Witbank Coalfields have similar aromaticity values such that the organic chemistry thereof is also comparable. However, since that study fails to report the seam from which the Witbank sample is obtained, it becomes difficult to make any significant comparisons with other samples from the Witbank. A sample from the Natal indicates that the organic chemistry of this coalfield is comparatively more aromatic than both the Ermelo and Witbank, such that it is less susceptible to low-temperature oxidation and spontaneous combustion.

## 5 CHAPTER 5: CONCLUSIONS

With regards to abandoned mines in particular, the modern, law-enforced process of mine rehabilitation along with topsoil replacement and re-cultivation hinders airflow resulting in reduced incidents of oxidation and spontaneous combustion. However, pre-rehabilitation legislation abandoned mines continue to be problematic. In addition, seams fires together with coal in spoil- or stockpiles will likely continue to be problematic in terms of low-temperature oxidation and spontaneous combustion. More information regarding the nature of oxidation products, therefore the oxygenated complexes will shed some light on molecular response of coal to oxidation.

In a study by Pone *et al.* (2007) substantial amounts of carbon dioxide, methane and carbon monoxide were produced by the Witbank and Sasolburg Coalfields through low-temperature oxidation and spontaneous combustion alone. The consequence of the emission of these greenhouse gases to the atmosphere is well-documented in literature. The emissions result in climate change and are carcinogenic for living organisms. In essence, low-temperature oxidation and spontaneous combustion are not just problems for coal producing and consuming industries but also in terms of the contribution thereof to greenhouse emissions and resultant climate change which is a problem for us all.

Van Nierkerk *et al.* (2008) determined petrographic composition and aromaticity of two samples from Highveld and Waterberg Coalfields based on the atomic ratio of hydrogen to carbon. The ratio is higher for the Waterberg sample meaning this sample has increased propensity to low-temperature oxidation. The lower H/C atomic ratio of the Highveld coal sample suggests this sample is less prone to spontaneous combustion. Maceral compositions at 91.8% vitrinite and 87.7% inertinite for the Waterberg and Highveld samples respectively supports the interpretation based on the aromaticity values. The vitrinite maceral group consists chiefly of aliphatic hydrocarbons (Falcon, 1986) which form oxygenated complexes that result in heat liberation upon thermal decomposition (McMurry, 1996). Aromatic hydrocarbons constitute the bulk of the inertinite maceral group (Falcon, 1986) and require high temperature aqueous solutions and a chemical catalyst for oxidation to progress (Enisov & Metelitsa, 1968).



Hydrogen and carbon as well as petrographic data for six Highveld coal samples were obtained from Wagner and Hlatswayo (2005). The aromaticities of these, calculated based on the H/C atomic ratio are similar to the one calculated by van Niekerk *et al.* (2008), indicative of the decreased susceptibility of the Highveld coals to low-temperature oxidation and spontaneous combustion. Petrographic data for the six samples also indicates that they are inertinite-rich with less than 30% vitrinite. Petrographic and ultimate analysis data for coals from the Waterberg was obtained from Wagner and Tlotleng (2012) for four ‘parent coals’ and their density fractions. Aromaticity for a sample from the Vryheid Formation is calculated as 0.69, and ranges between 0.98 and 1.06 for samples from the Grootegeeluk Formation. The latter samples are thus more prone to low-temperature oxidation whereas the former has an aromaticity value similar to Highveld coals. Petrographic data from Wagner and Tlotleng (2012) indicates that the Vryheid Formation sample is inertinite-rich whereas the Grootegeeluk Formation samples are relatively enriched in vitrinite.

Petrographic and aromaticity data from Hattingh *et al.* (2013) indicate that the various seams of the Witbank Coalfield have vastly different responses to low-temperature oxidation. The No. 2 and 4 seams are enriched in inertinite, oxidation of aromatic compounds therein will likely fail to progress at low temperatures. In contrast, the sample from the No. 5 seam is enriched in vitrinite with a corresponding aromaticity value of 0.83. Thus coal from the No. 5 seam possibly forms oxygenated complexes during oxidation which may subsequently decompose and release energy so that the coal self-heats. A sample from the Soutpansberg Coalfield was also collected and analysed in the Hattingh *et al.* (2013) study. The petrographic composition of this sample is 65.9% vitrinite and only 29.7% inertinite. Aromaticity in the study is determined using two techniques, H/C atomic ratio and nuclear magnetic resonance. Although the Soutpansberg sample is vitrinite-rich, its aromaticity is calculated at 0.66 based on the H/C ratio. The NMR results also indicate that this sample is more aromatic than the Witbank samples. This observation necessitates confirmation of the relationship between maceral and hydrocarbon group as vitrinite has largely been interpreted to be dominated by aliphatic compounds as per previous studies (e.g. Falcon, 1986).

Ultimate analysis data for samples from the Ermelo, Natal and Witbank Coalfields was obtained from Vassilev *et al.* (2010), following which the aromaticity values for the three samples is calculated. The Ermelo Coalfield sample has an aromaticity of 0.76, whereas samples from the Natal and Witbank Coalfields have aromaticities of 0.56 and 0.77

respectively. The aromaticity of the Natal sample is comparatively lower than those of Highveld samples suggesting the Natal Coalfield is richer in inertinite than the Highveld. However, Vassilev *et al.* (2010) does not report petrographic data for the three samples. The higher H/C atomic ratios of the Ermelo and Witbank samples indicate that these are more likely to spontaneously combust. The number of samples obtained from literature and then used in this study can never be considered statistically representative, thus more samples should be obtained if the findings of this study are to be validated.

In the whole, inertinite has been largely taken to be the main maceral group in South African Coalfields and those of other Gondwana Provinces. However, this appears to be untrue for the Waterberg Coalfield in general and several other seams in some of the other coalfields. It is these vitrinite-dominated coals, that based on the knowledge of organic chemistry of vitrinite appear to be most risk of spontaneous combustion. The Highveld Coalfield and the No. 2 and 4 seams of the Witbank Coalfield as well as the Vryheid Formation in the Waterberg at least, are dominated by inertinite resulting in what has been interpreted to be similar organic chemical makeup. On the other hand, vitrinite is the principal maceral group of samples from the Waterberg specifically the Grootegeluk Formation and the No. 5 seam of the Witbank. This study concludes that the Grootegeluk Formation of the Waterberg, No. 5 seam of the Witbank as well as the Ermelo Coalfield are dominated by aliphatic hydrocarbons and have an increased propensity towards to spontaneous combustion.

## **6 CHAPTER 6: THE WAY FORWARD...**

The variable petrographic composition of South African Coalfields, even in a single coalfield means that predicting low-temperature oxidation thereof is an extremely difficult although not impossible task. The occurrence of multiple seams in a single coalfield also exacerbates the problem. It might be simpler to determine ‘coal seam’ oxidation properties as opposed to ‘coalfield’ properties. If the existence of a seam can be correlated across multiple coalfields, presupposing that coal seam properties are constant as a result of similar depositional environments then oxidation properties for the entire seam can be determined. However, the properties, including coal rank across an individual seam have also been found to be highly varied. This observation necessitates analysis of samples from each individual seam in each coalfield if properties governing spontaneous combustion are to be accurately and comprehensively determined.

Petrographic composition is directly related to the structure of coal, referring specifically to the three dimensional assemblage of macromolecules, which in turn governs the resultant macro-porosity. Porosity and the interconnectedness thereof allows air-flow and oxygen storage, thus giving oxygen ample time to interact and react with hydrocarbon functional groups on the pore walls. In the event where moisture is also accommodated within the pores, low-temperature oxidation may be enhanced depending on the amount of water. In South African Coalfields, either one of two major maceral groups generally dominates any given coal, namely, inertinite and vitrinite. The study by van Nierkerk and Mathews (2010) is important because molecular models for two coals enriched in each of these macerals were constructed. However, the samples used were highly enriched in their respective maceral such that it might be prudent to construct models for lower inertinite and vitrinite contents so as to obtain a ‘combined structure’. Unsworth *et al.* (1989) as well as van Nierkerk and Mathews (2010) conclude that inertinite-rich coals have higher macro-porosity than vitrinite counterparts, but what happens to this porosity when a coal has 50% inertinite and 50% vitrinite (or anything similar)? The aforementioned ‘combined structure’ would answer this question so that the amount of air that can potentially be accommodated by the coal and available for oxidation of aliphatic hydrocarbons in vitrinite can be determined. In inertinite-rich coals which have been found to have higher oxygen contents (van Nierkerk & Mathews, 2010) although failing to spontaneously combust presumably due to the abundance aromatic

species, the effect of the increased oxygen content on coal quality should be quantitatively evaluated.

The aromaticities for the different coal samples determined in this study are indicative of highly varied coalfields. As previously mentioned, it may be advisable to determine elemental contents, at least so far as high ash content coalfields are concerned (e.g. Waterberg), on ‘cleaned’ samples. The contribution by inorganic constituents likely masks the aromaticity when run-of-mine samples are used for this computation. Future studies should where possible, evaluate aromaticity using both the hydrogen to carbon atomic ratios and nuclear magnetic resonance (technique that identifies different structural features in the organic matter in coals) owing to the observed complications of correlating results for the two techniques particularly in anthracitic coals. The inferred dominance of aliphatic and aromatic hydrocarbons in vitrinite and inertinite macerals respectively (Falcon, 1986), should be re-evaluated even if simply for confirmation owing to the Soutpansberg Coalfield sample from Hattingh *et al.* (2013). The coal sample (TSH; Table 4.6) has a vitrinite content of 65.9% and an aromaticity value of 0.66. This aromaticity value is lower than that of a sample in the same study from the Witbank with only 59.1% vitrinite. Perhaps the categorization of the coals as coking and non-coking has something to do with the observed contradiction.

Together with the ultimate analysis and petrographic data, the pyrite content of the different coal samples should be determined. This is mainly to evaluate the amount of possible sulphuric acid production, which is known to aid low-temperature oxidation. So far in this study, aromatic hydrocarbons have been interpreted to be entirely exempt from oxidation such that these do not contribute to self-heating at least at the temperatures typically accepted for spontaneous combustion initiation. However, according to Enisov and Metelitsa (1968), catalysts such as iron and copper ions, and liquid hydrofluoric acid may lead to oxidation of aromatic compounds. Whether these catalyst-induced oxidation reactions are exothermic, therefore whether these are able to contribute energy to the coal for self-heating is another question. The presence of the ions in particular, in different coals might thus be of interest to future studies regarding oxidation and spontaneous combustion. Liquid hydrofluoric acid and other solution-based catalysts may be more of a concern for coals with significant amounts of moisture such as those in stock- or spoil-piles thus directly exposed to rainfall. Admittedly, there may be too many factors to account for in any single study.

Hydrocarbon functional groups present in a coal before and following exposure to the atmosphere (i.e. under an inert gas and oxygen respectively) for both inertinite- and vitrinite-rich coals should be determined possibly using gas chromatography – mass spectroscopy (or similar techniques). This will yield information that can be used to directly compare coal constitution before and after oxidation. Identification of oxygenated hydrocarbons following oxidation will allow for investigations into the thermal decomposition requirements of the complexes. The vitrinite-rich samples should ideally come from coalfield(s) known to have a propensity to spontaneous combustion.

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