

Chapter 1

Review of Previous Work

1.1 Self-Heating and Spontaneous Combustion

Self-heating occurs when a reactive material, such as coal, experiences a rise in temperature due to the heat evolved from an exothermic reaction. Heating will occur when the rate of heat generation is greater than the rate at which it is dissipated. For small quantities of material where heat is readily lost to the surroundings, there is usually no noticeable temperature increase, however, for large structures such as coal stockpiles which have poor heat conduction properties, the temperature may rise significantly. Increasing temperature accelerates the reaction which in turn produces more heat raising the temperature still further. If unchecked, a runaway condition may develop which can ultimately lead to ignition or, in other words, spontaneous combustion.

The main source of heat that leads to self-heating is from the reaction of oxygen with coal or other carbonaceous material. Interaction with water vapour is also a potential source of heat but it is usually much less than that produced from oxidation.

Self-heating and spontaneous combustion have long been major problems in the coal industry. They may occur in stockpiles or during transportation resulting in deterioration of product coal or even the loss of the coal itself. There are also obvious safety risks associated with uncontrolled fires in coal piles. Waste material produced during mining frequently contains a high proportion of carbonaceous material and consequently is also often subject to spontaneous combustion. This can lead to safety hazards and environmental problems during mining. Because of the potential economic, safety and environmental problems associated with spontaneous combustion, there has been

considerable effort directed at attempting to develop practical methods to prevent or at least control the phenomenon. Many groups have, over a long period, studied the chemistry of coal-oxygen interaction to attempt to understand the fundamentals of the processes leading to self-heating. This research has led to the development of numerous mathematical models which have been used for predicting heating within stockpiles and mine waste (e.g. Sondreal and Ellman, 1974; Edwards, 1992; van Krevelen, 1993; Akgün and Arisoy, 1994; Carras and Young, 1994; Saghafi *et al.*, 1995). These models are necessarily complex and include, among other things, equations describing the heat and mass transfer within the structure.

Of great importance for any such model is a reliable kinetic model to describe the oxidation process. A number of kinetic models have been developed but none can yet be said to be universally applicable for all conditions because the oxidation process is very complex and is affected by many parameters. The heterogeneous nature of coal often means that the effect of these parameters is not the same for all coals. Because of the complexity of the problem, research into the kinetics of low temperature coal oxidation continues. Some of the most important of the variables which can affect oxidation kinetics and the current state of understanding are discussed in the following sections.

1.2 Oxidation of Coal

1.2.1 Coal Formation and Classification

Coal is formed from the remains of plant material which became buried and altered by the effects of heat and pressure over long periods of time. The characteristics of the resultant coal are determined by the geological conditions of heat and pressure (i.e. the coalification process) and also by the type of the plant material, the nature of its decay and subsequent weathering prior to it being buried (i.e. diagenesis).

Coal is a heterogeneous material consisting of a number of distinct organic components derived from the plant material from which the coal originated together with, usually, some inorganic mineral matter. Depending on the type of plant and the coalification processes involved, the organic components may have quite different chemical and physical properties. These components are known as macerals and are analogous to the minerals which constitute rocks. However, whereas minerals are crystalline in nature and have fairly well defined chemical compositions, macerals are not crystalline and may be quite variable in chemical make-up.

All coals are classified according to their “rank” which is a measure of the extent to which the coalification process has progressed. Lowest rank material is peat which has undergone the least alteration while at the other extreme is anthracite in which coalification is essentially complete. There are a number of chemical and physical properties of the coal which are used to assess its rank. The most common of these are the carbon content, volatile matter content, calorific value and the light reflected from vitrinite (a maceral of coal). The correlation of some these properties with rank is shown in Table 1.1 below.

Table 1.1 Correlation of some chemical and physical properties with coal rank (adapted from Stach *et al.*, 1982)

Rank	Volatile Matter (% daf)	Carbon (% daf)	Moisture (%)	Calorific Value (MJ/kg daf)
Peat	68			
	64	ca. 60	ca. 75	
Lignite	60			
	56		ca. 35	16.7
	52			
Sub-Bit. C	48	ca. 71	ca. 25	23.0
	44			
C	44	ca. 77	ca. 8-10	29.3
B	40			
A	36			
	32			
Med Volatile Bituminous	28	ca. 87		36.2
	24			
Low Volatile Bituminous	20			
	16			
Semi-Anthracite	12			
	8	ca. 91		36.2
Anthracite	4			
Meta-Anthracite				

It is generally agreed that lower rank coals are more susceptible to spontaneous combustion than high rank coals (Sondreal and Ellman, 1974).

1.2.2 Chemistry of Oxidation

The chemistry of interaction of oxygen with coal at low temperatures is very complex and, although having been studied extensively, is still not fully understood. Many researchers have investigated the fundamental chemistry of the process by using analytical techniques such as FTIR and NMR to probe the nature of the reactions occurring at the coal's surface. A discussion of these studies is beyond the scope of this thesis but there are several comprehensive reviews on the subject (e.g. Davidson, 1990; van Krevelen, 1993; Pànek and Taraba, 1996).

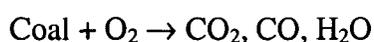
Because of the complexity of the reactions involved, more general reaction mechanisms have been proposed for the purposes of modelling the oxidation process. Kam *et al.*, 1976, suggested that low temperature oxidation of coal proceed by a two-step pathway:

1. a “burn-off” reaction similar to combustion in which CO₂, CO and water are produced and
2. a process involving chemisorption.

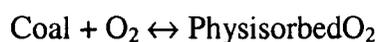
In the second step, oxygen chemisorbs onto active sites on the coal to produce an oxy-coal complex which can subsequently decompose to form more CO₂, CO and water. This mechanism was later expanded by Karsner and Perlmutter, 1982, to include physical adsorption of oxygen on the coal surface. Itay *et al.*, 1989, proposed an oxidation pathway similar to that of Karsner and Perlmutter, 1982, except that Itay *et al.* suggested that the burn-off reaction did not occur at low temperatures and that all of the gaseous products are formed by decomposition of oxy-coal complexes.

Although there remains some uncertainty about the exact nature of the coal oxidation reaction pathway, there is broad agreement (e.g. Carras and Young, 1994; Krishnaswamy *et al.*, 1996) that oxidation involves several discrete steps, namely:

- direct burn-off reactions to produce carbon oxides and water i.e.



- physical (reversible) adsorption of oxygen



- chemical (irreversible) adsorption leading to the formation of oxygen-coal complexes on the coal’s surface which can then decompose to produce gaseous products



Since the coal - oxygen reaction is the most important from the self-heating point of view, it is not surprising that the rate of reaction has been studied extensively. However, due to the heterogeneous nature of coal many of the results reported are confusing and sometimes appear to be contradictory. It is often difficult to directly compare results from different studies because of differences in the samples used and also because different techniques are used to measure the rate. For example, many researchers have used thermogravimetric analysis (TGA) to follow the reaction while others have measured the rate of heat generation with calorimetric methods. Still others have measured oxygen consumption of coal contained in fixed bed reactors. Differences also occur because experiments are conducted under either isothermal or adiabatic conditions.

Despite the differences, there are some variables in which there is general agreement that there is some effect on oxidation rate. Some of the main parameters that are known to affect the oxidation rate are discussed below.

1.2.3 Effect of Particle Size

Various groups have examined the effect of particle size on the rate of oxidation for at least several decades. Despite this, however, there is still no agreement on the exact nature of the effect and, at first glance, the results reported in the literature often appear to be contradictory. Many studies have shown that the rate of oxidation increases with decreasing particle size while others show no particle dependence. At least one group has reported that the rate *decreases* with decreasing particle size (Boyapati *et al.*, 1984). In a review of self-heating of coals and other materials, Carras and Young, 1994, concluded: “as the role of particle size on oxidation rate depends on the coal being studied, no simple generalisations are possible”. They suggested that in view of this, the rate of oxidation of a particular coal sample should be measured at a particle size typical of the application.

A summary of the research into the effects of particle size on the rate of oxidation is shown in the Appendix.

One of the earliest detailed studies appeared in 1966 by Carpenter and Sergeant. They measured oxygen consumption in an isothermal apparatus of 22 closely sized fractions of two Welsh coals ranging in size from 36 μm to 1866 μm and at temperatures from 37 to 105 $^{\circ}\text{C}$.

They found that the rate increased with increasing external surface area (i.e. decreasing particle size) until the mean particle diameter was between about 130 μm and 380 μm . Below this size the rate of oxidation was independent of particle size. It was shown that the rate of oxidation for particles larger than the critical size was proportional to the cube root of the specific external surface area. This is equivalent to approximately doubling the oxidation rate for a tenfold increase in external surface area.

The activation energy for the oxidation process was measured as a function of particle size in this study. It was found to increase from about 11.7 kJ/mol for 59 μm particles up to 23.4 kJ/mol for 273 μm particles although it should be noted that this range of particle sizes was close to or below the critical size range where the rate of oxidation was unaffected by particle size.

In another fairly wide ranging study (Sondreal and Ellman, 1974), the effect of particle size on the rate of low temperature oxidation of North Dakota lignite was examined. The results of this work showed that the oxidation rate was dependent on particle size in the range of 2 to 9.5 mm at 65 $^{\circ}\text{C}$ and, like Carpenter and Sergeant's results, correlated reasonably well with the cube root relationship. However, Sondreal and Ellman recognised that this

relationship predicts ever-increasing rate with decreasing particle size which implies that very small particles would ignite immediately on contact with air. To overcome this problem, they proposed an improved model with the form:

$$R_o = c / m(1 - e^{-km}) \quad (1.1)$$

where R_o is the of oxidation rate, m is the mean particle size and k and c are empirical constants. This model fitted the experimental data better than the cubic expression and showed a levelling off of rate as the particle size approached zero.

Rahman, *et al.*, 1986, also found that the oxidation rate of a US sub-bituminous coal decreased with increasing particle size. They noted that the reactivity of the coal they examined was approximately proportional to the one-fifth power of the particle external surface area (compared to the one-third power found by Carpenter and Sergeant and Sondreal and Ellman).

Itay *et al.*, 1989, considered the effect of particle size on low temperature oxidation rates of a South African coal. They found that at temperatures between 25 and 140 °C and for particles between about 45 and 710 µm, finer particles reacted faster than coarser material.

In a study of particle size effects on bituminous coals, Palmer *et al.*, 1990, measured oxidation rates at 200 °C of several US and Canadian coals as a function of particle size. These authors found that for particles between 38 µm and 2.0 mm the rate increased with decreasing particle diameter until about 50 µm, below which the rate remained constant. The effect, however, was not the same for all of the coals examined. For the highest sulphur samples the oxidation rate increased very rapidly with decreasing particle diameter whereas for the low sulphur coals, the effect was considerably less. The authors suggested that the higher amounts of pyrite present in the high sulphur coals might be responsible for

the higher oxidation rates observed in these coals. They also noted that differences in the H/C ratios (with presumably different chemical reactivities towards oxygen) may also account for the differences observed.

This group also measured activation energies of the oxidation reaction as a function of particle size for the coals they examined and found that there was little if any change in the activation energy with particle size.

Akgün and Arisoy, 1994, using a large-scale adiabatic reactor, examined the effects of coal particle size in relation to self-heating in coal stockpiles. They used a Turkish coal sample which was sieved into four relatively large size ranges: 2-5, 5-10, 15-20 and 20-50 mm - somewhat larger fractions than have generally been used in previous studies. As with the other studies referred to above, these authors found that the rate of oxygen consumption was highest for the smallest particle sizes and that rate of oxidation was proportional to the particle diameter raised to some exponent.

Although Akgün and Arisoy's experiments were not conducted under isothermal conditions, they were still able to determine the kinetic parameters for the oxidation reaction. Their results show decreasing activation energy with increasing particle size which is the opposite trend to that found by Carpenter and Sergeant, 1966.

Pànek and Taraba, 1996, made a thorough study of the effects of particle size on the rate of oxidation. They conducted a calorimetric study of 60 sub-bituminous and bituminous coals. Nine size fractions ranging from 0.075 to 1.125 mm were examined at temperatures between 30 and 50 °C.

The rate of oxidation was found to vary in proportion to the particle diameter according to the expression:

$$R_O \propto d^k \quad (1.2)$$

where R_O is the rate of oxidation, d is particle diameter and k is an empirical constant. This is similar to the results of other studies such as Carpenter and Sergeant, 1966, and Sondreal and Ellman, 1974. The values derived for k were usually between about -0.3 and -0.45, depending on the type of coal. However, for some sub-bituminous and oxidised coals the rate was essentially independent of particle size and in these cases k tended to zero.

Krishnaswamy *et al.*, 1996, found that for a Wyoming sub-bituminous coal the rate decreased with increasing particle size at temperatures between about ambient and 60 °C. The mean particle diameter in their experiments ranged from 0.4 to 1.5 mm.

All of the studies referred to above found strong particle size dependence on the oxidation rate for at least some of the coals examined, however, there have been numerous groups who have reported little or no effect. Karsner and Perlmutter, 1981 and 1982, measured the oxidation rates of various US coals and found that for temperatures up to about 150 °C, the rate was not affected by particle size when in the range of 0.7 to 2.3 mm. At higher temperatures, however, the rate began to decrease with increasing particle diameter. This shift in behaviour was attributed to diffusion of oxygen within the particles becoming the rate limiting process at higher temperatures. It was suggested that at lower temperatures, the kinetics were determined by purely chemical control. The apparent activation energy was also shown to be essentially independent of particle size under these conditions. The value determined was about 50 kJ/mol and varied by only about three percent over a two-fold change in diameter.

Another group which found no particle size effect was Polat and Harris, 1984. Using a microbalance technique, they measured oxygen uptake by Loy Yang coal at 35 °C in pure oxygen for several quite small particle sizes ranging from about 0.04 to 0.1 mm. Their experiments yielded similar oxidation rates for all of the particle sizes.

Kaji *et al.*, 1985 and 1987, measured the rate of oxygen consumption and heat generation for a series of coals of different ranks at temperatures from 30 to 250 °C. They found that both the rates of oxidation and heat generation were independent of particle size in the range of 74 µm to 1.0 mm

As mentioned above, Pànek and Taraba, 1996, also found that for some of the coals they examined, the rate of oxidation was not affected by particle size.

The apparently conflicting results from the studies described can be reconciled if the structure of coal is considered. Intuitively, one would expect the rate of coal oxidation to increase with decreasing particle diameter because the external surface area increases with decreasing particle diameter. However, coal is a porous material containing an extensive pore network ranging in size from cracks visible to the naked eye down to micropores with diameters of a few nanometres or less. The area of the internal surfaces is very much greater than the external surface area.

If oxygen was able to freely access all of the internal surface area, then the rate of oxidation may not be significantly affected by particle diameter since the increase in external area would be trivial compared to the reaction surface provided by the internal structure. In reality, however, the pore structure of the coal is unlikely to be fully accessible since not all of the pores are necessarily connected.

In studies where there was no particle size effect found, it is always the case that the range of particle sizes was small, usually less than 2 mm. In these cases the depth of penetration of the pore network (i.e. those that are connected to the outer surface) may be close to the radius of the particles so that most of the internal structure is exposed to the oxidation reaction. At larger diameter particles, less of the internal surface is available and consequently, the rate of reaction is slower. This could be the situation in those studies where significant particle size effects were observed.

Some workers have found that the temperature of measurements can determine whether or not particle size effects are observed. Karsner and Perlmutter, 1982, for example, reported that the rate of oxidation was unaffected by particle size at a temperature of 150 °C, but at 175 °C, the rate decreased with increasing particle diameter. The reason for this is that the rate of the oxidation process is determined by both the intrinsic rate of the chemical reaction as well as the rate at which oxygen can be transported to the reaction surface. When the temperature is low enough, the overall rate of the reaction is determined by the rate of chemical reaction between oxygen and the coal. As the temperature increases, however, the chemical rate increases and eventually a point is reached where oxygen can no longer diffuse to the surface fast enough to keep pace with the chemical rate. Under these conditions, oxidation is diffusion limited. When diffusion is the rate-limiting regime, particle size effects would be expected even with small particles because even though there may be full access to the internal area, the oxygen is consumed before it can reach the innermost sites.

The overall rate is usually determined by some combination of both chemical and diffusive control and some authors have attempted to quantify the contribution of each component. Karsner and Perlmutter, 1982, introduced the idea of an effectiveness factor to include the

effect of diffusive restrictions in the overall rate expression. The effectiveness factor is defined as the ratio of the overall rate to the rate had it been purely under chemical control. Akgün and Arisoy, 1994, also attempted to estimate the proportion of chemical and diffusive control occurring during their experiments but used a different approach. In their work, they found that the rate of reaction was proportional to the particle diameter raised to some power. They reasoned that if the reaction was confined to the external surface of the particle then the rate would be inversely proportional to the surface to volume ratio. In this case the value of the exponent would be -1. However, if the reaction was under chemical control with no pore diffusion limitations, the rate would be independent of particle size and so the exponent would be equal to zero. They evaluated the exponents at various temperatures and found that they ranged from -0.33 at 25 °C to -0.74 at 75 °C which is consistent with the assertion that at higher temperatures diffusive restrictions become the dominant rate limiting process.

1.2.4 Effect of Time

A characteristic of low temperature coal oxidation is that the rate of reaction decreases with time. This effect is illustrated by the example shown in Figure 1.1.

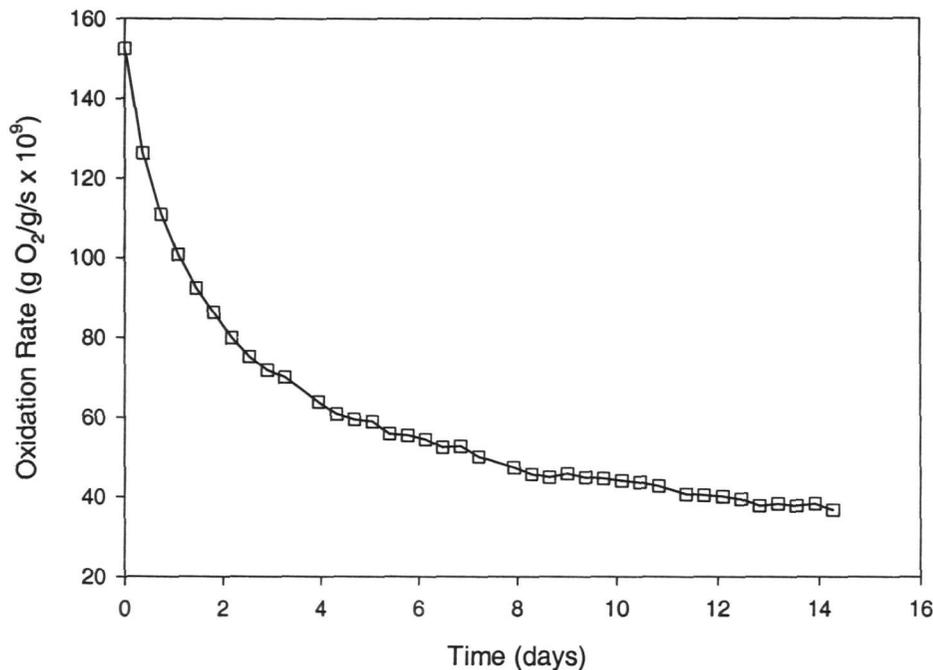


Figure 1.1. Oxidation rate as a function of time for Puxtrees coal at 120 °C

In the example above, the rate was measured in an isothermal fixed bed reactor where the oxygen concentration was essentially constant for the duration of the experiment. Despite the constant oxygen concentration, however, the rate is seen to rapidly decrease with time. The rate of decay slows with time and appears to approach some limiting value. Some authors have actually assumed that the rate does reach a steady state for the purposes of modelling the oxidation kinetics (Akgün and Arisoy, 1994). Although one would expect the rate to eventually decrease to zero as the coal is consumed, it has been shown that the time required to reach this state is very long indeed. Pànek and Taraba, 1996, measured a significant oxidation rate in a sample after three year's exposure to air. In an even longer-term experiment, Beier, 1994, reported that for small samples of coal (about 20 g) stored in air, oxidation was still continuing after more than 35 years.

Most of the studies of low temperature coal oxidation show similar behaviour to the example shown in Figure 1.1, however, an interesting variation was reported by Carpenter and Giddings, 1964. They measured the oxidation rates of several Welsh coals over relative short periods of up to about six hours and found that oxidation appeared to proceed in discrete stages during which the rate of oxygen consumption remained constant. The rate of the initial step was fastest with each successive step being progressively slower. It is not clear why these data should have steady state regions, however, if a line of best fit is drawn through all of the points, the form of the resultant curve is similar to those reported by other workers.

The ageing effect (i.e. the reduction of rate with time) is generally believed to be due to the sorption of gases by the active sites on the coal surface. As noted earlier, sorption may be either weakly bound physical adsorption (which is reversible) or much more strongly bound chemisorption (which is irreversible). It has been suggested by several groups (e.g. Kaji *et al.*, 1987; Allardice, 1966; Pànek and Taraba, 1996) that physical adsorption is the faster process and occurs during the initial stages of oxidation but at longer times, chemisorption dominates. The observed decrease in oxidation rate is thought to be a consequence of increasing surface coverage of the coal by oxygen or product gases.

There have been a number of mathematical treatments developed to describe the ageing effect. An early attempt was developed by Schimdt in 1945 who came up with a power law expression to relate the amount of oxygen consumed, q , to time:

$$q = Ct^b \quad (1.3)$$

where t is the time and C and b are empirical constants (cited in Hill, 1986). Since then, however, the Elovich equation has come to be used very widely to describe the oxidation

kinetics of coal and other carbonaceous materials (e.g. Allardice, 1966; Nordon *et al.*, 1979; Pànek and Taraba, 1996; Teng and Hsieh, 1999). The Elovich equation has the form:

$$R_O = \frac{dq}{dt} = ae^{-\alpha q} \quad (1.4)$$

where R_O is the rate of oxidation, q is the amount of oxygen consumed and a and α are constants. Although there have been attempts to assign physical significance to these constants they are usually regarded merely as curve fitting parameters (Nordon *et al.*, 1979; Carras and Young, 1994). A more detailed discussion of the Elovich equation is provided in Chapter 4 of this dissertation.

1.2.5 Effect of Temperature

The rate of coal oxidation, like most other chemical reactions, increases with increasing temperature. Virtually all studies of the effect of temperature (e.g. Carpenter and Giddings, 1964; Sondreal and Ellman, 1974; Karsner and Perlmutter, 1981; Carras and Young, 1994) have found that the temperature dependence of the oxidation reaction is well represented by an Arrhenius like relationship:

$$R_O = Ae^{-E/RT} \quad (1.5)$$

where R_O is the rate of oxidation, A is the pre-exponential factor (sometimes referred to the frequency factor), E is the activation energy, R is the gas constant and T is the absolute temperature. By plotting the logarithm of R_O against $1/T$, E and A may be easily determined.

The values of E reported in the literature for oxygen consumption by coal vary from less than about 20 kJ/mol (Pànek and Taraba, 1996) to about 80 kJ/mol (Carpenter and Giddings, 1964) but are typically between about 40 and 70 kJ/mol. Most of the studies report “overall” activation energies, i.e. the combined activation energies for all of the reactions occurring during the oxidation process. Some authors, however, have attempted

to measure the activation energies for at least some of the individual processes. Karsner and Perlmutter, 1981, measured rate constants at various temperatures for CO₂ and CO formation, physical adsorption of oxygen, physical oxygen desorption and oxygen chemisorption. The activation energies of these processes were determined to be 105, 42, 76 and 139 kJ/mol respectively. In a similar vein, Krishnaswamy, *et al.*, 1996, measured activation energies of 57.5 kJ/mol for the burn-off reaction (i.e. formation of CO₂ and CO), 53.1 kJ/mol for physical adsorption and 90.4 kJ/mol for decomposition of oxy-coal compounds.

Most of the overall activation energies should be considered to be “apparent” values since they include the effects of both chemical reaction and the mass transport limitations caused by the diffusion of oxygen to the reaction sites.

1.2.6 Effect of Moisture

Moisture can contribute to self-heating in two ways:

- by generating heat when it adsorbs onto the coal surface or when it condenses into liquid (conversely, heat is *absorbed* when moisture is desorbed or evaporated thereby lowering the temperature) and
- by affecting the oxidation reaction itself.

The effects of moisture adsorption and condensation are considered in more detail under a separate heading later in this chapter. This section is confined to the effect of moisture on the oxidation reaction.

The effect of moisture on the oxidation of coal is very complex and not particularly well understood. Davidson, 1990, noted in his review that water can affect not only the oxidation of the organic component of coal but can also react with minerals (e.g. pyrite).

The rate of oxidation of coal has been found to be both reduced and enhanced by the presence of moisture. Sondreal and Ellman, 1974, in their study of lignite found that the maximum rate of oxidation occurred when the moisture content was around its equilibrium value of about 20 percent. Pànek and Taraba, 1996, also found that a maximum oxidation rate was reached at a certain moisture content. In their study, using a bituminous coal, this moisture content was about 15 percent.

It has also been reported that oxidation can only occur in the presence of water. Itay *et al.*, 1989, in their adiabatic experiments found that prior to the addition of liquid water to completely dried coal in their reactor, virtually no oxidation occurred. However, upon the addition of water, the temperature of the sample rapidly increased. They discounted the effect of water adsorption as the reason for the temperature rise and concluded that water must have some catalytic effect on the oxidation reaction. Moxon and Richardson, 1985, also found that the rate of oxidation in the absence of moisture was very low.

Research conducted by the CSIRO (Carras and Young, 1994) suggests that the rate of oxidation is suppressed in coals which have moisture contents in excess of the equilibrium water content. However, as the coal is dried during the course of an experiment, the rate increases to about the level that would be measured had the excess moisture not been present in the first place. It was suggested that the rate suppression might be due to water physically blocking the pores of the coal and effectively preventing access of oxygen to the reaction sites. The physical blocking of pores by water to exclude oxygen is analogous to preserving coal samples by storing them under water to prevent oxidation.

1.2.7 Effect of Oxygen Concentration

At a constant temperature, the rate of a chemical reaction is a function of the concentration of the reactants (or products). The low temperature oxidation rate of coal can be expressed in terms of the oxygen concentration by the expression (Hill, 1986; Chen and Stott, 1997):

$$R_O = kC^n \quad (1.6)$$

where R_O , is the rate of oxygen consumption, k is the rate constant, C is the oxygen concentration and n is the reaction order. Taking logarithms, the equation becomes:

$$\log(R_O) = \log(k) + n \log(C) \quad (1.7)$$

The reaction order can then be readily established by measuring the rate of reaction at various oxygen concentrations and plotting $\log(R_O)$ against $\log(C)$ to yield a straight line with a slope equal to n .

Despite the simplicity of this experiment relatively few studies of the effect of oxygen concentration on the rate of oxidation have been made and of these, the results have been somewhat varied. Reaction orders ranging from zero (i.e. the rate is independent of oxygen concentration) to more than one have been reported. Allardice, 1966, in a study of an Australian brown coal, measured the oxidation rates at 65 °C at oxygen partial pressures ranging from 161 to 760 mm Hg (21 to 100 percent O₂). He found that the rate was not affected by the oxygen partial pressure under these conditions, i.e. zero order with respect to oxygen. It should be noted that the oxygen concentrations used in that work were above ambient levels and it is therefore unlikely that real coal stockpiles would be exposed to these levels.

In a more recent study, Keleman and Freund, 1990, measured the oxidation rate of a Wyoming sub-bituminous coal at 78 °C at various oxygen partial pressures ranging from about 10 to nearly 3000 mm Hg. This group found first order rate dependence up to O₂

pressures of 100 mm Hg, but as the pressure increased the reaction order decreased to ultimately approach zero order at the highest partial pressures. At the oxygen concentrations likely to be encountered in a coal stockpile the reaction order, based on these results, would be close to one.

Sondreal and Ellman, 1974, also found first order kinetics for a North Dakota lignite. The range of oxygen concentrations used in their study was not specified, however, the reaction was found to remain as first order over a temperature range of 25 to 95 °C. They noted that their results differed from some other studies and they suggested the possibility that the differences may have been related to the different amounts of oxygen already adsorbed by the samples thus affecting the measured rates. It was suggested that inherent differences in the chemistry of the different coal might also have contributed to the different reaction orders.

Most other authors have reported fractional reaction orders. For example, Karsner and Perlmutter, 1981, determined the order of reaction for a high volatile bituminous C coal at 160 °C to be 0.7. They reported that under the conditions of their experiments, the oxidation reaction was under chemical control. Interestingly, their results agreed very closely with those of Kam *et al.*, 1976, who found a reaction order of 0.74 for a higher rank coal (high volatile bituminous A) at 225 °C under diffusion control. The conclusion from this work was that the order of reaction is apparently unaffected by the rate controlling regime of the reaction.

Hill, 1986, also found a fractional reaction order of about 0.6 for a South African coal. Like Sondreal and Ellman, 1974, Hill also notes the importance of using initial rates to avoid ageing effects which may affect the reaction order determined.

Similar fractional orders of reaction were found by Carpenter and Giddings, 1964, who conducted a quite comprehensive study of the effect of oxygen concentration on the reaction rates of five Welsh coals and an anthracite of unknown origin. Oxidation rates were measured at 95 °C at O₂ concentrations of 21 percent to 100 percent. They found reaction orders ranging from about 0.3 to 0.7, however, most samples were close to 0.5. These results compared well with some much earlier work conducted by Winmill between 1913 and 1915 who had found that the reaction rate was proportional to the square root of the oxygen concentration (i.e. a reaction order of 0.5). Carpenter and Giddings postulated that oxygen molecules dissociated into atoms before chemisorption occurred in which case the reaction order would be expected to be 0.5.

Carpenter and Giddings also conducted what they called constant volume experiments in which a small amount of coal was placed into a sealed vessel and dosed with a fixed volume of oxygen. The reaction orders were again determined using this method, however, the results were considerably different to the results noted above. Here, reaction orders up to 2 were reported but it was suggested that these results might have been unreliable because the oxygen concentration within the vessel changed during the course of the experiment.

Despite the majority of studies finding fractional reaction orders, it is nevertheless often assumed that the reaction is first order with respect to oxygen (Carras and Young, 1994; Chen and Stott, 1997). This is an advantage when modelling the process because it simplifies the mathematics. Indeed, it may be a reasonable assumption since Karsner and Perlmutter, 1982, found that a model in which first order kinetics were assumed fitted their experimental data reasonably well even though they had measured the reaction order as 0.7.

1.3 Moisture in Coal

Coal generally contains a certain amount of water which can vary from a few percent in high rank coals to as much as 75 percent in some brown coals. The water may be present as either free (i.e. liquid water) or residual moisture. Free moisture is defined as that which is lost by the coal in attaining equilibrium with the surrounding atmosphere and residual moisture is that retained by the sample after it has reached equilibrium. (Maher and Barton, 1996).

Moisture in coal is important since it can affect many aspects of the production and ultimate use of coal. This discussion, however, will be limited to its effect on self-heating of coal. As noted earlier, the presence of moisture can affect the chemistry of the oxidation process but it can also provide a source of heat through the physical adsorption of water vapour onto the surface of the coal. While adsorption is an exothermic process which can potentially lead to a temperature rise in a coal stockpile, it must be remembered that it is a reversible process and consequently may act to reduce the temperature if desorption occurs.

Chen and Stott, 1992, measured the heat of drying (i.e. the heat of desorption) of a New Zealand coal using an isothermal calorimetric technique. They found that drying proceeded in three steps: removal of free water, removal of lightly bound moisture and removal of tightly bound moisture. The heats of drying associated with these steps increased with decreasing moisture content ranging from less than 2 kJ/kg of water content for the free water to more than 20 kJ/kg for the tightly bound moisture.

Like many of the variables that are known to influence self-heating and spontaneous combustion in coal, there is no general agreement on what the exact nature of what the effect may be. Some workers have suggested that wet coal inhibits the onset of self-heating

whereas others have reported that moisture acts as a trigger to spontaneous combustion. For example, in their review of moisture in coal, Maher and Barton, 1996, cite the results of a large scale experiment performed early in the twentieth century in which two bunkers of coal were subject to the same conditions except that one was dry while the other was thoroughly wetted. The temperature of the wet bunker remained below 50 °C whereas the dry bunker rose to 135 °C before it had to be dug out to prevent it from catching fire. In the same review, some anecdotal observations were quoted which suggested that spontaneous combustion frequently occurred after periods of rain immediately following warm sunny days.

In the first example, it may have been that excess moisture was preventing oxidation, or at least reducing it, by preventing oxygen from accessing the surface of the coal. As well, it is possible that during the course of the experiment some of the water was evaporating thereby reducing the temperature of the pile. In the second case, however, it is conceivable that adsorption of moisture from rain onto relatively dry coal provided the temperature increase necessary to start spontaneous combustion.

Various studies have found that the heat released as a result of the adsorption of moisture can be quite high. Schmidt, 1945, reported that for a particular coal, the temperature rose by 17 °C when sufficient water was adsorbed to raise the moisture content of the coal to one percent. Other work cited in Maher and Barton, 1996, also suggests that relatively large temperature increases are associated with adsorption of moisture from humid air. Some of these studies have even indicated that the heat released from the adsorption is greater than the oxidation reaction. This may, however, be due to the samples having been substantially “aged” so that the rate of oxidation would have been much lower than for fresh coal.

Although the amount of heat released from moisture adsorption is often substantial, most of the investigations which report significant temperature rises have used dry coal as the starting material. However, other work has shown that the amount of heat released is dependent upon the initial moisture content of the coal. Nordon and Bainbridge, 1983, found that the heat of wetting of a dry, Blair Athol low rank bituminous coal was substantial but it decreased rapidly with increasing moisture content. It is more likely that in reality, most coals would not be completely dry but would contain some amount of water. They estimated that at 65 percent humidity, the heat of wetting would cause a temperature rise of about 2 °C which they suggested would be unlikely to contribute significantly to self-heating.

Similar results were obtained by Moxon and Richardson, 1985, who showed that, using a calorimetric method, the heat generated during oxidation experiments decreased with increasing moisture content in the coal.

1.4 Aims of This Work

It is clear from the foregoing discussion that there is still considerable uncertainty surrounding low temperature oxidation kinetics of coal. In particular, the effect of particle size on the oxidation rate is not well defined. Particle size is an important parameter for any model of self-heating since, in practice, it can vary over many orders of magnitude from micron sized particles to boulder sized lumps in mine spoil piles.

Some of the apparently conflicting results obtained by the numerous particle size studies that have been conducted over the years seem to stem from the fact that the range of particle sizes examined in individual studies cover relatively small ranges. Most have tended to focus on small diameter particles usually ranging from a few tens of micrometres to perhaps one or two millimetres. Occasionally, larger fractions have been studied but in these cases finer material has not been examined.

One of the primary aims of the work presented in this thesis, therefore, was to examine the effect of particle size on the oxidation kinetics over a wide range of particle diameters for a coal which had been well characterised in terms of its chemical and petrographic composition and pore structure. The production of a set of closely sized coal fractions covering a wide range of particle diameters required for this study also meant that the effect of particle size on other coal properties could also be examined. Accordingly, the effect of particle size on the chemical and petrographic composition, surface area, porosity and density were examined. The results of these investigations are presented in Chapter 3.

As noted earlier, an important outcome from the study of low temperature oxidation of coal is the development of a reliable kinetic model for the reaction. Thus, another key aim of the work presented here was to evaluate three kinetic models which have been proposed for low temperature oxidation kinetics. In Chapter 4, the Elovich model, which is currently in widespread use, is compared to the experimental data. The more sophisticated shrinking core model (SCM) which, unlike the Elovich model, explicitly includes the effect of particle size is also examined. Finally, the pore-tree model, which was developed to mathematically represent the porous nature of coal, is tested against the experimental results.

Any comprehensive numerical model of self-heating in coal or other carbonaceous material must take into account the effects of heat generated when moisture is adsorbed by the material. Surprisingly, however, there is relatively little information available on the kinetics of moisture uptake by these materials. A further aim of this work was, therefore, to measure the adsorption of moisture onto coal over a range of temperatures likely to be

encountered in a real stockpile and to examine the kinetics of the process. The results of this investigation are described in Chapter 5.

1.5 References

- Akgün, F. and Arisoy, A. *Combustion and Flame*, 1994, **99**, 137-146.
- Akgün, F. and Arisoy, A. *Fuel*, 1994, **73**, 281-286.
- Allardice, D. J. *Carbon*, 1966, **4**, 255-262.
- Beier, E. *Fuel*, 1994, **73**, 1179-1183.
- Boyapati, E., Oates, W. A., Moxon, N. T., Day, J. C. and Baker, C. K. *Fuel*, 1984, **63**, 551-556.
- Carpenter, D. L. and Giddings, D. G. *Fuel*, 1964, **43**, 247-266.
- Carpenter, D. L. and Sergeant, G. D. *Fuel*, 1966, **45**, 311-327.
- Carras, J. N. and Young, B. C. *Prog. Energy Combust. Sci.*, 1994, **20**, 1-15.
- Chen, X. D. and Stott, J. B. *Journal of Fire Sciences*, 1992, **10**, 352-361.
- Chen, X. D. and Stott, J. B. *Combustion and Flame*, 1997, **109**, 578-586.
- Clemens, A. H., Matheson, T. W. and Rodgers, D. E. *Fuel*, 1991, **76**, 215-221
- Davidson, R. M., Natural oxidation of coal, *IEA Coal Research*, 1990
- Hill, C. R., MSc Thesis, University of Witwatersrand, 1986
- Itay, M., Hill, C. R. and Glasser, D. *Fuel Processing Technology*, 1989, **21**, 81-97
- Kaji, R., Hishinuma, Y. and Nakamura, Y. *Fuel*, 1985, **64**, 297
- Kaji, R., Hishinuma, Y. and Nakamura, R. *Fuel*, 1987, **66**, 154
- Kam, A. Y., Hixson, A. N. and Perlmutter, D. D. *Chem. Eng. Sci.*, 1976, **31**, 815
- Karsner, G. G. and Perlmutter, D. D. *AIChE*, 1981, **27**, 920-926
- Karsner, G. G. and Perlmutter, D. D. *Fuel*, 1982, **61**, 29-34
- Karsner, G. G. and Perlmutter, D. D. *Fuel*, 1982, **61**, 35-43
- Keleman, S. R. and Freund, H. *Energy and Fuels*, 1990, **4**, 165-171
- Krishnaswamy, B. S., Gunn, R. D. and Agarwal, P. K. *Fuel*, 1996, **75**, 344-352
- Maher, T. P. and Barton W. A., A review of literature on water in coal, *CSIRO Division of Coal and Energy Technology*, 1996, Investigation Report CET/IR456

Moxon, N. T. and Richardson, S. B. Proceeding of the Coal Research Conference, Wellington, New Zealand, Oct 15-17 1985.

Nordon, P. and Bainbridge, N. W. *Fuel*, 1983, **62**, 619-621

Palmer, A. D., Cheng, M., Goulet, J. C. and Furimsky, E. *Fuel*, 1990, **69**, 183-188

Pànek, P. and Taraba, B. Coal and its interaction with oxygen, Ostravskè Univerzity, Monograph 92, 1996

Polat, S. and Harris, I. J. *Fuel*, 1984, **63**, 669

Rahman, M., Hasan, A. R. and Baria, D. N., *Chemical Engineering Communications*, 1986, **46**, 209-226

Saghafi, A. Bainbridge, N. W. and Carras, J. C. Proceedings of the 70th US Mine Ventilation Symposium, June 5-7 1995

Schmidt, L. D., in *Chemistry of Coal Utilisation*, Lowry, H. H., Ed., Wiley and Sons Inc. New York, 1945, Vol 1, pp 627-676

Sondreal, E. A. and Ellman, R. C., Laboratory determination of factors affecting storage of North Dakota lignite, US Bureau of Mines Report of Investigation No 7887, 1974

Stach, E., Mackowsky, M.-Th., Teichmüller, M., Taylor, G. H., Chandra, D. and Teichmüller, R., in *Coal Petrology*, Gebrüder Borntraeger, Berlin, Stuttgart, 1982, pp 45

Teng, H. and Hsieh, C-T., *Ind. Eng. Chem. Res.* 1999, **38**, 292-297

van Krevelen, D. W., in *Coal - Typology, Physics, Chemistry, Constitution*, 3rd edition, Elsevier, 1993, pp 627

Chapter 2

Experimental Procedures

2.1 Experimental

2.1.1 Samples

A sample of freshly exposed (i.e. blasted the previous day) coal from the Puxtrees seam in the Greta coal measures from the Hunter Valley, NSW was used for the experimental program of this project. This is a high volatile, bituminous C coal.

To reduce any effects of ageing, care was taken to ensure that only large lumps of material were collected thus preventing the bulk of the sample from being exposed to oxygen. The coal was transported back to the laboratory in plastic bags and excess moisture was removed by allowing it to dry under nitrogen at ambient temperature overnight. The coal was then stored in a freezer at $-20\text{ }^{\circ}\text{C}$ until ready for use.

The entire sample was crushed to a top particle size of 32 mm. To study the effect of particle size, a portion of this crushed sample was sieved to produce 12 closely sized particle size fractions with average diameters ranging from $125\text{ }\mu\text{m}$ to 24 mm as shown in Table 2.1.

Table 2.1. Particle size fractions prepared from the Puxtrees sample

Size Range (mm)	Mean Particle Diameter (mm)
-0.250	0.125
0.250 – 0.355	0.303
0.355 -0.500	0.428
0.500 – 0.850	0.675
0.850 - 1.18	1.015
1.18 – 1.7	1.44
1.7 – 2.8	2.25
2.8 - 4.75	3.78
4.75 – 6.7	5.73
6.7 – 8.0	7.35
8.0 – 10.0	9.0
16 – 32	24

Approximately 2-3 kg of each fraction was prepared and immediately after processing, was purged with dry nitrogen and returned to the freezer where it was kept until required for testing.

A sub-sample of about 500 g was taken from the bulk material before preparation of the sized fractions. This sub-sample was crushed to $-212 \mu\text{m}$ and sent to Carbon Consulting International Pty Ltd (CCI) in Newcastle for ultimate and proximate analyses using Australian Standard methods. Analysis of each particle size fraction was also performed by CCI.

2.1.2 Mercury Porosimetry Measurements

Mercury porosimetry is a technique used to examine the pore structure of porous materials by forcing mercury into the material at very high pressures.

The theory of mercury porosimetry relies on the assumption that the pores are cylindrical in shape and that the meniscus of the mercury is a segment of a sphere (Figure 2.1).

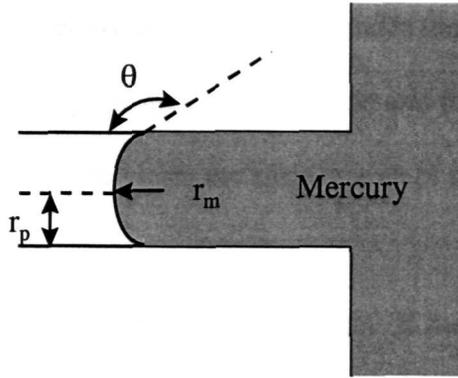


Figure 2.1. Representation of mercury penetrating a cylindrical pore (from Gregg and Sing, 1991)

The pore radius, r_p , is related to the pressure applied to the mercury, P , by the Washburn equation:

$$r_p = -\frac{2\gamma \cos\theta}{P} \quad (2.1)$$

where γ is the surface tension of the mercury and θ is the contact angle of mercury with the wall of the pore (Gregg and Sing, 1991).

In commercial porosimeters, the applied pressure is usually increased continuously from ambient (or in some cases from vacuum) to more than 200 MPa while the volume of mercury intruded into the sample is simultaneously measured. The range of pore sizes corresponding to these pressures is about 7.5 μm down to 3.5 nm (Gregg and Sing, 1991).

It is also possible to estimate the surface area of the pores contacted by the mercury from the porosimeter results. The cumulative surface area, S , of the pores can be calculated from the expression:

$$S = -\frac{1}{\gamma \cos\theta} \int_0^V P dV \quad (2.2)$$

where V is the intruded volume at pressure, P .

The integral in Equation 2.2 is equivalent to the area under the P versus V curve obtained for each sample. Thus, evaluating the area between zero and the total intruded volume and substituting into Equation 2.2 above yields the surface area of the pores.

A common problem with porosimetry is contamination of the mercury, which can affect the values of the contact angle and surface tension. To reduce the risk of contamination, distilled mercury was used in this study and the values of θ and γ used were 140° and 480 mN/m respectively.

Porosity measurements were made using a Quantachrome Autoscan Mercury Porosimeter from ambient pressure up to 33000 psi (~220 MPa). Prior to testing, samples were dried at 105°C under nitrogen then degassed under vacuum at 100°C using the degassing facility fitted to the instrument. Measurements were made on approximately 1 g of sample with mean diameters between 0.3 and 7.3 mm. The finest material (0.125 mm) was not amenable to porosimetry because the mercury did not fully wet the sample thus leaving regions where the mercury did not penetrate. The size of the glass sample tubes used with the apparatus limited the maximum particle diameters that could be tested to about 8 mm.

Data were collected and processed with a personal computer running proprietary software supplied by the manufacturer.

2.1.3 Helium Pycnometry Measurements

Helium pycnometry is used to measure the volume of irregularly shaped materials such as powders. If the weight of the sample is known then the density of the material can also be calculated. The principle of the technique is based on Boyle's Law. A known volume of gas, V_{ref} , at a known pressure, P_1 , contained in a reference cell is expanded into another cell containing the sample. By measuring the pressure of the expanded gas, P_2 , and

provided the volume of the empty sample cell, V_{cell} , is known, the volume of the sample, V_s , can be determined from:

$$V_s = V_{cell} - V_{ref} \left[\left(\frac{P_1}{P_2} \right) - 1 \right] \quad (2.3)$$

Helium is normally used for these measurements because it is close to being an ideal gas and, being a small molecule, can reach most of the pores within the sample. In the case of coal or other microporous materials, it has the added advantage that it does not adsorb onto the surface of the sample like most other gases.

In this study, a Quantachrome Multipycnometer was used to measure the true density of the all of the size fractions except the 16-32 mm sample (the particles of this fraction were too big to fit in the sample cell of the instrument). Samples were dried at 105 °C under nitrogen before testing. Approximately 1 g of sample was weighed to four decimal places into the sample cell and degassed by flushing with helium according to the manufacturer's instructions. Five individual measurements were made on each sample and the average value determined.

2.1.4 Surface Area Measurements

The measurement of surface areas of finely divided or porous solids is a well established technique which is now routinely performed using various commercially available instruments. All of these instruments rely on the principle of gas adsorption and the application of the Brunauer-Emmett-Teller (BET) equation to determine the surface area. The BET equation relates the relative pressure of the adsorbate, x , to the volume, v , adsorbed by the sample at that pressure:

$$\frac{x}{v(1-x)} = \frac{1}{v_m C} + \frac{(C-1)x}{v_m C} \quad (2.4)$$

where v_m is the volume of adsorbate in the monolayer and C is a constant. The relative pressure is defined as the pressure, P , divided by the saturated vapour pressure P_0 . If the

BET model holds, a plot of the left hand side of Equation 2.4 against x will yield a straight line from which v_m can be evaluated. Multiplying v_m by the cross-sectional area of the adsorbate molecule yields the surface area of the sample.

Most surface area determinations use nitrogen as the adsorbate at a temperature of $-196\text{ }^\circ\text{C}$, however, when coal is measured under these conditions, the results obtained are almost always very low despite the microporous nature of coal. This is generally explained in terms of activated diffusion in which it is thought that the thermal energy of nitrogen molecules is too low to allow them to enter the pore network of the coal (Mahajan, 1991). Surface area determinations of coal are therefore mostly performed using CO_2 as the adsorbate and at temperatures of either $-78\text{ }^\circ\text{C}$ or $0\text{ }^\circ\text{C}$. This usually yields surface areas one to two orders of magnitude higher than when N_2 is used. The higher values obtained with CO_2 are believed to be due to the higher thermal energy of the CO_2 molecules enabling them to fully access the micropore structure. However, Larsen *et al.*, 1995, have argued that it is also due to the high solubility of CO_2 in coal allowing it to access internal pores by diffusing through the solid.

The BET equation is usually linear only over a relative pressure range of 0.05 to 0.35 (Quantasorb, 1990), however, when using CO_2 at $0\text{ }^\circ\text{C}$ the range of relative pressures which can be accommodated in most commercial instruments is well below this range. An alternative model, the Dubinin-Radushkevich (DR) equation is therefore often used in place of the BET equation when CO_2 is used as the adsorbate. The DR equation is:

$$\log W = \log W_0 - D \log^2 \left(\frac{P_0}{P} \right) \quad (2.5)$$

where W is the pore volume at a given relative pressure (i.e. P/P_0), W_0 is the total pore volume, D is a constant and P and P_0 are the pressure and saturated vapour pressure respectively.

This model is thought to be valid over the relative pressure range of 10^{-5} to 0.1 (Clarkson, 1994).

The surface area determinations in this work were made with a Micromeritics ASAP 2400 surface area analyser at 0 °C using CO₂ as the adsorbate. The saturated vapour pressure was taken as 26142 mm Hg.

Between 1 and 2 g of sample was placed in the sample tube and degassed under vacuum at 100 °C overnight prior to starting the measurement. The diameter of the sample tubes used with the apparatus limited the maximum size of the particles which could be accommodated to less than 8 mm. Data were collected and analysed according to the DR model using a personal computer and software provided with the instrument.

2.1.5 Petrographic Analyses

A number of the sized fractions of coal were selected for petrographic analyses. Each sample was mounted and polished in an epoxy resin block. The polished blocks were then examined using a Ziess microscope using both normal incident reflected white light and reflected ultraviolet-blue light fluorescence mode. The proportion of macerals present in each block was determined by point count, with a minimum of 500 points.

The Australian Standards (AS2856-1986) maceral classification system was employed for the analyses of the coal composition.

Reflectance measurements were made under oil immersion (with a refractive index of 1.518 at 23±1°C) using plane polarised light with a wavelength of 546 nm. The photometer was calibrated against a synthetic yttrium aluminium garnet (YAG) standard of 0.92 percent reflectance.

2.1.6 Rate of Oxidation Measurements

Most of the oxidation rate measurements were made using an automated apparatus developed by the CSIRO Division of Energy Technology specifically for this purpose. This apparatus measures the rate of oxygen consumption of coal (or other carbonaceous material) under standard, isothermal conditions. It is a continuous, long term method based upon the work reported by Nordon *et al.*, 1979.

A schematic flow diagram of the oxidation apparatus is shown in Figure 2.2. Only one reactor is shown but the control software and the multi-port switching valve allowed up to 15 reactors to be run simultaneously if required.

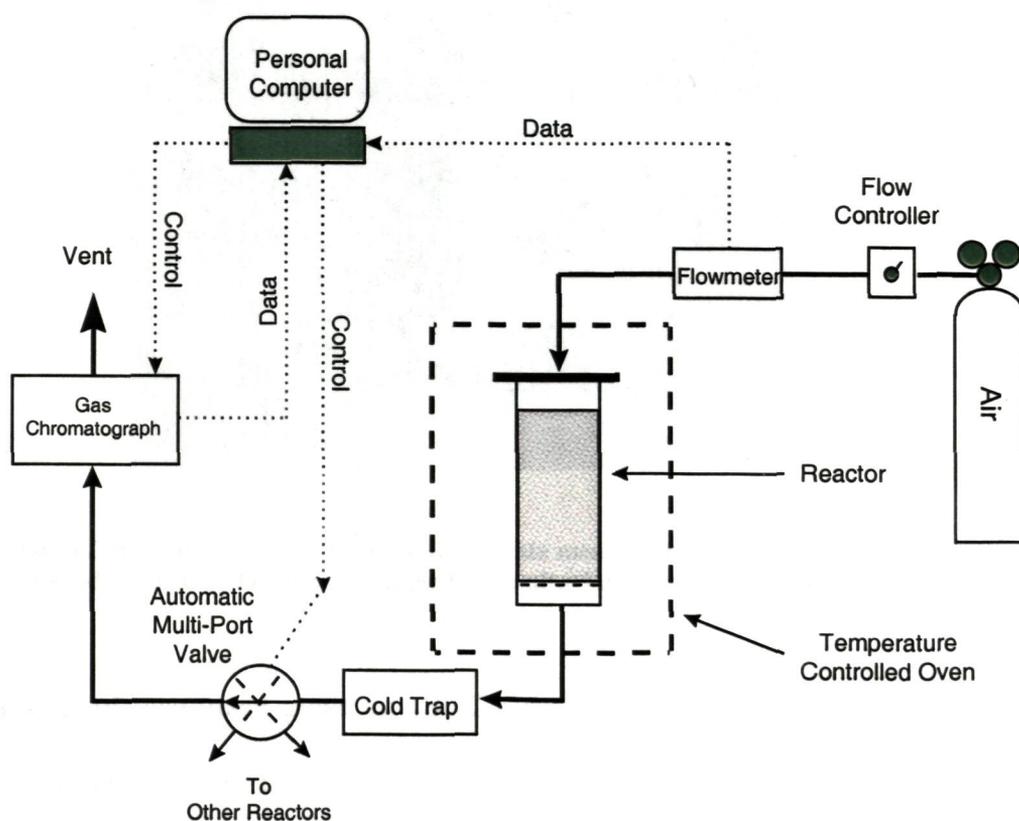


Figure 2.2. Schematic diagram of the automated apparatus used for measuring the rate of oxygen consumption

The sample was contained in a cylindrical reaction vessel and maintained at a constant temperature in an air oven which was controlled to within 0.1 °C of the set point. A

thermocouple was located in the centre of the sample to ensure that isothermal conditions were maintained.

In its original form, brass reactors each requiring about 1 - 1.5 kg of sample were used in the system. However, in this study the amount of each particle size fraction was limited and use of these reactors would have consumed the entire sample after only two or three runs. To accommodate the large number of experiments required, five smaller, stainless steel reactors were built which required only 50 to 100 g of material. A photograph of one of the smaller reactors is shown in Figure 2.3.



Figure 2.3. One of the reactors used for the oxidation rate measurements. Air entered at the bottom fitting and exited at the top. The thermocouple for monitoring the sample temperature is visible.

A steady stream of instrument grade air (BOC Gases) flowed via a calibrated flowmeter through the reactor as shown in Figure 2.2. Flow rates were typically of the order of 1 to 5 mL/min. Gas exiting the reactor passed through a cold trap (at about -5°C) to remove water and was then analysed for O_2 , N_2 and CO_2 with an MTI M200 Micro GC. This instrument operated under isothermal conditions up to a maximum temperature of 180°C and completed each analysis within 160 seconds. The unit was configured with a 10 m x 0.32 mm ID, 30 μm film thickness 5 Å molecular sieve column for the analysis of O_2 and

N₂ and an 8 m x 0.32 mm ID, 10 μm film thickness Poraplot Q column for analysis of CO₂.

The oxygen concentration of the outlet gas was kept within about 18 to 20 percent by adjusting the inlet air flow as necessary. This ensured that the concentration of oxygen within the reactor was known within reasonable limits.

Data from the GC and gas flow meter were collected on the system's computer which also controlled the operation of the GC and the multi-port valve.

Raw data (i.e. the GC analyses and gas flow measurements) were processed in a spreadsheet to calculate the rate of oxygen consumption, R_O , (in g O₂ consumed / g of sample / second) according to the expression:

$$R_O = (O_i - O_o)F\rho_{ox} / m \quad (2.6)$$

where O_i and O_o are the inlet and outlet concentrations of oxygen to the reactor respectively, F is the air flow rate to the reactor, ρ_{ox} is the density of oxygen at ambient temperature and pressure and m is the mass of coal.

Tests were performed by weighing between 50 and 100 g of fresh sample into the reactor which was immediately purged with nitrogen. The filled reactor was placed into the oven and connected to the gas supply/analysis system with stainless steel Swagelok fittings. When the sample reached the required temperature, the flow of air was started. Analysis of the off-gas was performed every few hours for the duration of the test. Tests were continued for at least 10 days, but in some cases much longer.

The temperature range used with this apparatus was 75 to 120 °C. Some lower temperature runs were also performed using the full range (i.e. -32 mm) material. For these, however, larger sample sizes were needed because the oxygen consumption of coal contained in the small reactors was so low that the flow rate required to maintain the required oxygen drop across the reactor was below the limit of the flow controller. To perform these tests, larger reactors were used. For the runs made at 35 and 45 °C, a 12 L brass reactor was used. One run was also made at room temperature (22 °C) but to get the required sensitivity, a 60 L steel drum was used for the reactor. These experiments were conducted using a separate laboratory oven and a Shimadzu gas chromatograph. In the case of the ambient run, the reactor was not contained in an oven but was maintained at temperature within about ± 2 °C in an air-conditioned laboratory. Gas analyses for all of the low temperature runs were performed by manually injecting a sample of the off-gas (via a gas sampling valve and 2 mL loop) using this system.

2.1.7 Adsorption of Moisture

Moisture adsorption by the Puxtrees coal was determined at five temperatures from 10 to 60 °C by measuring the moisture uptake of dried, sized coal at seven relative humidities. A range of relative humidities from about 10 to 100 percent was provided by using various saturated salt solutions as shown in Table 2.2.

Table 2.2. Relative humidities of saturated salt solutions at various temperatures (from Lange, 1988)

Salt	Relative Humidity (%)				
	10 °C	20 °C	30 °C	40 °C	60 °C
ZnCl ₂		10			
LiCl	13		12	11	11
KCH ₃ COOH	24		22	20	19
CaCl ₂		32			
MgCl ₂	34		33	32	30
K ₂ CO ₃	47	44			
Mg(NO ₃) ₂	57		52	49	43
NH ₄ NO ₃		66			
NaCl	76	76	75	75	74.9
KCl	88	85	84	82	80.7
Pb(NO ₃) ₂		98			
K ₂ SO ₄	98		96	96	96

Approximately 1 g of sample was weighed to the nearest 0.1 mg into a pre-weighed glass weighing jar and then dried at 105 °C under nitrogen. After drying, the jar and dried sample were placed into a glass desiccator containing one of the saturated salt solutions listed in Table 2.2. Four particle size fractions ranging from 0.125 to 9 mm mean diameter were placed in each desiccator so that the effect of particle size on the adsorption isotherm could be compared. Each desiccator was maintained at constant temperature for the duration of the experiment.

The samples were removed periodically from the desiccators and weighed to determine the moisture uptake. The frequency of these measurements varied from once each day for the first few days (when the rate of change was high) to about once every week near the end of the experiment. Measurements were continued until all of the samples in each desiccator had reached constant weight.

The final moisture contents of each sample were plotted against relative humidity to yield the isotherms. The rate of moisture uptake was calculated by dividing the mass of moisture adsorbed by the time since the previous weighing. This provided an average rate for each period.

2.2 References

Clarkson, C. 1994, University of British Columbia, MSc Thesis

Gregg, S. J. and Sing, K. S. W., in *Adsorption, Surface Area and Porosity* 2nd Ed, Academic Press, London, 1991

Lange, N. A., in *Lange's Handbook of Chemistry*, 13th Edition, Ed. Dean, J. A, McGraw-Hill, 1988

Mahajan, O. P., *Carbon*, 1991, **29**, 735-742

Nordon, P., Young, B. C. and Bainbridge, N. W. *Fuel*, 1979, **58**, 443-449.

Quantasorb Sorption System Manual, Quantachrome Corporation, 1990.

Standards Association of Australia. *Australia Standard AS 2856: Coal maceral analysis*.
Standards Association of Australia, Sydney, 1986