MATHEMATICAL MODELLING OF LARGE LOW-RANK COAL PARTICLE DEVOLATILIZATION

by

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in

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DECLARATION

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To my beloved Families
ACKNOWLEDGMENTS

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SUMMARY

The abundance of low-rank coals throughout Australia, and the world, ensures that low-rank coal will remain a major fuel for power generation in the ensuing years. Low-rank coals exhibit unique operating problems in both conventional p.f. fired and fluidised bed reactors which must be alleviated to ensure stable and economical operation. The emergence of processes utilising fluidised bed technologies has highlighted the need for an enhanced understanding of the behaviour of large coal particles in such systems. Coal devolatilization is the initial step in all high temperature coal conversion processes and, as such, is important in determining a number of factors which influence the operation of the aforementioned systems. These include the nature and location of volatiles evolution, the formation of specific flue gas emissions, and the effect of the volatile gases on the subsequent combustion and gasification of the coal char.

A number of mathematical models have been developed to predict the devolatilization behaviour of large low-rank coal particles. Numerous assumptions must be made during the development of these models and, at present, no consistency exists regarding the nature of these assumptions. Furthermore, many of these models do not consider the heat transfer environment within the reactor in detail, particularly when dealing with fluidised bed systems. A major limitation in the work presented to date lies in the model validation undertaken, which has traditionally focussed on volatile matter evolution. The dependence of devolatilization on the particle temperature suggests that validation of the particle temperature predictions generated by the model must also be undertaken to prove the reliability of the model.

An experimental investigation was undertaken to investigate the temperature response of both wet and dry, large low-rank coal particles in two reactors; a horizontal tube furnace and a fluidised bed reactor. It was found that the conventional technique
adopted throughout the literature for measuring the temperature response of large coal particles can in fact overestimate the actual particle temperature. A modified particle temperature measurement technique was developed which employed multiple particles at the end of the thermocouple and a water-cooled probe to insulate the thermocouple sheath. This technique was shown to yield more accurate particle temperature measurements and was subsequently used to collect the required particle temperature data.

The horizontal tube furnace represents a moderate heating environment while the fluidised bed reactor represents an excessive heating environment. Therefore, validation of the model using data collected in these reactors will indicate the ability of the model to predict the devolutilization behaviour of large coal particles under various operating conditions. Generally, the particle temperature data collected serves two purposes. Firstly it provides the particle temperature data necessary to validate the model predictions. Secondly, it is useful during the model development and sensitivity analysis stages to assist in elucidating the most appropriate assumptions pertinent to particular model parameters. To support the particle temperature data collected in the horizontal tube furnace, mass loss data was also collected to give an indication of the associated volatile matter evolution. Further experiments were conducted to investigate shrinkage of the wet coal particles during drying and devolatilization, and estimates of the particle density prior to, and on completion of, devolatilization. This data was also used during the model development and sensitivity analysis stages.

A model was proposed to predict the behaviour of large low-rank coal particles during devolatilization. Emphasis was placed on accurately representing the heat transfer environment surrounding the devolatilizing coal particle, and the model is subsequently capable of predicting the transient, radial temperature response of the coal particle. Based on this temperature response, the model estimates the extent of devolatilization from a number of “shells” which comprise the coal particle, and the density of the particle in any particular “shell” is proportional to the mass loss and the extent of shrinkage (for wet coal particles). The model has the capacity to account for
the enthalpy of devolatilization, and the influence of the volatile matter flux at the particle surface on the rate of external convective heat transfer. Drying is assumed to be limited by heat transfer such that the particle temperature does not exceed the effective drying temperature until drying is complete. Capacity was provided to enable both the effective drying temperature and the enthalpy of drying to be either constant or variable.

The sensitivity analysis conducted on the model indicated that, of the thermophysical properties, the specific heat capacity was found to have a significantly greater impact on the model predictions than either of the thermal conductivity or the emissivity. The convective heat transfer coefficient under fluidised bed conditions was found to have a minimal impact on the model predictions as the heating process is internally heat transfer controlled under these conditions. Despite this, heat transfer correlations determined from fixed beds or for pure convection must not be substituted for those developed uniquely for fluidised beds. Confusion regarding the magnitude and nature of the enthalpy of devolatilization results in the assumption that it has negligible impact on the model predictions. The surface volatile matter flux was found to have a minimal impact in the horizontal tube furnace or the fluidised bed reactor, however can be important in purely convective flow heating environments. Finally, the enthalpy of drying was found to be a critical parameter for modelling wet coal particle behaviour, and it was found that the trend observed by Chen of Auckland for the enthalpy of drying was most appropriate.

The predictions generated by the model were found to compare favourably with the experimental data collected in both the horizontal tube furnace and the fluidised bed reactor, particularly for dry coal particles. For wet coal particles, some discrepancy between the particle temperature measurements and predictions was observed during the early stages of heating and during the latter stages of devolatilization. The extent of this deviation was more pronounced in the fluidised bed and is more likely to be a result of limitations in the particle temperature measurements. The model predictions further confirm that the trend observed by Chen for the enthalpy of drying is appropriate given the ability of the model to estimate the total drying time using this
assumption. The accuracy of the model predictions, along with the rigorous model validation undertaken employing both particle temperature and volatile matter evolution data, indicates that the model is extremely capable of predicting the devolatilization behaviour of large coal particles. Note that the model validation undertaken in this study represents the most comprehensive testing regime performed on such a model in the literature to date.

Given the success of the model to date, the ability of the model to predict the evolution of individual volatile species, and to estimate the kinetic parameters for individual volatile species evolution, was investigated. It was found that the kinetic parameters for methane\(^1\) evolution proposed in the literature were unable to accurately predict the transient concentration of methane in the off-gas from a fluidised bed reactor. More particularly, these kinetics tend to underpredict the methane concentration during the latter stages of devolatilization, and predict higher maximum concentrations than those reported in the literature. In order to alleviate this, alternate kinetics have been proposed which were shown to accurately predict the methane concentration response for a wide range of particle sizes and fluidised bed temperatures. It should be noted that these alternate kinetics are applicable to predicting methane evolution from the coal employed for this part of the study. Given adequate data for the evolution of individual volatile species from any coal, it is possible to derive coal-specific kinetic parameters using the technique outlined in this study. This is further aided by the availability of thermophysical properties for the coal in question.

Many investigators have considered the relative roles of the chemical kinetics for devolatilization, and heat transfer, in controlling the devolatilization process. The conventional approach has been to distinguish between these regimes of coal devolatilization based purely on the particle size. However, such parameters as the reactor temperature, chemical kinetics, and heat transfer environment are also likely to influence the regime under which devolatilization is proceeding. A technique has been proposed to distinguish between chemical kinetically controlled and heat transfer

\(^1\) Methane was used as an example.
controlled devolatilization which employs the heat transfer Biot number, \( Bi \), and a modified Damkholer number, \( Da' \). Based on this technique, chemical kinetics dominate devolatilization when \( \log \left( \frac{Bi}{Da'} \right) < 4.5 \) while heat transfer is the dominant mechanism when \( \log \left( \frac{Bi}{Da'} \right) > 5.5 \). In the intermediate region, \( 4.5 < \log \left( \frac{Bi}{Da'} \right) < 5.5 \), devolatilization is controlled by a combination of chemical kinetics and heat transfer.

This study has highlighted the need for extensive testing of large particle coal devolatilization models with both volatile matter evolution and particle temperature data in order to ensure that the predictions generated by the model can be thoroughly trusted. By undertaking an in-depth investigation into the particle temperature measurements and associated model predictions, it has been shown that accurate model predictions can be obtained for the evolution of volatile matter, and of individual volatile species. The model is also capable of predicting the behaviour of wet coal particles by assuming that drying is heat transfer controlled and that the enthalpy of drying observed by Chen is applicable. Ultimately, this model forms a sound basis for the on-going development of a model encompassing all of the reactions required to model the behaviour of a typical coal particle in a fluidised bed combustor or gasifier. Such a model, when incorporated into a fluidised bed hydrodynamic model, will form a model for a fluidised bed gasifier or combustor which will aid in the design and scale-up of commercial fluidised bed reactors.
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Chapter 1

INTRODUCTION

1.1 CRC FOR NEW TECHNOLOGIES FOR POWER GENERATION FROM LOW-RANK COAL - MISSION AND OBJECTIVES

The Cooperative Research Centre for New Technologies for Power Generation from Low-Rank Coals was established in 1993 to carry out research and developmental studies to investigate alternative technologies and/or processes by which low-rank coals may be used more efficiently for power generation. Furthermore, the unique operational problems which arise during the utilisation of low-rank coal need to be addressed in order to meet the environmental and economic limitations required for cost effective power generation from low-rank coals.

The CRC for Low Rank Coals defined their mission and objectives as follows (CRC for Low Rank Coals, 1998):

Mission
Through cooperative R&D by Australian industry, research bodies and universities:

- promote the development and commercialisation of new, cost effective and environmentally acceptable technologies for power generation from low-rank coal;
• provide basic understanding of power generation processes and coal behaviour;
• provide scientific and engineering support for the development of process technologies and their commercial application;
• and become a leading world research centre in the area of power generation from low-rank coals.

Objectives

• Take a leading role in the development of new, efficient, cost-effective and environmentally acceptable technologies for electricity generation from low-rank coals.
• Enhance the potential of low-rank coal as a competitive fuel for future power generation by increasing the scientific understanding of its behaviour in advanced technology systems.
• Increase the effectiveness and collaborative synergy of low-rank coal research in Australia by strengthening the interaction between participants.
• Provide the necessary technical support for the export of such technologies which will have application in many developing nations where coal resources are low-rank and often low-grade.

1.2 LOW-RANK COAL RESERVES/RESOURCES IN VICTORIA AND SOUTH AUSTRALIA

1.2.1 SOUTH AUSTRALIA

South Australia has a number of low-rank coal resources with sub-bituminous coals found at Leigh Creek and Lock, and a number of lignites located in the south eastern corner of South Australia, namely Lochiel, Bowmans, Sedan, Anna, and Kingston etc (see Figure 1.1). At present, Leigh Creek coal is the only South Australian coal being actively utilised for power generation with an estimated 3 million tonnes per annum (Mackay, 1996) used to fuel the 500 MW Northern Power Station and the 240 MW
Thomas Playford B Power Station (Environmental Protection Council, 1992). This represents approximately 35% (as of 1992) of the total fuels used for power generation in South Australia and provides 27% (as of 1992) of the electrical energy generated (Environmental Protection Council, 1992). The Leigh Creek coal deposit occurs in a series of four isolated basins the largest of which, the Telford basin, is currently being mined and has an estimated resource of 500 million tonnes (Mackay, 1996). The bulk of the energy generated in South Australia is provided by the Torrens Island power station which generates around 65% (as of 1992) of the total electrical energy from a gas/oil fuel (Environmental Protection Council, 1992).

The Lock sub-bituminous coal deposit is located in the Polda Basin (Figure 1.1) and has an estimated resource of 320 million tonnes. The coal has an extremely high ash content, 20-25wt% (Mackay, 1996), which is likely to cause extensive fouling problems in conventional power stations. Two major lignite deposits are found in the Northern St. Vincent Basin; namely the Lochiel and Bowmans deposits. The Bowmans deposit is the largest lignite deposit in South Australia and has an estimated reserve of 1,250 million tonnes while the Lochiel deposit has an estimated reserve of 625 million tonnes (Mackay, 1996). Both deposits are ideally suited to open cut mining. However their high moisture and ash contents, along with their high levels of chlorine, sodium and sulphur, make them unsuitable for use in conventional power stations. Of the remaining deposits in South Australia, the Wintinna (4,000 million tonnes) deposit in the Ackaringa basin, the Sedan (184 million tonnes) and Anna (58 million tonnes) deposits on the western edge of the Murray basin, and the Kingston deposit (985 million tonnes) in the south of the Murray basin, are the largest in terms of their estimated reserves however they exhibit similar characteristics to the previous lignites and are not suited to conventional power generation facilities.
Figure 1.1 Low-rank coal deposits in South Australia (reproduced from Mackay, 1996)

1.2.2 VICTORIA

Victoria’s major low-rank coal deposits are located in the south eastern corner of the state in the Gippsland Basin which has an area of approximately 40,000 sq km (Gloe and Holdgate, 1991). The Gippsland Basin comprises both on-shore and off-shore sections with the off-shore section housing one of Australia’s largest oil and gas reserves, and accounts for 80% of the Gippsland Basin. The on-shore section of the Gippsland Basin is located in the Latrobe Valley and there are three major economic seams within the basin; namely the Yallourn seam, the Morwell seam, and the Traralgon seam (Figure 1.2). The Gippsland Basin itself has a total indicated resource estimated at 172,874 million tonnes and the Latrobe Valley coal fields have
a measured resource of approximately 64, 900 million tonnes (Gloe and Holdgate, 1991). Of the 64, 900 million tonne of coal in the Latrobe Valley, there is an economically winnable reserve of 35, 754 million tonnes. However, the presence of national parks and municipal infrastructure limit the readily recoverable reserve to 11 630 million tonnes (Gloe and Holdgate, 1991). There are two further, smaller coalfields within the Gippsland Basin; namely the Alberton coalfield (4, 887 million tonnes) and the Gelliondale coalfield (5, 200 million tonnes) (Gloe and Holdgate, 1991).

The Latrobe Valley also hosts the three brown coal fired power stations which provide a large proportion of the total electrical power capacity of Victoria. Three power stations are operational within the Latrobe Valley, the largest of which is the Loy Yang A power station which boasts four 500 MW units for a total output of 2000 MW (Gloe and Holdgate, 1991). The smaller Loy Yang B power station produces 1000 MW from two 500 MW units (Gloe and Holdgate, 1991). The Hazelwood power station combined eight 200 MW units for a peak capacity of 1600 MW while the Yallourn W power station generates 1450 MW from two 350 MW and two 375 MW units (Gloe and Holdgate, 1991). The capacity for utilisation of Victorian low-rank coals in conventional combustion systems is highlighted by the above figures, when compared to those of South Australia. Although this is also representative of demand, the capacity for electrical power generation from low-rank coals in Victoria is 10 to 12 times that of South Australia. This highlights the dependence of Victoria on low-rank coals for electrical power generation, as well as highlighting the potential for increased utilisation of the South Australian low-rank coals providing several critical operational problems can be overcome.

Victoria also has a number of smaller deposits located in the Otway and Murray basins (Figure 1.2). In the Otway basin there are several small discrete brown coal deposits such as the Wensleydale, Deans Marsh and Benwerrin deposits. The Benwerrin deposit is of some interest as it represents the highest in rank of the Victorian brown coals. The Anglesea coalfield, also in the Otway basin, is currently utilised to provide power for the nearby Alcoa aluminium smelter with approximately
Figure 1.2 Low-rank coal deposits in Victoria (reproduced from Glie and Holdgate, 1991)

1 million tonnes annually used to fuel a 175 MW power station (Gloe and Holdgate, 1991). The Anglesea deposit has an resource estimated at 390 million tonnes of which 160 million tonnes is considered economical and 70 million tonnes is readily available (Gloe and Holdgate, 1991). Near Bacchus Marsh is the Maddingly coal seam which has an estimated resource of 110 million tonnes and a readily recoverable
reserve of 30 million tonnes. The Maddingly coal seam is a part of the Port Phillip Sub-Basin which contains an extensive development of brown coal with a total estimated resource of 15, 110 million tonnes (Gloe and Holdgate, 1991). Large brown coal deposits are found in the Murray Basin, near the towns of Kerang and Shepparton (Figure 1.2). The deposits in the Murray basin have an estimated resource of 19, 599 million tonnes. However, due to their depth, the overburden-coal ratio of the deposits leaves them economically unsuitable for utilisation (Gloe and Holdgate, 1991).

1.3 LOW-RANK COALS: PROBLEMS FOR UTILISATION

Utilisation of many of the low-rank coals mentioned in Section 1.2 in conventional power station boilers presents several operating problems which must be overcome, or alternative technologies must be employed, before these coals can be effectively used for power generation.

1.3.1 MOISTURE

One of the major problems arising from the use of South Australian and Victorian low-rank coals is the extremely high moisture content of the as-mined coals. Typically, these coals contain between 25 wt% and 65 wt% water on an as-received basis. This severely impacts on the Net Wet Specific Energy (NWSE) of the coal which is a measure of the usable energy available from the combustion of the coal. Typical coals from the Gippsland Basin in Victoria have a NWSE of approximately 8.6 MJ kg\(^{-1}\) (Brockway and Higgins, 1991) compared to a Gross Dry Specific Energy (GDSE) of 26.86 MJ kg\(^{-1}\). This highlights the impact of moisture on the useful energy per kilogram of coal feed. This moisture can also be equated to yield a 1% reduction in efficiency for every 8 wt% moisture in the feed coal. This is reflected in the relative efficiencies of conventional black and brown (low-rank) coal fired power stations of 40% and 29%, respectively (Zhang, 1998).
Naturally, as the moisture content increases the NWSE decreases and the boiler flame temperature similarly decreases. To accommodate higher moisture content coals, larger boilers are required to facilitate the greater volume of gas/water vapour and provide sufficient heat transfer area, and greater feed rates are necessary to achieve the required output (Allardice and Newell, 1991). As a result the capital cost, maintenance and operating costs, and plant down-time are generally higher than for power stations fuelled by black coals (Allardice and Newell, 1991). Therefore, understanding the role of moisture during coal conversion processes, and developing techniques for pre-drying of low-rank coals, will be beneficial in the development of suitable low-rank coal power generation technologies.

1.3.2 Coal Ash

1.3.2.1 Fouling, Slagging and Deposition in Conventional Boilers

Another major limitation in the use of the aforementioned low-rank coals is their inherently high ash/inorganic matter contents. In conventional p.f. fired boilers, where flame temperatures of up to 1500°C are not uncommon, slagging, fouling and ash deposition become major operating problems, along with the additional problem of high temperature corrosion. Under the conditions prevalent in p.f. boilers, alkali and alkaline earth metals (e.g. Na, Ca, etc.) present in the coal ash vaporise. When these species come into contact with the cooler heat transfer surfaces they condense forming alkali sulphates. These sulphates act as a “glue” and capture ash particles which come into contact with the sticky alkali layer. As the ash layer grows, the surface temperature becomes hotter due to the decreased heat transfer eventually forming a molten layer which is able to trap further ash particles. This process results in the formation of deposits on the heat transfer surfaces which have the effect of reducing in the efficiency of these heat exchange operations (Zhang et al., 1998). Furthermore, as the boiler efficiency is reduced, the gas temperature in the convective heat exchange section increases which further increases the degree of fouling in these sections (Allardice and Newell, 1991). Subsequently, conventional power stations often
employ periodic shut downs to enable tube cleaning to be undertaken restoring boiler performance.

A major contributor to the initiation of fouling is sodium which, is often present in the form of a mineral chloride. At such high temperatures (~ 1500°C) the sodium can become volatilised and escape with the flue gas. However, both sodium and chlorine are highly corrosive in the vapor form. Due to the corrosive nature of the alkali metals, turbine manufacturers have strictly low levels for alkali metals in their turbine inlet gas streams (Allardice and Newell, 1991).

1.3.2.2 Agglomeration and Defluidisation in Fluidised Bed Combustion/Gasification

Compared with conventional p.f. fired boilers, fluidised bed combustors and gasifiers operate at much lower temperatures (ca. 700°C - 900°C). Hence they offer improved prospects for utilising low-rank coals as the ash related problems of p.f. boilers are greatly reduced (Zhang et al., 1998). However, low-rank coals exhibit alternate operating difficulties in fluidised bed reactors, namely agglomeration and defluidisation.

In a fluidised bed reactor, the bed of solids is suspended by a fluidising gas which provides for a rapid heat and mass transfer environment. The ash content of low-rank coals typically has a low melting point such that at typical fluidised bed temperatures the ash can become semi-molten. This semi-molten ash is able to adhere to the surface of the bed particles forming a sticky surface on the bed particles. It is further possible for bed particles to become attached to one another due to this sticky semi-molten ash layer. This process is known as agglomeration. As agglomeration continues, the effective bed particle size increases. As the bed particle size increases, the rate of the fluidising gas must also be increased to support the larger effective bed particles. If the fluidising gas rate is not increased, the bed particle size may reach a point at which the gas can no longer support the particles, and defluidisation results.
Under these conditions the normally stable operation of the fluidised bed is disturbed and the process must be shutdown.

1.3.3 **Flue Gas Emissions**

The flue gas from the South Australian low-rank coals is found to be high in the oxides of sulphur and nitrogen, SO\textsubscript{x} and NO\textsubscript{x}, respectively. While NO\textsubscript{x} emissions pose less of a problem, the SO\textsubscript{x} emissions are a direct result of the high sulphur content of the parent coals. Comparatively, the Victorian coals have a much lower sulphur content hence the resultant flue gas emissions are lower. The sulphur present in the parent coal is both inorganic and organic sulphur in origin and the nature of the SO\textsubscript{x} emissions is reliant on the origin of the sulphur and the combustion/gasification conditions to which the coal is exposed. During gasification hydrogen sulphide, H\textsubscript{2}S, is the main sulphur gas emission along with minor amounts of carbonyl sulphide, COS, carbon disulphide, CS\textsubscript{2}, and a number of trace sulphur bearing gases (Telfer and Zhang, 1997). During combustion however, due to the oxidising environment, the major sulphur emission is sulphur dioxide, SO\textsubscript{2} (Telfer and Zhang, 1997). These sulphur bearing gases are all found to be corrosive in downstream processes and are major contributors to air pollution.

NO\textsubscript{x} emissions, as stated, pose less of a problem than for SO\textsubscript{x} emissions due to the lower levels of nitrogen in the parent coals. The acceptance and signing of the *Kyoto* summit on greenhouse gas emissions limits any significant increase in the current levels of emissions within Australia over the next 8-10 years. Given that power usage will increase during this time, some effort will be required to maintain the NO\textsubscript{x} emissions at their current levels.

The problems discussed in-brief above are an example of the areas of research which must be further developed to enable an effective process for the utilisation of South Australian and Victorian low-rank coals to be developed. The CRC for Low-Rank Coals has identified specific areas within each of these unique problems and research
projects have subsequently been initiated. Using this approach, the CRC - Low Ranks Coals aims at achieving its objectives, as outlined in Section 1.1.

1.4 PROJECT SCOPE AND SIGNIFICANCE

The work presented in this study targets the first stage of an extensive project aimed at developing a comprehensive model for a bubbling fluidised bed coal gasifier and deals with the development of a mathematical model to describe devolatilization of large low-rank coal particles. The CRC for Low Rank Coal has a number of studies running in parallel to the study presented here. These studies deal with the subsequent in-bed behaviour of the volatiles once evolved from the coal particle, the gasification kinetics of the resulting chars to steam and carbon-dioxide and sophisticated computational fluid dynamic models to investigate the hydrodynamic behaviour of a bubbling fluidised bed. Ultimately, these individual studies form a long running project aimed at incorporating the information gained from each of the aforementioned areas to develop a comprehensive mathematical model for the hydrodynamic and kinetic behaviour of a bubbling fluidised bed gasifier.

The release of the volatile fraction of the parent coal during the heating of the coal as it is introduced to a gasifier/combustor has a number of implications in regards to the design and operation of low-rank coal combustion/gasification systems. The volatile matter content of typical South Australian and Victorian low-rank coals is between 25 and 50wt% on a dry basis. This represents a significant fraction of the useful fuel and as a result the volatile matter contributes a significant proportion of the total energy released during combustion (Agarwal et al., 1984a). The nature of the volatile products, along with their relative yields will be important in predicting the combustion behaviour of the gas phase inside the reactor as well as impacting on the fuel/oxygen ratio required in the feed.

In addition to the impact the volatile matter has on the energy parameters, the devolatilization process itself has important ramifications in terms of the gas emissions. Garcia-Labiano et al. (1996) noted that a large part of the sulphur present
in the parent coal is released during devolatilization. As would be expected, the reaction pathways which may lead to SO\textsubscript{x} formation differ significantly for the sulphur remaining in the coal, and for the sulphur evolved during devolatilization. Similarly, Johnsson (1994) stated that: "The division of nitrogen between char and volatiles and the type of nitrogen compounds formed during devolatilization are very important for the fate of coal-nitrogen in FBC, because the secondary reactions are quite different for char-N an volatiles-N, and also for the different volatile nitrogen species." This was further supported by Agarwal et al. (1984a) who also suggested that the volatile products also contribute significantly to the release of CO emissions. It follows then that understanding the process of devolatilization will further increase the knowledge of the origin and formation of various gas emissions during devolatilization, and aid in their minimisation.

A fundamental limitation in the present understanding of devolatilization is the role of heat transfer, mass transfer and chemical kinetics during devolatilization. Garcia-Labiano et al. (1996) reported that as the particle size increases, the effect of heat and mass transfer become more significant while for smaller particles chemical kinetics dominates the devolatilization mechanism. It is likely that understanding the way in which each of these mechanisms controls devolatilization, under a variety of operating conditions, will be a substantial step towards a greater understanding of the devolatilization process in general, and will be beneficial in the progression toward an accurate coal devolatilization model.

The coal devolatilization studies conducted are aimed at achieving the following:

- Measuring the temperature response of large low-rank coal particles during devolatilization under both fluid-bed and convective flow conditions.
- Investigate the effect of moisture on the particle temperature response under similar conditions.
- Propose a model to predict both the temperature response and evolution of volatiles from large low-rank coal particles, both wet and dry, during devolatilization.
• Perform a sensitivity analysis of the proposed model to aid in the selection of the appropriate assumptions pertaining to specific model parameters.

• Validate the model predictions using the experimental data collected in this study and appropriate data selected from the literature.

• Investigate the ability of the model to predict the evolution of individual volatile species from large low-rank coal particles during devolatilization, and assess the kinetic parameters proposed for volatile species evolution.

• Investigate the respective roles of chemical kinetics and heat transfer during devolutilization and propose a technique by which the dominant mechanism can be isolated.

It is proposed that developing an accurate model for large coal particle devolutilization is the first step in developing a single particle coal conversion model for predicting the behaviour of large coal particles under typical gasification conditions. The coal devolutilization model can be subsequently built on to include the effects of volatiles combustion at the particle surface and the reaction of the char particle with the combustion and gasification gases present in the gasification environment. However, it is not possible to consider the latter effects until the coal devolutilization model has been developed and tested to form the basis for the overall single particle conversion model. This model can subsequently be employed in either computational fluid dynamic models or mathematical models for the behaviour of a bubbling fluidised bed coal gasifier to give accurate predictions of the gasifier performance. Such models will be useful in the design and scale-up of commercial gasifiers.

The literature review of coal devolutilization presented in Chapter 2 will deal with the mechanism and transformations occurring during coal devolutilization as well as the products formed. The history of coal devolutilization modelling will be covered including the types of devolutilization models available, the kinetic of coal devolutilization, and large coal particle devolutilization modelling. Finally the status of large particle coal devolutilization modelling will be discussed giving a further indication of the scope of the present work in relation to the literature reviewed.
Chapter 3 will discuss the experiments conducted in support of the current work and the experimental techniques employed to generate the required data. The development of the large particle coal devolatilization model will be outlined in Chapter 4, and a sensitivity analysis will be conducted concerning specific model parameters in Chapter 5. The model developed in Chapter 4, considering the results of the sensitivity analysis of Chapter 5, will be employed in Chapter 6 to predict the experimental data collected in Chapter 3, as a means of validating the model predictions. This validation will be supported by comparisons between the model predictions and data selected from the literature, also in Chapter 6.

The ability of the model to predict the evolution of individual volatile species from large coal particles during devolatilization will be explored in Chapter 7. If necessary, the model will be employed to estimate alternate kinetics for the evolution of individual volatile species and the success of theses kinetics will subsequently be tested. Chapter 8 will deal with the mechanisms controlling devolatilization, namely chemical kinetics and heat transfer, and a technique will be developed to estimate which mechanism is dominant under specific operating conditions.

A summary of the work presented in this study will be given in Chapter 9 and the role of this work in terms of the overall development of a bubbling fluidised bed coal gasification model will be discussed. Also, implications of the present work for alternative areas of coal research will also be discussed.
Chapter 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter reviews the published literature with respect to the devolatilization of coal and its subsequent modelling, with particular emphasis on the devolatilization of low-rank coals (brown coals or lignites) which are of interest to the CRC for New Technologies for Power Generation from Low Rank Coals. A general review of coal devolatilization will cover the mechanism of devolatilization, the nature of the transformations occurring, and the products of devolatilization. The history of coal devolatilization modelling will subsequently be addressed, and will detail the types of models employed, chemical kinetics of devolatilization, large particle coal devolatilization models, and finally a comment on the status of coal devolatilization models will be made. Ultimately this review will present a broad and in-depth background to the present study, and assist in defining the scope of this work with respect to previous studies.
2.2 THE FUNDAMENTALS OF COAL DEVOLATILIZATION

2.2.1 THE STRUCTURE OF LOW-RANK COALS

An understanding of structural changes during devolatilization is greatly enhanced by some awareness of the chemical structure of low-rank coals, which is in turn related to the process by which coal is formed. Coal originates from peat, formed from plant matter that grows and/or is deposited in swamps. The transformation from peat to coal occurs via low grade metamorphosis, i.e. the application of heat and pressure. Generally the peat deposit is buried under sediments (sands, clays etc.) and it is the thickness of these sediments which determines the temperature and pressure to which the peat is exposed. The transformation process referred to here is termed coalification (Mackay, 1996).

Peat is composed of a significant amount of lignin and cellulose present in the original plant deposits. The first stage of coalification is one of dewatering which occurs due to a reduction in the porosity of the peat via a gradual increase in pressure (due to compaction), and the decomposition of hydrophilic functional groups (ie -OH groups). The cellulose present now begins to undergo decomposition while the lignins are preserved and become concentrated in the peat. Humification follows, whereby the formation of humic acid functional groups occurs, and to which such cations as Na, Ca, Mg, Fe, and Al can bond to form humates. The ensuing gelification stage involves the formation of colloidal humic gels which precipitate in void spaces resulting in a further reduction in porosity. As coalification progresses, the oxygen content of the coal is gradually reduced via the decomposition of carboxyl (-COOH), methoxyl (-OCH₃) and carbonyl (>C=O) functional groups, as well as ring oxygens. The final stages of coalification involve the condensation of humic acids to larger molecules, and the removal of aliphatic and alicyclic functional groups meaning the coal is becoming increasingly aromatic and carbon rich in nature (Stach et al., 1982).
Low-rank coals are at an early stage of coalification, and are at an intermediate stage between the original peat and sub-bituminous coal. Such coals have retained a large portion of their carboxyl, methoxyl, and carbonyl functional groups and these functional groups can explain much of the behaviour of these coals during processing (Mackay, 1996).

Previously, characterisation of the coal structure has been difficult due to the inherently complex nature of the structure, and the lack of adequate analytical techniques. More recently however, advanced techniques such as $^1$H NMR, $^{13}$C NMR, and TG-FTIR spectroscopy have enabled information on the structure of low-rank coals to be elucidated (Clemow et. al., 1998). $^{13}$C NMR spectroscopy has been applied to Victorian low rank coals by Russel et. al. (1983) and information regarding the fraction aromatic carbon content and the distribution of the carbon in various forms within the coal molecule have been deduced. By distinguishing between the aliphatic and aromatic carbon atoms, and the type and relative quantity of particular aliphatic and aromatic carbon atoms present, a general picture of the molecular structure of the coal molecules can be developed (Verheyen and Perry, 1991).

$^1$H NMR spectroscopy is able to provide further understanding of the coal structure by giving an indication of the mobility of the coal structure at various stages during thermal decomposition which, when combined with the $^{13}$C NMR results, further enhance the characterisation of the coal structure. FTIR spectroscopy, which can be used to distinguish particular functional groups, provides further information as to the coal molecular structure and, when combined with the forementioned techniques, a structural representation of low-rank (or other) coals can be developed (Verheyen and Perry, 1991).

A number of "hypothetical" models depicting the structure of coals have been developed, and a typical example of a structure proposed for a brown coal is displayed in Figure 2.1. As can be seen, the coal is composed primarily of groups of aromatic ring clusters which are cross-linked by aliphatic or etheric bridges. The aromatic ring cluster size for low-rank coals is in the range of one to four average rings per cluster,
and the rings have attached to them a variety of functional groups such as carbonyl, carboxyl, ether and phenol groups. The aromatic rings may also be monosubstituted with heteroatoms such as nitrogen, sulphur or carbon. This covalently bonded chain of aromatic ring clusters is commonly referred to as the immobile phase. Throughout this continuous chain of aromatic ring lusters exist small interstices, or holes, in which smaller molecules may be trapped. These molecules are generally aliphatic in nature, however minerals such as quartz (SiO₂) and kaolinitic clays (e.g. Al₂Si₂O₅(OH)₄) may also be present and these molecules constitute the mobile phase. Inorganics including Na, Ca, K, Al, and Fe etc. are also found within the coal structure and are typically attached to carboxylate (or similar) groups, or included as chelate type complexes (Solomon et al., 1993a; Solomon et al. 1993b; van Heek and Hodek, 1994).

Figure 2.1 Schematic of a proposed structure of a low-rank coal (after Lindner, 1988).
2.2.2 THE MECHANISM OF COAL DEVOLATILIZATION

The physio-chemical transformations occurring during devolatilization have been investigated by a number of authors (Juntgen. 1984; Serio et. al., 1987; Solomon et. al., 1993a; Solomon et al., 1993b; van Heek and Hodek, 1994) and mechanisms describing these transformations have been proposed. van Heek and Hodek (1994) proposed that devolatilization took place according to the mechanism described schematically in Figure 2.2. As the coal is heated, the first signs of thermal degradation are the desorption of moisture and selected light gases (mainly CH₄ and N₂) at ~120°C. Upon further heating, distillation of the mobile phase at temperatures above 250°C marks the commencement of tar formation and in particular the formation of the aliphatic tar component. Temperatures greater than 400°C promote the degradation of the immobile phase resulting in the formation of the aromatic tar fraction as well as a number of light gas species (H₂O, CO, CO₂) and low molecular hydrocarbons (CH₄, C₂H₄, C₃H₈, C₃H₆, C₃H₈ etc.). Finally, condensation of vaporised aromatics to char is evident above 600°C, and this is associated with the decomposition of heterocyclic compounds yielding N₂, H₂S and CO as well as hydrocracking of the aromatics releasing H₂ (van Heek and Hodek, 1994).

![Figure 2.2 Proposed mechanism for coal devolatilization. (after van Heek and Hodek, 1994)](image-url)
Solomon et al. (1993b) proposed the following theoretical mechanism describing the formation of the tar and char fractions:

Stage 1. Depolymerisation by rupture of weaker bridges in the coal macromolecule to release smaller fragments that make up the metaplast;

Stage 2. Repolymerisation (cross-linking) of metaplast molecules;

Stage 3. Transport of lighter molecules away from the surface of the coal particles by combined vaporisation, convection, and gas-phase diffusion; and

Stage 4. Internal transport of molecules to the surface of the coal particles by convection and diffusion in the pores of non-softening coals and by liquid-phase diffusion or bubble transport in softening coals. Char is formed from the unreleased or recondensed fragments. Various amounts of loosely bound guest molecules, usually associated with the extractable material, are also released during devolatilization.

This mechanism is indeed in accordance with that proposed by van Heek and Hodek (1994) considering that the metaplast referred to is essentially analogous to the mobile phase. An enhanced understanding of the structural changes occurring during pyrolysis can be obtained from Solomon et al. (1993a) who displayed a hypothetical structure for a sub-bituminous coal, and the subsequent coal structure during devolatilization. This can be seen in Figure 2.3. Comparing Figures 2.3a and 2.3b it is evident that the aliphatic bonds denoted by $\oplus$ in Figure 2.3a have been ruptured, and the carbon radicals formed have picked up hydrogen radicals to form either methyl or ethyl functional groups. The hydrogen radicals have been generated by the dehydrogenation of a hydroaromatic ring such as in the lower right hand side of the molecule in Figure 2.3a. These two aliphatic bond breakages have resulted in fragments which are light enough to evolve as tars (Solomon et al., 1993a).

The aliphatic ether bond denoted by $\ominus$ in Figure 2.3a has been disrupted with the fraction on the right hand side of the bond forming an aromatic ether linkage at the
position denoted by $\odot$ on the right hand side of Figure 2.3b. A hydroxyl functional group has also been formed on the left hand side of $\odot$ via a hydrogen radical. At the position labelled $\odot$ at the bottom of Figure 2.3b, condensation of two hydroxyl groups has resulted in the formation of a second aromatic ether bond and the release of $\text{H}_2\text{O}$. Other independent transformations have occurred such as the decomposition of the carboxyl group at the centre of Figure 2.3a to yield $\text{CO}_2$, an aliphatic ether bond has ruptured releasing a methyl group as $\text{CH}_4$ on the left hand side, and the mercaptan in the lower right hand corner of Figure 2.3a has has detached to form $\text{H}_2\text{S}$ (Solomon et al., 1993a). Again, these transformations are similar in nature to those described in the two previous mechanisms for devolatilization (van Heek and Hodek, 1994; Solomon et al., 1993b) thus giving us a generally accepted proposed mechanism for coal devolatilization.

![Hypothetical chemical structure of a sub-bituminous coal](image)

**Figure 2.3** Hypothetical chemical structure of a sub-bituminous coal: (a) parent coal; (b) during devolatilization (after Solomon et al., 1993a)
The structural changes presented in Figure 2.3 are indicative of those occurring during what is termed *primary devolatilization*. Primary devolatilization has been described as the decomposition of the macromolecular network of coal, which is disintegrated into fragments small enough to escape from the coal surface (Hayashi et al., 1992). This is distinct from the ensuing *secondary devolatilization* reactions which are described by the same author as the vapor-phase decomposition of the components produced during primary devolatilization.

Further to this, Pather (1996) proposed the following three-stage mechanism for devolatilization which summarizes the aforementioned mechanisms:

Stage 1 the release of *primary volatiles* at the solid-gas interface due to the thermal decomposition;

Stage 2 the production of *secondary volatiles* during the diffusion of gaseous products through the pores within the coal particles; and

Stage 3 the production of *tertiary volatiles* due to reactions occurring in the void spaces between the particles.

Secondary decomposition reactions are described by Pather et al. (1996) as those reactions which occur during Stages (2) and (3) of devolatilization and is essentially concerned with the transformation of the primary tar species, formed during primary devolatilization, via such reactions as tar cracking, dehydrogenation, aromatisation, and condensation (Hesp and Waters, 1970). The lighter fraction of the primary volatiles is generally stable, however at higher temperatures the decomposition of benzylic compounds can be detected (Hesp and Waters, 1970). While much work has been done in the area of thermal decomposition of tars (Hesp and Waters, 1970; Niksa, S., 1988; Xu and Tomita, 1989; Stiles and Kandiyoti, 1989; Jess, 1996), most of the work has concentrated on rationalization of the influence of various operating parameters on the secondary reaction products. A formal mechanism for tar decomposition has been proposed by Hesp and Waters (1970) and was elucidated by monitoring the product yields achieved when tars produced in a bench scale carbonizer were passed through a fixed-bed of coke particles at temperatures between
700°C and 1000°C. The mechanism suggests that tar decomposition takes place in three distinct phases which are summarised as follows Hesp and Waters (1970):

Phase 1. Phase of rapid gas formation: rapid decomposition into gas and carbon. The amount of tar decomposing in this first step is directly proportional, while the duration of the step is inversely proportional, to the temperature of cracking. Gas is the main product, indicating that gas forming reactions are quicker than carbon forming ones.

Phase 2. Phase of carbon formation: secondary decomposition of gas to yield mainly carbon and hydrogen, accompanied by slow decomposition of the tar which has survived the cracking reactions in the first place. Since a major part of the total carbon is obtained in this phase, it can be called the "phase of carbon formation". It is much longer than the first phase, and its duration is inversely proportional to the temperature of cracking.

Phase 3. Phase of slow gas evolution: slow evolution of gas from tar after the first two phases of decomposition. The amount of gas formed in the third phase is directly proportional to the amount of tar which enters this phase, i.e. inversely proportional to the temperature of cracking.

As is evident from Section 2.2, a substantial emphasis has been placed on developing a mechanistic understanding of the process of coal devolatilization, and how it relates to the parent coal structure. These structural and mechanistic models not only provide a physio-chemical description of the devolatilization process, but form the basis on which observations regarding the influence of various operating parameters on the devolatilization products can be analysed, and a rationale for the observed effect can be deduced.
2.2.3 Influence of the Operating Parameters on the Products of Coal Devolatilization.

Owing to the complexity of the devolatilization process, a majority of the conventional operating parameters have a direct influence over the nature and relative proportions of the products produced during devolatilization. Of these operating parameters, the most significant include the temperature, pressure, particle heating rate, and particle size. Factors such as particle moisture, coal rank and the presence of exchangeable cations also affect the ultimate product yields however these effects are coal dependant and, as this study is concerned primarily with a unique low-rank coal, these will not be discussed in detail. It has also been suggested that the gas environment can be a significant factor in determining the volatile yields however this effect is related to the homogeneous (gas-phase) reactions which the primary volatiles may be subjected to and also will not be dealt with. It should also be noted that a majority of the work carried out in this field is concerned with pulverised coal devolatilization. It is likely however, that the principles developed here can be extrapolated to rationalise the trends observed during large particle devolatilization.

2.2.3.1 Temperature

The operating parameter which exerts the greatest influence on the devolatilization process is the operating temperature (Xu and Tomita, 1987). The effect of the final temperature on the tar, gas and char yields is displayed graphically in Figure 2.4. It can be seen that the yield of C₁-C₃ hydrocarbons increases linearly with temperature, while the total volatile matter yield increases significantly up to approximately 700-800°C and begins to plateau thereafter. These results conform with those of other investigations (Hesp and Waters, 1979; Suuberg et al., 1979; Tyler, 1980; Cliff et. al., 1984; Niksa, 1988; Xu and Tomita, 1989; Jess, 1996). Figure 2.4 also indicates, conversely, that the yields of individual product species have differing trends as the devolatilization temperature increases. Xu and Tomita (1989) reported that the product yields are relatively constant up to 600°C, which is also observed in the results of Hesp and Waters (1979), Tyler (1980), and Cliff et al. (1984) for a majority
of the volatile products. From Figure 2.4 it is further noted that the tar yield tends to increase with temperature until approximately 600\(^\circ\)C, after which the yield decreases by almost 50\%. This trend was also observed by Cliff et al. (1984) and can be indirectly deduced from the results of both Xu and Tomita (1989) and Hesp and Waters (1979). Considering the previously discussed mechanisms for primary and secondary decomposition, this trend suggests that at T < 600\(^\circ\)C, secondary decomposition reactions are minimal and primary decomposition is dominated by Stage 1 reactions. Above 600\(^\circ\)C, primary decomposition via Stages 2, 3 and 4 begin to become increasingly more significant, as does the extent of the secondary decomposition reactions.

\[\text{Figure 2.4 Effect of temperature on the product yields during devolatilization (after Tyler, 1979).}\]
Similar studies have been conducted with a greater emphasis on low-rank coals (Scafer, 1979a,b; Scafer, 1980a,b) and it was found that the decomposition of the carboxyl and phenolic groups occurs at temperatures as low as 150°C yielding CO₂ and H₂O, and CO at temperatures above ~300°C (Scafer, 1979a,b). The maximum evolution rates for CO₂, H₂O, and CO occurred at temperatures of 300°C, 350°C, and 500-600°C respectively which were directly comparable with the temperatures observed by Carangelo et al. (1987) and Solomon et al. (1990b) for devolatilization of a lignite.

Xu and Tomita (1989) monitored the yields of specific gases produced when the primary volatiles from a bituminous coal were allowed to pass through a packed bed reactor at various operating temperatures. This enabled the extent of the secondary reactions to be investigated. The product yields, expressed as a wt% are summarised in Table 2.1 for a gas-phase residence time of 7s. Table 2.1 confirms that the assumption of minimal secondary decomposition reactions below 600°C is quite reasonable. Immediately above 600°C there is a noticeable increase in the yield of H₂, CO, CH₄, C₂H₄, C₃H₆, and benzene, while it becomes increasingly apparent that Phase 2 secondary decomposition is occurring due to the increase in coke formation. The yields of CO₂ and H₂O remain relatively constant while the majority of the remaining gases tend to show a steadily decreasing yield with temperature. The results also show that at 900°C the only gases present to a significant level are H₂, CO, CO₂, H₂O, CH₄, C₂H₄, and benzene. This agrees with the observations of others (Hesp and Waters, 1970; Tyler, 1980; Cliff et al., 1984).

The decrease in the yield of the heavier products (C₅-C₇'s, toluene - xylol) would indicate that Phase 2 secondary decomposition is occurring, however the products are not limited to hydrogen and include methane and ethylene, and to a lesser extent benzene. The continual increase in the formation of coke would indicate that Phase 3 decomposition has not been reached as this phase is characterised by the gradual release of H₂ and CO and only becomes predominant at longer residence times (Hesp and Waters, 1970). The thermal cracking of typical coal tar vapours was examined by Calkins et al. (1984) who measured the gas yields after passing tars produced at 600°C
through a tar cracker. Varying the cracker temperature enabled the thermal cracking reactions to be investigated. It was generally observed that the temperature at which thermal cracking became apparent decreased with increasing carbon chain length. Thermal cracking of butene-1 was observed at 650°C, while for methane the minimum cracking temperature was approximately 1000°C. It was interesting to note that the yield of ethylene increased consistently with temperature and would be considered to be a major product of the thermal cracking reactions.

It can be concluded that the trends observed in the yield and distribution of the products of devolatilization with varying temperature can be rationalised using the mechanisms which have been proposed by Solomon et al. (1993b) and Hesp and Waters (1970) for primary and secondary decomposition reactions respectively.

**Table 2.1** Effect of temperature on the product yields (wt%) from a bituminous coal *(reproduced from Xu and Tomita, 1989).*

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂O</th>
<th>CH₄</th>
<th>C₂H₄</th>
<th>C₂H₆</th>
<th>C₃H₆</th>
<th>C₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.4</td>
<td>2.1</td>
<td>1.7</td>
<td>4.0</td>
<td>3.5</td>
<td>0.8</td>
<td>0.9</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>600</td>
<td>0.4</td>
<td>2.0</td>
<td>1.6</td>
<td>4.3</td>
<td>3.6</td>
<td>0.9</td>
<td>1.0</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>700</td>
<td>0.5</td>
<td>2.5</td>
<td>1.4</td>
<td>4.1</td>
<td>4.6</td>
<td>1.9</td>
<td>1.0</td>
<td>1.3</td>
<td>0.2</td>
</tr>
<tr>
<td>800</td>
<td>0.6</td>
<td>2.7</td>
<td>1.9</td>
<td>4.1</td>
<td>5.4</td>
<td>3.0</td>
<td>0.5</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>900</td>
<td>0.9</td>
<td>3.4</td>
<td>2.0</td>
<td>3.6</td>
<td>5.7</td>
<td>2.0</td>
<td>0.05</td>
<td>0.03</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>C₃-C₇</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Xylene</th>
<th>Phenol</th>
<th>Cresol</th>
<th>Xylenol</th>
<th>Coke</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.6</td>
<td>0.1</td>
<td>0.3</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>600</td>
<td>0.7</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>0.6</td>
<td>1.4</td>
</tr>
<tr>
<td>700</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.6</td>
<td>0.4</td>
<td>2.3</td>
</tr>
<tr>
<td>800</td>
<td>0.1</td>
<td>0.8</td>
<td>0.5</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
<td>0.1</td>
<td>3.1</td>
</tr>
<tr>
<td>900</td>
<td>0.03</td>
<td>1.3</td>
<td>0.2</td>
<td>0.2</td>
<td>0.04</td>
<td>0.1</td>
<td>0.0</td>
<td>4.9</td>
</tr>
</tbody>
</table>
2.2.3.2 Pressure

The effect of the operating pressure on the products from devolatilization is most notably characterised by a decrease in the tar yield and a decrease in the total volatiles yield, most of which can be attributed to the reduced tar yield (Suuberg et al., 1979; Ladner, 1988). Ladner (1988) also noted that the decrease in tar yield was accompanied by an increase in the char yield. Suuberg et al. (1979) and Ladner (1988) both reported that the total hydrocarbon gas yield was observed to increase with increasing pressure, which was supported by Gokhale et al. (1986). Further investigation into the nature of the hydrocarbon gases being produced at various pressures suggests that a significant amount of the additional gases produced at higher pressures can be attributed to increased methane formation (Ladner, 1988; Gokhale, 1986). This suggests that the devolatilization mechanism at higher pressures is increasingly becoming controlled by Stages 3 and 4 primary, and Phase 2 secondary decomposition reactions. Note that Phase 2 rather than Phase 3 secondary decomposition has been suggested as the increase in the total char yield suggests that the process is remaining in the “phase of char formation”.

Increasing the external pressure results in a decrease in the differential pressure existing between the pores and the external particle surface during devolatilization. This suggests that the driving force for transport of the products out of the particle is reduced thus resulting in a longer residence time in the pore structure. This is further enhanced by the decrease in the molecular diffusivity of the product species arising from the increased pressures. Ultimately, the slowing of the transport processes within the particle extends the contact time of the products with the coal structure and exposes them to a greater opportunity for secondary reactions to occur. Thermal cracking reactions of the tar species, along with condensation to form char, predominate leading to the reduced tar, and increased hydrocarbon gas and char yields observed. It is not expected that the primary species formed from thermal decomposition of the initial coal structure are significantly altered, and it is during the subsequent transformations where the effect of pressure is realised.
2.2.3.3 Heating Rate

When considering the effect of the particle heating rate, care must be taken to ensure that no other dependent parameters are being incorporated into the experimental studies. Investigating devolatilization under various heating rates may be performed by varying the reactor type, however factors such as the gas-phase residence time must also be kept constant to ensure that the product yields derived are directly comparable. The most common technique for realising this situation has been through the use of wire mesh (Suuberg et al., 1979) or microsample strip (Niksa et al., 1984) reactors. Such reactors typically utilise either wire mesh grid or thin heating elements over which the coal sample is thinly dispersed to enable easy escape of the volatile products, hence reducing secondary decomposition. These reactors typically have variable heating rate control in the range of $10^2$-10$^4$ Ks$^{-1}$ and deal with sample sizes in the range of 20mg. Niksa et al. (1984) deduced that the effect of the heating rate was not uniform and was codependant on the system pressure. In a vacuum it was found that increasing the heating rate increased the total volatile yield and the magnitude of the increase was in the range of 10 - 20% when increasing the heating rate from $10^2$ to $10^3$ Ks$^{-1}$. At higher pressures, the effect of the heating rate is less apparent and can be considered negligible. This suggests that, at higher pressures, diffusion processes are becoming dominant and limiting the rates of the subsequent chemical kinetic steps i.e. Stages 3 and 4 primary decomposition are dominant. Suuberg (1979) also deduced that the heating rate has a negligible effect on the product yields. Ladner (1988) reported that an increase in oil and tar yield, as well as a corresponding decrease in the char yield, is obtained at higher heating rates according to the experimental results of Peters and Bertling (1965). This work was carried out in a fixed bed reactor and it is possible that secondary reactions related to the interaction of volatiles with adjacent char particles are evident in such a reactor. These results highlight the need for careful selection of the experimental arrangement used, with consideration given to the aims of the investigation.

The aforementioned results are limited to pulverised coal particles, and little work has been conducted to infer the effect of the heating rate on the products of large particle
devolatilization. Gavalas (1982) compared results obtained for fixed bed and fluidized bed devolatilization of coals and found that the tar yields increased significantly in the fluidized bed rig in comparison to the fixed bed rig. Higher heating rates are expected in a fluidized bed rig suggesting that higher heating rates favour tar evolution and limit secondary reactions. Again, the influence of the bed material cannot be isolated from the experimental results thus limiting the decisiveness of these results. It may be considered that the increased heating rate induces a more rapid release of volatiles from the particles, and accordingly there is a greater internal pressure build-up within the pore structure. This pressure build up causes the products to be expelled from the particles more rapidly and reduces their residence time in the pore structure. This in turn limits secondary tar cracking and condensation reactions thus explaining the observed trends.

2.2.3.4 Particle Size

In the transition from pulverised coal to large coal particles, the influence of the particle size is difficult to characterise as a number of factors become important. This is best described by Smoot (1985) who stated:

"... very large particles behave differently from finely pulverised coal. Larger particles will not heat rapidly or uniformly, so that a single temperature cannot be used to characterise the entire particle. The internal char surface provides a site where secondary reactions occur. Pyrolysis products generated near the centre of a particle must migrate to the outside to escape. During this migration, they may crack, condense, or polymerize, with some carbon deposition taking place. The larger the particle, the greater the amount of deposition, and hence the smaller the volatiles yield."

The suggestion here is that when dealing with large coal particle devolatilization, primary and secondary decomposition reactions are almost impossible to isolate due to the tendency for secondary decomposition reactions to proceed within the pore structure. Morris (1993) investigated the effect of the particle size on the total
volatile yield from particle in the range 38-45µm to 2000-2360µm. The findings support the previous statement above in that the volatile yield was found to decrease with increasing particle size, which is in accordance with the findings of Gokhale et al., 1986). The study of Morris (1993) was performed under mild heating rate conditions (10-30 Kmin\(^{-1}\) up to 900°C) and the trend in the total yield of various gas species was monitored as a function of particle size for a sub-biuminous coal. The results indicated that there was a slight increase in the tar yield with increasing particle size while the yields of H₂O, CO, CH₄, H₂, and CO₂ all decreased, and can account for the observed decrease in the total volatiles yield. A previous study by Morris (1990) under similar reaction conditions, however employing higher maximum temperatures and higher rank coals, produced slightly different results. At temperatures of 1000°C, 1100°C, and 1200°C the methane yield was found to increase consistently with particle size, as did the hydrogen yield. The yields of CO and CO₂, however, were found to decrease with particle size at the two higher temperatures and increase with particle size at 1000°C. This tends to suggest that the particle size effects are codependent on the maximum temperature and coal type, and that a transition in the dominating mechanism may be occurring at approximately 1000°C for the coals used in the earlier study.

The complexity of the particle size effect is again highlighted by Griffen et al.(1993) who noticed that the effect of the particle size on the tar yield was codependent on the heating rate employed, for 63-75 and 106-125 µm particles. At mild heating rates (10 Ks\(^{-1}\)), the increase in particle size decreased the tar yield by approximately 0.5wt%. Higher heating rates (1000 & 20,000 Ks\(^{-1}\)) resulted in a corresponding decrease in the tar yield of 3-4wt% and 5-6wt%, respectively. The explanation proposed is that larger particles induce competition between intraparticle transport and secondary reactions within the pore structure (Griffen, 1993). Further to this, Griffen et al. (1993) proposed that the heating rate may modify the particle size effect via any of the following reasons ; 1) larger heating rates may increase the driving force for internal mass transfer by increasing intraparticle concentration gradients, 2) changes in heating rate may change coal morphology and hence the accessibility, surface area, and chemistry of reactive interfaces, as well as the characteristic length scales for
physical transport - softening and volatiles generation may temporarily transform relatively porous coal into a molten material consisting of bubbles, mineral matter, and unsoftened macerals dispersed in a liquid continuum, which, before resolidification, may swell into a cenosphere or other shape drastically different from that of the original coal; one effect can be a major decrease in the distance tar must travel to escape the substrate internals, and 3) increasing heating rate increases contributions from chemical reactions with higher activation energies - tar yields would be affected when their generation and depletion reactions have significantly different activation energies.

What can be drawn from the sensitivity studies summarised above is that the devolatilization of large coal particles is complicated, and no single parameter (temperature, heating rate, or pressure) can explain the trends observed in the evolution of volatiles. Further investigation of the devolatilization process will require careful consideration of the role of each of these parameters in the study being undertaken, and the conclusions deduced from such a study must take into account the complex interactions between these parameters.

2.2.4 **Implications of Devolatilization for Fluidized Bed Combustion, Gasification and Carbonisation.**

The volatile matter content of low-rank coals, particularly after drying, can be as high as 50 to 60wt% of the raw coal feed. This implies that 50 to 60wt% of the feed entering a combustor, gasifier or carboniser is transformed to gaseous volatile matter, leaving the remaining fraction as char (the residual fixed carbon and ash). The sheer volume of these gases produced during devolatilization is likely to have a significant influence on the performance of these reactors, and in the subsequent design and scale-up of commercial scale processes.

The release of volatile gases into the gas-phase of a fluidised bed combustor, gasifier, or carboniser can have a number of consequences in terms of the homogeneous and heterogeneous reactions which take place in the bed (Pyatenko et al., 1992).
Chapter 2

Literature Review

Stubington et al. (1997) noted that the combustion of volatiles in a fluidized bed combustor influences their design and operation via the following means: it affects the distribution of oxygen across the bed, the coal particle feed point spacing, the split in heat release and hence heat transfer between the bed and the freeboard, and influences the release of nitrous oxide from the bed. In previous studies, Stubington and Linjewile (1993) and Stubington et al. (1991) both noted that inefficient in-bed volatiles combustion results in undesirably high freeboard temperatures and hence facilitates the need of larger heat transfer surfaces in the freeboard region. The evolution of volatiles within the bed is generally accepted to be dependent upon the mixing of the coal particle throughout the bed after injection and the rate of volatile matter release from the particles (Stubington and Linjewile, 1989; Stubington et al., 1997), and it is these factors which determine the split between the volatile released in-bed and in the freeboard. Borghi et al. (1985) noted that the oxygen and temperatures profiles in the bed are dependent on volatile release as concentrated evolution in particular regions of the bed can results in areas of oxygen depletion, and possibly cause "hot spots" within the bed. Furthermore it was suggested that the presence of in-bed volatile matter can extend the range of stable bed operation to lower temperatures due to their low ignition temperatures (Stubington et al., 1991). These comments tend to suggest that the in-bed combustion of volatiles is favoured over the combustion of volatiles in the freeboard. However, a balance must be maintained between the oxygen required for volatiles combustion, and that required to achieve sufficient char conversion.

From an environmental perspective, Borghi et al. (1985) reported that, based on pilot plant and laboratory scale studies, it has been verified that a major portion of the CO emission from fluidized beds is related to volatiles release and that most of the NO formed is derived from the oxidation of nitrogenous groups present in the volatiles. The significance of the volatiles in respect to NOx emissions was supported by Stubington and Chan (1990) while Johnsson (1994) emphasised this point in stating that the secondary reactions are quite different for char-N and volatiles-N, as well as for different volatile-N species. Garcia-Labiano et al. (1996) established that a large part of the sulfur present in the coal is released during the pyrolysis step hence having
a direct influence on SO\textsubscript{x} emissions. Agarwal et al. (1984) also noted that volatiles may contribute significantly to CO emissions and NO formation in fluidized beds, and added that the optimal design of fluidized-bed combustors and development of pollution control strategies rely intimately on understanding the mechanism of devolatilization in fluidized beds.

### 2.2.5 Summary

This review of the fundamentals of coal and coal devolatilization highlights the fact that significant work has been done into understanding the mechanisms which control coal devolatilization, and the structural changes which occur throughout the process. Structural models for the parent coal molecule have been developed via a number of analytical techniques (\textsuperscript{1}H n.m.r., \textsuperscript{13}C n.m.r., and TG-FT-i.r.) which provide a visual tool for characterising the nature of the thermally induced reactions taking place. The devolatilization process takes place via primary and secondary devolatilization reactions which in simple terms refer to the reactions which result in sections of the parent coal molecule detaching from the continuous structure, and subsequent reactions involving these detached sections, respectively. Several mechanisms for coal devolatilization have been proposed, and these mechanisms have proved to be extremely useful in rationalising the trends observed in the yields of individual gas species, as well as in the yield of char, tar, and total volatiles, when various operating parameters such as the temperature, pressure, heating rate, and particle size are varied. This work has enabled an improved understanding of the coal devolatilization process to be developed however the complexity of the process, and of the structure of low-rank coals, limits this understanding to a level at which distinct reactions cannot be comprehensively characterised.

Further to this, an increased understanding of the devolatilization process has at least two potential benefits in advanced power generation systems. Firstly, the design and scale-up of the process from pilot plant to commercial scale will depend on a thorough understanding of the influence of volatile release on the heat transfer requirements, operating conditions and dimensions of the process units required. Furthermore, the
growing demand for environmentally sound technologies, combined with the increasingly stringent emission standards being implemented, brings about the need for a greater understanding of the formation of pollutant species in such technologies with the objective of developing techniques for reducing their levels in the subsequent off-gas.

2.3 COAL DEVOLATILIZATION MODELLING

When dealing with modelling of the coal devolatilization process there are two fundamental types of models which may be employed; empirical models, or structural models. Empirical models have been used extensively throughout the literature with both pulverised coal, and large coal particle devolatilization models being developed. While these models do not rely on any detailed physio-chemical understanding of the process, they have been found to be useful in predicting the devolatilization products, and their evolution rates with a reasonable degree of accuracy. Structural models, conversely, model the thermal decomposition process based on the structure of the parent coal with a knowledge of the functional groups present and the nature of the coal macromolecule itself. Such models are not as common due mainly to their inherent complexity and their dependence on the chemical structure of the parent coal. The development of each of these model types will be addressed in the following section, along with their advantages and disadvantages.

2.3.1 STRUCTURAL MODELS FOR COAL DEVOLATILIZATION

The common thread which runs through all structural models is that they are based on a fundamental understanding of the coal structure. Much of the interest in these models lies in predicting the yields of char and tars produced during coal pyrolysis, and predicting the variations in the yields under different operating conditions. A number of structural based models have been developed including the functional group - depolymerisation, vaporisation, and cross-linking (FG-DVC) model (Solomon et al., 1988, 1990a, 1993), and the chemical percolation devolatilization (CPD) model
(Grant et al., 1989; Fletcher et al., 1990, 1992), which will be considered in more detail below.

2.3.1.1 Chemical Percolation Devolatilization (CPD) Model

The Chemical Percolation Devolatilization (CPD) model for coal devolatilization was first investigated by Grant et al. (1989) as a means for describing and predicting coal conversion behaviour based on the chemical structure of the parent coal. Using the structure as a starting point, percolation lattice statistics are employed to estimate the yield and mass distribution of the devolatilization products which emanate from the break-up of the macromolecular coal network. The CPD model requires three groups of input parameters, namely coal-independent kinetic parameters which are essentailly rate parameters, coal-dependent parameters which are used to define the chemical structure of the parent coal, and an elemental analysis of the parent coal. The kinetic rate parameters in the model are assumed to be identical for all coals, and the variation in the devolatilization behaviour for different coals is dependent on the structural parameters (Fletcher et al., 1990, 1992)

The CPD model assumes that the parent coal can be described as a macromolecular array composed of clusters of fused aromatic rings which vary in size and nature. Associated with the ring clusters are various side chains and loops, and the clusters are interconnected by a number of bridge configurations. Typically the side chains are carboxyl, hydroxyl or short chain aliphatics. The bridges connecting adjacent aromatic ring clusters are either charred bridges, or labile bridges. The char bridges remain intact throughout any given thermal process and are aromatic in nature with no substituted heteroatoms. The bridges which contribute to the break-down of the macromolecular structure are the labile bridges which contain the aliphatic carbon, oxygen, and sulphur content of the parent coal. As a labile bridge is broken, two side chains are formed which represent precursors to the formation of light gas species. If an aromatic ring cluster is completely freed from the macromolecular structure, ie all of its attached bridges are broken, this ring cluster may escape from the coal in the form of a tar. Hence the breakdown of the parent coal structure, or primary
devolatilization, is controlled by the structural model parameters (Fletcher et al., 1992).

The five structural parameters which characterise the structure of the parent coal in the CPD model are (Fletcher et al., 1992):

1. The co-ordination number (total attachments per cluster): $\sigma + 1$, which represents the average number of bridges and side chains per cluster.

2. The initial fraction of intact bridges: $P_0$, which represents the initial population of labile bridges and char bridges, and is associated with the percolation lattice statistics.

3. The initial fraction of char bridges: $C_0$.

4. The average cluster molecular weight: $MW_{\text{cluster}}$, which consists of contributions by aromatic nuclei and aliphatic moieties, and reflects the configuration of the cluster.

5. The side chain molecular weight: $MW_s$, which reflects the molecular weight of the light gases.

The kinetic rate parameters for the CPD model are derived from experimental techniques such as TG-FTIR or GC-MS, and from thermochemical kinetics. Coal structure parameters are derived directly from NMR data, except for the initial fraction of char bridges ($C_0$) which is assumed to be 0.0 for high rank coals and is determined empirically for low-rank coals by comparing the CPD model predictions with experimental tar yields (Fletcher et al., 1992). In order to simulate the breakdown of the coal structure, bonds are randomly broken within the coal macromolecule depending on the thermal treatment of the coal, and the corresponding probability of any given bond being ruptured. In this manner the formation of "loose" aromatic ring clusters which lead to tars, and of light gases from the labile bridges and side chains which result in light gas formation can be predicted (Solomon et al., 1990a).
2.3.1.2 Functional Group - Depolymerisation, Vaporisation, and Cross-linking (FG-DVC) Model.

The Functional Group - Depolymerisation, Vaporisation, and Cross-linking (FG-DVC) model has some similarities with the CPD model, however is far more extensive in its treatment of tar formation and of the behaviour of the char during devolatilization. The starting point of the model, that is the parent coal structure, is defined almost identically in principle to the CPD model. In the FG-DVC model, linear oligimers of \( l \) aromatic ring clusters having a molecular weight distribution defined by an average, \( M_{\text{avg}} \), and a standard deviation, \( \Delta M \), are linked by \( m_o \) “crosslinks” per monomer. Crosslinks are defined as points at which more than two attachments connect a cluster to another cluster. During thermal decomposition, bridges are broken and cross-links may be formed, and the molecular weight of the resultant oligimers is calculated by randomly distributing these changes (Solomon et al., 1990a).

The decomposition of the coal macromolecule is based on the following six concepts (Solomon et al., 1990a; Solomon et al., 1993a; Solomon et al., 1993b):

1) The decomposition of functional group sources in the coal yields the light gas species in thermal decomposition. The amount and evolution kinetics can be measured by t.g.-FT-i.r., the functional group changes by FT-i.r. and n.m.r.

2) The decomposition of a macromolecular network yields tar and metaplast. The amount and kinetics of the tar evolution can be measured by t.g.-FT-i.r. and the molecular weight by f.i.m.s. The kinetics of metaplast formation and destruction can be determined by solvent extraction, by Gieseler plastometer measurements, and by proton magnetic resonance thermal analysis (p.m.r.t.a.).

3) The molecular weight distribution of the metaplast depends on the network coordination number (average number of attachments per ring cluster). The coordination number can be determined by solvent swelling and n.m.r.
4) The network decomposition is controlled by bridge breaking. The number of bridges broken is limited by the available donatable hydrogen.

5) The network solidification is controlled by cross-linking. The changing cross-link density can be measured by solvent swelling and n.m.r. Cross-linking appears to occur with evolution of both CO₂ (before bridge breaking) and CH₄ (after bridge breaking). Thus low-rank coals (which evolve much CO₂) cross-link before bridge breaking and are thus thermosetting.

6) The evolution of tar is controlled by mass transport in which the tar molecules evaporate into the light gas or tar species and are carried out of the coal at rates proportional to their vapour pressure and the volume of light species. High pressures reduce the volume of light species and hence reduce the yield of heavy molecules with low vapour pressures. These changes can be studied with f.i.m.s.

As with the CPD model, a network coordination number is defined in the FG-DVC model, along with a starting probability of bridges being unbroken. As these concepts demonstrate, the evolution of light gas species is directly related to the nature of the functional groups present in the parent coal. The evolution of tars or heavier gas species however, is comparatively more complicated. In order to model tar release, it is proposed that the coal is made up of clusters of fused aromatic rings (as described in section 2.1) which have a specific number of attachments linking the cluster to the macromolecular network. The "macromolecular network coordination number" is a critical parameter in the model and is defined as the number of possible attachments which exist per aromatic ring cluster. The extent of decomposition can be predicted by the probability that an attachment is broken at any particular time. Subsequently, the rate of decomposition is controlled by the rate at which the attachments are broken and the retrogressive rate at which cross-linking occurs. The resulting tar is defined by the molecular weight of the aromatic ring cluster which has been released. It must be noted that the incorporation of diffusion allows for further breakdown of the primary tar as it is released from the pore structure as well as the possibility of repolymerisation with the macromolecular network (Solomon et al., 1993a).
Due to the slight variations in the characterisation of the parent coal structure between the CPD and FG-DVC models, the initial parameters describing the coal structure differ accordingly (Solomon et al., 1990a). In the FG-DVC model, the average molecular weight of an oligomer of aromatic ring clusters is in the range of $M_{avg} = 256\text{amu}$, while such a value is not specified in the CPD model. For a high-volatile bituminous coal the CPD model employs a network coordination number of $(\sigma+1) = 4.6$, while a value of $(\sigma+1) \sim 2.1$ is utilised in the FG-DVC model. The initial bridge population also varies and for the CPD model takes on a value of approximately $p_0 \sim 0.6$ while the FG-DVC model incorporates a value of $p_0 \sim 0.9$.

Along with variations in the structural parameters, there are some differences linked to the nature of the decomposition reactions which are assumed to contribute to devolatilization. The rate of bridge breaking in both the CDP and FG-DVC models are assumed to be coal independent and are similar in magnitude, $K_{B,CPD} = 2.6 \times 10^{15} \exp(-55 \text{ 400/RT})$ and $K_{B,FG-DVC} = 0.8 \times 10^{15} \exp(-55 \text{ 400/RT})^\dagger$. The FG-DVC model assumed that three distinct types of bridges are present; labile bridges, unbreakable bridges, and cross-links. When a labile bridge is broken, the FG-DVC requires that donatable hydrogen be available to stabilize the radicals formed. It is further assumed that all the donatable hydrogen is located in the labile bridges such that effectively only half the labile bridges can be broken. Crosslinks are also considered in the FG-DVC model and are bridges which cannot be broken which are not formed in the manner of the previous unbreakable bridges. The CPD considers the existence of both labile and unbreakable bridges, with probabilities of $L_0$ and $c_0$ respectively, such that $(c_0 + L_0) = p_0$. During devolatilization the labile bridges can break and react to form either unbreakable "char" bridges, or broken bridges.

The phenomenon of cross-linking has been dealt with intimately within the FG-DVC model via the assumption of two independent cross-linking reactions. At low temperatures, below those necessary for bridge breaking to be prevalent (ca. 250°C), cross-linking is associated with the evolution of CO$_2$ in low-rank coals. At temperatures slightly above those at which bridge breaking initiates, a second cross-

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$^\dagger$ The FG-DVC model utilised a distributed activation energy dependence, the value presented is for the centre of the distribution.
linking reaction takes place and is responsible for CH$_4$ evolution. It is assumed that one cross-link is formed per molecule of CH$_4$ and CO$_2$ released from these reactions. Conversely the CPD model does not consider cross-linking reactions explicitly, however branch points may occur when three or more attachments are formed with any individual cluster (Solomon et al., 1990a).

The distinction between the devolatilization products in the FG-DVC and CPD models also differs, with the CPD model taking the simplest approach in assuming that all molecules not attached to the macromolecular network are essentially evolved as tars. In the FG-DVC model, mass transport equations have been included and it is assumed that the molecular weight dependent vapour pressure controls whether or not the molecules are released into the gas phase, and then convective transport allows these gases to escape from the coal particle. Thus the tar fraction comprises that in the lower molecular weight region with sufficiently high vapour pressures. The remaining fraction is trapped within the coal as either solvent extractable material, or liquids.

### 2.3.1.3 Advantages and Disadvantages of Structural Models

Structural models for predicting coal devolatilization behaviour have been shown to be extremely effective in predicting a number of coal properties. The CPD and FG-DVC models are useful in predicting tar, light gas, and char evolution during devolatilization (Fletcher et al., 1990, 1992; Solomon et al., 1990a; Solomon et al., 1993a; Solomon et al., 1993b), while the FG-DVC model has also been shown to predict behaviour such as cross-linking, hydrogen utilisation, and fragmentation during devolatilization (Solomon et al., 1990a; Solomon et al., 1993a; Solomon et al., 1993b). Furthermore the FG-DVC model has been applied to predict the solvent swelling and insolubility behaviour of coals, and can distinguish between the evolved tars, solvent extractable and liquid products generated during devolatilization with reasonable success, which highlights the robustness of these models (Solomon et al., 1990a; Solomon et al., 1993a; Solomon et al., 1993b).
The robustness of these models can be related directly to the detailed information regarding the structure of the parent coals which are required as model input parameters. The CPD model utilises data obtained using NMR techniques to characterise the coal structure, while TG-FTIR or GC-MS results, along with thermochemical analysis, are utilised to determine the kinetics rate parameters. Similarly, techniques including t.g.-FT-i.r., n.m.r., solvent extraction, Gieseler plastometry, p.m.r.t.a., and f.i.m.s. have all been used to provide specific information regarding the coal behaviour for the FG-DVC models. While these experimental techniques are all sufficiently developed and the data may be readily obtained, the quantity of data required is significant and highly coal-specific which reduces the scope of the model to a unique coal type which corresponds to the input data. In other words, for each coal type investigated a large amount of input data is necessary in order to apply these structural models. The major success of these models is in the prediction of relative tar and char evolution trends with operating conditions, due to their ability to consider the coal structural behaviour. As will be discussed in Section 2.3.2, empirical models can be reliably used to predict the release of light gas species (up to ~ C₃ hydrocarbons), however are limited in their applicability to tar and char yield predictions. Computationally, structural models present a significant challenge, particularly the FG-DVC model which has included mass transfer processes into the model thus enhancing the model complexity. The CPD model is generally considered to be more computationally efficient than the FG-DVC model in its treatment of the coal structure (Solomon et al., 1990a) however, as mentioned, is not as complex in its consideration of the structural changes occurring, and is consequently limited in this aspect.

2.3.2  **Empirical Models for Coal Devolatilization**

While structural models have been developed based on an appreciation of the structure of coals and the nature of the transformations which are occurring, empirical models take a less sophisticated approach and refer to a more global approach to devolatilization modelling. Empirical models have been used extensively throughout the literature and were originally developed to model pulversied, bituminous coal
particle devolutilization. This section will deal with several empirical modelling techniques, varying in complexity, which have been employed in models for both pulverised and large coal particle devolutilization. A more detailed review of aspects pertinent to large coal particle devolutilization will be considered later in Chapter 2, while this section provides a more general review of empirical modelling approaches.

2.3.2.1 Single First Order Arrhenius Models

In early attempts to model coal devolutilization, the complex nature of the chemical reactions and transport phenomena occurring within the particle were not as well understood as at this time. Consequently, simplified approaches to modelling were considered with the simplest being the use of single first order Arrhenius type models. Such models have been used by Van Krevlin et al. (1951), Stone et al. (1954), Shapatina et al. (1960), Howard and Essenhigh (1967), Wiser et al. (1967), Badzioch and Hawsely (1970), Anthony et al. (1975), Kobayashi et al. (1978), Moloney and Jenkins (1984), Niksa et al. (1984), Sandhu et al. (1985), Gokhale et al. (1986), Fu et al. (1987), and Sharma et al. (1994) for coals ranging from bituminous to brown coals, and the general form of the model is presented in Equation (2.1).

\[ \frac{dV}{dt} = k(V^* - V) \]  

where, \( V^* \) is the ultimate yield of volatiles (g/g dry coal) and \( V \to V^* \) as \( t \to \infty \). The kinetic rate constant, \( k \), takes on the conventional Arrhenius form, namely,

\[ k = k_0 e^{-\frac{E}{RT}} \]  

A major focus of the experimental work into devolutilization has been to provide data in support of these models. More specifically, information regarding the ultimate volatile yield, \( V^* \), the rate constant, \( k_0 \), and the activation energy, \( E \), have been sought using a number of experimental techniques.
In the investigation of Badzioch and Hawksley (1970), experimental data for coal thermal decomposition was collected in a laminar flow furnace in which nitrogen is introduced at the top of the vertical reactor along with a stream of 20µm coal particles. The particles are collected in a water cooled collection probe which can be adjusted vertically to enable the particle residence time to be varied and the mass loss with time to be determined. The furnace temperature could be controlled up to 1000°C enabling the Arrhenius parameters to be determined. The rationale behind using such a reactor was to simulate as closely as possible the conditions within a p.f. boiler. Using the transient mass loss data collected for a number of coal types, Badzioch and Hawksley (1970) determined the kinetic parameters and found that the activation energy could be considered to be constant at ~17.8 kcal mol\(^{-1}\) (74.5 kJ mol\(^{-1}\)). This value was found to be applicable to both swelling and non-swelling bituminous coals. The rate constant for the non-swelling coals was found to range between 0.836×10\(^{5}\) s\(^{-1}\) and 2.81×10\(^{5}\) s\(^{-1}\), while that of the swelling coals was somewhat higher and in the range 3.12×10\(^{5}\) s\(^{-1}\) to 6.51×10\(^{5}\) s\(^{-1}\) for the coals investigated.

Kobayashi et al. (1977) also utilised the laminar flow furnace of Badzioch and Hawksley (1970) to deduced kinetic parameters for the devolutilization of a lignite and a bituminous coal. The devolutilization rates were found to be similar and could be described by a rate constant of 6.6×10\(^{4}\) s\(^{-1}\), and an activation energy of 25 kcal mol\(^{-1}\) (104.7 kJ mol\(^{-1}\)), and these parameters were also used by Sandhu et al. (1985) in their modelling studies. Maloney and Jenkins (1984) used an entrained flow reactor to study a high-volatile bituminous coal and deduced that the rate parameters were dependant on the extent of devolutilization with the rate constant increasing from 1.9×10\(^{4}\) s\(^{-1}\) to 9.1×10\(^{4}\) s\(^{-1}\), and the activation energy increasing from 15 kcal mol\(^{-1}\) (62.8 kJ mol\(^{-1}\)) to 22 kcal mol\(^{-1}\) (92.1 kJ mol\(^{-1}\)) as the extent of devolutilization increased from 20% to 70%. Sharma et al. (1994) reported activation energies of approximately 32 kcal mol\(^{-1}\) for two Indian lignites, Winter et al. (1997) reported parameters ranging from \(k_o = 1.7×10^3\) s\(^{-1}\) to \(k_o = 5.3×10^5\) s\(^{-1}\) and \(E = 14.9\) kcal mol\(^{-1}\) (62.4 kJ mol\(^{-1}\)) to \(E = 28.9\) kcal mol\(^{-1}\) (121 kJ mol\(^{-1}\)) for a bituminous and a sub-bituminous coal respectively, whilst Niksa et al. (1984) reported rate constants of \(k_o = 7050\) s\(^{-1}\) and \(E = 17.2\) kcal mol\(^{-1}\) (72 kJ mol\(^{-1}\)).
Anthony et al. (1975) used a mire mesh apparatus to investigate the devolatilization of 70μm coal particles. The apparatus utilises an electrically heated stainless steel screen (325 mesh) onto which a thin layer (approximately monolayer) of less than 10mg of coal was dispersed. The apparatus is housed inside a vessel which can be evacuated to remove oxygen prior to heating. Upon heating, purified helium is used to carry the product gases away from the coal to reduce secondary reactions. The apparatus is heated at a set heating rate (controlled by variable resistors) to a specified temperature, maintained at the specified temperature for a controlled time, prior to being cooled by natural convection. The weight of the combined screen and coal sample is recorded before and after each run in order to obtain the weight loss profiles (Anthony et al., 1975).

Based on an analysis of the data, Anthony et al. (1975) deduced that the Arrhenius parameters were sensitive to the heating rate employed. For a lignite it was found that the activation energy increased from 9.0 kcal mol\(^{-1}\) (37.7 kJ mol\(^{-1}\)) to 11.1 kcal mol\(^{-1}\) (46.5 kJ mol\(^{-1}\)) as the heating rate increased from 650°C s\(^{-1}\) to 10\(^4\)°C s\(^{-1}\), while the rate constant increased from 60.7 s\(^{-1}\) to 283 s\(^{-1}\). Contrastingly for a bituminous coal, the activation energy decreased from 13.3 kcal mol\(^{-1}\) (55.7 kJ mol\(^{-1}\)) to 11.8 kcal mol\(^{-1}\) (49.5 kJ mol\(^{-1}\)) and the rate constant decreased from 1800 s\(^{-1}\) to 706 s\(^{-1}\) over an identical range of heating rates. Furthermore it was found that the kinetic parameters were sensitive to the surrounding gas pressure with both the activation energy and rate constant decreasing substantially at increased pressures. It was concluded that, although good fits can be achieved using the single first order reaction model with variable kinetic parameters, the applicability of the model is limited to the availability of experimental data from which kinetic parameters can be derived. In addition, Anthony et al. (1975) found that the ultimate volatile yield was also dependent on the experimental conditions which further diminishes the models credibility.

Fu et. al. (1987) used a single first order model to predict the devolatilization behaviour of large coal particles however assumed the activation energy and rate constant were temperature dependant. Using this technique it was proposed that the temperature dependent activation energy and rate constant values were applicable to
modelling volatiles release from all coal types (Fu et al., 1987), which is in contrast with previous reports (Badzioch and Hawksley, 1970; Anthony et al., 1975; Maloney and Jenkins, 1984). Gokhale et al. (1986) also used a single first order model in their large particle devolatilization model into which diffusion effects were considered. Activation energy values derived from fixed bed experiments were found to be quite low (4 to 11 kcal mol\(^{-1}\), 16.7 to 46.1 kJ mol\(^{-1}\)) which was concluded to be due to the diffusion mechanisms controlling the devolatilization process. The activation energy was found to be a complex function of the particle size and pressure, and it would suggest from this that the controlling mechanism may be changing over the range of parameters tested. For example, particles in the range -2.0 +1.0 mm were found to have activation energies which varied from 11.4 kcal mol\(^{-1}\) (47.7 kJ mol\(^{-1}\)) at 30 psig, to 4.8 kcal mol\(^{-1}\) (20.1 kJ mol\(^{-1}\)) at 300 psig, to 11.9 kcal mol\(^{-1}\) (49.8 kJ mol\(^{-1}\)) at 375 psig. For the same range of operating pressures, the activation energies for -9.0 + 6.0 mm particles were 7.08 kcal mol\(^{-1}\) (29.6 kJ mol\(^{-1}\)), 10.6 kcal mol\(^{-1}\) (44.4 kJ mol\(^{-1}\)), and 11.7 kcal mol\(^{-1}\) (50.0 kJ mol\(^{-1}\)). At 30 psig, activation energies of 11.4 kcal mol\(^{-1}\) (47.7 kJ mol\(^{-1}\)), 3.9 kcal mol\(^{-1}\) (16.3 kJ mol\(^{-1}\)), and 7.08 kcal mol\(^{-1}\) (29.6 kJ mol\(^{-1}\)) were obtained for particles in the ranges -2.0 + 1.0 mm, -4.0 + 3.0 mm, and -9.0 + 6.0 mm respectively. At 300 psig the corresponding activation energies are 4.8 kcal mol\(^{-1}\) (20.1 kJ mol\(^{-1}\)), 3.4 kcal mol\(^{-1}\) (14.2 kJ mol\(^{-1}\)), and 10.6 kcal mol\(^{-1}\) (44.4 kJ mol\(^{-1}\)).

Badzioch and Hawksley (1970) noted that, in accordance with Anthony et al. (1975), the ultimate volatile yields from devolatilization were sensitive to the operating conditions, and formulated a correlation to account for the variation in the volatile yield with temperature. They correlated the actual volatile yield with the volatile matter content of the original coal obtained by standard techniques according to:

\[
\frac{V^*}{VM_o} = 1 - C
\]

(2.3)

where \(C\) was found to be temperature dependent and could be represented as:

\[
C = \exp[-K_1(T - K_2)]
\]

(2.4)
For the non-swelling coals $C$ was found to be relatively constant at $C \sim 0.14$. For the swelling coals $C$ was found to be coal dependent with values of $K_1$ and $K_2$ ranging from 0.00277 K$^{-1}$ to 0.00374 K$^{-1}$, and 438 K to 746 K, respectively.

It is apparent that single first order reaction models have been used extensively in the literature to model coal devolatilization. These studies have highlighted that, although effective, the kinetic parameters of the model are extremely sensitive to the operating conditions, and must be varied accordingly in order to provide a reasonable fit. The model is subsequently limited in its application to conditions at which supporting experimental data is available, which reduces the overall scope of these model types. The simplicity of these models however is a strength, which would be advantages in more complicated models incorporating char combustion or gasification reactions such as that of Winter et al. (1997).

### 2.3.2.2 n$^{th}$ Order Reaction Models

An extension of the first order reaction models is to consider that devolatilization can be modelled by a single n$^{th}$ order Arrhenius model ie.

\[
\frac{dV}{dt} = k(V^* - V)^n
\]

(2.5)

This technique was used by Peeler and Poynton (1992) in their attempt to predict large particle devolatilization, as well as in the work of Li et al., (1996) in a model for simulating pulverised coal behaviour. Peeler and Poynton (1992) deduced that the n$^{th}$ order model was extremely useful in predicting their mass loss data for particle in the size range 1.4-29mm, and ranging in rank from sub-bituminous to semi-anthracite. Data was obtained by suspending the coal particles from a microbalance in a hot gas stream and recording the transient weight loss profile. Experiments were conducted at only one temperature (900°C) and it was that the rate constant, $k$ in Equation (2.5), was related to the particle size via:
\[ k = aD^b \]  \hspace{1cm} (2.6)

where \( a \) and \( b \) are coal dependent parameters. The reaction order was found to vary between \( n = 0.4 \) and \( n = 0.6 \) depending on coal type.

Li et al. (1996) used t.g.a techniques to obtain transient mass loss profiles from -125 + 75 \( \mu \text{m} \) coal particle at various heating rates, from which activation energy and reaction order data could be obtained. Activation energies were found to be heating rate dependant, as previously deduced (Anthony et al., 1975), as was the apparent reaction order. In contrast to the reaction orders of Peeler and Poynton (1992), Li et al. (1996) found reaction orders of between \( n = 1.27 \) and \( n = 4.5 \) which is most likely due to the massive discrepancy in the particle sizes used in the two studies. The lower reaction orders would seem to infer that the devolatilization of larger coal particles is becoming increasingly less kinetically controlled as the particle size increases, and phenomena such as heat and mass transfer are becoming increasingly important.

### 2.3.2.3 Two-competing Reaction Models.

The inability of the single first order and \( n^{th} \) order reaction models to replicate the devolatilization behaviour of coals over a range of operating conditions lead to the use of more sophisticated reaction models such as the two-competing reaction models. An example of this approach is the model of Doolan et al. (1982) who combined the single first order volatile evolution model with a similar term describing volatiles decomposition according to Equation (2.7).

\[
\frac{dV_i}{dt} = k_{yi}(V_i^* - V_i) - k_{di}V_i \tag{2.7}
\]

\( V_i \) represents the yield of species \( i \) and \( V_i^* \) represents the ultimate yield of species \( i \). \( k_{yi} \) denotes the rate of evolution of species \( i \) which is proportional to the amount of species \( i \) remaining in the coal \( (V_i^* - V_i) \), while \( k_{di} \) refers to the decomposition rate of species \( i \) which is related to the amount of species \( i \) which has been formed \( (V_i) \).
similar approach was used by Cliff et al. (1984), and Yang and Wang (1990) in their devolatilization modelling studies. Sprouse and Schuman (1981) and Jamaluddin et al. (1985) also used the two-competing reaction model in studies comparing the effectiveness of a variety of model types.

Doolan et al. (1982) concluded that the two-competing reaction model was useful for describing the evolution of individual volatile species, and the varying trends with temperature, for particles of  \( d_p < 50 \mu m \) in a shock tube furnace. Cliff et al. (1984) deduced kinetic parameters for the two-competing reaction model from experimental data obtained from two reactor types; a shock tube furnace and a fluid-bed reactor. It was found that the "best-fit" kinetic parameters varied significantly between the two reactors. This then suggests that the two-competing reaction model has limitations relating to the applicability of kinetic parameters derived under specific conditions.

Jamaluddin et al. (1985) investigated the ability of the two-competing reaction model to predict devolatilization data, and a comparison was made between the effectiveness of the two-competing reaction model and the single first order reaction model. The two-competing reaction model was able to provide better predictions over a range of heating rates and final temperatures than the single first order reaction model, using constant kinetic parameters for each individual model, thus suggesting some advantages in using the two-competing reaction model. A major improvement which arises from utilising the two-competing reaction model is in predicting the yields of various volatile species at higher temperatures. Heavier volatiles, such as \( C_3H_6 \), \( C_3H_8 \), \( C_4H_6 \), and \( C_4H_8 \), undergo secondary cracking reactions at higher temperatures which can be accounted for by the volatiles decomposition term in the two-competing reaction model (Doolan et al., 1982). Similarly the variation in the tar, char, and total volatile yields with increasing reactor temperature can be predicted with greater accuracy using the two-competing reaction model (Cliff et al., 1984).
2.3.2.4 Multiple Parrayl Reaction Models

Tomeczek and Kowol (1990), in the development of a large particle coal devolatilization model, proposed a devolatilization model in which particular volatile species were evolved via a number (4 to 6) of simultaneous, independent, first order reactions. Each species could be considered to be derived from a number of “sources” within the coal structure each of which yielded the species according to differing chemical kinetics. Accordingly, the evolution of any gas species was given by (Tomeczek and Kowol, 1990):

$$\frac{dm_i}{dt} = \sum_{k=1}^{4 \text{or} 6} k_{o,i} \exp\left(\frac{-E_{i,k}}{RT}\right)(m_{i,k,\infty} - m_{i,k})$$  (2.8)

where $m_i$ is the total yield of species $i$, $k_{o,i}$ is the Arrhenius frequency factor for species $i$, $E_{i,k}$ is the activation energy for evolution of species $i$ from source $k$, $m_{i,k}$ is the yield of species $i$ from source $k$, and $m_{i,k,\infty}$ is the ultimate yield of species $i$ from source $k$. As can be seen it was assumed that the frequency factor was constant regardless of the respective volatile sources leaving $E_{i,k}$ and $m_{i,k,\infty}$ as variables for each volatiles source. Therefore for each volatile species effectively eight or twelve variables were used to describe the volatile evolution. Tomeczek and Kowol (1990) were able to achieve relatively good model predictions for a number of volatiles species as would be expected considering the number of variables. This was based on data collected for particles ranging in size from 0.75-0.9mm to 10mm in a fluidised bed at 870K.

While Tomeczek and Kowol (1990) considered that individual volatiles could be derived via several (4 to 6) simultaneous, independent, first order reactions, a large number of models have been developed in which coal devolatilization is described by an infinite number of simultaneous, independent, first order reactions (Anthony et al., 1975, Agarwal et al., 1984a; Agarwal et al., 1984b; Borghi et al., 1985; Agarwal, 1985; Agarwal, 1986; Agarwal et al., 1987; Wildeger-Gaissmaier and Agarwal, 1990; Andres et al., 1991; Wang et al., 1994; Adesanya and Pham, 1995; Miura, 1995; Maki et al., 1997). Anthony et al. (1975) showed that if coal devolatilization is
considered to take place via a large number of independent first order Arrhenius reactions, each of which can be represented by Equation (2.1), then the transient yield of species \( i \) with time can be represented by:

\[
\frac{V_i^* - V_i}{V_i^*} = \int_{-\infty}^{\infty} \exp \left( \frac{-E_{a,i}}{RT} \right) dt f(E) dE
\]  

(2.9)

where \( E_{a,i} \) is the mean activation energy for the infinite independent first order reactions, and \( \sigma_i \) is the corresponding standard deviation in activation energies. The term \( f(E) \) refers to the distribution of the activation energies around the mean activation energy. For example, if a Gaussian distribution of activation energies is assumed, then \( f(E) \) is given by Equation (2.10).

\[
f(E) = \frac{1}{\sigma_i \sqrt{2\pi}} \exp \left( -\frac{(E - E_{o,i})^2}{2\sigma_i^2} \right)
\]  

(2.10)

Anthony et al. (1975) reported the following pressure independent kinetic data for mass loss from a lignite; \( k_o = 1.67 \times 10^{13} \text{ s}^{-1} \), \( E_o = 236 \text{ kJ.mol}^{-1} \), and \( \sigma = 45.7 \text{ kJ.mol}^{-1} \).

Wang et al. (1994) studied the devolatilization of two lignite coals in a heated grid reactor using particle in the size range \( d_p < 70 \mu m \). The devolatilization kinetics were found to be dependent on both the final temperature and the coal type and as with Anthony et al. (1975) a frequency factor of \( k_o = 1.67 \times 10^{13} \text{ s}^{-1} \) was used. Mean activation energy values of 170.2 kJ.mol\(^{-1}\) and 179.7 kJ.mol\(^{-1}\) were calculated for Hulinhe lignite at final temperatures of 600\(^\circ\)C and 800\(^\circ\)C respectively, at a heating rate of 600\(^\circ\)C s\(^{-1}\). At a similar heating rate, Yima lignite recorded mean activation energies of 193.4 kJ.mol\(^{-1}\) and 205.1 kJ.mol\(^{-1}\), at 600\(^\circ\)C and 800\(^\circ\)C respectively. This was explained by the slightly higher rank of the Yima coal. As the coal rank increases the structure becomes more aromatic in nature and thus more tightly bound. Therefore the decomposition on higher rank coals requires more energy to break the stronger bonds hence the higher observed mean activation energies (Wang et al., 1994). The
increase in the mean activation energy with temperature is due to the shift in the overall distribution of reactions occurring. When the coal is heated to 600°C, not all of the coal devolatilization reactions proceed. Upon further heating, reactions take place which have higher activation energies and these are accounted for by the increase in the overall mean activation energy. While the variation in the activation energies was well accounted for, the standard deviation in activation energies did not show similarly rational trends. For the Hulinhe lignite, $\sigma$ was reasonably constant at 32.6 kJ.mol$^{-1}$ and 31.8 kJ.mol$^{-1}$ at final temperatures of 600°C and 800°C respectively, yet for Yima lignite $\sigma$ varied from 22.1 kJ.mol$^{-1}$ to 31.1 kJ.mol$^{-1}$ over the same temperature range. This result was not explained however generally it could be concluded from this study that the devolatilization kinetics applicable to the multiple parallel reaction model remain dependent on the temperature and coal type.

Adesanya and Pham (1995) investigated the devolatilization of large bituminous coal particles using a model which incorporated a multiple parallel coal devolatilization model. It was found that a mean activation energy of 217 kJ.mol$^{-1}$ and a standard deviation in activation energies of 49 kJ.mol$^{-1}$ produced model predictions comparable with the supporting experimental data derived from 16mm particle in a convective flow reactor at 650°C. Comparing these kinetic parameters with those of Wang et al. (1994) it would seem to further support that higher mean activation energy values are essential to describe the devolatilization behaviour of higher rank coals. This may not strictly be true as the frequency factor was not reported in the study of Adesanya and Pham (1995) however a general trend is apparent.

A significant amount of work utilising the multiple parallel reaction models has been conducted by Agarwal and co-workers over a number of years with an emphasis on the modelling of primarily large particle coal devolatilization, and to a lesser extent combined drying and devolatilization, devolatilization and combustion, and drying, devolatilization, and combustion modelling. Agarwal et al. (1984a) developed the initial large particle coal devolatilization model and concluded that this approach was able to predict both the overall mass loss and the evolution of individual gas species from large coal particles with reasonable accuracy thus confirming the applicability of
the model. It is obvious from Equation (2.9) that as time increases the computational time necessary for calculating the volatile yield will become increasingly larger and, to alleviate this, Agarwal et al. (1984b) proposed an alternative approach for reducing the complexity of the calculation although it is apparent that this approach has not been continued in the further studies. The overall devolatilization of a Mississippi lignite was subsequently modelled with success, generating kinetic parameters of $k_o = 1.67 \times 10^{13} \text{s}^{-1}$, $E_o = 192 \text{kJ.mol}^{-1}$, and $\sigma = 40 \text{kJ.mol}^{-1}$ which again are comparable with those reported in previously reviewed work (Wang et al., 1994; and Adesanya and Pham, 1995).

Agarwal (1985) continued this work by considering modelling of the evolution of methane from two high-volatile bituminous, and one sub-bituminous coal. Again this modelling approach proved to be reasonably successful however an over-riding assumption was formed suggesting that the devolatilization kinetics for methane evolution were coal independent. While the previously reviewed studies have dealt mainly with the total volatile yields (Agarwal et al., 1984b; Wang et al., 1994; and Adesanya and Pham, 1995), it has generally been observed that the devolatilization kinetics were at least coal rank dependent, if not dependent on the coal type which is in contrast to the assumption of Agarwal (1985). This model was then extended by Agarwal et al. (1987) to consider the evolution of a range of volatile species ($\text{H}_2$, $\text{CO}$, $\text{CO}_2$, $\text{CH}_4$, $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_6$, $\text{C}_3\text{H}_6$, and $\text{C}_3\text{H}_8$) and the estimation of appropriate kinetic parameters. Again it was concluded that the kinetic parameters were insensitive to the coal type and comparisons between the model predictions and experimental data obtained using a variety of reactor types showed encouraging results. Table 2.2 outlines the kinetic parameters suggested by Agarwal et al. (1987) for evolution of the various volatile species. In Table 2.2, $V_i^*$ refers to the fraction of the total yield of a volatile species which is derived from a particular source. For example, CO evolves during devolatilization from two sources each of which has different kinetic parameters and 33% of the total CO yield is evolved from one source with a second source contributing the remaining 67%.
As extensions of the aforementioned devolatilization modelling studies, Agarwal (1986) developed a combined devolatilization and volatile combustion model for single large coal particles, and Wildegger-Gaissmaier and Agarwal (1990) reported a model for the drying, devolatilization and volatile combustion of single large, wet coal particles while Borghi et al. (1985) developed a model combining the multiple parallel devolatilization reaction model with models for volatiles and char combustion. These studies highlight the flexibility of the multiple parallel models for integration into more comprehensive models depicting the high temperature behaviour of coal particles. In the two former cases the models were found to be reasonably successful which confirms this as a feasible coal devolatilization modelling approach while no direct comparison with experimental data was reported for the latter case.

Andres et al. (1991) determined multiple parallel reaction model kinetic parameters for the evolution of CO₂, CH₄ and S-compounds from four coals ranging in rank from peat to a sub-bituminous coal. It was considered that each species was derived from two sources within each coal type, and that unique kinetics could be used to describe gas evolution from the individual coal types. For CO₂, mean activation energies ranging from 144 kJ.mol⁻¹ to 183 kJ.mol⁻¹ and 181 kJ.mol⁻¹ to 228 kJ.mol⁻¹ were obtained for the two respective sources, while the corresponding ranges for CH₄ were 175 kJ.mol⁻¹ to 208 kJ.mol⁻¹ and 208 kJ.mol⁻¹ to 223 kJ.mol⁻¹. These values are slightly lower than those of Agarwal et al. (1987). However the frequency factors are lower for Andres et al. (1991) which will partially compensate for this difference. It should be noted that the mean activation energies for CO₂ evolution differed significantly for the coals tested, while those for methane evolution were far less varying. In fact, based on the kinetic parameters reported for all the coals tested, at least 65% of the methane yield was derived from a source whose mean activation energy was between 205.9 kJ.mol⁻¹ and 206.7 kJ.mol⁻¹ which would suggest that methane evolution kinetics may be considered insensitive to coal type. Conversely it would follow that CO₂ evolution kinetics remain coal dependent.

Recent work by Miura (1995) and Maki et al. (1997) has focussed on modelling coal devolatilization with a multiple parallel reaction model, with the over-riding
assumption that the distribution of activation energies around the mean activation energy may not be limited to a Gaussian distribution. Under this assumption, the activation energy distribution can be skewed either side of the mean which gives the model greater flexibility providing the nature of the distribution can be determined. Furthermore, the assumption of a constant $k_o$ value was also discounted and the authors were able to provide a technique which enabled both the distribution function, $f(E)$, and $k_o$ to be determined from relatively easy to obtain t.g.a data. The frequency factor was related to the activation energy according to:

$$k_o = \alpha e^{\beta E}$$  \hspace{1cm} (2.11)

**Table 2.2** Kinetic parameters for the evolution of individual gas species (*after Agarwal et al., 1997*)

<table>
<thead>
<tr>
<th>Species</th>
<th>Model parameter</th>
<th>Recommended Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>$V_i$</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>$E_{o,i}$ (kJ.mol⁻¹)</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>$\sigma_i$ (kJ.mol⁻¹)</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>$\log_{10}k_{o,i}$</td>
<td>13.22</td>
</tr>
<tr>
<td>CO</td>
<td>$V_i$</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>$E_{o,i}$ (kJ.mol⁻¹)</td>
<td>216</td>
</tr>
<tr>
<td></td>
<td>$\sigma_i$ (kJ.mol⁻¹)</td>
<td>28.8</td>
</tr>
<tr>
<td></td>
<td>$\log_{10}k_{o,i}$</td>
<td>13.22</td>
</tr>
<tr>
<td>CO₂</td>
<td>$V_i$</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>$E_{o,i}$ (kJ.mol⁻¹)</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>$\sigma_i$ (kJ.mol⁻¹)</td>
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<td></td>
<td>$\log_{10}k_{o,i}$</td>
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<td>CH₄</td>
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<td>$\sigma_i$ (kJ.mol⁻¹)</td>
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<td></td>
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<td>13.22</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>$V_i$</td>
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</tr>
<tr>
<td></td>
<td>$E_{o,i}$ (kJ.mol⁻¹)</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>$\sigma_i$ (kJ.mol⁻¹)</td>
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<tr>
<td></td>
<td>$\log_{10}k_{o,i}$</td>
<td>12.23</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>$V_i$</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>$E_{o,i}$ (kJ.mol⁻¹)</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>$\sigma_i$ (kJ.mol⁻¹)</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>$\log_{10}k_{o,i}$</td>
<td>12.23</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>$V_i$</td>
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<td></td>
<td>$E_{o,i}$ (kJ.mol⁻¹)</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>$\sigma_i$ (kJ.mol⁻¹)</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>$\log_{10}k_{o,i}$</td>
<td>13.22</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>$V_i$</td>
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<td></td>
<td>$E_{o,i}$ (kJ.mol⁻¹)</td>
<td>235</td>
</tr>
<tr>
<td></td>
<td>$\sigma_i$ (kJ.mol⁻¹)</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>$\log_{10}k_{o,i}$</td>
<td>13.22</td>
</tr>
<tr>
<td>C₅H₈</td>
<td>$V_i$</td>
<td>1.0</td>
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<tr>
<td></td>
<td>$E_{o,i}$ (kJ.mol⁻¹)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>$\sigma_i$ (kJ.mol⁻¹)</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>$\log_{10}k_{o,i}$</td>
<td>13.22</td>
</tr>
</tbody>
</table>
Miura (1995) found that the distribution function \( f(E) \) for total volatile release was approximately Gaussian however the distribution was skewed thus confirming their initial hypothesis of a non-uniform activation energy distribution. Maki et al. (1997) went one step further and considered the distribution function for the evolution of particular volatile species and again found some deviation from the assumed Gaussian distribution. No statistical analysis was presented to quantify the magnitude of the variation in the distribution function. Based on these studies (Miura, 1995; and Maki et al., 1997), the technique presented does enable the evolution trends of both the total and of individual volatile species to be estimated with reasonably high precision, and improvements on the more conventional Gaussian assumption have been shown.

Sprouse and Schuman (1981) compared the effectiveness of the two-competing and multiple parallel reaction models, and Jamaluddin et al. (1985) compared the effectiveness of the single, two-competing, and multiple parallel reaction models for predicting coal devolatilization behaviour. Sprouse and Schuman (1981) concluded that the multiple parallel reaction model was the most robust devolatilization model based on its ability to predict the devolatilization trends over a range of particle heating rates, maximum temperatures, and particle residence times. Jamaluddin et al. (1985) observed no appreciable improvement in the model predictions for the multiple parallel model when compared to the two-competing reaction model, however both of these models were significantly better than the single reaction model. The conclusion of Jamaluddin et al. (1985) was based on a limited range of heating rates (\( 10^4 - 10^6 \) K s\(^{-1}\)) and maximum temperatures (1273 - 1773 K) while Sprouse and Schuman (1981) covered a wider range of operating conditions (1000 - 2100 K, 180 - 10000 K s\(^{-1}\)) which would give a greater appreciation for the overall effectiveness of the respective models. Ultimately it would be reasonable to suggest that the multiple parallel reaction model can be favoured over the two-competing reaction model given the robust nature of the model, as observed by Sprouse and Schuman (1981).
2.3.2.5 Advantages and Disadvantages of Empirical Models

The greatest benefit to coal devolatilization modelling presented by empirical coal devolatilization models is their relative simplicity when compared with the more sophisticated structural based models. This simplicity is derived directly from the general assumption that, rather than considering the breaking of individual bonds within the coal macromolecule, the entire process can be represented on a more global scale by a simplified overall reaction rate. This has a second important advantage for modellers in that extensive data relating to the structure of the coal being modelled is not required. In order to model the process only the necessary kinetic parameters and particle temperature data are required. Information regarding the kinetic parameters are readily available in the literature (Agarwal et al., 1987). However, it may be necessary to generate appropriate kinetic data in which case mass loss and volatile evolution data is required under controlled conditions. The data necessary to supplement empirical models can be obtained with far simpler techniques than for structural models due mainly to the nature of the data required.

Empirical models, while providing a more computationally more simple problem, have a major drawback in that there is no distinct relation with the parent coal structure. This limits the applicability of these models to purely modelling devolatilization, and other coal properties related to the structural changes during devolatilization (such as solvent swelling etc.) can not be predicted. Furthermore, empirical models are less effective in predicting relative yields of tar, char, and volatile gases due to their total independence of the coal structure and of the coal devolatilization mechanism in general. In structural devolatilization models, the formation of tars and subsequent volatiles can be replicated relatively accurately and thus the trends can also be reproduced.

2.3.3 SUMMARY

Two distinctly different types of models for predicting coal devolatilization behaviour have been presented, and their general development, assumptions, advantages and
disadvantages have been discussed. Structural models have been shown to be based on the chemical structure of the parent coal and devolatilization is modelled by modelling the breakdown of particular bonds within this coal structure which then leads to the freeing of large sections of the coal macromolecule which are the precursors of volatiles evolution. These precursors can either breakdown further, or undergo re-attachment to the coal structure, and by following these transformations the devolatilization process can be modelled. Development of structural devolatilization models relies on specific information pertaining to the structure of the parent coal and a number of different analytical techniques are employed. These models have been proven to be quite effective in modelling not only coal devolatilization, but a number of subsequent properties of the coal/char which highlights their overall robustness.

Empirical models are based on a simplified approach to coal devolatilization modelling in which the devolatilization process can be represented holistically using a global reaction rate model. The reaction rate model itself can range in complexity from single first order Arrhenius type reaction models, through single $n^{th}$ order reaction models and two-competing reaction models, and ultimately multiple parallel reaction models. These models have no link with the structure of the parent coal and in this way are limited in their fundamental description of the devolatilization process. Despite this, these models have been shown to also be effective in modelling the evolution of both total volatiles and individual volatile species. Their ability to predict relative tar, char and volatile gas yields however is less than that of the structural models. Computationally the empirical models are far less taxing than structural models which makes them favourable when considering the development of more complex models which consider volatile combustion, char combustion, and drying in addition to coal devolatilization. In some cases it may be necessary to produce volatile evolution data under controlled conditions to provide data on which appropriate kinetic parameters can be derived. This is an easier prospect than producing the structural information required for development of a structural model, however deriving the kinetic parameters from the data requires some manipulation.
It can be concluded that both the structural and empirical coal devolatilization models have been shown to be suitable to modelling coal devolatilization. Whether a structural model should be employed in preference to an empirical model will be dependent on a number of factors including the requirements of the model (tar, char and gas yields, or volatile gas yields), the available information regarding the coal structure, the scope of the overall model (purely a devolatilization model, incorporating drying, volatiles combustion, char combustion etc.), and the computational limitations as they apply to the overall model complexity. Ultimately, these factors must be considered in order to make an informed choice regarding the type of coal devolatilization model which will be ideally suited to meet all the modelling requirements.

2.4 LARGE PARTICLE COAL DEVOлатILIZATION MODELLING

The development of advanced technologies for power generation from low rank coals within the CRC for Power Generation has indicated that further technologies will utilise coal particles in the mm size range, rather than conventional power stations in which pulverised coal particles are employed. This then directs the modelling studies toward the development of large coal particle devolatilization models. As will be discussed later in this chapter, modelling of large coal particles differs from that of pulverised coal particles in that the particle temperature can no longer be assumed to be uniform during heating. This is particularly relevant in fluid-bed systems where the high external heat transfer rates deliver heat rapidly to the particle surface, however internal heat conduction limitations result in slower transfer of heat to the centre of the particle resulting in the formation of large temperature gradients within the coal particle. This section will consider the implications of large coal particles with respect to both kinetic and heat transfer modelling, and previously reported large particle coal devolatilization models will also be reviewed.
2.4.1 KINETIC MODELLING

From a fundamental viewpoint, the effect of large coal particles on the devolatilization process has been discussed in Section 2.2.3.4. The most significant change to the devolatilization mechanism relates to the secondary devolatilization reactions, or the reactions of the primary volatiles as they are transported out of the coal particle. During this stage the primary volatiles are able to undergo reactions which include cracking, condensation, polymerisation and char formation. This is further enhanced by the temperature gradient existing within the particle. As primary volatiles formed at the particle centre migrate out of the particle, they encounter higher temperature regions at the outer surface of the particle. The cracking etc. reactions are promoted at higher temperatures thus facilitating enhanced secondary decomposition.

The FG-DVC model for coal devolatilization, as discussed in Section 2.3.1.2, represents the most comprehensive structural coal devolatilization model due to the incorporation of transport processes into the overall model. This model would thus seem ideally suited to large particle coal devolatilization modelling as it is capable of considering all the major contributing physio-chemical processes. A major limitation of this process will be the complexity of the model considering the co-dependence of the particle temperature and devolatilization models. As will be discussed below, devolatilization results in changes in the thermophysical coal properties and the coal density which directly impacts on the particle temperature response. Hence in the solution algorithm of the model, the devolatilization and heat transfer processes must be coupled which significantly increases the solution complexity.

It was concluded earlier (Section 2.3.3) that empirical models present a far less complicated solution to coal devolatilization modelling and may be suited to integration into large coal particle devolatilization models. This has been done in several studies (Agarwal et al., 1984a; Agarwal et al., 1984b; Stubington and Sumaryono, 1984; Agarwal, 1985; Agarwal et al., 1987; Fu et al., 1987; Tomeczek and Kowol, 1990; Tia et al., 1991; Peeler and Poynton, 1992; Adesanya and Pham, 1995; Garcia-Labiano et al., 1996). These studies have shown that these models have
had reasonable success in predicting both the total mass loss and evolution of individual volatile species from large coal particles during devolatilization which indicates they are suitable for this application. These models have not been used to attempt to characterise the yields of tar, char and volatile gases during devolatilization as this has not been the intended focus of these studies.

Rather than selecting the devolatilization model type based purely on the success of previous modelling efforts, a comprehensive set of selection criteria will be established and the various devolatilization models will be reviewed in relation to each selection criteria. Using this approach the most appropriate devolatilization model will be selected for the purposes of this study. Chapter 4 details the choice of selection criteria and an assessment of each model type relevant to the selection criteria, along with the favoured devolatilization model for this study.

2.4.2 PARTICLE TEMPERATURE MODELLING

As mentioned, a major implication of large coal particles is the presence of large temperature gradients within the coal particles during heating which has been reported by Agarwal et al. (1984), Tomeczek and Kowol (1990), Adesanya and Pham (1995), and Garcia-Labiano et al. (1996). Tomeczek and Kowol (1990) further highlighted the importance of the particle temperature response by commenting that any model verification by mass loss alone is not sufficient and model verification by means of the predicted and measured temperature response is also necessary. This seems logical given that devolatilization is essentially a thermally induced decomposition and would thus be highly dependent on the particle temperature history. It follows then that a significant contribution to the development of a large particle coal devolatilization model should be the development of a suitable particle temperature model.
2.4.2.1 Particle Energy Balance Equations

The unsteady-state heat conduction equation in spherical co-ordinates, given by Equation (2.12), has commonly been used as the basis for models to predict the temperature response of coals during devolatilization (Agarwal et al., 1984a; Agarwal et al., 1984b; Fu et al., 1987; Tomeczek and Kwokol, 1990; Kilic et al., 1993; Adesanya and Pham, 1995; and Garcia-Labiano et al., 1996). Agarwal et al. (1984a) also found that when a constant thermal diffusivity, $\alpha_c$, is assumed an analytical solution to Equation (2.12) is possible and takes the form of Equation (2.13).

$$\frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \alpha_c \frac{\partial T}{\partial r} \right)$$

(2.12)

$$\frac{T_a - T(r,t)}{T_a - T_0} = 2.0 \sum_{i=1}^{\infty} \frac{\sin \beta_i - \beta_i \cos \beta_i}{\beta_i - \sin \beta_i \cos \beta_i} \left[ \sin \left( \frac{\beta_i r}{R_0} \right) \right] e^{-\frac{\theta r}{k_c R_0}}$$

(2.13)

where $\beta_i$ are the roots of $\beta \cos \beta = (1 - Bi) \sin \beta$

The Biot number, $Bi$, describes the ratio of the external to the internal particle heat transfer rates according to:

$$Bi = \frac{h d_p}{k_c}$$

(2.14)

This solution applies uniquely to cases in which the Biot number can also be assumed to be constant.

If this cannot be assumed, two boundary conditions must be specified in order to solve Equation (2.12). Firstly, the boundary condition denoted by Equation (2.15) describes the rate of heat transfer at the particle surface due to convective and radiative heat
transfer, while Equation (2.16) refers to the centre of the particle where the radial temperature gradient is zero.

\[
k_c \left. \frac{\partial T}{\partial r} \right|_{r=R_0} = h\left(T_a - T\right)_{r=R_0} + \sigma_{rad} \varepsilon_{rad} \left(T_a^4 - T_{r=R_0}^4\right)
\]

(2.15)

\[
\left. \frac{\partial T}{\partial r} \right|_{r=0} = 0
\]

(2.16)

Equations (12) to (16) above represent the most basic form of the particle temperature models, and these equations have been used by Agarwal et al. (1984a), Agarwal et al., (1984b), Agarwal (1985), Agarwal et al. (1987), and Garcia-Labiano et al., (1996) to model coal devolatilization. In none of the aforementioned studies has an attempt been made to verify the particle temperature predictions with experimental data. Furthermore, a number of assumptions relating to these equations are questionable which has led to other studies producing particle temperature models with a number of variations.

### 2.4.2.2 Coal Thermophysical Properties

When modelling heat transfer in solids, the thermophysical properties of the solids play a major role in controlling the accumulation and transfer of heat through the solid. The thermophysical properties relevant to the situation of heating of a coal particle are the specific heat, \(C_{p,c}\), and thermal conductivity, \(k_c\), of the coal which are related to the thermal diffusivity via \(\alpha_c = k_c / \rho_c C_{p,c}\). Therefore, the assumption of a constant thermal diffusivity in Equation (2.12) is inherently dependent on constant thermophysical properties, as well as a constant coal density during pyrolysis.

The thermophysical properties reported in the literature vary significantly. Garcia-Labiano et al. (1996) commented that coal thermal diffusivities ranging between \(0.4 \times 10^{-7}\) m² s⁻¹ and \(50 \times 10^{-7}\) m² s⁻¹ have been reported, which agrees with the value of \(2 \times 10^{-7}\) m² s⁻¹ used by Agarwal et al. (1984a).
Stubington and Sumaryono (1984) reported thermal conductivity and volumetric heat capacity correlations based on the work of Badzioch et al. (1964) which are represented by Equations (17) and (18) respectively.

\[ k_c = \begin{cases} 
0.23 \text{ Wm}^{-1}\text{K}^{-1} \text{ for } T \leq 400^\circ \text{C} \\
0.23 + 2.24 \times 10^{-5} (T - 400)^{1.8} \text{ Wm}^{-1}\text{K}^{-1} \text{ for } T > 400^\circ \text{C} 
\end{cases} \]  \hspace{1cm} (2.17)

\[ \rho_c C_{p,c} = \begin{cases} 
1.92 \times 10^6 \text{ Jm}^{-3}\text{K}^{-1} \text{ for } T \leq 350^\circ \text{C} \\
1.92 \times 10^6 - 2.92 \times 10^3 (T - 350) \text{ Jm}^{-3}\text{K}^{-1} \text{ for } T > 350^\circ \text{C} 
\end{cases} \]  \hspace{1cm} (2.18)

These correlations were also used by Adesanya and Pham (1995) in their modelling studies. As can be seen these correlations describe the temperature dependence on the thermal conductivity and heat capacity. However the heat capacity has been linked with the coal density. Based on these correlations the coal thermal diffusivity varies from \(1.2 \times 10^{-7} \text{ m}^2\text{s}^{-1}\) at \(25^\circ\text{C}\) to \(2.16 \times 10^{-6} \text{ m}^2\text{s}^{-1}\) at \(800^\circ\text{C}\). This is comparable with the values reported by Garcia-Labiano et al. (1996), however, it is difficult to elucidate the true heat capacity and density values from Equation (2.18).

Tomeczek and Kowol (1990) and Kilic et al. (1993) used the following correlations reported by Agroskin (1957) and Agroskin et al. (1970), respectively, for the thermal conductivity and specific heat of coal in their models:

\[ k_c = 0.19 + 2.5 \times 10^{-4} (T - 300) \text{ Wm}^{-1}\text{K}^{-1} \]  \hspace{1cm} (2.19)

\[ C_{p,c} = 1.15 + 2.03 \times 10^{-3} (T - 300) - 1.55 \times 10^{-6} (T - 300)^2 \text{ Jkg}^{-1}\text{K}^{-1} \]  \hspace{1cm} (2.20)

Based on these correlations and an initial coal density of \(1300 \text{ kg m}^{-3}\), the coal thermal diffusivity varies between \(1.27 \times 10^{-7} \text{ m}^2\text{s}^{-1}\) and \(3.3 \times 10^{-7} \text{ m}^2\text{s}^{-1}\) over a temperature range of \(25^\circ\text{C}\) to \(800^\circ\text{C}\) assuming a volatile matter loss of approximately half the original coal mass. Again these values lie within the range reported by Garcia-Labiano et al. (1996). However the high temperature thermal diffusivity calculated
here is much lower than that calculated using the correlations of Stubington and Sumaryono (1984).

A number of researchers have quoted constant values or alternative correlations for the coal thermophysical properties in their work, and these are summarised in Table 2.3. From these values it can be seen that the thermal diffusivities calculated based on these thermophysical properties lie well within the range of values reported by Garcia-Labiano (1996). The thermal conductivities quoted are generally in the range $k_c = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$ which agrees with the two correlations presented above. The correlation of Agroskin (1957) yields thermal conductivities of $0.19 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.38 \text{ W m}^{-1} \text{ K}^{-1}$ for temperatures of $25^\circ \text{C}$ and $800^\circ \text{C}$ respectively, while the correlation used by Stubington and Sumaryono (1984) generates values of $0.23 \text{ W m}^{-1} \text{ K}^{-1}$ and $1.31 \text{ W m}^{-1} \text{ K}^{-1}$ over the same temperature range.

Tomeczek and Palugniok (1996) performed a rigorous investigation of the heat capacity and enthalpy of coal pyrolysis, given that the processes governing these two cannot be dealt with separately. A technique was proposed by which the heat capacity and enthalpy of devolatilization could be differentiated and heat capacity measurements were obtained for a number of coals were calculated. Based on these measurements the heat capacity of the coals were correlated according to Equation (2.21). The coefficient $A$ - $D$ for use in Equation (2.21) for each of the coals are given in Table 2.4.

$$C_{p,c}(T) = A + BT + CT^2 + DT^3 + ET^4 \quad \text{kJ kg}^{-1} \text{ K}^{-1} \quad (2.21)$$

The results of this study suggest that, along with the correlations presented above and in Table 2.3, the heat capacity and thermal conductivity of coal is not constant and in fact varies with the particle temperature. A consequence of this assumption is that the work of Agarwal et al. (1984a), Agarwal et al. (1984b), Agarwal (1985), Agarwal (1986), and Agarwal et al. (1987) where Equations (12) - (14) have been employed to calculate the particle temperature response may be compromised by the assumption of a constant thermal diffusivity. This is clearly not the case. It is difficult however to
experimentally determine the heat capacity of coals at elevated temperatures due to the mass loss associated with thermal decomposition and the possible confusion with the enthalpy of devolatilization (Tomeczek and Palugniok; 1996). The influence of the coal thermal properties on the particle temperature response and evolution of volatiles should be investigated in order to gain some knowledge on their relative importance.

<table>
<thead>
<tr>
<th>Reference</th>
<th>( C_{pe} ) (kJ kg(^{-1}) K(^{-1}))</th>
<th>( k_e ) (W m(^{-1}) K(^{-1}))</th>
<th>( \alpha_{25C} ) (m(^{2}) s(^{-1}))(^{c})</th>
<th>( \alpha_{800C} ) (m(^{2}) s(^{-1}))(^{d})</th>
</tr>
</thead>
<tbody>
<tr>
<td>James and Mills (1976)</td>
<td>1.465</td>
<td>0.67</td>
<td>3.52 \times 10(^{3})</td>
<td>5.38 \times 10(^{-7})</td>
</tr>
<tr>
<td>Borgh et al. (1985)</td>
<td>1.047</td>
<td>1.26</td>
<td>9.26 \times 10(^{3})</td>
<td>1.42 \times 10(^{6})</td>
</tr>
<tr>
<td>Gat (1986)</td>
<td>4.187</td>
<td>1.256</td>
<td>2.3 \times 10(^{8})</td>
<td>3.53 \times 10(^{8})</td>
</tr>
<tr>
<td>Sandhu and Hashemi (1985)</td>
<td>1.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Perry and Green (1984)</td>
<td>0.921 - 0.963(^{A})</td>
<td>0.26</td>
<td>1.84 \times 10(^{3})</td>
<td>2.81 \times 10(^{7})</td>
</tr>
<tr>
<td></td>
<td>1.004 - 1.088(^{B})</td>
<td>-</td>
<td>2.17 \times 10(^{7})</td>
<td>3.32 \times 10(^{7})</td>
</tr>
<tr>
<td>Lopez-Peinado et al. (1989)</td>
<td>1.1 - 1.5 @ 300 - 400K</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.5 - 2.0 @ 500 - 600K</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.5 - 4.5 @ 900 - 1000K</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wang et al. (1994)</td>
<td>1.52</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Yang and Wang (1990)</td>
<td>-</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tia et al. (1991)</td>
<td>0.87 + 2.55 \times 10(^{3})(T-273)</td>
<td>0.25</td>
<td>2.06 \times 10(^{7})</td>
<td>1.32 \times 10(^{-7})</td>
</tr>
</tbody>
</table>

\(^{A}\) Anthracite coal  
\(^{B}\) Bituminous coal  
\(^{c}\) Based on an initial coal density of 1300 kg m\(^{3}\)  
\(^{d}\) Based on a final coal density of 850 kg m\(^{3}\) as calculated in this study.
Table 2.4 Coefficients of the heat capacity correlation given by Equation (2.21) (after Tomeczek and Palugniok, 1996)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Czeczot</th>
<th>Boleslaw Smialy</th>
<th>Rydultowy</th>
<th>Wawel</th>
<th>Gliwice</th>
<th>Anthracite</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.22</td>
<td>1.17</td>
<td>1.13</td>
<td>1.08</td>
<td>1.01</td>
<td>0.91</td>
</tr>
<tr>
<td>B×10^1</td>
<td>2.99</td>
<td>3.15</td>
<td>3.58</td>
<td>3.81</td>
<td>4.19</td>
<td>3.49</td>
</tr>
<tr>
<td>C×10^6</td>
<td>5.30</td>
<td>4.35</td>
<td>2.28</td>
<td>0.548</td>
<td>-2.01</td>
<td>-1.24</td>
</tr>
<tr>
<td>D×10^9</td>
<td>-12.00</td>
<td>-11.70</td>
<td>-9.81</td>
<td>-7.83</td>
<td>-5.63</td>
<td>-4.43</td>
</tr>
<tr>
<td>E×10^12</td>
<td>4.92</td>
<td>5.10</td>
<td>4.63</td>
<td>3.99</td>
<td>3.58</td>
<td>2.63</td>
</tr>
</tbody>
</table>

2.4.2.3 Coal Particle Density

The changing density of the coal particle which results from the thermal degradation process is another parameter which will be integral in particle temperature calculations. For coals of high volatile matter content, such as those of interest to the CRC for Power Generation, the mass loss due to devolatilization can represent anywhere between 30 and 50 wt% of the initial mass of coal feed. This would tend to suggest that the bulk particle density is likely to vary significantly during devolatilization.

According to their assumption of a constant thermal diffusivity, Agarwal et al. (1984a), Agarwal et al. (1984b), Agarwal (1985), Agarwal (1986), and Agarwal et al. (1987) have effectively assumed that the density is also constant. It may be that their assumption is based on a situation where the coal density variation is negating any changes in the thermophysical properties thus producing an apparently constant thermal diffusivity. If the correlations of Agroskin (1957) and Agroskin et al. (1970) are used as a basis, for an initial coal density of 1300 kg m\(^{-3}\) a final coal density of 1680 kg m\(^{-3}\) is required in order to achieve an approximately constant thermal diffusivity. This is obviously not possible which raises enormous doubt regarding the assumption of a constant thermal diffusivity and a constant density for coals during pyrolysis. Others to assume a constant density are Kilic et al. (1993), Wang et al., (1994), and Garcia-Labiano et al. (1996).
Conversely a number of researchers have accounted for variations in the particle density during devolatilization via a number of techniques. Adesanya and Pham (1995) proposed that the density varied in direct proportion to the mass loss, while the particle diameter is assumed to remain constant. This approach seems reasonable however the assumption of a constant particle size is questionable and will be discussed later. Borghi et al. (1985) allowed for particle density variation to occur by including phenomena such as pore destruction in their model. This enabled variations in the effective particle volume to be calculated, as well as the devolatilization mass loss, which in turn enabled the particle density to be determined. Tia et al. (1991) also enabled particle density variations to be accounted for by considering the mass loss via devolatilization, however no comments were made regarding the change in particle size during devolatilization. Gat (1986) investigated the devolatilization of 70μm coal particles under high heating rate conditions and, from modelling studies, found that variations in the particle density were prevalent across the particle radius at specific time intervals. This was related to the temperature gradients which also existed within the coal particle affecting the extent to which devolatilization had progressed at various radial positions. This adds further to the suggestion that the coal particle density changes during devolatilization, and further to that suggests that density variations across the particle radius are also possible. This is far more likely to be evident in coal particles in the mm-size range given that it occurs in pulverised coal particles.

2.4.2.4 Coal Emissivity

When coal particles are inserted into a hot environment, radiation heat transfer is likely to take place. This is particularly relevant to fluid-bed applications where the bed material, at high temperatures, represents a suitable medium for radiative heat transfer. In order to quantify the magnitude of the heat transferred to the particle via radiation, the emissivity, εc, of the particle must be known which is indicative of the amount of energy absorbed by the particle relative to that which is incident on the particle surface (Holman, 1990).
A number of researchers have quoted emissivity values for coal with the values generally ranging from $\varepsilon = 0.8$ to $\varepsilon = 1.0$. Specific emissivity values quoted for particular coals are summarised in Table 2.5.

Linjewile (1993) investigated the emissivity of petroleum coke particles and found that the emissivity was temperature dependent. Based on the data presented (Linjewile, 1993) the temperature dependent emissivity can be represented by Equation (2.22) which gives emissivity values of $\varepsilon = 0.493$ and $\varepsilon = 0.795$ at temperatures of 25°C and 800°C respectively. These values are significantly lower than those quoted in Table 2.5 which raises doubt as to the correct range of emissivity values for use in coal devolatilization models.

$$\varepsilon_c = 0.377 + 0.00039T_p \bigg|_{T_r = T_p} \quad (2.22)$$

<table>
<thead>
<tr>
<th>Reference</th>
<th>Coal type</th>
<th>Emissivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perry and Green (1984)</td>
<td>-</td>
<td>0.8</td>
</tr>
<tr>
<td>Sandhu and Hashemi (1985)</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Fu et al. (1987)</td>
<td>Bituminous/lignite</td>
<td>0.9</td>
</tr>
<tr>
<td>Tia et al. (1991)</td>
<td>Lignite</td>
<td>1.0</td>
</tr>
<tr>
<td>Kilic et al. (1993)</td>
<td>-</td>
<td>0.93</td>
</tr>
<tr>
<td>Wang et al. (1994)</td>
<td>Lignite</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Agarwal et al. (1984a) in the description of their model development accounted for the contribution of radiation to the particle heating via assuming a 30% increase in the Nusselt, $Nu$, and Biot numbers calculated based purely on convective heat transfer. The reliability of this approach is questionable however can be considered as a simplified technique by which radiation can be considered. Several researchers have failed to account for radiation at all in their modelling work (Stubington and Sumaryono, 1984; Borghi et al., 1985; Tomeczek and Kowol, 1991; and Adesanya and Pham, 1995).
In the experimental investigations of Adesanya and Pham (1995), an insulating tube was employed to protect the coal particle from the hot walls of their convective flow furnace. The particle, surrounded by the insulating tube, was inserted into the furnace so that effectively the coal particle and insulating tube underwent simultaneous heating thus radiation heat transfer would be kept to a minimum. This is only applicable if the two objects heat up at identical rates. In this case, however, it would appear that the extent of radiation heat transfer would be minimal. Borghi et al. (1985) presented a model which was not based on any particular experimental system and no comparisons were made with experimental data. While there is no definite need to include radiation in the particle temperature equations, a comprehensive model would be developed in such a way as to enable radiation to be considered if necessary. The work of Tomeczek and Kowol (1991) and Stubington and Sumaryono (1984) both involved experiments conducted in a fluidized bed environment in which case the coal particles are undergoing heating in the immediate vicinity of the hot bed material. It is certain that there would be a heat transfer component due to radiation in this situation. Therefore the affect of radiation should be considered.

The treatment of radiation in current models remains unresolved in that some researchers have incorporated radiation explicitly into their model, some have accounted for radiation by simplified means, and some have either ignored radiation or assumed it is not significant. Whether or not radiation is significant is dependent on the physical environment under which devolatilization is occurring. However unless extensive precautions are undertaken it would be envisaged that radiation would contribute to some extent to the particle heating in most heating environments.

2.4.2.5 Convective Heat Transfer

While radiation heat transfer is likely to contribute to the heating of coal particles in high temperature environments, in systems where the particle experiences gas flow convective heat transfer will certainly play a significant role. For single spherical particles in a stream of hot gas the heat transfer rate to the particle can be estimated from the correlation of Ranz and Marschall (1952) given by Equation (2.23), while for
a fixed bed of particles subject to gas flow the gas-particle convective heat transfer coefficient, $h_{\text{conv}}$, can be determined via Equation (2.24) as reported by Kunii and Levenspiel (1969).

$$\frac{Nu_p}{k_g} = \frac{h_{\text{conv}} d_p}{k_g} = 2 + 0.6 \frac{1}{Re_p^2} Pr^{\frac{1}{3}} \quad (2.23)$$

$$\frac{Nu_p}{k_g} = \frac{h_{\text{conv}} d_p}{k_g} = 2 + 1.8 \frac{1}{Re_p^2} Pr^{\frac{1}{3}} \quad \text{Re}_p > 100 \quad (2.24)$$

Fu et al. (1987), Yang and Wang (1990), Tia et al. (1991), and Adesanya and Pham (1995) all used Equation (2.23) to define the rate of heat transfer to the coal particle from the surroundings in their modelling work. The model of Fu et al. (1987) was developed to describe coal devolatilization in an inert argon plasma jet stream while Adesanya and Pham (1995) aimed to describe devolatilization in a convective flow of hot nitrogen. Yang and Wang (1990) and Tia et al. (1991) developed models for combined devolatilization and combustion in hot convective air streams. In each case the specific mode of heating is by pure gas convection in which case the use of Equation (2.23) is justified.

Stubington and Sumaryono (1984) developed a model to predict the devolatilization of large coal particles in a fluidized bed environment. While no specific correlation was used to determine the external heat transfer coefficient, it was noted that heat transfer coefficients in the range of 460 W.m$^{-2}$K$^{-1}$ to 500 W.m$^{-2}$K$^{-1}$ have been quoted in the literature which are significantly greater than those calculated by Equation (2.23). The models developed by Agarwal et al. (1984a), Kilic et al. (1993), and Dincer et al. (1996) were aimed at representing coal devolatilization in fluidized-bed environments. Agarwal et al. (1984a) determined the heat transfer coefficient based on the assumption that it lies within the limits presented by Equations (2.23) and (2.24), while Kilic et al. (1993) and Dincer et al. (1996) calculated the heat transfer coefficient using Equation (2.23) exclusively. Given the comments of Stubington and Sumaryono (1984) it is questionable as to whether this approach is reliable.
Linjewile (1993) presented a summary of correlations presented in the literature for calculating the heat transfer to mobile spheres inserted into fluidized bed. These have been included in Table 2.6. Linjewile (1993) further proposed a mechanistic model for heat transfer to mobile spheres in which the overall heat transfer rate, \( \bar{h} \), is composed of a number of contributions which relate to the motion of the particle within the bed. This model can be summarised by Equation (2.25) in which \( h_{pc,a} \) and \( h_{pc,d} \) refer to the convective heat transfer coefficients for a sphere as it rises and sinks respectively during its circulation within the bed. The convective heat transfer coefficient for the particle in the bubble and gas phase are represented by \( h_{pc} \) and \( h_{bub} \) respectively. The probability parameters \( p \) and \( p' \) relate to the probability of the particle residing in the dense phase during one whole circulation, and of residing in the dense phase during its rise in the bed respectively. Greater details of the respective heat transfer coefficient correlations will be presented later.

\[
\bar{h} = p'h_{pc,a} + (p - p')h_{pc,d} + ph_{gc} + (1 - p)h_{bub}
\]  

(2.25)

Using this heat transfer model, and experimental temperature data from petroleum coke spheres in a fluidized bed, Linjewile (1993) was able to compare the heat transfer coefficients of the model with those determined from the experimental data. The model was found to provide reliable predictions for the heat transfer coefficient and typically values in the range of 200 W m\(^{-2}\) K\(^{-1}\) to 600 W m\(^{-2}\) K\(^{-1}\) were obtained. The heat transfer coefficient was found to increase rapidly with the fluidisation velocity immediately above the minimum fluidization velocity, and began to plateau as the fluidization velocity reached approximately twice the minimum fluidization velocity. A number of factors were found to influence the heat transfer coefficient including the fluidization velocity as mentioned, the particle size, the size of the fluidized bed material, the bed temperature, the nature of the bed material and its thermophysical properties, and the bed geometry including the bed diameter and static bed height (Linjewile, 1993).

Heat transfer to the particle from the surrounding environment provides the initial driving force for devolatilization. As such, accurate estimation of the magnitude of
the heat transfer will be critical in the overall devolatilization model. A number of researchers have used correlations developed for single spheres to predict the rate of heat transfer to coal particles in a fluidized bed heating environment. It has been shown, however, that the nature of the heating is far more complex in fluidized beds and that much higher heat transfer rates are commonly present. Therefore all attempts at modelling the high temperature behaviour of coal must ensure that appropriate heat transfer correlations are used, or that suitable values are assumed.

Table 2.6 Correlations for predicting the heat transfer coefficient for active spheres in fluidized beds (reproduced from Linjewile, 1993)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ross and Davidson (1982)</td>
<td>( \frac{(h \cdot d_a)}{k_e} = (\frac{k_a}{d_a})(D_e \varepsilon_{mf})(\frac{k_e}{k_s}) )</td>
</tr>
<tr>
<td>Tamarin et al. (1982)</td>
<td>( (hd_a) / k_s = 5Ar^{0.207}(d_i / d_a)^{0.65} )</td>
</tr>
<tr>
<td>Pal’chenok and Tamarin (1983)</td>
<td>( \bar{h}_{\text{max}} = (k_s / d_i)[0.41Ar^{0.3}(d_i / d_a)^{0.2} (\rho_i / \rho_a)^{-0.07}] )</td>
</tr>
<tr>
<td>Baskakov et al. (1987)</td>
<td>( \bar{h} = h_1 + (h_2 - h_1)\exp[-d_a / (4d_i)] )</td>
</tr>
<tr>
<td></td>
<td>( h_1 = (k_s / d_i)[0.85Ar^{0.19} + 0.006Ar^{0.5}Pr^{1/3}] )</td>
</tr>
<tr>
<td></td>
<td>( h_2 = (k_s / d_i)[10 + 0.23(ARPr)^{1/3}] )</td>
</tr>
<tr>
<td>Prins (1987)</td>
<td>( \bar{h}_{\text{max}} = (k_s / d_i)[3.539Ar^nf_T(d_a / d_i)^{0.257}] )</td>
</tr>
<tr>
<td></td>
<td>( n = 0.105(d_a / d_i)^{0.082} )</td>
</tr>
<tr>
<td></td>
<td>( f_T = 0.844 + 0.0756(T_b / 273) )</td>
</tr>
</tbody>
</table>

2.4.2.6 Enthalpy of Devolatilization

Throughout the models presented in the literature, the enthalpy of devolatilization has been inconsistantly dealt with. The particle energy balance equation denoted by Equation (2.12) can be suitably modified to account for the energy required to drive the devolatilization reaction i.e.
\[ \rho_c C_{p,e} \frac{dT}{dt} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \alpha_e \frac{dT}{dr} \right) + Q_{dev} \]  

(2.26)

The term \( Q_{dev} \) is proportional to both the devolatilization rate and the enthalpy of devolatilization. While the devolatilization rate can be derived from the kinetics of devolatilization, much speculation remains as to the magnitude of the enthalpy of devolatilization, \( \Delta H_{dev} \). Agarwal et al. (1984a) commented that while endothermic values of the heat of pyrolysis have been reported it is common to assumed that it is negligible, ie \( \Delta H_{dev} \approx 0 \). This was also assumed by Tia et al. (1991) and Winter et al. (1997). Wang et al. (1994) also commented that primarily endothermic enthalpy of devolatilization values have been quoted and based on their modelling work they deduced that the particle temperature was relatively insensitive to the enthalpy of devolatilization (for \( \Delta H_{dev} = 400 \text{ kJ kg}^{-1} \)) thus could effectively be ignored in the model calculations. Fu et al. (1987), based on an order of magnitude assessment of their model, also deduced that the enthalpy of devolatilization was negligible in the overall context of the model. Tomeczek and Kowol (1991) determined the "best fit" value of the enthalpy of devolatilization and found that the required value was in the range of \( \Delta H_{dev} = 10 \text{ - } 40 \text{ kJ kg}^{-1} \) which was considered sufficiently low that it could effectively be ignored.

Conversely, few investigators have ultimately accounted for the enthalpy of devolatilization in their modelling work. Sandhu and Hashemi (1985) used an enthalpy of devolatilization of \( \Delta H_{dev} = 627.6 \text{ kJ kg}^{-1} \) which was based on the recommendation of Baum and Street (1971), while Adesanya and Pham (1995) employed an exothermic heat of reaction equivalent to \( \Delta H_{dev} = 300 \text{ kJ kg}^{-1} \) in their modelling work. In neither of these studies was the significance of the enthalpy of devolatilization in terms of the model predictions investigated or commented on.

Merrick (1983) investigated the enthalpy of devolatilization and specific heat of coal and deduced that the endothermic enthalpy values obtained previously, for temperatures below 650°C, may be due to inaccurate estimation of the coal specific heat. As a result it was concluded that in this temperature range the magnitude of the
enthalpy of devolatilization is negligible. At higher temperatures Merrick (1983) calculated exothermic enthalpy of devolatilization values which varied with the volatile matter content of the coal. For coals with volatile matter contents of 15wt%, 25wt% and 35wt%, the calculated enthalpy of devolatilization values were -465, -616, and -653 kJ kg\(^{-1}\). These were found to be slightly greater than previously reported values of -424 and -299 kJ kg\(^{-1}\) (Merrick, 1983).

Lopez-Peinado et al. (1989) used differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.) techniques to investigate the enthalpy of devolatilization. It was found that in general the heat effects associated with coal devolatilization are endothermic, however some exothermic heat effects were discovered exclusively for low-rank coals. The results indicated that between 300 K and 450 K the heat effects are endothermic for all coals and are related to moisture desorption, particularly in the case of low-rank coals. From 450 K to 750 K the heat effects are mostly endothermic and are relatively minimal, except in the case of low-rank coals where larger exothermic enthalpy of devolatilization values were obtained. Finally, above 750 K, the heat effects are endothermic for all the coals tested with the apparent magnitude of the endothermicity decreasing with decreasing coal rank. These results suggest that the enthalpy of devolatilization is temperature dependent which is highly likely given that the nature of the reactions occurring varies with the particle temperature. Furthermore, the enthalpy of devolatilization also seems to be coal rank dependent which is also acceptable based on a similar theory.

Tomeczek and Palugniok (1995) also carried out an experimental investigation into the magnitude of the enthalpy of coal devolatilization and found that between 300°C and 800°C the reactions are endothermic for all coals. This is in contrast to the conclusions of Lopez-Peinado (1989) who observed almost negligible endothermic or exothermic enthalpy of devolatilization values. Within this region the average magnitude of the enthalpy of devolatilization was \(\Delta H_{\text{dev}} = 120\) kJ kg\(^{-1}\). Above 800°C both endothermic and exothermic enthalpy of devolatilization values were obtained depending on coal type. Low-volatile coals typically displayed exothermic enthalpy of devolatilization values in this range while the result was mixed for higher-volatile
coals. Within this range, the magnitude of the exo- or endothermic enthalpy of devolatization values was $\Delta H_{dev} \sim 200 \text{ kJ kg}^{-1}$.

Based on these reports it can be seen that significant confusion exists regarding both the use of, and the magnitude and nature of, the enthalpy of devolutilization in existing devolatilization models. It would appear that the enthalpy of devolutilization is dependent on both the coal rank, and the particle temperature, which is quite reasonable given that both influence the nature of the reactions which may be occurring.

### 2.4.2.7 Surface Volatile Matter Flux

As volatiles are evolved from the particle they are emitted from the particle surface and enter the boundary layer surrounding the particle. Tomeczek and Kowol (1991) reported the conclusion of Peters and Berling (1965) which proposed that devolatilization is controlled by heat transfer to the particle surface due to the ten fold decrease in the heat transfer coefficient resulting from the intensive outflow of products from the particle. Gat (1986) commented that when coal particles undergo uneven heating (ie laser heating on one side only) they have been observed to be propelled by the "rocketing" of volatile gases from the high temperature region of the particle. It can be elucidated from these observations that the volatile gases can have an influence on the conditions in the boundary layer surrounding the particles, which in turn will impact on the temperature response of the particle during devolatilization.

Kalson (1985) performed a sensitivity analysis of this phenomenon as it applies to pulverised coal particles. The Ackermann correction factor, which was previously used to determine the reduction in the heat transfer across the boundary layer resulting from the mass flux at the surface of flat plates, was modified to consider the situation of a spherical outer surface which is the situation relevant to coal devolatilization. The Ackermann correction factor describes the ratio of the actual rate of heat transfer to the particle surface, to that when the surface flux is zero or as calculated by
conventional means (Section 2.4.1.5.). According to Kalson (1985) for spherical geometry the Ackermann correction factor is given by:

\[
A_h' = \frac{h}{h_{N=0}} = \frac{C_0'}{\exp(C_0') - 1}
\]  \hspace{1cm} (2.27)

where

\[
C_0' = \frac{C_0}{1 + \frac{2}{Nu_0}} \quad \text{and} \quad C_0 = \frac{N_R C_{p,e}}{h_0}
\]  \hspace{1cm} (2.28-2.29)

The mass flux at the particle surface is denoted by \(N_R\) (kg.m\(^{-2}\).s\(^{-1}\)) and \(C_0\) is a dimensionless parameter relating the heat carried from the particle surface by the volatiles to the heat transfer to the particle surface via convection. Using these equations Kalson (1985) found that the convective heat transfer coefficient to a 74 \(\mu\)m coal particle under conditions prevailing in an entrained-flow gasifier may be reduced by between 7\% and 67\% which is likely to cause some significant reduction in the overall particle heating rate. Note that this applies only to convective heat transfer coefficients and no reduction in the radiation heat transfer will result.

This technique was incorporated into the model of Saastamoinen et al. (1993) which was developed to predict the pyrolysis and char combustion behaviour of coals however the influence of the surface volatile matter flux on the model predictions was not discussed. While it has been proposed that the surface volatile matter flux may have an impact on heat transfer to the particle surface, no conclusion can be drawn at this stage as to the extent of this reduction for mm-sized coal particles, or on the resulting impact on the model predictions.
2.4.2.8  Moisture

Coals, particularly low-rank coals, typically contain inherent moisture within the pore structure which is removed during the heating process. The moisture is present in a number of forms which can be summarised as (Allardice, 1991):

**Bulk Water**: Normal liquid water condensed in voids and capillaries, representing water from 0.725 to 2.0 kg / kg dry coal.

**Capillary Water**: Water condensed in capillaries with slightly abnormal thermodynamics in the small capillaries, representing water from 0.175 to 0.725 kg / kg dry coal.

**Multilayer Water**: Weakly hydrogen bonded water on top of monolayer water, representing water from 0.08 to 0.175 kg / kg dry coal.

**Monolayer Water**: Water hydrogen bonded to oxygen containing functional groups on the coal surface, representing water from 0.0 to 0.08 kg / kg dry coal.

Drying of solids is a function of the internal diffusion mechanisms working within the particle, along with external parameters such as temperature, pressure, and humidity etc. The internal mechanisms relative to solids drying are (Perry and Green, 1994):

1. **Internal diffusion** of liquids/vapours due to concentration/pressure gradients within the pores.
2. Liquid movement due to **capillary flow**.
3. Liquid/vapour movement due to particle **shrinkage** or pressure gradients within the porous particle.
4. Liquid flow due to gravity.
5. **Surface diffusion** due to condensation/vaporisation.

The external parameters represent the driving force for drying. For example in a fluidised-bed the driving force is the temperature gradient, while in vacuum drying the driving force is the pressure differential.
Jung and Stanmore (1980) investigated the behaviour of wet coal particles during fluidised bed combustion and, more specifically, measured the transient water and volatile matter contents of particles ranging in size from 5mm to 8mm under both inert and combustion conditions. It was discovered that the removal of moisture and then evolution of volatiles overlapped to some extent. The drying rate was able to be correlated with the equation of McIntosh (1976) which proposed that the transient moisture content could be calculated according to:

\[
\frac{C_t}{C_0} = \exp(-nt)
\]  

(2.30)

where

\[
n = \frac{12h(T_a - T_w)}{\lambda \rho_c \left[ \frac{C_0}{1 + C_0} \right] R}
\]  

(2.31)

Based on a shrinking core model, McIntosh (1976) also developed a correlation to predict the required particle drying time which was defined as:

\[
t = \frac{\lambda d_c \rho_c C_0}{2 h(T_a - T_w)} \left[ \frac{1}{3} (1 - Bi) \left( 1 - \frac{C}{C_0} \right) + \frac{Bi}{2} \left( 1 - \left( \frac{C}{C_0} \right)^{\frac{2}{3}} \right) \right]
\]  

(2.32)

Agarwal et al. (1984c) developed a model to predict the drying behaviour of coals during fluidized bed combustion. It was assumed that drying takes place from the surface of a receding wet core which is similar to the shrinking core assumption of McIntosh (1976). Based on their model prediction Agarwal et al. (1984c) proposed that the total drying time could be estimated via:

\[
t = \frac{0.14}{\alpha_{eff}} \left[ C_0 \left( \frac{Bi + 4}{Bi} \right)^{1.1} \left( \frac{\lambda}{C_{p,c}(T_a - T_{wd})} \right)^{1.09} \right] R^2
\]  

(2.33)
Wildegger-Gaissermaier and Agarwal (1990) extended the previous work of Agarwal et al. (1984c) to consider a combined drying/devolatilization/volatiles combustion model. Drying occurs at a wet/dry interface which recedes into the particle as drying progresses leaving a moisture-free outer shell, as per Agarwal et al. (1984c). The model was found to provide reasonable predictions for the transient moisture and volatile matter loss, based on supporting experimental results, however significant improvements in the model predictions could still be achieved.

Winter et al. (1997) incorporated drying into their model for predicting the drying, devolatilization, and char combustion of coal under fluid-bed conditions. It was assumed that the evaporation temperature of the moisture increased with the capillary pressure and this resulted in evaporation temperatures ranging between 100°C and 200°C. Their modelling results suggested that the effect of moisture is to delay the onset of the subsequent devolatilization and char combustion processes. Also, once char combustion has begun, the earlier presence of moisture had no effect of the particle behaviour (Winter et al., 1997).

Golonka and Rhodes (1997) proposed an alternative coal drying model to predict the behaviour during pressurised superheated steam drying of low-rank coals. The model incorporates capillary flow, bound water diffusion, and Knudsen diffusion terms which describe the movement of moisture within the pore structure. During the constant drying rate period the drying rate is assumed to be convective heat transfer limited while in the falling rate period the drying rate is controlled by a combination of heat transfer and diffusion mechanisms. No comparison between the model predictions and experimental data were presented. It was further assumed that no substantial pressure build up occurs within the particle thus the evaporation temperature remains at approximately 100°C. This model is far more complex than those reviewed earlier and accordingly would be difficult to integrate into a model for drying and devolatilization, or drying, devolatilization, and volatile combustion.

A factor which has a significant affect on the particle drying time is the amount of energy required to remove the moisture from the coal particle. Chen (1994) investigated the heat of drying as a function of the moisture content for a sub-
bituminous coal and found that the heat of drying increases dramatically, from the latent heat of vaporization, as the moisture content decreases below a critical level. For moisture above this critical level, the heat of drying is equivalent to the enthalpy of vaporization. Chen (1994) found that the heat of drying varied with the moisture content according to Figure 2.5 and for the sub-bituminous coal tested found that $MC_1 = 7\%$ (dry basis) and $MC_2 = 11\%$ (dry basis). These values are indicative of the tightly bound and loosely bound moisture fractions of the total coal moisture. The heat of drying was found to increase from the latent heat of vaporisation (2334 $kJ$ (kg $H_2O$)$^{-1}$) at $MC_1$ to 8000 $kJ$ (kg $H_2O$)$^{-1}$ at $MC_2$, and then to 20000 $kJ$ (kg $H_2O$)$^{-1}$ at 0 $kJ$ (kg $H_2O$)$^{-1}$. This represents an increase of up to 750% in the heat of drying from the latent heat of vaporisation which has not been considered in any coal drying/devolatilization models to date.

![Figure 2.5](image)

Figure 2.5 The heat of drying as a function of the moisture content of coal (as reproduced from Chen, 1994).

Drying is an integral part of high temperature coal applications due to the inherent moisture present in as-mined coals. Models have been proposed to predict the drying behaviour of coals, however, except in the case of Wildegger-Gaismaier and Agarwal
(1990), no substantial validation of these models has been undertaken. In this case it was found that substantial improvements in the model predictions remain to be made.

2.4.3 Summary

It is evident that modelling the devolatilization of large coal particles poses a number of additional problems to that of pulverised coal particles. The particle size has a significant effect on the mechanism of coal devolatilization and effectively increases the residence time of the primary volatiles within the particle thus providing additional opportunity for subsequent secondary reactions. These reactions include reactions which lead to the thermal degradation of larger molecules as well as char forming reactions where tars are able to re-bond to the macromolecular structure. The result of these reactions is a general decrease in the overall tar yield and an increase in the yield of lighter gases (H₂ - C₃ hydrocarbons).

Modelling of these secondary reactions is complex and ideally should be coupled with mass transfer equations such that the rate of these reactions and the rate of mass transport of the primary volatiles out of the particle can be considered concurrently. This substantially increases the complexity of the kinetic model however it has been shown that this can be achieved with the use of the FG-DVC model. The FG-DVC model has not to date been combined with a sophisticated large particle temperature model and it is envisaged that such a model would be highly complex. This would diminish the capacity of the model to be combined into models including drying, volatiles combustion, and char combustion. The simplicity of empirical models, and their robustness, would serve to reduce the complexity of the overall model however their ability to predict relative char, tar and volatile gas yields are inferior to the FG-DVC model.

A significant factor in modelling of large coal particle devolatilization is the prediction of the temperature response of the particles during heating. Due to the thermal resistance of the particle, large temperature gradients have been found to be apparent during the heating of large coal particles and the isothermal particle...
assumption is no longer valid. A number of models have been developed to predict the temperature response of large coal particle during heating and the unsteady-state heat conduction equation in spherical co-ordinates has commonly been used as the basis for the calculations. While this is an acceptable approach, there are a number of factors relating to this model which need to be further addressed in order to produce reliable model predictions. These include the thermophysical properties (heat capacity and thermal conductivity) of the coal particles, the variation in particle density during pyrolysis, the emissivity of the particle, the rate of external heat transfer, the enthalpy of devolatilization, the surface volatile matter flux and the presence of moisture. Each of these parameters and assumptions regarding their use in the unsteady-state heat conduction equation in spherical co-ordinates may impact on the model predictions. At present there is no consistent method for utilising these parameters in coal particle temperature models and the relative importance of these parameters has not been addressed.

2.5 CONCLUSIONS FROM LITERATURE REVIEW AND OBJECTIVES OF THE PRESENT STUDY

2.5.1 COAL STRUCTURE AND DEVOLATILIZATION

The literature review presented in this chapter has revealed the following points with regard to the structure and devolatilization of low-rank coals:

- recent advancements in analytical techniques such as of $^1$H NMR, $^{13}$C NMR, and TG-FTIR spectroscopy has enabled information on the structure of coals to be elucidated.
- low-rank coals are composed of groups of aromatic ring clusters which are cross-linked by aliphatic or etheric bridges.
- functional groups such as carbonyl, carboxyl, ether, and phenol groups are attached to the aromatic ring clusters, and inclusions such as small aliphatics or mineral species trapped with the coal macromolecule.
• during devolatilization the products produced include light gases (H₂O, CO, CO₂), low molecular weight hydrocarbons (CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈ etc), tars, and the residual char.
• devolatilization takes place via primary and secondary devolatilization.
• primary devolatilization involves the breakdown of the parent coal into smaller fragments.
• secondary devolatilization refers to transformations involving the products of primary devolatilization.
• the products of devolatilization are dependent on the temperature, pressure, and heating rate of devolatilization, as well as the coal particle size.
• the products of devolatilization influence the performance of the fluidized-bed as well as contributing to the formation of CO, NOₓ and SOₓ gases which are environmentally unacceptable.

2.5.2 COAL DEVOLATILIZATION MODELLING

The review of existing models for predicting the behaviour of coal during devolatilization has indicated that:

• the models developed to describe coal devolatilization can be classed as either empirical or structural models.
• structural models are based on a theoretical representation of the coal structure and predict the changes occurring during coal devolatilization by considering this structural representation.
• structural models require significant input information relating to the structure of the parent coal, therefore such models are dependent on the accuracy and availability of this input data.
• structural models are capable of predicting yields of tar, char and volatile species, as well as solvent swelling and fragmentation etc. properties, however, these models are highly computationally intensive.
• empirical models represent a global model for devolatilization in which the reactions are lumped into a simplified kinetic description.
• empirical models range in complexity from single first order models to multiple parallel reaction models.

• empirical models utilise devolatilization kinetic parameters which are determined from particle mass loss and individual species evolution data.

• empirical models are unable to predict relative tar, char, and total volatile yields as effectively as structural models, however are far more computationally efficient.

• empirical models have been used effectively in models for predicting coal devolatilization, coal drying and devolatilization, and coal drying, devolatilization and char/volatiles combustion, which indicates the flexibility of these models.

• when developing a coal devolatilization model, the choice of the model type employed should be made with a consideration of the aims of the model, the availability of data to support the model, and the nature of model which is being developed.

2.5.3 LARGE COAL PARTICLE DEVOLATILIZATION MODELLING

Reviewing the existing information relating to modelling of large coal particle devolatilization has revealed the following:

• modelling of large coal particle devolatilization relies on predicting both the particle temperature response and the evolution of volatile matter.

• several large coal particle devolatilization models have been developed and the majority have utilised empirical devolatilization kinetic models.

• predicting the particle temperature response during devolatilization has been found to be critical in the development of accurate coal devolatilization models.

• few of the models developed to date have considered, in detail, the accuracy of their particle temperature predictions.

• the devolatilization of large coal particles is influenced by factors such as the external heat transfer environment, the thermophysical properties of the coal, the coal emissivity, the surface volatile mattet flux, the enthalpy of devolatilization, and the moisture content of the coal.
• in order to definitively validate large coal particle devolatilization models, the model predictions must be tested against particle temperature and mass loss data, as well as individual species evolution data where appropriate.

• in order for this validation to occur, reliable experimental data must be available which has been collected under controlled operating conditions.

2.5.4 CURRENT LIMITATIONS IN COAL DEVIOLATILIZATION MODELLING

Based on the literature review presented in this chapter it is possible to highlight several areas which require significant improvement in existing coal devolatilization modelling studies. The most distinctive of these areas is the prediction of the particle temperature response during devolatilization. As reported, very few modellers have performed any substantial validation of their model with experimental data for the coal particle temperature response and, of those who have done so, there has been none who have been able to generate consistently reliable results.

The inability of modellers to predict the coal particle temperature response can be attributed to two factors. Firstly, minimal experimental data exists with which devolatilization models can be refined, and secondly, there are a number of factors which may be affecting the particle temperature response which are not being considered in the models developed to date. While several of these factors may not impact significantly on the model predictions, no comprehensive sensitivity analysis has been performed to act as a basis for the omission of these factors in existing and future models.

The inability of existing models to the particle temperature response during devolatilization has an added impact on the ability of the model to predict volatile evolution trends under similar operating conditions. Given that the evolution of volatile matter is essentially a thermal degradation process, devolatilization will depend highly on the time-temperature history of the particle and thus accurate
prediction of this time-temperature will enhance the ability of the model to predict the coal devolatilization behaviour.

However, predicting the time-temperature history of coal particles does not ensure that volatiles evolution trends will be accurately predicted as these trends will be further dependent on the kinetic used to describe the devolatilization of each volatile species. Previously, these kinetics have been deduced from models in which the particle temperature response has not been accurately predicted which in itself can result in unreliable kinetic parameters. It is possible that the inability of present models to predict volatile evolution behaviour over a wide range of operating conditions is a combination of the inability to predict the particle time-temperature history and the utilisation of unreliable kinetics. This same situation may also be a factor leading to the suggestion that the kinetics for evolution of particular volatile species are relatively coal independent. Therefore by enabling the particle temperature history to be more accurately determined will enable more reliable devolatilization kinetics to be determined which in turn will lead to more accurate predictions for volatile evolution trends from large coal particles.

2.5.5 Objectives of the Present Study

Based on the literature review presented here, and the limitations in coal devolatilization modelling discussed in the previous section, the objectives of the present study are as follows:

- to develop a coal devolatilization model which is capable of accounting for all the factors which may be influencing the devolatilization behaviour of large coal particles.
- to perform a comprehensive sensitivity analysis of the model to test the affect of the various factors on the devolatilization behaviour, most notably the predicted particle temperature response and volatile evolution trends.
• to collect experimental data for the particle temperature response and evolution of volatile matter under controlled operating conditions in order to generate a sufficient data set to achieve model validation.

• to validate the coal devolatilization model using both the particle temperature and volatile evolution data.

• based on the validated coal devolatilization model, elucidate devolatilization kinetics for select individual gas species using appropriate experimental data.

• to compare the devolatilization kinetics determined above with those proposed in the literature.

• to investigate the controlling mechanism/s during large coal particle devolatilization and to distinguish between chemical kinetic and heat transfer controlled devolatilization.
Chapter 3

EXPERIMENTAL WORK

3.1 INTRODUCTION

As has been mentioned, coal devolatilization is an important stage in all high temperature coal conversion processes. As such, a practical understanding of the behaviour of low-rank coals during heating is necessary in order to gain an appreciation of the specific requirements of models developed to simulate this process. In particular, this section of work focuses on gaining accurate measurements for the particle temperature response during heating which is an area that has not been dealt with extensively in the current literature. Furthermore, this data is to be complimented by mass loss data collected under identical conditions to the aforementioned temperature data in order to yield a comprehensive experimental data set for the subsequent verification of a coal devolatilization model.

Although some experimental data for the temperature response of large coal particles is present in the literature, less emphasis has been placed on accurate prediction of the particle temperature response than on predicting volatile evolution. This is primarily due to the uncertainty surrounding the model predictions for the particle temperature response and the number of influencing parameters, as well as the uncertainty relating to the particle temperature measurements. A fundamental aim of this section of work then is to develop a reliable technique for measuring the temperature response of low-
rank coal particles during heating. Once a suitable measurement technique has been established, it can be implemented to collect the desired temperature data. Due to the rising tendency toward the utilisation of fluidized bed combustion, gasification, and carbonisation systems, temperature data collected under fluidized bed conditions would be ideally suited to verification of coal particle behaviour during fluidised-bed devolatilization. Unfortunately, despite the proposal of a number of correlations to predict heat transfer to coal particles in a fluidised-bed environment, the heat transfer mechanism is not particularly well defined. Therefore it was deemed necessary to utilise a far more controlled heating environment, such as that observed in a horizontal tube furnace. The horizontal tube furnace was not only beneficial in enabling temperature data to be collected under well defined heating conditions, it was also used in the development of a reliable temperature measurement technique due to its moderate heating environment. Subsequent temperature measurements obtained from coal particles under fluidised-bed conditions were also necessary, however such data cannot be used for model development purposes and are limited to validation of the corresponding model predictions.

In presenting the experimental work conducted in this study, a description of the experimental apparatus used in this study will be followed by description of the steps leading to the development of a reliable technique for measuring the temperature response of low-rank coal particles during heating. The application of this technique for the collection of particle temperature data in both the horizontal tube furnace and a fluidized bed reactor will then be described and results from this work presented, along with the corresponding mass loss data. This chapter will conclude with a summary of the work presented and implications of the results of this work for coal devolatilization models.
3.2 EXPERIMENTAL APPARATUS

3.2.1 HORIZONTAL TUBE FURNACE

The horizontal tube furnace used in this study is distinctive in that it is able to provide a relatively constant and well defined heating environment for studying the devolatilization of large coal particles. The second advantage of this apparatus is its inherent simplicity which makes it ideal for handling delicate situations such as those existing in this study when bone dry particles are employed. These particles are prone to fragmentation in coarse environments and thus temperature measurements are extremely difficult to obtain. This was overcome with the use of the horizontal tube furnace.

The horizontal tube furnace, as depicted in Figure 3.1, comprises a 25 mm i.d. \times 500 mm long non-porous "Pythagorus" type ceramic which is housed inside a refractory lined Carbolite CFM 14/2 furnace. The furnace is heated by four Kanthal silicon carbide heating elements capable of delivering a maximum of 2.25 kW. Gas is supplied to the system directly from G size high purity N₂ gas bottles and the gas flow rate is controlled by a Metric Series Tube Size 7 Rotameter with a Type A Duralumin float. Prior to entering the horizontal tube furnace the gas passes through a moisture trap packed with silica gel to ensure the stream is moisture free. The furnace can be heated to a maximum of 1400°C and the temperature is controlled by a Eurotherm 91e temperature controller.

The gas enters at the back of the furnace directly into the heating zone while the particles are inserted via the exhaust hood. A stainless steel tube (25 mm i.d.) passes through the exhaust hood to meet the ceramic tube. The stainless steel tube has an entry point at the base of the tube into which purge N₂ can be injected, and has an open section between the ceramic tube and the purge N₂ injection point to allow the off-gas to flow into the exhaust system. The purge N₂ serves two purposes. Firstly it provides a N₂ rich environment in the stainless steel tube thus reducing the likelihood of air entering the heated zone and compromising the experimental measurements via
Figure 3.1 Schematic diagram of the horizontal tube furnace.
char or volatiles combustion. Secondly, hot coal particles could be rapidly quenched in the stainless steel tube via the cold purge N₂ gas stream. This is extremely useful when mass loss studies are being undertaken to ensure no substantial mass loss takes place on removal of the hot coal particles from the horizontal tube furnace.

3.2.2 **Fluidized Bed Reactor.**

The fluidized bed reactor used in this study has been used elsewhere (Linjewile, 1993) for an investigation into the combustion behaviour of coal chars. The rig has five main sub-units including the gas pre-heater, the calming section, the fluidizing chamber, the electric furnace, and the control panel. A schematic of the rig is shown in Figure 3.2 and a description of the various sub-units is given below (Linjewile, 1993).

The gas pre-heater is an electrically heated Leister type 5000 hot air tool with a heating capacity equivalent to 5 kW. The pre-heater is capable of providing 500 L min⁻¹ of hot air at 873 K and acts to reduce the load on the furnace section as well as to reduce the start-up time of the rig by enabling stabilisation at the set-point temperature to be reached much earlier.

The calming section, or plenum chamber, comprises a 102 mm i.d. by 300 mm high stainless steel tube which has a perforated distributor plate with 1mm distributor holes at the base of the tube. The distributor plate supports a bed of 2 mm diameter sand particles. The calming section is required to ensure that the gas entering the subsequent fluidization vessel is distributed evenly over the bed cross-section and smooth fluidization can be achieved. Note that the gas pre-heater, the piping leading to the calming section and the calming section itself are all lagged with Kaowool insulation to minimise heat loss.
Figure 3.2 Schematic diagram of the Fluidized Bed Reactor
The fluidizing chamber comprises a 102 mm i.d. by 500 mm long stainless steel tube and is fitted with a perforated gas distributor plate with 121 holes of 0.4 mm diameter arranged in an $8 \times 10^{-3}$ m standard pitch. The temperatures at various bed heights within the fluidizing chamber are monitored by five K-type thermocouples while the pressure drop can be measured at various bed heights via three manometer tappings. The thermocouple outputs are displayed on a digital readout unit on the control panel. The entire fluidizing chamber is enclosed within an electrically heated furnace.

The furnace, lined with refractory bricks, is heated by four Kanthal type DS silicon carbide heating elements capable of delivering a maximum of 8 kW. The elements are supported such that a clearance of 50 mm existed between the elements and the wall of the fluidizing chamber. Two of the four heating elements are connected to a Dimmerstat 28D-3P variable transformer enabling the input voltage to be regulated between 0% and 100% of the maximum. These heating elements provide a base heating load to the fluidizing chamber. The remaining two heating elements are connected to the temperature controller via a PAC-15 series thyristor to provide any additional heating load required to maintain the set-point bed temperature.

The control panel consists of a Shimaden SR17 PID type temperature controller and the furnace is capable of operating at temperatures up to 1100°C. The bed temperatures are displayed on a Shimaden SD10 digital display unit via a Shimaden KR10 thermocouple selection unit. The supply and apparatus pressures are monitored by Blackwoods 400 kPa pressure gauges while the pressure drop over the bed can be measured via two water filled manometers. The gas flow to the bed can be supplied from either gas bottles, or via an air compressor, and is regulated by a Metric Series Tube Size 7 Rotameter with a Type A Duralumin float. The volumetric flowrate of gas to the bed can further be measured by a MT-5 Toyo Gas Meter.
3.2.3 **Temperature Measurement System**

The temperature measurements obtained in this investigation have been collected via the use of a 1.0 mm K-type Chrome-Alumel thermocouple with a 310 stainless steel sheath. Such thermocouples are capable of withstanding temperatures of up to 1370°C making them suitable for the purposes of this work. The thermocouple is connected to a Pico TC-08 8 channel thermocouple input device which is in turn linked to the serial port of a standard 386 Personal Computer. The signal from the TC-08 input device is analysed by the Picolog Data Logging Software installed on the PC. The software has in-built cold junction compensation algorithms as well as algorithms for thermocouple curve normalisation based on the type of thermocouple in use thus enabling temperature measurements to be recorded automatically at predetermined intervals. Temperature readings can be taken at sampling rates up to 100 s\(^{-1}\) however for the purposes of this work samples were recorded at intervals of between 3 s and 5 s which enabled the signal filter to be used. The signal filter uses the signal from both the thermocouple and the cold junction and based on the cold junction signal determines the relative amount of electrical noise and adjusts the thermocouple signal accordingly.

3.2.4 **Mass Loss and Particle Size Measurement System**

In all the experiments performed in this study, measurements of the particle diameter and particle mass were recorded prior to, and on completion of, the particle temperature measurement experiments. In the horizontal tube furnace the particles were quenched with the purge N\(_2\) gas stream upon completion of the experiments to minimise further mass loss, as per Figure 3.1. For the fluidized bed reactor experiments, the hot particles were immersed in a dry ice filled container achieving similar results. Particle diameter measurements were taken with electronic digital callipers accurate to 0.01 mm while the particle mass was measured via a Sartorius GMBH Type 1702 electronic balance accurate to 0.1 mg.
3.3 SAMPLE PREPARATION

While much of the focus of this study is aimed at investigating the devolatilization behaviour of dry coal particles, some work has been done with wet coal particles to investigate the influence of moisture on the devolatilization behaviour. As the coal particles were prepared from as-received coal, the procedure for preparing the wet coal particles will be outlined first, prior to detailing the drying procedure leading to the preparation of the dry coal particles.

3.3.1 WET COAL PARTICLES

The particular coal which has been used in this study is Bowmans coal which is located in the mid-north region of South Australia. The ultimate and proximate analysis of Bowmans coal are summarised in Table 3.1. Bowmans coal was selected for a number of reasons. Firstly, the relatively high ash content of Bowmans coal is useful in that it acts to "bind" the particles at high temperatures such that minimal fragmentation is observed. Secondly, a previous study has been conducted analysing the devolatilization behaviour of Bowmans coal (Wildegger-Gaissmaier, 1990) with emphasis on the particle mass loss and evolution of volatiles. No particle temperature data was collected in the study of Wildegger-Gaissmaier (1990). However, the mass loss and volatiles evolution data may be useful for model validation purposes.

Spherical, wet Bowmans coal particles were prepared from large lumps of Bowmans coal. The lumps were initially cut into squares of appropriate size and then the sides were smoothed using a rotating belt sander. Spherical particles in the size range of -11 + 10 mm and -9 + 8 mm were prepared using this technique. Once prepared the particles were stored in an air tight container to avoid any substantial drying taking place. Prior to the temperature measurements, 1mm holes were drilled to slightly beyond the centre of the coal particles. Note that the thermocouple junction is located approximately 0.5 - 1mm from the tip of the thermocouple sheath hence the need to extend the hole slightly beyond the particle centre.
Table 3.1 Proximate and Ultimate Analysis of Bowmans Coal (Wildegger-Gaismaier, 1990)

<table>
<thead>
<tr>
<th>Proximate Analysis (wt%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total moisture (as received)</td>
<td>52.0</td>
</tr>
<tr>
<td>Ash (db)</td>
<td>11.6</td>
</tr>
<tr>
<td>Volatile Matter (db)</td>
<td>49.2</td>
</tr>
<tr>
<td>Fixed Carbon (db)</td>
<td>39.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate Analysis (% daf)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>69.4</td>
</tr>
<tr>
<td>H</td>
<td>4.6</td>
</tr>
<tr>
<td>N</td>
<td>0.5</td>
</tr>
<tr>
<td>S</td>
<td>4.6</td>
</tr>
<tr>
<td>O (by difference)</td>
<td>20.9</td>
</tr>
</tbody>
</table>

3.3.2 DRY COAL PARTICLES

The dry coal particles were prepared by drying the wet coal particles produced via the technique outlined in Section 3.3.1. Due to the brittleness of the dried coal particles it was observed that the holes must be drilled prior to drying. Also, significant shrinkage was observed upon drying thus necessitating the need for larger initial holes. Drying of particles with different initially sized holes indicated that 1.2 mm holes were required in order to produce dry coal particles into which a 1 mm thermocouple could be inserted maintaining a reasonably tight fit. Therefore in generating the dry coal particles, 1.2 mm holes were drilled to just beyond the centre of the wet coal particles.

The coal particles at this stage were placed into a temperature controlled oven at ~40°C. The particles were allowed to dry in air overnight in the oven. A number of air dried particles were subsequently placed into a platinum crucible and inserted into the horizontal tube furnace at 150°C using N₂ as the feed gas. The particles were allowed to dry for up to 1 hr under these conditions after which they were quenched using the purge N₂ stream and stored in a desiccator for future use. Interestingly it was found that wet coal particles dried directly in the horizontal tube furnace
developed severe cracking and were almost impossible to use for temperature measurements. This less severe drying technique enabled the dry particles to be effectively used for temperature measurement applications.

To ensure that the particles were sufficiently dried, measurements of the particle mass prior to and during drying were taken. These measurements are shown in Table 3.2 and show that drying is complete within approximately 45 minutes in the horizontal tube furnace at 150°C. This data also serves to confirm the initial moisture content of the wet coal particles. Based on these calculations it can be seen that the wet coal particles have an average initial moisture content of 1.052 g (g dry coal)$^{-1}$ which is slightly lower than that of Wildegger-Gaismaier (1990) (52wt% H₂O - 1.08 g (g dry coal)$^{-1}$).

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mass of crucible* + particles, M₁ (g)</th>
<th>Mass loss, ΔM₁ (g)</th>
<th>Coal Moisture Content, X_{H₂O} (g (g dry coal)$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.6779</td>
<td>0</td>
<td>1.044</td>
</tr>
<tr>
<td>15</td>
<td>14.1157</td>
<td>0.5622</td>
<td>0.371</td>
</tr>
<tr>
<td>30</td>
<td>13.8384</td>
<td>0.8395</td>
<td>0.039</td>
</tr>
<tr>
<td>45</td>
<td>13.8067</td>
<td>0.8712</td>
<td>0.001</td>
</tr>
<tr>
<td>60</td>
<td>13.8057</td>
<td>0.8722</td>
<td>0.001</td>
</tr>
</tbody>
</table>

3 x 10 mm Coal Particles

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mass of crucible* + particles, M₁ (g)</th>
<th>Mass loss, ΔM₁ (g)</th>
<th>Coal Moisture Content, X_{H₂O} (g (g dry coal)$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.7805</td>
<td>0</td>
<td>1.059</td>
</tr>
<tr>
<td>15</td>
<td>13.9880</td>
<td>0.7925</td>
<td>0.206</td>
</tr>
<tr>
<td>30</td>
<td>13.8181</td>
<td>0.9624</td>
<td>0.005</td>
</tr>
<tr>
<td>45</td>
<td>13.8156</td>
<td>0.9649</td>
<td>0.002</td>
</tr>
<tr>
<td>60</td>
<td>13.8140</td>
<td>0.9665</td>
<td>0.002</td>
</tr>
</tbody>
</table>

5 x 8 mm Coal Particles

* The crucible mass for both experiments was 12.9701g

The moisture content at any time in Table 3.2 was determined according to:

\[
X_{H₂O} = \frac{ΔM_{60} - ΔM₁}{M_{60} - M_{crucible}}
\]  

(3.1)
3.4 DEVELOPING A RELIABLE TECHNIQUE FOR PARTICLE TEMPERATURE MEASUREMENTS

3.4.1 CONVENTIONAL TEMPERATURE MEASUREMENT TECHNIQUE

A number of investigators (Stubington and Sumaryono, 1984; Tomeczek and Kowol, 1990; Tia et al., 1991; Kilic et al., 1993; Adesanya and Pham, 1995; Dincer et al., 1996; and Winter et al., 1997) have measured the temperature response of large particles during heating and in each case the measurement technique used was identical. This "conventional" technique involves the insertion of a thermocouple into the centre of the coal particle via an appropriately drilled hole. Tomeczek and Kowol (1990), Kilic et al (1993), and Dincer et al. (1996) used 0.1mm thermocouples and Linjewile (1993) used a 0.5 mm thermocouple while Stubington and Sumaryono (1984), Tia et al. (1991), and Winter et al. (1997) did not specify the size of the thermocouples employed in their studies. Adesanya and Pham (1995) did not specify the size of the thermocouple used either, however based on a photograph of their experimental system it would appear that a 1mm or similar thermocouple was employed.

Due to the lack of availability of finer thermocouples, and their significantly higher costs, 1mm K-type thermocouples were used to perform temperature measurements on -11 + 10 mm Bowmans coal particles in the horizontal tube furnace at 600°C using the aforementioned "conventional" technique. Such experiments were conducted using both wet and dry coal particles and the results are displayed in Figure 3.3. It can be seen that, as expected, the wet coal particles undergo much slower heating than the dry coal particles. It is interesting to note the temperature response obtained for the wet coal particle and the point at which the influence of moisture is most apparent. Up to approximately 150°C the wet particle observes a slightly lower heating rate than that of the dry particle taking almost double the time to reach this temperature. However it is above 150°C where the temperature responses begin to deviate substantially. The heating rate of the wet coal particle decreases substantially at this
point and it is not until the centre temperature reaches 300°C that the heating rate substantially increases again.

![Graph showing temperature response vs time for dry and wet particles.]

Figure 3.3 Measured temperature response at the centre of -11 + 10 mm Bowmans coal particles in the Horizontal Tube Furnace at 600°C. Data obtained using the conventional measurement technique for both wet and dry particles.

While this phenomenon is not completely unexpected, there are some inconsistencies with observations made regarding the drying of wet coal particles in the literature. As reported in Section 2.2.2.8, the moisture present in coals between 2.0 and 0.725 g (g dry coal)^{-1} is bulk water which has properties identical to that of moisture in its free state (Allardice, 1991). Based on an initial moisture content of 1.052 g (g dry coal)^{-1}, this would suggest that approximately 31% of the moisture present initially in the coal particles used here would behave similarly to free moisture and hence would evaporate at ~100°C. Under these conditions it would be expected that some significant change in the wet particle heating rate would be expected at 100°C consistent with bulk moisture evaporation. Capillary moisture, which has only slightly different thermodynamic properties to the bulk moisture (Allardice, 1991), represents a further 57% of the total moisture present which further increases the likelihood of a significant reduction in the heating rate at, or near, 100°C.
Further evidence of this was observed by McIntosh (1976) who measured the temperature within large coal particles during drying and observed interface temperatures of between 62°C and 83°C. The interface temperature referred to here is the temperature at the wet/dry interface which forms as moisture is progressively removed from the particle. Moisture is removed from the outer surface of the particle first, and as the particle dries the moisture “front” recedes into the particle thus producing a wet/dry interface. Also, Winter et al. (1997) calculated the moisture evaporation temperature based on the capillary pressure and found that the evaporation temperature ranged between 100°C and 200°C.

These results all allude to the formation of a plateau in the temperature response at, or near, 100°C due to moisture evaporation. Figure 3.3 indicates that this phenomenon could not be measured using the “conventional” particle temperature measurement technique. Therefore the factors leading to deviation from the expected temperature response must be determined, and subsequent action taken to minimise their effect. It is difficult to observe any unexpected results from measuring the dry particle temperature. However, any factors influencing the measured temperature response of wet coal particles is likely to also influence that of dry coal particles given that the experimental technique employed is identical. Therefore this has implications for both wet and dry coal particles and prior to any modelling work being undertaken, a technique must be developed to measure the temperature response of wet and dry coal particles with reasonable accuracy. Without such a technique any modelling work becomes redundant as validation of the model predictions with reliable temperature data is not possible.

In order to develop an effective measurement technique, the “conventional” technique will be critically assessed to isolate factors which may be leading to deviation from the expected measurements. Improvements to the existing technique will be assessed using measurements obtained from wet coal particles and the ability of the measurement technique to reproduce the expected trends in the particle temperature response. Once a suitable measurement technique has been established it will be applied to the measurement of the temperature response of dry coal particles in order
to ascertain the improvements in the dry particle measurements relative to the "conventional" measurements technique.

### 3.4.2 WATER-COOLED PROBE EXPERIMENTS

Given that the conventional temperature measurement technique was unable to measure the expected temperature response for wet coal particles, based on the expected trends, and those obtained in Figure 3.3, it is apparent that the conventional technique is over-estimating the actual particle temperature. Figure 3.4 shows a schematic of the arrangement of the coal particle and thermocouple within the horizontal tube furnace, and also indicates the heat transfer mechanisms which are taking place.

![Schematic diagram of the thermocouple/particle arrangement in the horizontal tube furnace.](image)

**Figure 3.4** Schematic diagram of the thermocouple/particle arrangement in the horizontal tube furnace. Also shown are the heat transfer mechanisms possible during the experiments.

The heat transfer mechanisms shown in Figure 3.4 are summarised as:

\[ h_{p,\text{conv} + \text{rad}} \]

- **External heat transfer to the particle surface via convection and radiation. These are dependent on the heat transfer environment.**

\[ h_{p,\text{cond}} \]

- **Internal heat transfer through the particle via conduction. This is likely to be significant for large coal particles.**

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Experimental Work

\( h_{p,T} \): Heat transfer from the particle to the thermocouple at the point of contact arising from the thermal contact resistance between the two materials.

\( h_{T,\text{conv} + \text{rad}} \): External heat transfer to the thermocouple via convection and radiation. These are dependent on the heat transfer environment.

\( h_{T,\text{cond}} \): Heat transfer along the thermocouple due to conduction. This is likely to be rapid due to the high thermal conductivity of the thermocouple material.

The heat transfer mechanisms involving the particle, namely external convection/radiation (\( h_{p,\text{conv} + \text{rad}} \)) and internal conduction (\( h_{p,\text{cond}} \)) are inherent to the coal particle and represent the mechanisms which are to be characterised by measuring the particle temperature response. The heat transfer resulting at the particle/thermocouple interface due to their thermal contact resistance is generally accepted to be significantly faster than the rate of internal heat transfer via conduction (Holman, 1990). This is desirable given that it leads to rapid heating of the thermocouple to the adjacent particle temperature. If the thermal contact resistance was greater the thermocouple temperature would, in fact, lag behind the particle temperature thus resulting in an underprediction of the actual particle temperature. This then discounts the thermal contact resistance as a significant contributor to the overprediction of the actual particle temperature in the current measurement technique.

While the first three heat transfer mechanisms are unlikely to be adversely affecting the measured particle temperature response, this cannot be said for the remaining two mechanisms. Generally thermocouples are constructed of materials which have high thermal conductivities and low thermal capacities such that they heat rapidly to the required temperature. It is likely that the rate of heat transfer to the thermocouple is lower than that of the particle due to its much smaller diameter, however the lower thermal capacity of the thermocouple implies that the thermocouple is likely to heat more rapidly than the coal particle. An implication of this is that there will be a temperature gradient existing along the length of the thermocouple from the region
outside of the particle, which is exposed to the hot environment, to the tip of the thermocouple inside of the particle. This temperature gradient is the driving force for thermal conduction along the thermocouple as denoted by $h_{T,\text{cond}}$ in Figure 3.4. If this occurs, the thermocouple temperature is likely to exceed that of the particle thus leading to an over-estimation of the measured particle temperature response. Based on this conclusion it can be proposed that by minimising $h_{T,\text{conv}} + \text{rad}$ and $h_{T,\text{cond}}$ a more reliable measurements of the particle temperature may be obtained.

A logical starting point is to consider minimising the heat transfer to the thermocouple from the surroundings ($h_{T,\text{conv}} + \text{rad}$) given that it is this mechanism that leads to the formation of a temperature gradient along the thermocouple thus inducing thermocouple conduction. In order to minimise this effect a suitable means by which the thermocouple can be insulated from the surrounding environment was required. A convenient tool for this purpose was a water cooled probe, the details of which are given schematically in Figure 3.5. The probe essentially consists of a 1.4 mm i.d. stainless steel tube which has a double jacketed outer cover. Cooling water enters the inner jacket and passes down along the length of the probe where it passes into the outer jacket and travels back along the probe and exits to the drain. The probe is approximately 1050 mm in length and has been shown to be extremely efficient in cooling gases sampled directly from fluidized bed combustion systems (Linjewile, 1993). The diameter of the probe is sufficient to enable a 1 mm thermocouple to be threaded through the probe thus acting as an ideal tool for insulating the thermocouple from the surroundings.

Experiments were conducted in which the thermocouple was threaded through the water-cooled probe extending out of the probe sufficiently to enable the wet coal particles to be placed onto the thermocouple tip as per the "conventional" technique. The cooling water was turned on and the particle/thermocouple/water-cooled probe arrangement was subsequently inserted into the horizontal tube furnace at 600°C and the particle temperature measurements were recorded. The results of this experiment are compared with those obtained using the conventional measurements technique in Figure 3.6. It should be noted that in this experiment approximately 1 equivalent
particle diameter was allowed between the tip of the water-cooled probe and the coal particle. The influence of this distance will be discussed later.

**Figure 3.5** Schematic of the Water-Cooled Probe used for reducing External Heat Transfer to the Thermocouple.
Figure 3.6 Measured temperature response at the centre of -11 + 10 mm Bowmans coal particles in the Horizontal Tube Furnace at 600°C. Data obtained using the conventional measurement technique, and with the additional use of the water-cooled probe.

Figure 3.6 shows that the additional use of the water-cooled probe has a definite impact on the measured temperature response with the effect being to lower the temperature at which the particle temperature response begins to plateau and maintaining this temperature plateau over a consistently lower temperature range. The time over which this plateau in the temperature response is maintained is quite similar for both measurement techniques. While it appears that significant improvements in the model predictions have been obtained, there remains some question over the reliability of these measurements. From Figure 3.6 it can be seen that the particle temperature response begins to plateau at approximately 125°C as opposed to the “conventional” technique where an initial plateau temperature of 150°C was observed. It has previously been established that a significant change in the temperature response should be apparent at 100°C consistent with moisture evaporation. It can therefore be concluded that, while the temperature measurements obtained using the water-cooled probe show some improvement over those obtained using the conventional technique, they still deviate from the trends which are expected. This suggests that that the
water-cooled probe is unable to fully alleviate the heat transfer mechanisms which lead to an overestimation of the actual particle temperature. Therefore an alternative measurement technique, or further modification of the existing measurement technique must be sought.

3.4.3 **Multiple-Particle Experiments**

In order to propose an alternative technique, or further modify the technique proposed in Section 3.4.2, the inability of the water-cooled probe to eliminate the heat transfer mechanisms which lead to overestimation of the actual particle temperature must be analysed. Consider the experimental arrangement outlined in Figure 3.7 which schematically represents the arrangement of the water-cooled probe, thermocouple and coal particle in the previous experiment. Here \( T_p \) is the required particle temperature, \( T_M \) is the temperature measured by the thermocouple, \( T_{TI} \) is the temperature of the thermocouple between the tip of the water-cooled probe and the particle a distance \( L \) from the thermocouple tip, and \( T_{T2} \) is the temperature of the thermocouple inside the water-cooled probe.

![Figure 3.7](image.png)

**Figure 3.7** Experimental arrangement of the thermocouple, water-cooled probe and coal particle during the experiments in Section 3.4.2.

From Figure 3.7 it can be seen that there remains a section of the thermocouple between the tip of the water-cooled probe and the particle which will be exposed to the external heating environment. If we consider that the thermocouple temperature in
this region, denoted by $T_{T1}$, is greater than the temperature at the tip of the thermocouple, $T_M$, then thermal conduction along the thermocouple will be evident. Also, thermal conduction will occur along the thermocouple toward the region housed within the water-cooled probe which can be assumed to remain at ambient temperature i.e $T_{T2} \sim 25^\circ$C. The rate of heat conduction toward the thermocouple tip can be approximated by:

$$h_{\text{cond}} \propto \frac{1}{L} (T_{T1} - T_M) \quad (3.2)$$

Therefore in order to minimise the rate of heat conduction toward the thermocouple tip, given that the temperature $T_{T1}$ is difficult to control, it may be suitable to increase the distance, $L$, over which the temperature gradient exists. This is difficult given that fixed size particles are being employed. A possible means of achieving this is to consider a second particle which is placed between the existing particle and the tip of the water-cooled probe in such a way that the thermocouple passes directly through this second particle. This particle then acts as a thermal barrier in that it is able to absorb part of the heat transferred along the thermocouple via conduction as well as effectively increasing the total distance, $L$, over which the temperature gradient exists. The overall result is that the temperature gradient existing at the tip of the thermocouple is significantly reduced and less thermal conduction is able to occur. Ultimately a more accurate measurement of the actual particle temperature response is possible.

In order to experimentally investigate this hypothesis, two wet coal particle were prepared. One of the particles was prepared as previously in that a hole was drilled to just past the centre of the particle while the second particle was prepared with the hole drilled directly through the particle and the particle was forced onto the thermocouple is such a way that a sufficient length of thermocouple protruded from the second particle to enable the first particle to be inserted onto the tip of the thermocouple as previously. Subsequent experiments were conducted using this "two particle" technique for the situation in which the water-cooled probe was present as well as when it was not employed. When the water-cooled probe was present, one effective
particle diameter was maintained between the second particle and the tip of the water-cooled probe. The measurements obtained from these two experiments are shown in Figure 3.8 along with those obtained using the "conventional" measurement technique.

Figure 3.8 shows that the measured temperature response has been altered dramatically by the addition of the second particle and there is much similarity between the results obtained when the water-cooled probe has been used and when it was not employed. This indicates that the bulk of the problem leading to overestimation of the actual particle temperature was directly related to thermal conduction in the region near the end of the thermocouple. The addition of a second particle in this region to act as a thermal barrier as well as to increase the conduction distance, $L$, is effective in reducing the magnitude of conduction near the thermocouple tip thus enabling the particle temperature, $T_p$, to be measured with greater accuracy.

Despite the effectiveness of the second particle in eliminating thermal conduction, it is evident that the measurements obtained when the water-cooled probe was employed do differ slightly from those when the water-cooled probe was not considered. As can be seen, the temperature response obtained when the water-cooled probe was employed is consistently lower than that when no water-cooled probe was utilised until particle drying is complete and the temperature approaches the furnace temperature. At 40s, when it would appear that drying has commenced, the temperature measured using the water-cooled probe is 92°C while that measured in the absence of the water-cooled probe is 100°C. At 100s the corresponding temperatures measured are 100°C and 114°C while at 130s, where drying would be assumed to be almost complete, the measured temperatures are 126°C and 180°C, respectively. Therefore while both experiments yielded much improved results, some differences are evident and the appropriateness of both techniques must be critically assessed.
Figure 3.8 Measured temperature response at the centre of -11 + 10 mm Bowmans coal particles in the Horizontal Tube Furnace at 600°C. Data obtained using the conventional measurement technique, and with the two particle technique under conditions in which the water-cooled probe was both present and when it was not employed.

Referring to the information presented in Section 3.4.1 regarding drying, it is possible to rationalise which of these two techniques provides the more reliable data. As mentioned, much of the moisture present is likely to evaporate at, or slightly above, 100°C. If moisture present near the particle surface is undergoing evaporation at 100°C, the thermal resistance of the particle itself would suggest that the temperature at the centre of the particle is likely to be somewhat lower than 100°C. Also, given that approximately 80% of the moisture present behaves similarly to free moisture (ie. would evaporate at 100°C), it is likely that for a similar fraction of the drying time the centre temperature is likely to be at or slightly below 100°C. These two observations agree well with the measurements obtained in the case in which the water-cooled probe was employed and suggest that the two-particle technique employing the water-cooled probe may provide a suitable technique for measuring the temperature response of large coal particles during heating.
While the previous results suggest that the two particle and water-cooled probe technique is effective, there are two factors which must be investigated in order to make a confident assessment of this technique. The two factors referred to here are the effect of the number of particles as well as the effect of the spacing between the second particle and the tip of the water-cooled probe on the particle temperature response. Using the water-cooled probe, three particles were placed on the end of the thermocouple such that the thermocouple passed directly through two of the particles, and one was placed on the tip of the thermocouple as per the conventional technique. Here the distance between the third particle and the tip of the water-cooled probe was maintained at one particle diameter. A further experiment was performed in which the two particle technique employing the water-cooled probe was repeated however the second particle was located directly adjacent the tip of the water-cooled probe. The particle temperature measurements obtained using these two techniques are shown in Figure 3.9. Also shown are the measurements from Figure 3.8 for the two particle technique employing the water cooled probe with a one particle diameter gap between the second particle and the probe tip.

The measurements in Figure 3.9 indicate that there is no discernible difference in the measured temperature responses obtained using either the two or three particle and water-cooled probe techniques in the horizontal tube furnace. The implication of this conclusion is that the presence of the third particle is not greatly influencing the behaviour of the first two particles. If this is the case it may be similarly suggested that the second particle is also having minimal effect on the behaviour of the first particle. The improvement in the temperature measurements is directly related to the influence of the second particle on the thermocouple behaviour only.

Comparing the temperature measurements for the two particle and water-cooled probe techniques in which either no gap or a one particle diameter gap was maintained between the second particle and the tip of the water-cooled probe, it can be observed that the final temperature obtained when no gap existed is significantly lower than that when the one particle diameter gap was employed.
Figure 3.9 Measured temperature response at the centre of -11 + 10 mm Bowmans coal particles in the Horizontal Tube Furnace at 600°C.

The data in Figure 3.9 was obtained using the two particle and water-cooled probe technique with no gap between the particles and the probe tip, as well as the three particle and water-cooled probe technique. Also shown are the measurements from Figure 3.8 for the two particle and water-cooled probe technique in which a one particle diameter gap is allowed between the second particle and the probe tip.

By allowing the bare thermocouple without the water-cooled probe to reach a steady-state temperature in the furnace under identical operating conditions revealed a thermocouple temperature of 605°C which is comparable with the final temperature observed when a one particle diameter gap was utilised. Thus the temperature measurements obtained when no gap is employed are under-estimating the final particle temperature. It is likely that this is due to thermal conduction taking place away from the thermocouple tip toward the region of the thermocouple inside the water-cooled probe which is maintained at ~25°C. Therefore in order to eliminate thermal conduction of this form, sufficient space must be maintained between the tip of the water-cooled probe and the second particle and it is suggested that a one particle diameter gap is sufficient for particles in the current size range.
3.4.4 **FINE THERMOCOUPLE EXPERIMENTS**

The experiments performed to date have been conducted using a 1mm thermocouple while it has previously been reported that many investigators have used finer (0.1 - 0.5 mm) thermocouples in their investigations. The advantage of finer thermocouples is that they are less influenced by the external heat transfer environment and thus give more reliable measurements for the particle temperature response. A further experiment was conducted in which the thermocouple wires from a thermocouple, identical to that used previously, were obtained without the outer sheath and associated insulation. The wires (~0.2 mm), which were covered in plastic insulation† to eliminate any intimate contact, were passed directly through a 0.5 mm hole drilled to the centre of a -11 + 10 mm Bowmans coal particle such that the thermocouple junction was located at the centre of the coal particle. Because the hole was larger than the thermocouple wires, the hole was packed with pulverised coal in order to eliminate excessive heat transfer into the hole. The thermocouple wires were subsequently passed through the water-cooled probe. Note that the plastic outer covering around each wire was stripped such that it extended to near the particle surface. Care was taken to ensure that the wires would not contact at any point outside of the water-cooled probe except at the junction point. The experimental arrangement used in this experiment is depicted in Figure 3.10.

Temperature measurements were obtained using this technique for similar conditions as previously and the results are compared with those of the conventional technique and the single particle technique utilising the water-cooled probe in Figure 3.11. These measurements show that the temperature response obtained using this technique is almost identical to that obtained using the one particle and water-cooled probe technique in Section 3.4.2. This suggests that, despite the fineness of the thermocouple wires used, heat transfer along the thermocouple wires is still evident. The plastic insulation located between the tip of the water-cooled probe and the particle was observed† to melt quite rapidly (within 20s of insertion into the furnace)

† The plastic insulation served to ensure electrical contact between the thermocouple wires was prevented and some melting was apparent during the experiments.
† Using a torch the interior of the horizontal tube furnace could be visually monitored.
thus indicating rapid heat transfer to these regions of the thermocouple wires. It is highly likely then that this results in overestimation of the actual particle temperature in a similar way to the one particle and water-cooled probe technique in Section 3.4.2. This result has implications relating to the reliability of the “conventional” technique and this will be further discussed in Section 3.4.7.

Figure 3.10 Experimental arrangement of the coal particle, water-cooled probe and thermocouple wires used to measure the particle temperature response in Section 3.4.4.

Figure 3.11 Measured temperature response at the centre of -11 + 10 mm Bowmans coal particles in the Horizontal Tube Furnace at 600°C. Data obtained using the conventional technique, the one particle and water-cooled probe technique, and the thermocouple wire and water-cooled probe technique.
3.4.5 APPLICATION OF THE MODIFIED TECHNIQUE TO DRY COAL PARTICLES IN THE HORIZONTAL TUBE FURNACE.

The experiments detailed above clearly indicate that the modified technique, which incorporates the use of a water-cooled probe to insulate the thermocouple from the surrounding heat transfer environment along with a second particle to minimise thermal conduction along the thermocouple, is extremely effective in eliminating any factors which may compromise the temperature measurements. Thus, the modified technique is capable of generating reliable particle temperature measurements. This has been verified based on wet coal particle measurements however the effect of this measurements technique on the temperature response of dry coal particles, if any, is yet to be established. Subsequently experiments were conducted using dry coal particles in the horizontal tube furnace at 600°C, and employing both the conventional measurement technique and the modified technique proposed in this study. The particle temperature measurements obtained from these experiments are presented in Figure 3.12.

The results confirm that the modified technique also produces significantly different temperature measurements than the "conventional" technique for dry coal particles. Note that the magnitude in the improvement in the temperature measurements is lower than that for the wet coal particles, which is as expected. Due to the presence of moisture the wet coal particles heat up much slower than the dry coal particles. Under the conventional technique the subsequent driving force for thermal conduction, $T_{T1} - T_M$, is generally greater for the wet coal particle as $T_{M, wet} < T_{M, dry}$ during the majority of the heating time. Thus the magnitude of the over-estimation of the particle temperature is lower for the dry coal particles which is reflected in the improvements gained in Figure 3.12. These results confirm that the modified technique is also applicable to dry coal particles and significant improvements in the temperature measurements are possible.
Figure 3.12 Measured temperature response at the centre of -11 + 10 mm dry Bowmans coal particles in the Horizontal Tube Furnace at 600°C. Data obtained using the conventional technique and the modified technique proposed in this study.

3.4.6 APPLICATION OF THE MODIFIED Technique TO THE FLUIDIZED BED REACTOR

The modified particle temperature measurement technique has been shown to be suitable for use in the horizontal tube furnace which displays a relatively moderate heating environment. In a fluidized bed reactor, however, the heating environment is particularly coarse and involves the constant contact between the solid particle and the bed material as well as between the thermocouple and the bed material. The resulting heat transfer rates are significantly larger and as a result the modified technique must be tested to ensure it is able to generate reliable temperature measurements under such coarse operating conditions.

Figure 3.13 shows the temperature measurements obtained from wet coal particles undergoing devolatilization in the fluidized bed at 600°C using three experimental techniques. The conventional technique, as with similar experiments in the horizontal tube furnace, is unable to generate measurements which depict the expected plateau in
the temperature response at 100°C consistent with moisture removal. This is expected given that there is intimate contact between the thermocouple and the bed material which will rapidly increase the thermocouple temperature and facilitate thermal conduction along the thermocouple resulting in the observed over-estimation of the actual particle temperatures. Consequently, the modified technique proposed above was utilised to generate experimental data under identical conditions to the previous case, and the results are shown in Figure 3.13. It is apparent that there is a distinct temperature plateau at 100°C corresponding to moisture release. Also shown is the experimental data obtained when the three particle and water-cooled probe technique was employed which again shows the distinctive temperature plateau at 100°C. However, the temperature plateau in this case is far more substantial than for the two particle and water-cooled probe experiment.

![Graph showing temperature response](image)

**Figure 3.13** Measured temperature response at the centre of -11 + 10 mm wet Bowmans coal particles in the Fluidized Bed Reactor at 600°C. Data obtained using the conventional technique, the two particle and water-cooled probe technique, as well as the three particle and water-cooled probe technique.
Based on the results presented in Figure 3.13 it can be concluded that the modified technique proposed to measure the temperature response of large coal particle during heating is applicable to fluidized bed applications. However rather than employing two coal particles, three coal particles were required with two of the particles necessary to ensure that thermal conduction along the thermocouple is minimised. The need for an additional particle under fluidised-bed conditions is quite reasonable given the enhanced heat transfer environment existing within a fluidized bed. This causes a much more rapid increase in the thermocouple temperature and consequently the driving force for thermal conduction \((T_{TL} - T_M)\) is increased. Thus in order to minimise thermal conduction the conduction distance, \(L\), must be increased which is effectively achieved via the extra particle.

![Temperature response graph](image)

**Figure 3.14** Measured temperature response at the centre of -11 + 10 mm dry Bowmans coal particles in the Fluidized Bed Reactor at 600°C. Data obtained using the conventional technique as well as the three particle and water-cooled probe technique.

A final test of this temperature measurement technique is to apply it to measuring the temperature response of dry coal particles under fluidized bed heating conditions. The measurements obtained using the three particle and water-cooled probe technique are
compared with those of the conventional technique in Figure 3.14, above. Again, there is a distinct variation in the temperature measurements obtained using the three particle and water-cooled probe technique relative to the conventional technique. As in the horizontal tube furnace, the magnitude of this variation for dry coal particles in the fluidized bed is less than that for wet coal particles for similar reasons to those discussed in Section 3.4.5. Thus it can be concluded that this technique can also be utilised to generate improved particle temperature measurements from dry coal particles under fluidized bed heating conditions.

3.4.7 **Statistical Analysis of the Modified Particle Temperature Measurement Technique**

Sections 3.4.2 to 3.4.6 have detailed the development of a particle temperature measurement technique, based on the conventional measurement technique outlined in Section 3.4.1, which has been modified to minimise any external factors that may act to compromise the temperature measurements obtained. While these sections have shown that this modified technique is capable of generating significantly improved temperature measurements, the reliability of this technique must be established and the accuracy to which this technique is able to measure the temperature response must be compared with the relative improvement in the measurements in order to ascertain if the technique can be confidently employed. Due to the coarse nature of the heating environment and the rapid heating rates encountered by the particles it was envisaged that from a practical outlook the most difficult measurements to reliably obtain would be in the case of dry coal particles undergoing devolutilization in a fluidized bed environment. Subsequently, several repeat runs were conducted utilising the three particle and water-cooled probe technique, to investigate the repeatability of the particle temperature measurement technique under these conditions. The measurements obtained from five repeat runs are presented in Figure 3.15.
Figure 3.15 Measured temperature response at the centre of -11 + 10 mm dry Bowmans coal particles in the Fluidized Bed Reactor at 600°C. Data obtained using the three particle and water-cooled probe technique with results from five repeat runs displayed.

It is difficult to perform a standard statistical test on this data in order to ascertain, from a statistical viewpoint, whether or not the data presented in Figure 3.15 differs significantly from that in Figure 3.14 for the conventional measurement technique. It would be convenient to describe the data collected from each run with a single value which would be representative of the data, and furthermore allow the data to be analysed with a standard statistical test. A convenient parameter for this purpose was the weighted mean heating rate which was defined as (Megalos, 1998):

$$\frac{dT}{dt}_{\text{mean}} = \frac{\sum \left( \frac{dT}{dt}.t \right)}{\sum t}$$ (3.3)

The parameter given in Equation (3.3) has been effectively used to investigate reactivity data for various coals obtained from various experimental techniques.
(Megalos, 1998) which is analogous to the situation presented here. Using Equation 3.3, the data presented in Figure 3.15 was analysed and the results are presented in Table 3.3.

Table 3.3 Statistical data based on the temperature data presented in Figure 3.15.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>( \frac{dT}{dt} ) (K.s(^{-1}))</th>
<th>( \frac{dT}{dt} ) (K.s(^{-1}))</th>
<th>( \sigma \left( \frac{dT}{dt} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.271</td>
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<td></td>
</tr>
<tr>
<td>3</td>
<td>3.457</td>
<td>3.327</td>
<td>0.1023</td>
</tr>
<tr>
<td>4</td>
<td>3.368</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.351</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the conventional technique presented in Figure 3.14, the weighted mean heating rate calculated is 2.409 K s\(^{-1}\). Based on these values a simple z-test can be carried out to determine if the conventional technique differs significantly from the modified technique (Perry and Green, 1984). The z-test parameter is defined as:

\[
z = \frac{\bar{x} - \mu_0}{\sigma / \sqrt{N}}
\]  

(3.4)

Here \( \bar{x} \) is the population mean based on the conventional measurement technique, and \( \mu_0 \) is the proposed population mean which is that of the modified measurement technique. \( s \) is the standard deviation of the population mean as per Table 3.3, and \( N \) is the number of sample points used to obtain \( \bar{x} \). Therefore the z-test parameter is:

\[
z = \frac{3.327 - 2.409}{0.1023 / \sqrt{1}} = 8.974
\]

The hypothesis tested here are:
H₀ : \( \bar{x} = \mu_0 \) vs H₁ : \( \bar{x} \neq \mu_0 \)

From the normal tables we get \( P(z > 8.974) \approx 0.0\% \). Thus we effectively have no statistical probability that the data from the conventional technique is similar to that of the modified technique and we reject hypothesis H₀ in favour of H₁.

Furthermore it would be useful to test whether or not the data reported in Table 3.3 are similar statistically to add further support to the above result. Considering that the sample has five data points, the probability statistic for a 95\% confidence interval from the T-distribution Tables is \( P_{0.995,4} = 2.132 \) (Perry and Green 1984). This tells us that 95\% of the data are likely to lie between the limits of:

\[
-2.132 \leq \frac{\bar{x} - \mu_0}{\sigma / \sqrt{N}} \leq 2.132
\]

(3.5)

Given that \( \mu_0 = 3.217 \), \( \sigma = 0.1023 \), and \( N = 5 \), then 95\% of the data should lie between the limits of 3.229 and 3.425. Given that only one of the data points lie outside of these limits it is reasonable to conclude that the data presented are statistically similar. Therefore there is no statistical difference between the temperature responses presented in Figure 3.15.

Based on the data presented in Figures 3.14 and 3.15, as well as the statistical evidence outlined above, we can confidently deduce that the temperature measurements obtained using the conventional measurement technique differ significantly from those obtained via the modified technique proposed in this study. Furthermore the modified measurement technique is capable of generating data which has been shown to be repeatable from a statistical basis.

3.4.8 COMPARISON WITH LITERATURE TEMPERATURE DATA

The modified technique which has been proposed and critically assessed in Sections 3.4.2 to 3.4.7 can now be confidently employed to measure the temperature response
of large coal particles, and the data can be used for model validation with similar confidence. Also, this technique has been shown to yield measurements which differ significantly from those measured using the conventional measurement technique frequently used in the literature. These two results then imply that the data presented in the literature to date, derived using the conventional measurement technique, may not be accurate. The literature data must then be examined, along with the experimental technique, in order to assess its reliability.

The basis of the development of the modified temperature measurement technique was to develop a technique which could predict the temperature plateau expected at \(-100^\circ\text{C}\) during the drying of wet coal particles due to moisture evaporation. Due to the complications which arise from the presence of moisture in the coal particles, the majority of the data presented in the literature has been collected using either low moisture coals (Stubington and Sumaryono, 1984; Tia et al., 1991; Adesanya and Pham, 1995) or dried coal particles (Tomczek and Kowol, 1990). Only Kilic et al. (1993) and Winter et al. (1997) performed any in-depth investigation of the temperature response of wet coal particles. The work of Dincer et al. (1996) employed an inert material rather than coal, however the conventional temperature measurement technique was employed. The difference between these studies and the present study is that finer thermocouples were utilised which in theory should act to minimise any compromising heat transfer effects, thus giving more reliable temperature measurements.

A similar approach will be used to assess the reliability of the data presented in the literature as was used to develop the modified temperature measurement technique, i.e. the ability of the measurement technique to predict the temperature response of wet coal particle temperature will be reviewed. Winter et al. (1997) reported temperature data at the centre of a sub-bituminous coal having a moisture content of 25.3 wt% (0.339 g (g dry coal)\(^{-1}\)) for particle sizes of 5.5 mm, 10 mm, and 15 mm in a fluidized bed combustor obtained from the conventional measurement technique. The combustor operated at \(-800^\circ\text{C}\) with an oxygen partial pressure of 10 kPa (i.e. combustion conditions). The measured temperature data indicated that a distinctive
temperature plateau at \( \sim 100^\circ \text{C} \) was observed for the 15 mm particles, while a significant moisture effect was also apparent for the 10 mm particles. In the latter case, however, the effect was observed between particle temperatures of 100\(^\circ\)C and 400\(^\circ\)C. Further data was presented for the temperature response of 10 mm sub-bituminous coal particle at combustor temperatures of 700\(^\circ\)C, 800\(^\circ\)C, and 900\(^\circ\)C. Again the moisture effect was evident between 100\(^\circ\)C and 400\(^\circ\)C for combustor temperatures of 700\(^\circ\)C and 800\(^\circ\)C, while at a combustor temperature of 900\(^\circ\)C there was a slight reduction in the particle heating rate between 400\(^\circ\)C and 600\(^\circ\)C. Finally, data from a second sub-bituminous coal having a moisture content of around 52.7 wt\% (1.11 g (g dry coal)\(^{-1}\), 10 mm), obtained in the combustor at 800\(^\circ\)C, showed no distinctive temperature plateau despite having a similar moisture content to the coal used in the present study.

Given that a distinctive temperature plateau is evident for the 15 mm particle and becomes less apparent as the particle size decreases tends to suggest that the conventional temperature measurement technique may not be reliable. Based on the argument presented in Section 3.4.3, a larger particle effectively has a larger thermal conduction distance, \( L \), which would thus act to reduce the rate of thermal conduction to the tip of the thermocouple thus minimising any adverse effects on the temperature measurements. Also, the investigation into the applicability of the modified technique in fluidized bed systems (Section 3.4.6) has indicated that the thermal conduction distance, \( L \), must be greater than that in more moderate heating environments such as the horizontal tube furnace due to the excessive external heat transfer rates. It would be expected that a similar situation would apply in the fluidized bed combustor of Winter et al. (1997). All of this supports the suggestion that the conventional particle measurement technique can not produce reliable temperature measurements under fluidized bed heating conditions.

Further evidence of this can be gained from the data reported by Kilic et al. (1993). Kilic et al. (1993) used a 0.1 mm thermocouple to measure the temperature response of a 20 mm lignite particle in a fluidized bed at \( \sim 860^\circ \text{C} \). Unfortunately the details of the coal type was not included in the report. Once again the experimental data did not
show the distinctive plateau in the temperature response at 100°C, however, a significant deviation in the temperature response was evident between 350°C and 600°C. Based on the data reported by Winter (1997) and Kilic et al. (1993) it becomes increasingly apparent that the conventional particle measurement technique is unable to provide reliable particle temperature data due to excessive thermal conduction effects along the thermocouple.

While making a definite deduction as to the reliability of the conventional measurement technique is difficult based on data presented for dry coal particles, there are some distinctive trends which may be used as a basis for such a judgement. The most distinctive of these is the particle heating rate during the initial stages of devolatilization or heating. Figure 3.14 shows that the modified temperature measurement technique shows a significantly slower initial particle heating rate then the conventional measurement technique for the dry coal particles. It would be expected that early in the heating the effect of thermal conduction may be large as the thermocouple temperature increases rapidly while the particle centre temperature is cool thus leading to a large driving force for thermal conduction ($T_{T1} - T_M$). The data reported by Adesanya and Pham (1995) is expected to be somewhat more reliable than the majority of the remaining literature data reported due to the precautions taken to eliminate external heat transfer forces acting on the thermocouple. The data of Winter et al. (1997) indicates that the conventional technique may be applicable to large coal particles and Adesanya and Pham (1995) have used particles between 10.2 mm and 16 mm in their studies. Also, the particle and thermocouple were protected from the furnace walls by a ceramic tube thus reducing radiation heat transfer which is significant at low particle and thermocouple temperatures. The data of Adesanya and Pham (1995) also exhibited the low initial heating rates observed using the modified temperature measurement technique, particularly for the 16 mm particles. Thus it can be suggested that, in the case of particles in the range 10 - 20 mm, a reliable particle measurement technique should be capable of predicting the low initial heating rates expected during heating.
The temperature data reported by Tia et al. (1991) for 11.1 mm coal particles did not show this low initial heating rate and the temperature response increased almost linearly from the start and only slowed as the temperature approached the final temperature. The resulting data was comparable to that presented for the conventional technique in Figure 3.14. A similar temperature response was reported by Dincer et al. (1996) for an inert material in a fluidized bed at 860°C. Dincer et al. (1996) used a relatively large particle (20 mm) and the centre temperature response would be expected to show low initial heating rates based on the reported particle Biot number\(^1\) (Bi = 1.9). Tomeczek and Kowol (1991) measured the temperature response of dry 15 mm coal particles under fluidised-bed conditions (950K) using a 0.1 mm thermocouple and, conversely, the data showed a low initial heating rate. The temperature response of air-dried particles, which retain a fraction of the initial moisture, was also presented and the distinctive temperature plateau expected at 100°C is indeed observed.

Ultimately it can be concluded that the majority of the particle temperature data presented to date in the literature may not be reliable due to the effects of excessive thermal conduction along the thermocouple. While some of the data reported follows the expected trends, the same technique is producing data which do not exhibit these trends in alternate studies, which questions the reliability of the technique in general. As a result, the data presented in the literature may not be useful for model validation purposes in the present study. Based on the argument outlined above it cannot be conclusively concluded that all of the particle temperature data presented in the literature is unreliable. However, there are a number of inconstancies which exist between the data reported despite the fact that an almost identical measurement technique was employed. It can however be stated with confidence that when measuring the temperature response of large particles during heating, much care must be taken to ensure that the measurement technique employed is capable of generating reliable measurements. Also, care should be taken when considering using the particle temperature data presented in the literature for purposes such as model validation to ensure that reliable particle temperature data is selected.

\(^1\) Temperature gradients are expected to exist with particles having Biot numbers in the range Bi>0.1 (Holman, 1990). Thus the centre of the particle will show a slow initial heating rate.
3.4.9 Summary

A systematic investigation has been undertaken to develop a technique for measuring the temperature response of large coal particles during devolatilization. Initially, the reliability of the conventional measurement technique used widely in the literature was assessed and it was concluded that this measurement technique was not reliable for 1 mm thermocouples. This conclusion was based on the inability of the conventional technique to predict the temperature plateau expected at 100°C due to moisture evaporation from wet coal particles. Thus an alternative, or modified technique, was explored.

It was deduced that the conventional technique was likely to be over-estimating the actual temperature response due to heat transfer to the thermocouple for the surroundings and subsequent thermal conduction along the thermocouple from the region of the thermocouple external to the particle, to the tip of the thermocouple inside the particle. In order to minimise external heat transfer to the thermocouple a water-cooled probe was employed to shield the thermocouple from the external environment and maintain it at ambient conditions. This was show to have a slight improvement on the temperature measurements and it could be further deduced that much of the problem was related to thermal conduction effects near the end of the thermocouple.

Based on this conclusion it was deduced that the thermal conduction effects could be minimised by the presence of a second particle between the first particle and the water-cooled probe to act as a thermal barrier to thermal conduction. This technique, in combination with the water-cooled probe, was found to generate extremely reliable particle temperature measurements and the temperature plateau due to moisture evaporation at 100°C was distinctively apparent. Fine thermocouple experiments were conducted using the thermocouple wires from a K-type thermocouple and the water-cooled probe. The wires were in the order of 0.1 mm in diameter which are comparable with thermocouples used in the literature, however, this technique did not show any improvement over the measurement collected using the 1mm thermocouple
and water-cooled probe. It was proposed then that the modified technique employing
the water-cooled probe and multiple particles on the thermocouple tip be used in
preference to the conventional particle temperature measurement technique.

While the modified technique has been shown to be applicable to wet coal particles in
the horizontal tube furnace, it was also used to measure the temperature response of
dry coal particles in the horizontal tube furnace showing significantly different results
from similar measurements obtained via the conventional technique. Similarly, the
measurements obtained for both wet and dry coal particles in the fluidized bed
differed significantly from those of the conventional technique. It was also shown that
the much more severe heat transfer environment in the fluidised-bed necessitates the
use of a third particle on the thermocouple tip to minimise thermal conduction.
Ultimately this technique has been shown to be effective under the conditions
prevalent in both the horizontal tube furnace and the fluidized bed reactor.

In order to validate this particle temperature measurement technique, analysis was
undertaken to ensure that the accuracy of this measurement technique was sufficient
that the measurements were statistically different from those of the conventional
measurement technique. It was envisaged that producing repeatable measurements for
dry coal particle in the fluidized bed reactor would be the most difficult due to the
rapid heating rate, hence measurements under this condition were used as the basis for
the analysis. It was found that even under these conditions, the particle temperature
measurements obtained from the modified measurement technique were statistically
similar, and furthermore they were statistically different from those obtained using the
conventional measurement technique. Given this result then it is possible to use the
measurements obtained from the modified measurement technique with confidence
given that they are repeatable, they are statistically different from those of the
conventional measurement technique, and they give more reliable measurements of
the particle temperature response for the conditions of this study.

Finally, the temperature data reported in the literature was analysed to assess the
reliability of this data given the knowledge gained in the development of the modified
particle temperature measurement technique. It was found that the conventional technique employing much finer thermocouples was unable to consistently predict the trends predicted during the heating of both wet and dry coal particles in a variety of heat transfer environments. While all of the temperature data reported cannot be repudiated, caution must be taken when using this data, particularly for model validation purposes, to ensure that the data is sufficiently accurate for the objective in mind.

3.5 EXPERIMENTAL RESULTS

3.5.1 PARTICLE TEMPERATURE DATA

3.5.1.1 Horizontal Tube Furnace

Particle temperature measurements were carried out using the modified particle temperature measurement technique proposed in Sections 3.4.2 and 3.4.3 in the horizontal tube furnace at furnace temperatures of 600°C, 700°C, and 800°C. Measurements were recorded using both -11 + 10 mm and -9 + 8 mm wet coal particles and the results of these experiments are displayed in Figures 3.16 and 3.17 for the -11 + 10 mm and -9 + 8 mm particles, respectively. Two repeat runs were conducted for each particle size at each temperature to ensure the repeatability of the measurements.

The data in Figures 3.16 and 3.17 follow the expected trends in that drying appears to be complete earlier as the furnace temperature increases for both particle sizes. Also, at the same furnace temperature it is observed that drying occurs earlier for the -9 + 8 mm particles than for the -11 + 10 mm particles which is also as expected. The measurements obtained were highly repeatable for both particle sizes which adds further support to the reliability of the modified particle temperature measurement technique.
Further temperature measurement experiments were conducted under identical conditions to those above, however in these experiments, dry coal particles formed from the drying of wet coal particles identical to those above were used. The dry particles were generated using the drying procedure outline in Section 3.3.2 and the data obtained from dry coal particles generated from -11 + 10 mm and -9 + 8 mm wet coal particles are displayed in Figures 3.18 and 3.19, respectively. Note that the dry coal particles did not have the same initial diameters as the wet coal particles as a direct result of shrinkage during the drying process. The extent of the shrinkage will be discussed in Section 3.5.3.

The data in Figures 3.18 and 3.19 also follow the trends expected in that the particles heat up more rapidly at higher furnace temperatures, and the smaller particles in Figure 3.19 heat up quicker than the larger particles in Figure 3.18. Again the data is highly repeatable despite the higher heating rates evident. A point of interest is that in Figure 3.19, the temperature responses measured at 700°C (HTF700g & HTF700h) appear to be closer to those at 600°C than for the particles in Figure 3.18. It is expected that the data would be more consistent however it must also be conceded that gaining accurate measurements for smaller particles at higher temperatures will be more difficult, especially for dry coal particles, due to the thermal conduction effect explained in Section 3.4.3. Despite this, the data appear to be consistent and repeatable and thus can be confidently used for model validation purposes.
Figure 3.16 Experimental data for the temperature response at the centre of -11 + 10 mm wet Bowmans coal particles in the Horizontal Tube Furnace at 600°C, 700°C, and 800°C.

Figure 3.17 Experimental data for the temperature response at the centre of -9 + 8 mm wet Bowmans coal particles in the Horizontal Tube Furnace at 600°C, 700°C, and 800°C.
Figure 3.18  Experimental data for the temperature response at the centre of dry coal particles, generated from -11 + 10 mm wet Bowmans coal particles, in the Horizontal Tube Furnace at 600°C, 700°C, and 800°C.

Figure 3.19  Experimental data for the temperature response at the centre of dry coal particles, generated from -9 + 8 mm wet Bowmans coal particles, in the Horizontal Tube Furnace at 600°C, 700°C, and 800°C.
3.5.1.2 Fluidized Bed Reactor

The data presented in Section 3.5.1.1 is ideally suited to model development purposes given that the heat transfer environment is reasonably well defined and the modified particle temperature measurement technique has been employed to ensure accuracy of the particle temperature measurements. However, as much of the future emphasis is on fluidized bed applications, similar data is necessary in order to test the ability of the model to predict the behaviour of large coal particles in a fluidized bed environment. Subsequently, temperature measurements were collected using the modified temperature measurement technique outlined in Section 3.4.6 in a fluidized bed reactor at temperatures of 650°C, 750°C, and 850°C. Measurements were carried out using -11 + 10 mm coal particles only as it was extremely difficult to obtain reliable measurements from the -9 + 8 mm particles regardless of the moisture content. Figures 3.20 and 3.21 show the experimental data obtained from wet and dry coal particles, respectively, where once again the dry particles were derived from drying of the -11 + 10 mm wet coal particles.

The experimental data for the wet coal particles in the fluidized bed reactor (Figure 3.20) exhibits a trend which is not apparent in the data from the horizontal tube furnace (Figures 3.16 & 3.17). The temperature plateau due to drying is evident, however, immediately after drying would appear to have ceased, there is a period in which a moderate heating rate exists lasting up to a centre temperature of 400°C. After this period the heating rate becomes much more rapid. In the horizontal tube furnace the particle temperature increases rapidly immediately after drying has apparently finished and this phenomenon is not observed. It is likely that this is due to the influence of thermal conduction, which is more difficult to be evident in the fluidized bed than in the horizontal tube furnace, becoming significant during the final stages of drying.
Figure 3.20 Experimental data for the temperature response at the centre of -11 + 10 mm wet Bowmans coal particles, in the Fluidized Bed Reactor at 650°C, 750°C, and 850°C.

The uncertainty surrounding this phenomenon adds to the conclusion that the data derived under fluidized bed conditions is not particularly suited to model validation purposes. It is reasonable to suggest that this data can be utilised as a means of comparing the model predictions for the temperature response under fluidized bed heating conditions, however the limitations of this data should be carefully considered when any comparisons are made.

Figure 3.21 shows the experimental data obtained from the fluidised-bed reactor under similar conditions to the experiments in Figure 3.20, however employing dry coal particles. At each reactor temperature a distinct region is evident at the initial stages where the heating rate is low, as is expected. Again, it is difficult to ascertain the extent to which overprediction of the actual particle temperature is occurring. Thus the data presented in Figure 3.21 is limited to comparative purposes and is not applicable to model validation purposes.
Figure 3.21 Experimental data for the temperature response at the centre of dry coal particles, generated from -11 + 10 mm wet Bowmans coal particles, in Fluidized Bed Reactor at 650°C, 750°C, and 850°C.

3.5.2 Mass Loss Experiments

To supplement the particle temperature data presented in Sections 3.5.1.1 and 3.5.1.2, particle mass loss data was collected under identical conditions to the particle temperature experiments. Individual particles were weighed and their initial weight ($M_0$) was recorded. The particles were inserted into a wire mesh basket which was subsequently inserted into the horizontal tube furnace and allowed to remain for a specified time interval. Once the required time was complete, the wire mesh basket was positioned above the quench nitrogen stream to rapidly quench the particles ensuring minimal additional mass loss took place. The particle was then weighed and the final mass recorded ($M_t$) which enabled the fractional mass remaining ($M_t / M_0$) to be determined. This was repeated over a number of time intervals until minimal additional mass loss was observed.

The data obtained for the -11 + 10 mm and -9 + 10 mm wet Bowmans coal particles in the horizontal tube furnace are shown in Figures 3.22 and 3.23, respectively. This data represents the mass loss data analogous to the temperature data in Figures 3.16
and 3.17, respectively. Figures 3.24 and 3.25 exhibit the mass loss data derived from the dry coal particles analogous to the temperature data reported in Figures 3.18 and 3.19. The lines in Figures 3.22 to 3.25 represent trend lines only and are included to enable the data at different temperatures to be clearly distinguished. Once again the general trends expected are observed, in that the weight loss occurs more rapidly as the temperature increases and as the particle size decreases. The fractional mass remaining for the wet coal particles is significantly lower than that for the dry coal particles due to the significant mass of moisture present in the parent coal. For the wet coal particles the fractional mass remaining upon completion of devolatilization is in the range of 0.23 - 0.26. The analysis of Bowmans coal presented earlier (Table 3.1, Section 3.3.2) indicates that Bowmans coal has a volatile matter content of 49.2 wt% (db) and the drying experiments conducted in Section 3.3.2 revealed an average moisture content of 52 wt% moisture. Given this then the expected mass fraction remaining after devolatilization is 0.236 which agrees well with the experimental data.

Figure 3.22 Experimental data for the fractional mass remaining from -11 + 10 mm wet Bowmans coal particles in the Horizontal Tube Furnace at 600°C, 700°C, and 800°C. Data is complimentary to the temperature data in Figure 3.16.
Figure 3.23 Experimental data for the fractional mass remaining from -9 + 8 mm wet Bowmans coal particles in the Horizontal Tube Furnace at 600°C, 700°C, and 800°C. Data is complimentary to the temperature data in Figure 3.17.

Figure 3.24 Experimental data for the fractional mass remaining from dry coal particles, generated from -11 + 10 mm wet Bowmans coal particles, in the Horizontal Tube Furnace at 600°C, 700°C, and 800°C. Data is complimentary to the temperature data in Figure 3.18.
Figure 3.25  Experimental data for the fractional mass remaining from dry coal particles, generated from -9 + 8 mm wet Bowmans coal particles, in the Horizontal Tube Furnace at 600°C, 700°C, and 800°C. Data is complimentary to the temperature data in Figure 3.19.

Furthermore, for the dry coal particles the mass fraction remaining is expected to be \( \sim 0.508 \) which also agrees with the data presented in Figures 3.24 and 3.25 except for the data at 600°C. Based on the experimental observations reviewed in Section 2.2.3.1, it is expected that at 600°C the volatile matter will not be totally removed which explains this observation.

It is interesting to compare the observed devolatilization times based on the fractional mass remaining with the heating times based on the corresponding temperature data. For the -11 + 10 mm wet coal particles in Figure 3.22, the estimated devolatilization times are 250s, 200s, and 180s at 600°C, 700°C, and 800°C, respectively. These times compare well with the times required for the centre of the particle to reach the furnace temperature in Figure 3.16. Similarly for the -9 + 8 mm particles in Figure 3.23, the observed devolatilization times of 200s, 150s, and 120s at 600°C, 700°C, and 800°C, respectively correlate extremely well with the observed heating times in Figure 3.17.
The same can be said for the dry coal particles. The dry coal particles generated from the $-11 + 10$ mm wet coal particles exhibit devolatilization times of 120s, 100s, and 80s, while those generated from the $-9 + 8$ mm wet coal particles have devolatilization times of 120s, 90s, and 70s for a similar range of furnace temperatures. Figures 3.18 and 3.19 indicate that the heating times are again quite similar. These observations suggest that, for particles of this size range under heating conditions prevalent in the horizontal tube furnace, the devolatilization process may be heat transfer controlled. This has been suggested throughout the literature (Agarwal et al., 1984a, Stubington and Sumaryono, 1984). While the data presented here supports this hypothesis, this will be investigated further later in this study.

### 3.5.3 Shrinkage Experiments

The effect of particle shrinkage during drying was found to be significant for Bowmans coal and, as such, it was deemed necessary to determine the extent to which shrinkage was occurring. The extent of shrinkage was characterised by measuring the particle size before and after devolatilization and defining a parameter termed the shrinkage factor (SF) which is simply defined as:

$$SF = 1 - \frac{\overline{d}_w}{\overline{d}_0}$$  (3.6)

where $\overline{d}_w$ is the average particle diameter after devolatilization and $\overline{d}_0$ is the average particle diameter before devolatilization. Up to three particle diameter measurements were taken from each particle before and after devolatilization in order to obtain the average diameters. Measurements were taken using both $-11 + 10$ mm particle and $-9 + 8$ mm wet Bowmans coal particles at temperature of 600°C, 700°C, and 800°C in the horizontal tube furnace. The particle residence times in these experiment was 600s which was sufficient for devolatilization to be assumed to be complete based on the data presented in Figures 3.22 and 3.23. The data and calculated shrinkage factors are summarised in Table 3.6.
From this data a number of statistical test was employed to determine whether or not the shrinkage factor was dependent on the particle size as well as on the devolatilization temperature. This analysis was conducted via a two-way ANOVA test (with replication) using Microsoft Excel© Version 5.0c. The results of the two-way ANOVA are summarised in Table 3.5. The standard hypothesis for an ANOVA test are:

\[
\begin{align*}
H_{0,\text{row}} &: \quad \text{there is no row factor effect} \\
H_{0,\text{column}} &: \quad \text{there is no column factor effect} \\
H_{0,\text{row} / \text{column}} &: \quad \text{there is no interaction effect between rows and columns}
\end{align*}
\]

For the temperature and particle-size data, the F-statistic is greater than the critical F value \((F_{\text{crit}})\) in which case the null hypotheses are rejected. This then indicates that the shrinkage factor is statistically dependent on both the temperature and the initial particle size. The F-statistic for the row/column interaction is lower than the critical F value which infers that the variations between the shrinkage factors at any temperature and particle size are consistent for all the possible combinations which indicates that there are no unusual trends within any particular data set. Therefore average shrinkage factors were calculated for each set of particle size and temperature, and these are characteristic of the particle behaviour under the respective conditions. The shrinkage factors are presented in Table 3.4.

**Table 3.4** Average shrinkage factors calculated at each set of experimental conditions.

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Temperature</th>
<th>Shrinkage Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>-11 + 10 mm</td>
<td>600°C</td>
<td>0.200</td>
</tr>
<tr>
<td>-11 + 10 mm</td>
<td>700°C</td>
<td>0.206</td>
</tr>
<tr>
<td>-11 + 10 mm</td>
<td>800°C</td>
<td>0.230</td>
</tr>
<tr>
<td>-9 + 8 mm</td>
<td>600°C</td>
<td>0.213</td>
</tr>
<tr>
<td>-9 + 8 mm</td>
<td>700°C</td>
<td>0.242</td>
</tr>
<tr>
<td>-9 + 8 mm</td>
<td>800°C</td>
<td>0.235</td>
</tr>
</tbody>
</table>
### Table 3.5 Summary of results from a two-way ANOVA test conducted on the shrinkage factors in Table 3.6.

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size</td>
<td>0.002327</td>
<td>1</td>
<td>0.002327</td>
<td>7.351824</td>
<td>0.0143</td>
<td>4.413863</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.003106</td>
<td>2</td>
<td>0.001553</td>
<td>4.905492</td>
<td>0.01993</td>
<td>3.554561</td>
</tr>
<tr>
<td>Interaction</td>
<td>0.000884</td>
<td>2</td>
<td>0.000442</td>
<td>1.396753</td>
<td>0.272962</td>
<td>3.554561</td>
</tr>
<tr>
<td>Within</td>
<td>0.005698</td>
<td>18</td>
<td>0.000317</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>0.012015</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 3.6 Summary of experimental data and calculated shrinkage factors for -11 + 10 mm and -9 + 8 mm Bowmans coal particles in the horizontal tube furnace at 600°C, 700°C, and 800°C.

<table>
<thead>
<tr>
<th>Particle Size (mm)</th>
<th>Temperature (°C)</th>
<th>Initial Diameter (mm)</th>
<th>Final Diameter (mm)</th>
<th>Shrinkage Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>-11 + 10</td>
<td>600</td>
<td>10.0 10.6 11.4</td>
<td>8.7 8.4 8.7</td>
<td>0.194</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>600</td>
<td>10.5 11.1</td>
<td>9.0 8.2</td>
<td>0.204</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>700</td>
<td>10.4 10.9 11.0</td>
<td>8.5 8.2</td>
<td>0.224</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>700</td>
<td>11.0 11.4 10.4</td>
<td>8.3 8.8</td>
<td>0.219</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>700</td>
<td>10.9 11.4 10.8</td>
<td>8.4 8.2</td>
<td>0.218</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>700</td>
<td>11.7 10.3 10.4</td>
<td>9.2 8.9</td>
<td>0.162</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>800</td>
<td>10.3 10.0 10.4</td>
<td>8.6 7.0 8.7</td>
<td>0.244</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>800</td>
<td>10.7 10.6 10.3</td>
<td>8.4 8.2</td>
<td>0.212</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>800</td>
<td>10.5 10.3</td>
<td>7.8 8.0</td>
<td>0.240</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>800</td>
<td>10.4 11.2 10.6</td>
<td>8.5 8.2</td>
<td>0.222</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>600</td>
<td>9.4 8.7 8.6</td>
<td>7.5 6.2</td>
<td>0.230</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>600</td>
<td>9.3 8.5</td>
<td>7.0 7.4</td>
<td>0.191</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>600</td>
<td>8.7 8.6 9.2</td>
<td>7.1 6.7</td>
<td>0.219</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>700</td>
<td>8.9 9.0</td>
<td>6.5 7.0</td>
<td>0.246</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>700</td>
<td>8.7 8.5</td>
<td>6.9 6.5</td>
<td>0.221</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>700</td>
<td>8.8 9.4</td>
<td>6.4 6.9</td>
<td>0.269</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>700</td>
<td>8.7 9.1 8.4</td>
<td>6.4 7.0</td>
<td>0.233</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>800</td>
<td>8.5 8.4 9.2</td>
<td>6.5 7.0</td>
<td>0.224</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>800</td>
<td>8.8 8.6 9.2</td>
<td>6.9 6.5</td>
<td>0.244</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>800</td>
<td>8.9 8.5 8.7</td>
<td>6.6 6.7</td>
<td>0.236</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>800</td>
<td>9.5 8.6 8.4</td>
<td>6.6 6.7</td>
<td>0.247</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>800</td>
<td>8.8 8.6 9.6</td>
<td>7.1 6.9</td>
<td>0.222</td>
</tr>
</tbody>
</table>
3.5.4 PARTICLE DENSITY EXPERIMENTS

A change in the bulk particle density during devolatilization is also likely to be taking place, due to a combined effect of the mass loss associated with coal drying and devolatilization, and the shrinkage referred to in Section 3.5.3. To gain an appreciation for the change in the particle density, experiments were carried out, using both wet and dry coal particles, in which the initial and final particle mass and particle sizes were measured and the corresponding particle densities were determined. As in Section 3.5.3, up to three measurements were taken in order to obtain an average particle diameter. The particle density was determined via Equation 3.7 and the resulting densities are summarised in Table 3.7.

As in the previous section a number of statistical tests were conducted to determine whether the final particle density was dependent on either the initial particle size or the furnace temperature. Two-way ANOVA tests (with replication) were performed on the data from the wet and dry coal particles separately to ascertain any dependence on either the particle size or temperature within each group. The resulting ANOVA tables from Microsoft Excel® Version 5.0c for the wet and dry coal particles are displayed in Tables 3.8 and 3.9, respectively. The hypothesis used in this analysis are similar to those in Section 3.5.3. Tables 3.8 and 3.9 clearly show F-statistics lower then the critical F value, thus indicating that the final particle density is totally independent of the initial particle size and furnace temperature.

A one-way ANOVA test was conducted in order to ascertain whether or not the final particle densities were dependent on whether the particles were wet or dry initially. This is valid given the results of the previous analysis. The results of this ANOVA test are summarised in Table 3.10 and again the F-statistic is lower than the critical F-value. Therefore it can be conclude that the final particle density is not dependent on the initial state of the particle.

The results of the above ANOVA tests indicate that the final density of the coal particle, after devolatilization, is independent of the initial particle condition, initial
particle size, and the furnace temperature. Therefore it is convenient to characterise the final particle density with an average density based on the entire data set. This density has a value of 626 kg m\(^{-3}\).

Table 3.7  Densities determined from -11 + 10 mm and -9 + 8 mm wet and dry coal particles prior to and on completion of devolutilization in the Horizontal Tube Furnace at 600°C, 700°C, and 800°C.

<table>
<thead>
<tr>
<th>Particle Size (mm)</th>
<th>Temp (°C)</th>
<th>Wet Coal Particles</th>
<th>Dry Coal Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial Density (kg m(^{-3}))</td>
<td>Final Density (kg m(^{-3}))</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>600</td>
<td>998</td>
<td>539</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>600</td>
<td>1104</td>
<td>617</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>600</td>
<td>1106</td>
<td>757</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>700</td>
<td>1094</td>
<td>657</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>700</td>
<td>977</td>
<td>631</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>700</td>
<td>1141</td>
<td>639</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>800</td>
<td>1070</td>
<td>616</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>800</td>
<td>1163</td>
<td>635</td>
</tr>
<tr>
<td>-11 + 10</td>
<td>800</td>
<td>1226</td>
<td>687</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>600</td>
<td>1189</td>
<td>619</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>600</td>
<td>1076</td>
<td>646</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>600</td>
<td>1152</td>
<td>612</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>700</td>
<td>1128</td>
<td>619</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>700</td>
<td>1120</td>
<td>640</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>700</td>
<td>1219</td>
<td>614</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>800</td>
<td>1186</td>
<td>600</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>800</td>
<td>994</td>
<td>601</td>
</tr>
<tr>
<td>-9 + 8</td>
<td>800</td>
<td>1030</td>
<td>641</td>
</tr>
</tbody>
</table>
Table 3.8 Summary of results from a two-way ANOVA test conducted on the final particle densities from wet coal particles given in Table 3.7.

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>33.3333</td>
<td>2</td>
<td>16.6667</td>
<td>0.006762</td>
<td>0.993265</td>
<td>3.88529</td>
</tr>
<tr>
<td>Particle Size</td>
<td>1922</td>
<td>1</td>
<td>1922</td>
<td>0.779751</td>
<td>0.394563</td>
<td>4.747221</td>
</tr>
<tr>
<td>Interaction</td>
<td>316</td>
<td>2</td>
<td>158</td>
<td>0.0641</td>
<td>0.93823</td>
<td>3.88529</td>
</tr>
<tr>
<td>Within</td>
<td>29578.67</td>
<td>12</td>
<td>2464.889</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>31850</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.9 Summary of results from a two-way ANOVA test conducted on the final particle densities from dry coal particles given in Table 3.7.

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial state (wet/dry)</td>
<td>322.3333</td>
<td>2</td>
<td>161.1667</td>
<td>0.226871</td>
<td>0.800365</td>
<td>3.88529</td>
</tr>
<tr>
<td>Columns</td>
<td>24.5</td>
<td>1</td>
<td>24.5</td>
<td>0.034488</td>
<td>0.855774</td>
<td>4.747221</td>
</tr>
<tr>
<td>Interaction</td>
<td>313</td>
<td>2</td>
<td>156.5</td>
<td>0.220302</td>
<td>0.80545</td>
<td>3.88529</td>
</tr>
<tr>
<td>Within</td>
<td>8524.667</td>
<td>12</td>
<td>710.3889</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>9184.5</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.10 Summary of results from a one-way ANOVA test conducted on the final particle densities from wet and dry coal particles given in Table 3.7.

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1332.25</td>
<td>1</td>
<td>1332.25</td>
<td>1.103864</td>
<td>0.30083</td>
<td>4.130015</td>
</tr>
<tr>
<td>Particle Size</td>
<td>41034.5</td>
<td>34</td>
<td>1206.897</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>42366.75</td>
<td>35</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.6 SUMMARY

This section has dealt with the techniques and apparatus used in the experimental investigations carried out in this study in order to provide data to support the development of a coal devolatilization model which will be discussed shortly. It was found that the conventional technique used in the literature to measure the temperature response of large coal particles during heating may not be totally reliable and hence a modified technique was developed and rigorously tested to ensure it was capable of generating measurements with an acceptable accuracy. This modified technique
makes use of a water-cooled probe to insulate the thermocouple from the surrounding heat transfer environment as well as a number of particle on the thermocouple tip to act as a thermal barrier to heat conduction along the thermocouple. This technique was subsequently used to obtain the following particle temperature data:

- -11 + 10 mm wet Bowmans coal particles in the horizontal tube furnace at 600°C, 700°C, and 800°C.
- -9 + 8 mm wet Bowmans coal particles in the horizontal tube furnace at 600°C, 700°C, and 800°C
- Dry coal particles, generated from -11 + 10 mm wet Bowmans coal particles, in the horizontal tube furnace at 600°C, 700°C, and 800°C.
- Dry coal particles, generated from -9 + 8 mm wet Bowmans coal particles, in the horizontal tube furnace at 600°C, 700°C, and 800°C.
- -11 + 10 mm wet Bowmans coal particles in the fluidized bed reactor at 650°C, 750°C, and 850°C.
- Dry coal particles, generated from -11 + 10 mm wet Bowmans coal particles, in the fluidized bed reactor at 600°C, 700°C, and 800°C.

This data will play a critical role in both the development and the validation of the large particle coal devolatilization model to be developed in this study. The data collected in the horizontal tube furnace is ideally suited to model development purposes as the horizontal tube furnace presents a well controlled heating environment. As a consequence, the uncertainty which may arise from the external heating environment is minimised and factors such as the coal properties, heat of pyrolysis, etc. can be investigated under these conditions with greater confidence. Hence any conclusions made regarding these factors can be made with confidence given that the external heating conditions are known.

The fluidized bed data, as has been explained, is far less suited to model validation due to the uncertainty which surrounds the heat transfer environment as well as limitations in the experimental data. While this data cannot be used here, it can be
used for model validation and comparison purposes as the data represent reasonably accurate estimates of the particle temperature response under the given conditions.

The mass loss data in Section 3.5.2 complement the particle temperature data in Section 3.5.1 and together represent a comprehensive data set for the validation of the large particle coal devolatilization model to be developed in this study. Furthermore, this data set is significantly more advanced than a majority of the data available in the literature in that it considers both temperature and mass loss data collected at a variety of temperatures, for a variety of particle sizes, and in two different heat transfer environments. Therefore this data forms an excellent basis for the impending model development stages and also provides a perception of the physio-chemical processes being modelled.

The particle shrinkage experiments are critical to the model development as they provide an understanding of the magnitude of the shrinkage encountered during the drying and devolatilization of wet coal particles. As shrinkage may be a factor which influences the ultimate model predictions, these experiments therefore provide insight into how shrinkage may be affecting the devolatilization as well as enabling the relevant sensitivity analysis to be performed using realistic shrinkage factors. Similar can be said for the particle density experiments, however, the particle density is not an explicit parameter within the model and is dependent on the mass loss and the particle size. Therefore, while no sensitivity analysis would be performed directly on the density, the density can be used as a means of elucidating the applicability of any assumptions relating to the mass loss and the particle size or shrinkage.

The experiments conducted in this chapter have enabled several of the measurable variables which are potentially important during coal devolatilization to be measured and these measurements can subsequently be used for either model development, sensitivity analysis, or model validation purposes. As mentioned in Section 2.4.2, there are a number of other factors which may influence the devolatilization process and thus must be considered during devolatilization modelling. However, factors such as the heat of pyrolysis and the surface volatile matter flux etc. are difficult to measure
experimentally. The advantage of modelling then, is that such factors can be considered within a model, and the relevant sensitivity analysis is capable of ascertaining to what extent these factors are influencing the model predictions.
Chapter 4

MODEL DEVELOPMENT

4.1 INTRODUCTION

The Literature Review presented in Chapter 2, along with the Experimental Work detailed in Chapter 3, have laid the foundation for the development of a comprehensive large particle coal devolutilization model. The Literature Review has revealed that emphasis must be placed on both the devolutilization kinetic modelling as well as the coal particle temperature modelling in order to generate a representative model for the behaviour of large coal particles during devolutilization. From a kinetic modelling perspective, there have been many models developed to replicate devolutilization and the appropriate model type must be selected in order to achieve the aims of the current study. The selection of the kinetic model and the criteria on which this selection was based will be presented in this chapter, followed by a more detailed description of the kinetic model development.

A number of parameters have been shown to potentially influence the particle temperature model predictions in both the Literature Review and the Experimental Work. These factors, including the coal/char thermophysical properties, emissivity, the enthalpy of devolutilization, and etc., should be considered during the model development such that their effect on the model predictions can be examined via a comprehensive sensitivity analysis. The development of the particle temperature
model will subsequently be discussed detailing the technique by which these factors have been incorporated into the model. Ultimately, this will enable a list of explicit parameters which can be tested within the model to be collected. These parameters subsequently form the basis for the sensitivity analysis to follow, in Chapter 5. This chapter will conclude with a summary of the solution algorithm used to operate the model, as well as a summary of the capabilities of the model.

4.2 KINETIC MODEL DEVELOPMENT

4.2.1 SELECTION OF THE APPROPRIATE KINETIC MODEL

As was discussed in the Literature Review (Chapter 2), there are two distinctive types of model which have been used to describe coal devolatilization; namely empirical models and structural models. Hence the initial step in the development of the model describing the kinetic aspects of coal devolatilization is to deduce which of these two model types is best suited to the purposes of this modelling work.

Whilst a number of objectives have been defined which relate to the scope of the work to be conducted in this study, this study itself is designed to support an extensive research effort which is aimed at developing a comprehensive model for a fluidised bed coal gasification/combustion facility via the efforts of a number of researchers within the CRC for Power Generation (Yan et al., 1998). Therefore the model to be developed in this study not only needs to fulfil the objectives of this study, it must also satisfy the requirements of the overall research programme and as such the selection of the kinetic model type must ultimately be guided by the aims of this programme which have been summarised in Chapter 1.

Given the aims of the research programme, and the objectives of this particular study, several factors have been isolated which must be considered when deciding on the most appropriate type of devolatilization model to use for this particular application. These factors subsequently become the selection criteria when selecting the model type to be employed. These factors include:
1. *Model complexity*: Refers to the ease at which the model can be converted into an operating computer code. This is influenced by several factors including the type and number of calculations required by the model, applicability of the model to various coal types, and the level of understanding of the model basis.

2. *Availability of data/information to construct and utilise the model*: The capacity of the model is limited by the information which is available to aid in the development of the model, as well as the availability of the appropriate model parameters or experimental data required to utilise and validate the model.

3. *Accuracy of the model predictions*: The model must be able to predict the evolution of particular gas species and the total mass loss with a reasonable accuracy under various operating conditions and for a variety of coal types.

4. *Computational time*: The computational time required by the devolutilization model must not severely corrupt the computational time of the overall model.

5. *Integratability of the model*: The ultimate goal of this section of work is to integrate the devolutilization model into the overall gasifier model (Yan et al., 1998). This step must not have any detrimental effects on the predictability of the overall gasifier model and the model should be capable of integrating into the existing model framework easily.

Table 4.1 examines each of these factors as they apply to the devolutilization model types. As can be elucidated from this table, empirical models have an advantage over structural models in respect to their modelling complexity and the availability of data.
Table 4.1 Comparison between the fundamental types of models available for coal devolutilization modelling based on the designated selection criteria.

<table>
<thead>
<tr>
<th>Selection Criteria</th>
<th>Empirical models</th>
<th>Structural models</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model complexity</strong></td>
<td>Generally these models are easy to understand and are based on a minimal number of customary equations. The equations generally contain parameters which are variable for different coal types and do not upset the basic structure of the model.</td>
<td>These models require a detailed understanding of the chemical structure of the coal, particularly the functional groups present. There are a large number of calculations required as the breaking and reforming of the bonds present must be continually determined. For each coal, a new coal structure is required which alters the basis of the model.</td>
</tr>
<tr>
<td><strong>Availability of information to construct and utilise the model</strong></td>
<td>Much work has been carried out using these models hence there is an abundance of information for both the development of the model, and for the kinetic parameters required.</td>
<td>There is some information available regarding the development of such models. Information regarding the structure of various coals is not as readily available and the experiments necessary to generate this data are expensive, sophisticated and not readily accessible.</td>
</tr>
<tr>
<td><strong>Accuracy of the model predictions</strong></td>
<td>The more complex models have been shown to give quite accurate predictions. Estimating relative tar, char and total volatile yields is not possible however this is not a particular aim of the current model.</td>
<td>The accuracy of such models is usually good, provided the data necessary to operate the model is available and can be accurately determined.</td>
</tr>
<tr>
<td><strong>Computational time</strong></td>
<td>Dependent on the complexity of the model chosen and the algorithms employed in the solution method. In general they are simple to solve thus are expected to have relatively small computational times.</td>
<td>It is envisaged that there would be no advantage of such models over empirical models and, if anything, they would be more time consuming given the complexity of the model structure.</td>
</tr>
<tr>
<td><strong>Integratability of the model</strong></td>
<td>It has been proven in previous studies that these models can be integrated into larger and more sophisticated models (refer Chapter 2)</td>
<td>This is unknown at present.</td>
</tr>
</tbody>
</table>
for various coals. Both model types are capable of similar accuracy. In both cases, however, the accuracy is dependent on the input parameters whether they be kinetic parameters, or experimental data in the case of structural models. There is a marginal advantage for structural model in respect to estimating the respective tar, char and total volatile yields (Fletcher et al., 1990, Fletcher et a., 1992; Solomon et al., 1990a; Solomon et al., 1990b; Solomon et al., 1993a; Solomon et al., 1993b). This is not an integral requirement of the model as low-rank coals generally have low tar yields (Tyler, 1979) hence this capability is not as critical.

The computational time required by each model type is difficult to characterise as no direct information is given. The computational time is then judged based on the complexity of the model which gives some indication of the number and nature of calculations involved in the model algorithm. Given the decisively more sophisticated nature of the structural models, they are expected to have enhanced computational times when compared with the empirical models. Due to the uncertainty which surrounds this selection criteria it should not be used as a critical criteria in the ultimate selection of the model type. Finally, the integratability of the respective model types tends to favour the empirical models as some work has been undertaken previously in which such models have been incorporated into more complex models. Conversely, little information exists regarding the integratability of structural models. Therefore the proven success of the empirical models tends to favour their use based on this particular selection criteria.

Based on these conclusions, empirical models are the preferred choice as the most appropriate model type for modelling coal devolatilization. Their moderate complexity, availability of supporting data, and the proven integratability of these models exists as definite indicators of their precedence over structural models. The remaining selection criteria either show no distinct advantage of either model type or represent criteria which are difficult to characterise based on a lack of knowledge and can thus be exempt from the selection process.
4.2.2 EMPIRICAL KINETIC MODEL DEVELOPMENT

Whilst there are a number of empirical models which have been developed to represent coal devolatilization, ranging in complexity from single first order reaction models to multiple parallel reaction models, the multiple parallel reaction models are clearly the most robust of the empirical models developed to date (as discussed in Section 2.3.2). In fact, much of the large particle coal devolatilization work carried out to date has employed some form of multiple parallel reaction model. Given the success of this model type in the work conducted to date it seems feasible to employ a multiple parallel reaction model in the present study.

The most widely used of the multiple parallel reaction models is the Distributed Activation Energy Model (DAEM) which predicts the fraction of the total volatile matter remaining in a spherical coal particle as a function of time according to (Agarwal et al. 1984a, Agarwal et al., 1984b):

\[
\left( \frac{V^* - V}{V^*} \right)_{\text{avg}} = \frac{3}{R_0^3} \left( \int_0^r \frac{1}{r} \exp \left( - \int_0^t k_o e^{\left( -\frac{E}{RT(t)} \right)} dt \right) f(E) dE \right) r^2 dr
\]

where

\[ f(E) = \frac{\exp \left( -\frac{(E - E_o)^2}{2\sigma^2} \right)}{\sigma \sqrt{2\pi}} \quad (4.1) \]

The kinetic parameters required to solve Equation (4.1) are the frequency factor, \( k_o \), the mean activation energy, \( E_o \), and the standard deviation in activation energies, \( \sigma \).

The integration limits \( r_1 \) and \( r_2 \) refer to the radial distance from the particle centre over which the fractional volatile yield is calculated. Generally \( r_1 = 0 \) and \( r_2 = R_0 \) where \( R_0 \) is the radius of the particle. As will be discussed later, the calculations will be conducted over a number of radial shells which comprise the entire particle. In this way the mass loss can be determined at local positions within the coal particle enabling the particle density to vary across the radius of the particle as has been
observed by (Gat, 1986). Therefore the radial integration limits are given by \( r_1 = m \Delta r \) and \( r_2 = r_1 + \Delta r \) where \( m = 0, \ldots, n \) given that \( n \) is the shell number and \( \Delta r \) is the shell size. Note that the shell representing the centre of the particle has a shell number of \( n = 0 \). This is represented schematically in Figure 4.1.

![Diagram](image)

**Figure 4.1** Schematic representation of the shell arrangement used to define the coal particle in the model calculations.

The model denoted by Equation (4.1) has been used extensively with reasonable success throughout the literature (Anthony et al., 1975; Agarwal et al., 1984a; Agarwal et al., 1984b; Borghi et al., 1985; Agarwal, 1985; Agarwal, 1986; Agarwal et al., 1987; Wildegger-Gaismaier, 1990; Andres et al., 1991; Wang et al., 1994; Adesanya and Pham, 1995; Miura, 1995; Maki et al., 1997), as has been presented in the Literature Review. In addition to the kinetic parameters, the time-temperature history of the particle, \( T(r,t) \), is also required to calculate the fractional volatile yield. The technique used to calculate \( T(r,t) \) will be discussed later in this chapter.

A further parameter in Equation (4.1) is the ultimate volatile yield, \( V^* \). This represents the total mass of volatiles released from the coal during devolatilization under a specific set of operating conditions. Generally, the volatile matter content of the parent coal is used to characterise \( V^* \), however, it has been shown that the ultimate
volatile yield is dependent on the operating temperature Tyler (1979), particle size (Morris, 1993), and etc. In fact, Agarwal et al. (1987) stated

"It would be interesting to consider whether the observed effects of pressure and heating rate could be conveniently lumped into the estimation of the maximum yield, the kinetic parameters remaining the same as those determined under a standard set of conditions"

This suggests that the ultimate volatile yield is highly dependent on the operating conditions and may well be further dependent on the coal type. In order to alleviate this problem, the experimental data can be modified where possible such that the fractional mass loss due to devolatilization will be used for model development/validation purposes. This is achieved by normalising the experimental data with respect to the ultimate volatile yield to yield $V/V^*$ versus time. In this way the predictions of the DAEM can be compared directly with the modified experimental data without the need to estimate a value for the ultimate volatile yield, $V^*$.

While Equation (4.1) is applicable to determining the fractional total volatile yield, it can also be used to estimate the yield of individual volatile species provided the appropriate kinetic parameters are known. An example of these parameters has been presented in Chapter 2 (Table 2.2). It is noticeable from this table that, for some of the species listed, there exist more than one set of kinetic parameters. These sets of parameters relate to the evolution of the specific volatile species from a particular source within the coal structure from which the species is derived. Equation (4.1) must be modified accordingly to account for the presence of more then one set of kinetic parameters (more than one source) and the modified version is given by Equation (4.2).

$$\left(\frac{V_i^* - V_i}{V_i^*}\right)_{ave} = \frac{3}{R_0^3} \sum_{j=1}^{S} \left( X_{i,j} \int_0^{r_j} \int_0^{T_j} \exp \left(-\int_0^t k_{o,i,j} \left[\frac{-E}{RT(r,t)}\right] \, dt\right) f(E) \, dE \right) r^2 \, dr$$
\[
    f(E) = \frac{\exp\left(-\frac{(E - E_{0,i,j})^2}{2\sigma_{i,j}^2}\right)}{\sigma_{i,j}\sqrt{2\pi}}
\]

where

Here, \(X_j\) refers to the fraction of the total yield of species \(i\), \(V_i^*\), which is derived from the particular source \(j\). \(n\) is the total number of sources from which species \(i\) is generated. The frequency factor, \(k_{0,i,j}\), the mean activation energy, \(E_{0,i,j}\), and the standard deviation in activation energies, \(\sigma_{i,j}\), all refer to the kinetic parameters which define the evolution of species \(i\) from the particular source, \(j\).

Assuming that the time-temperature history of the particle is known, Equations (4.1) and (4.2) requires a triple nested integration calculation to be performed for each time interval in order to determine the fractional volatile yield. For each integration step, the commonly used Simpsons Integration Rule has been used which is defined as (Perry and Green, 1984):

\[
    \int_a^b f(x) dx = \frac{h}{3} [f_0 + 4f_1 + 2f_2 + 4f_3 + \ldots]
    
    \ldots + 4f_{n-3} + 2f_{n-2} + 4f_{n-1} + f_n] + E_n
\]

(4.3)

According to Simpsons Integration Rule the interval \(a < x < b\) is divided into \(n\) subintervals where \(n\) is an even integer, that is, \(n = 2m\) for some integer \(m\). The value of \(h\) is given by \(h = (b - a) / 2m\). This technique approximates the function to be integrated, \(f(x)\), as a parabola over each subinterval and is generally accepted to be one of the most accurate integration formulas. Figure 4.2 shows schematically the concept of Simpsons rule for the simple case of \(n = 2\). The error term in Equation (4.3), \(E_n\), is defined by Equation (4.4) (Perry and Green, 1984).

\[
    E_n = \frac{(b - a)^5}{180n^4} f^{(5)}(\varepsilon), \quad a < \varepsilon < b
\]

(4.4)
Throughout the calculations the integral step size, defined by \((b - a)\), was kept to a minimum and large values of \(n\) were employed. By maintaining these conditions it was assumed that the error could be ignored. In order to determine whether the significance of the error, model predictions were obtained for high temperature conditions (800°C) after an extended period of time, under conditions prevailing in both the horizontal tube furnace and the fluidised bed reactor. At 800°C it is reasonable to expect that devolatilization would proceed to completion. The model predicted values of \((V^*_m - V_m) / V^*_m = 0.00\) which indicates the residual volatile matter content of the particle is 0.00 ie. devolatilization is complete. If the magnitude of the error value was significant it is likely that the model would be unable to predict a value of \((V^*_m - V_m) / V^*_m = 0.00\) hence this result confirms the aforementioned assumption that the error term (Equation (4.4)) can be ignored in Equation (4.3).

\[\text{Figure 4.2} \quad \text{Schematic diagram depicting the concept of Simpsons integration formula when } n = 2.\]
4.3 PARTICLE TEMPERATURE MODEL DEVELOPMENT

4.3.1 PARTICLE ENERGY BALANCE EQUATIONS

The success of the unsteady-state heat conduction equation in spherical co-ordinates (Equation 2.12) in previous modelling studies (Agarwal et al., 1984a; Agarwal et al., 1984b; Fu et al., 1987; Tomecek and Kowol, 1990; Kilic et al., 1993; Adesanya and Pham, 1995; and Garcia-Labiano et al., 1996) indicates it is a suitable basis for the coal particle temperature model in the present study. However, due to the uncertainty surrounding the contribution of the enthalpy of devolatilization and the effect of moisture on the time-temperature history of the particles, additional energy terms must be added to the standard unsteady-state heat conduction equation which yields Equation 4.5.

$$\rho_c C_{p,c} \frac{dT}{dt} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 k_c \frac{dT}{dr} \right) + Q_{pyrolysis} + Q_{drying} \tag{4.5}$$

Equation (4.5) differs from Equation (2.12) in that the thermal diffusivity, $\alpha_c$, in Equation (2.12) has been substituted according to Equation (4.6) in Equation (4.5), and terms describing the energy associated with devolatilization, $Q_{dev}$, and the energy associated with moisture removal, $Q_{drying}$, have been added.

$$\alpha_c = \frac{k_c}{\rho_c C_{p,c}} \tag{4.6}$$

Equation (4.5), in its present form, enables a number of parameters within the model to be individually tested during the sensitivity analysis. These parameters include the coal thermophysical properties, $k_c$ and $C_{p,c}$, and the coal density, $\rho_c$.

As mentioned in Section 2.4.2.1, the solution to Equation (4.5) is facilitated by the specification of appropriate boundary conditions which define the heat transfer
behaviour associated with the particle. Boundary conditions must be specified at the surface and the centre of the coal particle as these represent the physical limits over which the particle temperature calculations are to be conducted. The boundary condition at the particle surface is given by Equation (2.15):

$$k_c \frac{\partial T}{\partial r} \bigg|_{r=R_0} = h_{conv} (T_u - T|_{r=R_0}) + \sigma \varepsilon \varepsilon_{rad} (T_u^4 - T|_{r=R_0}^4)$$  \hspace{1cm} (2.15)$$

Equation (2.15) enables the heat transfer to the particle surface via both convection and radiation heat transfer to be considered within the particle temperature model. Individually specifying these heat transfer mechanisms has added significance with regard to the model sensitivity analysis. Firstly, the effect of the various correlation for the convective heat transfer rate under fluidised bed conditions can be directly examined, as can the influence of the coal particle emissivity. Furthermore, the surface volatile matter flux has been shown to have an effect on the convective heat transfer rate at the particle surface (Kalson, 1983) and Equation (2.15) enables this phenomenon to also be considered. This will be discussed in greater detail later in this chapter.

Finally, the boundary condition at the centre of the particle is defined such that the temperature gradient at the particle centre is zero (Equation 2.16). Equation (2.16) ensures that the temperature profile across the particle radius is uniform for the entire particle which substantially reduces the complexity of the model.

$$\frac{\partial T}{\partial r} \bigg|_{r=0} = 0$$  \hspace{1cm} (2.16)$$

The final boundary condition to be specified relates to the initial condition of the coal particle, i.e., the intial particle temperature. It is assumed that the particle temperature is intially uniform therefore Equation (4.7) applies:

$$T(r, t) = T_0 \text{ at } t = 0$$  \hspace{1cm} (4.7)$$
Therefore, Equations (4.5), (2.15), (2.16), and (4.7) represent the fundamental equations comprising the particle temperature model. The following sections detail the model equations which contribute to the particle energy balance, and their relationship to the aforementioned particle temperature model.

4.3.2 COAL THERMOPHYSICAL PROPERTIES

Section 2.4.2.2 reviewed the correlations or constant values which have been quoted in the literature for both the heat capacity, $C_{p,c}$, and thermal conductivity, $k_c$, of various coals. Based on the reported data, it appears that both thermophysical properties are temperature dependent. Therefore, rather than assume either a constant or a temperature averaged value for the thermophysical properties, consideration will be allowed within the model framework to enable the thermophysical properties to be calculated based on the particle temperature at any time, at the appropriate position along the radius of the coal particle. This technique provides the closest analogy to the actual behaviour of the coal particle during devolatilization.

When dealing with wet coal particles, the thermophysical properties of the coal particle cannot be assumed to be equivalent to those presented in Section 2.4.2.2 as they represent the properties of dry coal particles. The presence of moisture was accounted for, when applicable, by using the following mass averaged values for the heat capacity and thermal conductivity in each individual shell:

$$
\overline{C_{p,m}} = \frac{[1 - W^* - V^*(1 - \nu_m)] C_{p,c} + W^* (1 - X'_{H_2O,m}) C_{p,H_2O}}{1 - W^* X'_{H_2O,m} - V^*(1 - \nu_m)} \tag{4.8}
$$

$$
\overline{k_m} = \frac{[1 - W^* - V^*(1 - \nu_m)] k_c + W^* (1 - X'_{H_2O,m}) k_{H_2O}}{1 - V^*(1 - \nu_m) - W^* X'_{H_2O,m}} \tag{4.9}
$$
In these equations, $W^*$ is the original moisture content of the coal particle on a wet basis, $X'_{v,0,m}$ is the fraction of the original moisture which has been removed from a particular shell, and $\nu_m$ is the fraction of volatile matter remaining in the same shell (see Equation 4.11). The values for the heat capacity and thermal conductivity of water used in Equations (4.8) and (4.9) were 4.19 kJ kg$^{-1}$ K$^{-1}$ and 0.65 W m$^{-1}$ K$^{-1}$, respectively.

### 4.3.3 Coal Particle Density

The assumption of a constant coal particle density was discussed in Section 2.4.2.3 while an experimental investigation into the change in the coal density during devolatilization was conducted in Section 3.5.4. The conclusion which can be drawn from these sections is that the coal particle density is definitely changing during devolatilization and as such, provision must be made within the model to account for the changing density of the coal particle. However, the coal particle density is not an explicit parameter in itself, and is related to both the mass and the volume of the particle. Furthermore, the density varies across the radius of the coal particle and the model must be structured to enable this behaviour to be considered.

Corresponding to the shell arrangement used to model the coal particle as depicted in Figure 4.1, the coal particle density can be calculated for each individual shell for each time increment thus enabling the particle density to vary across the particle radius. Mass loss from the particle can result from the loss of both moisture and volatile matter. The mass of coal remaining in any shell at any time then can be represented by:

$$M_{t,m} = M_{0,m}(1 - V^*(1 - \nu_m) - W^*X'_{v,0,m})$$  \hspace{1cm} (4.10)

where $M_{t,m}$ is the mass of coal remaining in shell $m$ after time $t$, $M_{0,m}$ is the original mass of coal in shell $m$, and $V^*$ is the ultimate volatile yield (g/g raw coal). \hspace{1cm} (1 - \nu_m)
represents the fraction of volatiles removed from the coal particle where $v_m$ is calculated via Equation (4.1) and Equation (4.11).

$$v_m = \left( \frac{V^*_m - V_m}{V^*_m} \right)$$  \hspace{1cm} (4.11)

The diameter of the coal particle, for the coal used in this study, was found to decrease during drying as was investigated in Section 3.5.3. Experimentally it was found that the shrinkage factor was dependent on both the temperature and the initial particle size and, for each set of experimental conditions, a shrinkage factor was defined which indicates the reduction in the particle size due to drying. The shrinkage factor was defined by Equation (3.6). The shrinkage factor was found to vary between $SF_{\infty} = 0.200$ and $SF_{\infty} = 0.242$, which suggests a 20.0% to 24.2% reduction in the particle size.

$$SF = 1 - \frac{d_m}{d_0}$$  \hspace{1cm} (3.6)

If it is assumed that the degree of shrinkage is directly proportional to the residual moisture content then the degree of shrinkage in any particular shell at any time, $SF_{t,m}$, is given by:

$$SF_{t,m} = SF \cdot X_{H_2O,m}$$  \hspace{1cm} (4.12)

The volume of each shell is proportional to $(r_{2,m}^3 - r_{1,m}^3)$, hence it can be assumed that the shell volume varies with the degree of shrinkage according to Equation (4.13).

$$V_{t,m} = V_{0,m} \left( 1 - SF_{t,m} \right)^3$$  \hspace{1cm} (4.13)

The coal particle density at any time then can be calculated from Equations (4.7) and (4.13), yielding Equation (4.14).
\[ \rho_{t,m} = \frac{M_{0,m}(1 - V^*(1 - \nu_m) - W^*X'_{H_{2}O,m})}{V_{0,m}(1 - SF)^3} \]

\[ = \rho_{0,m} \frac{(1 - V^*(1 - \nu_m) - W^*X'_{H_{2}O,m})}{(1 - SF_{t,m})^3} \quad (4.14) \]

In Equation (4.14), \( \rho_{0,m} \) is the initial particle density. When modelling dry coal particles, the moisture term in the numerator of Equation (4.14) can be neglected and minimal shrinkage is assumed\(^1\).

Equation (4.14) serves two purposes. Firstly, it enables the particle density variation across the coal particle radius to be considered within the model, consistent with previous observations (Gat, 1986). Also, a sensitivity analysis can be carried out to characterise the influence of the assumption of a constant particle density on the model predictions and therefore ascertain the most appropriate assumption.

### 4.3.4 Coal Emissivity

The role of the coal emissivity in determining the time-temperature history is critical in both the horizontal tube furnace and the fluidised bed reactor as in both cases radiation heat transfer is significant. The sensitivity of the model predictions to the coal emissivity must subsequently be determined such that an informed decision can be made regarding the coal emissivity value used in Equation (2.15). In Section 2.4.2.4 a range of emissivity values were quoted for a variety of coal types. However, the only direct experimental investigation aimed at characterising the emissivity of coal was conducted by Lineweile (1993) who proposed a temperature dependent emissivity given by Equation (2.22). Therefore the sensitivity analysis to follow can investigate the effect on the model predictions resulting from using a constant emissivity value \((\varepsilon = 0.8 \text{ to } \varepsilon = 1.0)\) compared to the temperature dependent emissivity of Lineweile (1993).

\(^1\text{The shrinkage of dry coal particles was difficult to measure due to fragmentation of the devolatilized particles. The data collected suggested that minimal shrinkage was apparent.}\)
\[ \varepsilon_c = 0.377 + 0.00039T_p \bigg|_{r=R_0} \] (2.22)

### 4.3.5 Convective Heat Transfer

The horizontal tube furnace presents a basic convective heat transfer environment and is analogous to the situation of a spherical particle in a convective gas stream. This condition has been well documented and can be adequately represented by the correlation of Ranz and Marshall (1952) as given by Equation (2.23). Due to the relative certainty regarding the convective heat transfer coefficient for the conditions pertaining to the horizontal tube furnace, it is unnecessary to conduct a sensitivity analysis with respect to the convective heat transfer coefficient, \( h_{\text{conv}} \). However, the role of the surface volatile matter flux in reducing the effective rate of convective heat transfer will be considered, and is directly related to the convective heat transfer coefficient.

\[ Nu = \frac{h_{\text{conv}}d_p}{k_t} = 2 + 0.6 \text{Re}_{\rho}^{\frac{1}{2}} \text{Pr}^{\frac{1}{3}} \] (2.23)

While the convective heat transfer rate under conditions relevant to the horizontal tube furnace has been well established, the opposite can be stated for the convective heat transfer rate under fluidised bed conditions. The complex mixing patterns and the presence of both solid and gaseous phases ensures that the heat transfer environment remains far more difficult to characterise. As a result there have been a number of correlations developed to estimate the convective heat transfer coefficient under fluidised bed conditions, as presented in Table 2.6.

Linjewile (1993) developed a comprehensive model for the overall convective heat transfer coefficient under fluidised bed conditions which is summarised by Equation (2.25). For an explanation of each of the parameters in Equation (2.25), refer to Section 2.4.2.5.
\[ \bar{h} = p' h_{pc,a} + (p - p') h_{pc,d} + ph_{gc} + (1 - p) h_{bub} \]  

(2.25)

The particle convective heat transfer coefficient for a solid rising through the bed, \( h_{pc,a} \), is given by:

\[
h_{pc,a} = \left\{ \frac{d_i}{\delta_p k_t} + 0.5 \sqrt{\frac{\pi \rho}{k_t \rho_x C_{p,i}}} \right\}^{-1}
\]

where \( t_c = f_i^{-1/3} U_B^{-2/3} \left( U_B - U_R \right) \) \( U_B + U_R \)  

(4.15)

The particle convective heat transfer coefficient for a solid moving downward through the bed, \( h_{pc,d} \), is given by:

\[
h_{pc,d} = \left\{ \frac{d_i}{\delta_p k_t} + 0.5 \sqrt{U_B k_t \rho_x C_{p,i}} \right\}^{-1}
\]

where \( \frac{X}{H} = 0.012(\xi - \xi_m)^{1/2} \)  

(4.16)

The gas convective heat transfer coefficient for the solid in the emulsion phase, \( h_{gc} \), is given by:

\[
h_{gc} = \frac{k_x}{d_p} \left\{ 2 + \frac{k_x}{k_t} + 0.693 \frac{(1 + Re_x Pr) - 1}{(Re_x Pr)^{1/3}} \left( \frac{C_{Dea}}{8} \right)^{1/3} \left( \frac{q}{\varepsilon_{mf}} Re_x \right)^{2/3} \right\}^{1/3}
\]

(4.17)

The gas convective heat transfer coefficient for the solid in the bubble phase, \( h_{bub} \), is given by:

\[
h_{bub} = \frac{k_x}{d_p} \left\{ 2 + \frac{k_x}{k_t} + 0.693 \frac{(1 + Re_b Pr) - 1}{(Re_b Pr)^{1/3}} \left( \frac{C_{Dea}}{8} \right)^{1/3} \left( Re_b \right)^{2/3} Pr^{1/3} \right\}
\]

(4.18)
The probability parameters, \( p \) and \( p' \), can be determined from Equations (4.19) and (4.2), respectively.

\[
p = \frac{U_B}{U_B + U_D} \tag{4.19}
\]

\[
p' = \frac{U_D(U_B - U_R)}{(U_B + U_D)(U_R + U_D)} \tag{4.20}
\]

The correlations required to estimate the remaining parameters in Equations (4.15) to (4.20) are summarised in Appendix A. Linjewile (1993) showed that the convective heat transfer model represented by Equations (2.25) and (4.15) to (4.20) were able to estimate the experimentally derived heat transfer coefficients over a wide range of operating conditions including the bed temperature, fluidising velocity, active particle size, inert particle size and inert bed material. Therefore, this model will be used to determine the effective convective heat transfer coefficient under fluidised bed conditions and the sensitivity analysis will investigate the effect on the model predictions of utilising the correlations in Table 2.6 in place of the model of Linjewile (1993).

4.3.6 ENTHALPY OF DE VOLATILIZATION

The energy required to drive the coal devolatilization reactions, \( Q_{dev} \), is proportional to both the rate of mass loss due to devolatilization, \( \dot{M}_{dev} \), and the magnitude of the enthalpy of devolatilization, \( \Delta H_{dev} \), according to Equation (4.21).

\[
Q_{dev} = \dot{M}_{dev} \Delta H_{dev} \tag{4.21}
\]

The rate of mass loss due to devolatilization can be determined from Equation (4.1) and is given by:
\[ M_{\text{dev}} = M_0 V^* \frac{d}{dt} \left( 1 - \left( \frac{V^* - V^*}{V^*} \right) \right) \]  

(4.22)

Here \( V_m \) is the volatile matter which has been released from shell \( m \). When substituting into Equation (4.21), it must be noted that Equation (4.5) represents a volume based equation. Consequently, Equation (4.22) must be adjusted accordingly. Upon substitution into Equation (4.21) this yields:

\[ Q_{\text{dev}} = \rho_0 V^* \frac{d}{dt} \left( 1 - \left( \frac{V^* - V^*}{V^*} \right) \right) \Delta H_{\text{dev}} \]  

(4.23)

While Equation (4.20) enables the effect of the enthalpy of devolatilization to be investigated within the model, the magnitude of the enthalpy of devolatilization is itself a difficult parameter to quantify. As a result, the sensitivity analysis will focus on the effect of varying the magnitude of \( \Delta H_{\text{dev}} \) on the model predictions.

Often throughout the literature, constant values for the enthalpy of devolatilization have been assumed which represents a direct substitution of the appropriate value into Equation (4.23). However, the results of Lopez-Perinado et al. (1989) suggest that, for lignites, the enthalpy of devolatilization varies with temperature according to the trend displayed in Figure 4.3.

\( \Delta H_{\text{max,1}} \) is the maximum endothermic value for the enthalpy of devolatilization between 300K and \( T_1 \), where \( T_1 \) is the temperature at which the transition from an endothermic enthalpy of devolatilization to an exothermic enthalpy of devolatilization occurs. \( \Delta H_{\text{max,2}} \) is the maximum exothermic value of the enthalpy of devolatilization between \( T_1 \) and \( T_2 \) where \( T_2 \) is the temperature at which the enthalpy of devolatilization returns to \(-0 \) kJ kg\(^{-1}\). Note that above 750K the enthalpy of devolatilization can be either endothermic or exothermic. This region is not as significant as the lower temperature regions since the majority of the mass loss occurs in the lower temperature region hence the mass loss rate is less pronounced (Lopez-
Peinado et al., 1989). Therefore, the sensitivity analysis will focus on the temperatures range below $T_2$.

![Diagram showing enthalpy of devolatilization vs temperature with $\Delta H_{\text{max,1}}$, $\Delta H_{\text{max,2}}$, $T_1$, and $T_2$ indicated.]

**Figure 4.3** General trend in the Enthalpy of Devolatilization based on the results of Lopez-Peinado et al. (1989).

Based on the data reported by Lopez-Peinado et al. (1989), $T_1$ has a value of approximately 450K while $T_2$ has a value of 750K. The values of $\Delta H_{\text{max,1}}$ and $\Delta H_{\text{max,2}}$ are coal dependent hence will be treated as variables in the sensitivity analysis. According to the trends observed in Figure 4.3, the temperature dependent enthalpy of devolatilization values could be represented by Equation (4.24) over the specified temperature ranges.

$$
\Delta H_{\text{dev}} = \begin{cases} 
\sin\left(\pi \frac{T - 300}{T_1 - 300}\right) \Delta H_{\text{max,1}} & 300 < T < T_1 \\
\sin\left(\pi \frac{T - T_1}{T_2 - T_1}\right) \Delta H_{\text{max,2}} & T_1 < T < T_2 
\end{cases}
$$

(4.24)
4.3.7 **SURFACE VOLATILE MATTER FLUX**

The emission of volatiles from the surface of coal particles has been proposed to impact on the rate of convective heat transfer to the particle due to a disruption of the boundary layer surrounding the particles (Peters and Bertling, 1965). As discussed in Section 2.4.2.7, Kalson (1983) investigated this phenomenon and proposed that the reduction in the heat transfer coefficient due to the surface volatile matter flux could be represented by Equation (2.27).

\[
A_h' = \frac{h}{h_{N=0}} = \frac{C_0'}{\exp(C_0') - 1}
\]  

(2.27)

The parameters \( C_0' \) is given by:

\[
C_0' = \frac{C_0}{1 + \frac{2}{N\mu_0}}
\]  

(2.28)

where \( C_0 \) is calculated from Equation (2.29).

\[
C_0 = \frac{N_R C_{p,vol}}{h_0}
\]  

(2.29)

The critical parameter in these correlations (Equations (2.27) to (2.29)) is the volatile matter flux at the particle surface, \( N_R \) (kg m\(^{-2}\) s\(^{-1}\)). The surface volatile matter flux can be calculated from Equation (4.1) according to:

\[
N_R = \frac{M_0}{A|R=r_0|} \sum_{m=0}^{a} \left[ \frac{d}{dt} \left[ 1 - \left( \frac{V^* - V_m}{V^*} \right) \right] \right]
\]  

(4.25)
Note that the effect of the surface volatile matter flux is pertinent to the convective heat transfer coefficient only. Although it is possible that the extent of radiation heat transfer may be effected by the presence of the volatile gases, this effect is difficult to quantify and will not be considered. Furthermore, this approach cannot be employed under fluidised bed heating conditions where the gas solid contacting pattern is significantly different. While it has been shown that the surface volatile matter flux may influence the rate of convective heat transfer to pulverised coal particles (Kalson, 1983), no investigation has characterised the corresponding influence on mm-sized coal particles which will be an aim of the sensitivity analysis.

4.3.8 MOISTURE

The modelling of wet coal particles takes on added significance due to the impact of the moisture on the model predictions, in particular the particle temperature response. The effect of moisture can be modelled using a similar approach to that of the enthalpy of devolatilization in Equation (4.23), hence the energy associated with drying to be employed in Equation (4.5) is given by:

\[ Q_{\text{drying}} = \rho_0 \frac{d}{dt} \left( X_{H_2O} \right) \Delta H_{\text{drying}} \]  \hspace{1cm} (4.26)

The enthalpy of drying, \( \Delta H_{\text{drying}} \), varies with the moisture content according to the trend observed by Chen (1994) in Figure 2.5. According to this trend there are three regimes of drying which correspond to the free moisture, loosely bound moisture, and tightly bound moisture. For the free moisture, \( MC > MC_1 \), the enthalpy of drying can be approximated by the latent heat of vaporisation of water, i.e. \( \Delta H_{\text{drying}} = H_{w,1} = 2334 \text{ kJ kg}^{-1} \). For moisture contents below \( MC_1 \), it was assumed that the enthalpy of drying increased linearly within the respective ranges according to Equation (4.27).

\[
\Delta H_{\text{drying}} = \begin{cases} 
H_{w,1} + (H_{w,2} - H_{w,1}) \frac{MC_1 - MC}{MC_1 - MC_2} & \text{if } MC_2 < MC < MC_1 \\
H_{w,2} + (H_{w,3} - H_{w,2}) \frac{MC_2 - MC}{MC_2} & \text{if } 0 < MC < MC_2
\end{cases}
\]  \hspace{1cm} (4.27)
The critical moisture contents, $MC_1$ and $MC_2$, and the enthalpy of drying parameters, $H_{w,2}$ and $H_{w,3}$, are coal dependent parameters and therefore can be investigate within the sensitivity analysis. The values reported by Chen (1994) can be used as a basis for comparing the sensitivity of the model predictions to these parameters.

A far more challenging task involves determining the actual drying rate, $\frac{d}{dt}(X_{H_2O})$, to be used in Equation (4.26). Section 2.4.2.8 reviewed the existing models developed to predict coal drying. The model of McIntosh (1976) is useful in describing the residual moisture content of the entire coal particle with time, however in the current model it is required that the moisture content remaining in the individual shells be determined. Golonka and Rhodes (1997) proposed a drying model which incorporates comprehensive diffusion phenomena. The added complexity imposed by such a model, combined with the fact that volatile diffusion has not been considered, limits its applicability in this instance.

Wildegger-Gaismaier (1990) and Winter et al. (1997) assumed the drying process was heat transfer controlled i.e. the particle temperature response was limited to the effective drying temperature until the moisture had been completely removed. Once drying was complete the particle was able to undergo further heating and subsequent devolatilization. This assumption is useful in that it is representative of the trends observed in the present study (Chapter 3), and it can be readily incorporated into the current model framework.

Wildegger-Gaismaier (1990) further assumed that the effective drying temperature was constant at 100°C, however, Winter et al. (1997) assumed that the effective drying temperature was dependent on the capillary pressure which resulted in drying temperatures as high as 200°C. Therefore, while the drying rate is heat transfer controlled and thus cannot be explicitly investigated, the influence of the effective drying temperature can be investigated. This can be achieved by defining the effective drying temperature as a function of the residual moisture content, i.e. $T_{drying} = f(MC)$. The effective drying temperature is subsequently used as the limiting temperature for determining the drying rate in any particular shell.
4.3.9 Summary

The development of the particle temperature model has revealed a number of parameters or assumptions which may influence the model predictions. Many of these parameters are either not well defined, or have not been considered in previous coal devolatilization models. As a result, a sensitivity analysis will be useful in determining which of these parameters has a significant influence on the model predictions, as opposed to those which have a minimal impact and can thus be ignored in future modelling applications.

The parameters and assumptions to be considered in the sensitivity analysis include:

- coal heat capacity, \( C_{p,c} \)
- coal thermal conductivity, \( k_c \)
- coal particle density, \( \rho_c \)
- coal emissivity, \( \varepsilon_c \)
- convective heat transfer coefficient, \( h \)
- enthalpy of devolatilization, \( \Delta H_{dev} \)
- surface volatile matter flux, \( N_R \)
- enthalpy of drying, \( \Delta H_{drying} \)
- effective drying temperature, \( T_{drying} \)

4.4 Solution Algorithm

The solution algorithm employed to solve the model developed in Sections 4.2 and 4.3 is divided into two sections. Figure 4.4 gives a schematic of the general solution algorithm for the entire model, while Figure 4.5 details the solution algorithm employed to determine the radial particle temperature profile, \( T(r,t) \), at STEPs 2 and 4 in Figure 4.4.
Figure 4.4 indicates that the coal devolatilization sub-model and the particle temperature sub-model are coupled within the overall model structure and thus must be solved simultaneously for each time increment. The volatile yield in each shell and the residual moisture content in each shell are directly related to the time-temperature history of the particle. Therefore it was concluded that, for each time increment, the radial temperature profile, $T(r, t)$, could be used as a single test parameter in order to ensure that each of the aforementioned parameters have been adequately solved. This is the test carried out in STEP 5 in Figure 4.4. The convergence criterion was defined such that the maximum difference between the temperatures calculated in STEP 2, $T'(r, t)$, and STEP 4, $T''(r, t)$, at any corresponding radial positions, is less than 0.5°C.

In Figure 4.4, the calculations performed above the dashed line are those used to calculate the temperature at the particle surface, $T(R_0, t)$, at any time. Calculations below the line are used to determine the temperature at successive radial increments, $\Delta r$, from the particle surface until the centre of the particle is reached. STEPs 5 to 7 and STEPs 12 to 14 are used to determine the fraction of moisture evolved from each shell, at each time increment, using the assumption of heat transfer controlled drying. The correction factor denoted by $\delta X_{H_2O, m}$ in STEP 6 and STEP 13 in Figure 4.4 is calculated from the absolute error between the calculated temperature, $T'(r, t)$, and the required drying temperature, $T_{drying}$, according to:

$$\delta X_{H_2O, m} = F(T'(r, t) - T_{drying})$$ (4.28)

The factor $F$ in Equation (4.28) acts as a relaxation factor to modify the fraction of moisture present in each shell until the drying temperature is reached, when appropriate. A convenient value for $F$ was found to be $F = 0.0025$. Note that the length of the time increments also effects the required value of the relaxation factor.

As discussed in the following paragraph, it was found that modifying the length of the time increments enabled a constant relaxation factor to be utilised. This is useful when excessive drying rates are encountered.
Figure 4.4 Schematic of the solution algorithm used to solve the overall coal devolatilization model.
From **STEP 1 or 3 in Figure 4.3**

**STEP 1**
Calculate $k_{e,m} = C_{pc,m} \cdot \rho_{e,m}$

**STEP 2**
Calculate $\Delta H_{d,e} = f(T(R_{0,t}))$
Calculate $Q_{d,e,m}$ using Equation

**STEP 3**
Calculate $T'(R_{0,t})$ using Equation 2.15 and $T(r,t-1)$

**STEP 4**
Calculate $T_{drying,m} = f(X_{H_2O,m=n})$
Test: $T'(R_{0,t}) > T_{drying,m}$

NO
Accept $T'(R_{0,t})$

$\Delta H_{d,e} = f(T(r,t))$
Calculate $Q_{d,e,m}$ using Equation

**STEP 5**
Test: $X_{H_2O,m=n} = 1$

NO

**STEP 6**
$X_{H_2O,m=n} = X_{H_2O,m=n} + \delta X_{H_2O,m=n}$

NO

**STEP 7**
Test: $X_{H_2O,m=n} > 1$

**STEP 8**
Calculate $k_{e,m} \cdot C_{pc,m} \cdot \rho_{e,m}$

**STEP 9**
Calculate $\Delta H_{d,e} = f(T(r,t))$
Calculate $Q_{d,e,m}$ using Equation

**STEP 10**
Calculate $T'(r,t)$ using Equation 4.5 and $T(r,t-1)$

**STEP 11**
Calculate $T_{drying,m} = f(X_{H_2O,m})$
Test: $T'(r,t) > T_{drying,m}$

NO
Accept $T'(r,t)$

Test: $k = n$

NO
$k = k + 1$

Test: $T(r,t) = T'(r,t)$

YES

**STEP 12**
Test: $X_{H_2O,m} = 1$

**STEP 13**
$X_{H_2O,m} = X_{H_2O,m} + \delta X_{H_2O,m}$

NO

**STEP 14**
Test: $X_{H_2O,m} > 1$

YES
Accept $T'(r,t) = T'(r,t)$

To **STEP 3 or 4 in Figure 4.3**

---

**Figure 4.5** Schematic of the solution algorithm used to calculate the radial particle temperature profile, $T(r,t)$, at **STEPS 2 and 4 in Figure 4.3**

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As with the test conducted in Figure 4.4, the maximum difference between the calculated temperatures $T(r,t)$ and $T'(r,t)$ at any corresponding radial positions must be less than 0.5°C in order for convergence to be accepted. When convergence is not achieved, the temperatures used to calculate the thermophysical properties in STEP 1 and STEP 8 are set to the temperatures calculated within this algorithm. It was found that this technique enabled convergence to be achieved with a maximum of 5 repeats of the entire algorithm denoted by Figure 4.5. Generally however, only 2 or 3 iterations were required and thus it was deemed unnecessary to utilise a Newton-Raphson type iteration method. Similar was observed for the iteration method used to correct for the fraction of moisture in Equation (4.28). As mentioned, however, the model predictions were found to be extremely sensitive to this parameter. This was particularly applicable under fluidised bed heating conditions where rapid drying was prevalent. For such conditions it was deemed necessary to reduce the length of the time increments such that the change in the fraction of moisture evolved from each shell for successive time increments was less pronounced.

For the entire model algorithm depicted in Figure 4.4, the number of iterations required was found to be highly dependent on the length of the time increments and the heat transfer environments. As with the fraction of moisture evolved, it was necessary to adjust the time increments such that the change in the residual volatile content in each shell, $V_m$, did not decrease overly rapidly. Generally it was found that for the conditions prevailing in the horizontal tube furnace, time increments of between 2 and 3 seconds at 800°C and 600°C, respectively, were able to achieve adequate model predictions with a reasonable solution time. For the fluidised bed, where the heat transfer rate is much higher, the time increments were reduced to 1 second. The overall calculation time was not effected, however, due to the decrease in the overall devolutilization time.

Furthermore it was found that the number of shells, and therfore the number of nodes at which the radial temperature profile was calculated, also effected the model predictions. For particles of up to 10 mm in diameter, 10 shells were observed to be the minimum required such that the addition of further shells did not dramatically
influence the calculated particle temperature response. Therefore, in order to minimise the overall computational time, 10 shells were used in all of the subsequent modelling work to be presented.

4.5 CAPABILITIES OF THE PROPOSED MODEL

In order to depict the capabilities of the current model, model predictions were generated using the conditions prevalent in the horizontal tube furnace at 800°C. Note that the model predictions generated here are only useful to illustrate the predictions generated by the model.

Figure 4.6 compares the particle temperature response predictions generated at the particle surface, the centre of the particle, and at a radial position half way between the surface and the centre. Also in Figure 4.6 are the corresponding values of the fraction of moisture released from the corresponding shells within the coal particle. It can be observed that the surface heats up quite rapidly and there is no noticeable plateau in the temperature response and this is reflected in the rapid release of moisture from this shell. The remaining temperature response predictions do indicate the presence of the temperature plateau due to moisture evolution. Note that the time at which moisture has been completely removed from each shell is equivalent to the time at which the respective particle temperature rises above the drying temperature.

Figure 4.7 compares the temperature response predictions of Figure 4.6, with the predicted fraction of volatiles evolved from the coal particle in the corresponding shells. Comparing Figures 4.6 and 4.7 indicate that, in any particular shell, devolatilization does not occur until drying is complete which is expected given the temperature range over which these phenomena occur. It is also apparent that devolatilization occurs in the shell nearest the surface of the particle at the same time as drying is apparent at the centre of the coal particle. Figure 4.7 tends to suggest that devolatilization becomes significant at temperatures greater than 400°C, which is consistent with that reported previously (Section 2.2.3.1). Also, the time required for
the particle to reach the furnace temperature is comparable with the time required for devolutilization to be complete in each individual shell.

**Figure 4.6** Model predictions for the temperature response and fraction of moisture released from three radial positions within the coal particle.

**Figure 4.7** Model predictions for the temperature response and fraction of volatiles released from three radial positions within the coal particle.
Ultimately, Figures 4.6 and 4.7 give an indication of the nature of the results which can be obtained from the current model, as well as the variation in the predictions across the radius of the particle. The predictions indicate that there are indeed significant temperature gradients existing across the radius of the particle during devolatilization, which confirms the need for a sophisticated particle temperature model. Furthermore the model is capable of predicting the evolution of both moisture and volatile matter from the coal particle, and can predict variations in the evolution profiles across the particle radius. Devolatilization and drying can be seen to be occurring simultaneously in different shells within the coal particle, and the temperatures over which drying and devolatilization are observed are consistent with the literature.

4.6 SUMMARY

A comprehensive coal devolatilization model has been developed in this chapter, with the model designed to predict both the particle temperature response and the evolution of both moisture and volatile matter in a number of shells which comprise the entire coal particle. Throughout the development of the model, a number of parameters have been identified which are either dealt with inconsistently, or have not been thoroughly assessed, in the literature. In order to determine the influence of these parameters on the model predictions, a sensitivity analysis will be conducted in the following chapter in order to deduce the most appropriate assumption relating to the use of these parameters within the overall devolatilization model.

An example of the capabilities of the model was also presented, and the model has been shown to be capable of predicting the temperature response at various radial positions within the coal particle. These predictions have indicated that large temperature gradients do exist within mm-sized coal particles which is consistent with the literature. The model is also able to predict the expected trends of both moisture and volatile matter evolution, and the trends of each of these are comparable with the particle temperature predictions. It is interesting to note the model predictions indicate that, for a 10 mm particle, the overall devolatilization time was comparable
with the time required for the particle to reach the furnace temperature. This implies that devolatilization of large coal particles takes place in the heat transfer controlled regime. Further work is necessary to confirm this observation. Ultimately, the model presented in this chapter is capable of generating the model predictions required for the present study and, as such, subsequent validation and testing of the model can proceed with confidence.
Chapter 5

SENSITIVITY ANALYSIS

5.1 INTRODUCTION

Throughout the development of the large coal particle devolatilization model in Chapter 4, a number of model parameters were detected which were considered to require a sensitivity analysis. The need for a sensitivity analysis may arise from uncertainties in the magnitude of a particular parameter, inconsistent assumptions relating to the use of a particular parameter in models presented in the literature, and etc. The focus of this chapter of work is to perform the required sensitivity analysis with respect to the parameters in question, and to conclude on the appropriate utilisation of each parameter within the current model. The parameters to be tested as a part of this sensitivity analysis are:

- coal specific specific heat capacity, $C_{p,c}$
- coal thermal conductivity, $k_c$
- coal particle density, $\rho_c$
- coal emissivity, $\varepsilon_c$
- convective heat transfer coefficient, $h$
- enthalpy of devolatilization, $\Delta H_{dev}$
- surface volatile matter flux, $N_R$
- enthalpy of drying, $\Delta H_{drying}$
• effective drying temperature, $T_{\text{drying}}$

Prior to performing the sensitivity analysis, a reference set of model predictions must be obtained. Subsequently, model predictions generated as a result of a variation in one of the parameters listed above can be compared with the reference set of model predictions. This section of work will detail the assumptions made when defining the conditions used to obtain the reference set of model predictions. Following this, each of the aforementioned model parameters will be independently tested in order to ascertain their effect on the model predictions. Note that parameters such as the temperature of the surroundings, the initial particle size, the initial moisture content, and the heat transfer environment will have an impact on the model predictions. These parameters are not intrinsic to the model and are defined by the conditions of any particular experiment. However, the magnitude of the effect on the model predictions of some of the variables to be tested in this chapter may depend on the experimental conditions and this will be taken into account where appropriate. Ultimately, the results of the sensitivity analysis performed in his chapter will govern the use of the aforementioned parameters in the existing model and enable model predictions corresponding to the experimental measurements in Chapter 3 to be performed with greater confidence.

5.2 REFERENCE MODEL PREDICTIONS

In order to generate the reference set of model predictions, it is necessary to define a typical set of experimental conditions on which the subsequent sensitivity analysis can be performed. Furthermore, a reference set of assumptions must be made relating to each of the model parameters to be tested in the sensitivity analysis. Therefore, the influence on the model predictions of a variation in any of the model parameters to be tested can be directly related to the magnitude of the change in the model parameter itself.
5.2.1 Reference Experimental Conditions

Chapter 3 details the experimental work which was conducted as part of this study. It is logical, therefore, that the experimental conditions employed to obtain the reference model predictions be directly related to the experimental conditions employed. Two experimental apparatus were utilised to generate the experimental data appearing in Chapter 3, namely the horizontal tube furnace and the fluidised bed reactor. As stated in Chapter 3, the heat transfer environment in the horizontal tube furnace is far more confidently defined when compared to that in the fluidised bed reactor. As a result, the reference model predictions will be based on the conditions pertinent to the horizontal tube furnace. However, when investigating the convective heat transfer coefficient under fluidised bed conditions these reference model predictions will not be useful.

When considering the heat transfer environment within the horizontal tube furnace, the majority of the heating results from radiation form the interior surface of the ceramic tubes. Equation (2.15) which defines the total rate of heat transfer from the surrounding environment employs the term $\varepsilon_{rad}$ which refers to the effective amount of radiant heat leaving the ceramic tube which is absorbed by the coal particle. The effective emissivity is given by:

$$
\varepsilon_{rad} = \varepsilon \varepsilon_{F_{rad}}
$$

(5.1)

where $F_{rad}$ is the radiation shape factor between the ceramic tube and the coal particle which refers to the amount of radiant heat leaving the ceramic tube which is incident on the coal particle. For the situation particular to a spherical particle inside a relatively long cylinder, the expected radiation shape factor is $F_{rad} = 1$ (Holman, 1990) which then gives $\varepsilon_{rad} = \varepsilon_{c}$. The flowrate of $N_{2}$ through the horizontal tube furnace in all of the experiments conducted was equivalent to 5 cm on the Metric Series Tube Size 7A Rotameter Chart which correspond to a flowrate of 2.25 L min$^{-1}$ under reference conditions. This can be used to determine the gas velocity in the tube by correcting the gas flowrate with respect to the furnace temperature and accounting for
the cross-sectional area of the tube. This gas velocity is used in Equation (2.23) to
determine the convective heat transfer coefficient for use in Equation (2.15).

Chapter 3 also indicates the bed temperatures and particle sizes employed during the
experimental investigation. Data was obtained in the horizontal tube furnace for both
-10 + 11 mm and -8 + 9 mm coal particles at furnace temperatures of 600°C, 700°C,
and 800°C. Due to the relative similarity of the trends observed for both the -10 + 11
mm and -8 + 9 mm particles in Chapter 3, the influence of the parameters to be tested
on the model predictions for these particle sizes is also likely to be similar. Therefore,
the reference model predictions will be generated assuming -10 + 11 mm coal
particles only. In cases where the influence of the parameter being tested may be
dependent on the particle size, it will be more appropriate to employ much smaller
particle sizes during the sensitivity analysis in order to better gauge the particle size
effect.

While the horizontal tube furnace experiments were conducted over a relatively
narrow temperature range, 600°C ≤ T ≤ 800°C, this temperature range is significant
when considering with the trends observed during devolatilization (Tyler, 1980).
Therefore, a single temperature cannot be employed to characterise the typical
devolatilization behaviour, and it is more appropriate to consider the model
predictions obtained at 600°C and 800°C in order to observe any unexpected
behaviour which results from variations in the model parameters being examined.

Finally, the reference model predictions will be generated by assuming that the coal
particles are initially completely dry. This eliminates any conflicting effect of the
drying process on the influence of the parameters to be tested, with the exception of
the enthalpy of drying and the effective drying temperature. When assessing the
influence of these two parameters, the particles will be assumed to be wet. This
assumption is also pertinent to dealing with the changing particle density as discussed
in Section 3.5.3 hence this parameter will be considered after the aforementioned
moisture parameters.
5.2.2 Reference Parameter Assumptions

Due to the number and variation in the thermophysical properties reported for coal in the literature, it is difficult to define a reference set of values for generating the reference model predictions. While most of the specific heat capacity and thermal conductivity data have been reported separately, and by different researchers, the correlations presented by Agroskin et al. (1970) and Agroskin (1957) represent thermophysical property correlations which have been produced by a single research group. These correlations are given by Equations (2.20) and (2.19), respectively.

\[ k_c = 0.19 + 2.5 \times 10^{-4} (T - 300) \]  \hspace{1cm} (2.19)

\[ C_{p,c} = 1.15 + 2.03 \times 10^{-3} (T - 300) - 1.55 \times 10^{-6} (T - 100)^2 \text{ J kg}^{-1} \text{ K}^{-1} \]  \hspace{1cm} (2.20)

The work of Linjewile (1993) represents the most thorough investigation into the emissivity of coal particles and, as such, Equation (2.22) can be confidently used when generating the reference model predictions.

\[ \varepsilon_c = 0.377 + 0.00039 T_p \bigg|_{r = R_e} \]  \hspace{1cm} (2.22)

Investigating the influence of the convective heat transfer coefficient on the model predictions is applicable to the fluidised bed reactor where the heat transfer environment is not well defined. Consequently the reference model predictions generated in this section of work will not be applicable as they pertain to the conditions in the horizontal tube furnace. In this case model predictions will be generated using the correlation of Linjewile (1993) (Equations (2.25) and (4.12) to (4.17)) to estimate the heat transfer coefficient. The sensitivity of the model predictions to this parameter can then be tested by using alternate correlations for the heat transfer coefficient.
When generating the reference model predictions, it will be assumed that the enthalpy of devolatilization is negligible. Accordingly, the effect of employing of a non-zero enthalpy of devolatilization will be easily observed via a direct comparison with the reference model predictions.

Similarly, it will be assumed initially that the effect of the surface volatile matter flux is negligible. The effect of considering the volatile matter flux on the model predictions will again be evident from a direct comparison with the reference model predictions. Note that the heat transfer environment in the horizontal tube furnace is not a purely convective flow environment and, in fact, radiation heat transfer is dominant. Hence comparisons will be made between the influence the volatile matter flux has under the conditions prevailing in the horizontal tube furnace and that when a purely convective heating environment is assumed.

Observing the effect of the enthalpy of drying and the effective drying temperature can only be facilitated by assuming that the particles are initially wet. Hence the reference model predictions do not apply to these two parameters. However, to investigate the effect of these parameters a second set of reference model predictions will be generated which will be applicable to wet coal particles. These predictions will employ the same assumptions mentioned above for the experimental conditions and the aforementioned model parameters, and will further assume that the effective drying temperature is equivalent to 100°C and that the enthalpy of drying remains constant at the free moisture enthalpy of vaporisation.

The incorporation of moisture into the model enables the effect of shrinkage, or the effect of the particle density, to be considered. While it is evident that shrinkage is occurring, the reference model predictions generated for wet coal particles will neglect shrinkage however will take into account the effect of the weight loss on the particle density. This will enable to effect of assuming a constant density and the effect of considering shrinkage to be assessed via a direct comparison with the reference model predictions for wet coal particles.
5.2.3 **REFERENCE MODEL PREDICTIONS**

Table 5.1 indicates the experimental conditions and assumptions relating to the various parameters being investigated which were used to generate the reference model predictions.

<table>
<thead>
<tr>
<th>Experimental condition/parameter</th>
<th>Assumed Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat transfer environment</td>
<td>Horizontal tube furnace</td>
</tr>
<tr>
<td></td>
<td>Radiation shape factor = 1</td>
</tr>
<tr>
<td></td>
<td>( N_2 ) flowrate @ 2.25 L min(^{-1}) ((25^\circ C, 1) atm)</td>
</tr>
<tr>
<td>Particle size</td>
<td>-10 + 11 mm</td>
</tr>
<tr>
<td>Furnace temperature</td>
<td>600(^\circ)C and 800(^\circ)C</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>Equation (2.20)</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>Equation (2.19)</td>
</tr>
<tr>
<td>Emissivity</td>
<td>Equation (2.22)</td>
</tr>
<tr>
<td>Convective heat transfer coefficient(^a)</td>
<td>Linjewile (1993)</td>
</tr>
<tr>
<td>Enthalpy of devolatilization</td>
<td>0 kJ kg(^{-1})</td>
</tr>
<tr>
<td>Surface volatile matter flux</td>
<td>Negligible</td>
</tr>
<tr>
<td>Enthalpy of drying(^b)</td>
<td>2334 kJ kg(^{-1})</td>
</tr>
<tr>
<td>Effective drying temperature(^b)</td>
<td>100(^\circ)C</td>
</tr>
<tr>
<td>Particle density(^c)</td>
<td>Proportional to mass loss only</td>
</tr>
</tbody>
</table>

\(^a\) Applies only when considering the environment prevailing in the fluidised bed reactor.

\(^b\) Applies only when considering wet coal particles.

\(^c\) Applies only when considering wet coal particles, shrinking is ignored.

Figure 5.1 shows the reference model predictions obtained at a furnace temperature of 800\(^\circ\)C, while Figure 5.2 shows similar model predictions generated at a furnace temperature of 600\(^\circ\)C. The model predictions displayed in these two figures will be
used as the reference model predictions in the sensitivity analysis which follows in Section 5.3.

**Figure 5.1** Reference model predictions obtained using the assumptions listed in Table 5.1 at a furnace temperature of 800°C.

**Figure 5.2** Reference model predictions obtained using the assumptions listed in Table 5.1 at a furnace temperature of 600°C.
5.3 PARAMETER SENSITIVITY ANALYSIS

5.3.1 THERMOPHYSICAL PROPERTIES

5.3.1.1 Thermal Conductivity

The value of the coal thermal conductivity used to generate the reference model predictions was assumed to be that of Agroskin (1957), which yields a thermal conductivity which ranges from 0.19 W m\(^{-1}\) K\(^{-1}\) to 0.38 W m\(^{-1}\) K\(^{-1}\) between temperatures of 300 K (27°C) and 1073 K (800°C), respectively. As can be seen in Table 2.3 (Chapter 2), Perry and Green (1984), Yang and Wang (1990), and Wang et al. (1994) all quote a constant thermal conductivity of \(k_c \approx 0.25\) W m\(^{-1}\) K\(^{-1}\). This value is approximately equivalent to the average of the thermal conductivity values obtained from the correlation of Agroskin (1957). Figures 5.3 and 5.4 exhibit the model predictions generated assuming a constant thermal conductivity of \(k_c \approx 0.25\) W m\(^{-1}\) K\(^{-1}\) at furnace temperatures of 600°C and 800°C, respectively. Also shown in these figures are the corresponding set of reference model predictions generated using the correlation of Agroskin (1957).

It is evident from Figures 5.3 and 5.4 that assuming a constant value of the coal thermal conductivity which is approximately equal to the temperature averaged thermal conductivity has only a minor effect on the model predictions relative to the reference model predictions. The magnitude of the effect can be seen to be marginally more pronounced at 800°C. Furthermore, the model predictions are effected to a greater extent at the particle surface where the predicted particle temperature response in Figure 5.3 deviates from the corresponding reference temperature response with an average absolute error of 3.1%, and the volatile matter released deviates on average by approximately 6.1% The corresponding average absolute error values at the centre of the particle are 1.5% and 4.4%, respectively. In Figure 5.4, the average deviations in the temperature response and volatile matter evolved at the particle surface are 3.6% and 7.0%, respectively, while at the centre of the particle values of 1.8% and 4.4%,
respectively, were obtained. The average absolute deviation in the thermal conductivity over the temperature ranges of the model predictions displayed is approximately 14% in Figure 5.3, and 18% in Figure 5.4.

**Figure 5.3** Comparison between the model predictions obtained for the HTF at 600°C assuming $k_c = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$ and those of the corresponding reference model predictions. (A) refers to the reference model predictions. (B) refers to the predictions assuming $k_c = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$.

**Figure 5.4** Comparison between the model predictions obtained for the HTF at 800°C assuming $k_c = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$ and those of the corresponding reference model predictions. (A) refers to the reference model predictions. (B) refers to the predictions assuming $k_c = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$.
It is evident that the maximum error resulting from varying the coal thermal conductivity will arise at the particle surface when furnace temperatures of 800°C are assumed. From Figure 5.4 it can be seen that the maximum error occurs at approximately 25 seconds which corresponds to the time at which the particle surface is undergoing significant devolatilization. According to the model predictions, the magnitude of the absolute error in the predicted temperature response at $t = 25$ s is 8%, while the magnitude of the absolute deviation in the fraction of volatile matter evolved is approximately 35%. Note that the deviation in the fraction of volatile matter evolved is higher due to the dependence of the fraction of volatile matter evolved on the entire time-temperature history of the particle.

Ultimately, while there are isolated instances where deviations in the model predictions of as high as 35% can be observed, the model predictions in general are only marginally influenced by the variation in the thermal conductivity displayed in Figure 5.3 and 5.4. This is expected given that the thermal conductivity employed was approximately equivalent to the temperature averaged thermal conductivity. Figures 5.5 and 5.6 display the model predictions obtained at the surface and the centre of the coal particle, respectively, by assuming a much higher thermal conductivity being that proposed by James and Mills (1976), $k_c = 0.67$ W m$^{-1}$ K$^{-1}$. Model predictions using this thermal conductivity were only generated at 800°C as it is at this temperature that the maximum deviation from the reference model predictions is expected.

Figure 5.5 indicates that the model predictions at the particle surface are not drastically affected, yet Figure 5.6 suggests that the centre of the particle is undergoing significantly faster heating, and devolatilization, as a result of assuming a higher thermal conductivity. The temperature at the particle surface is lower than the reference particle surface temperature during the initial heating period which is a direct result of the increased rate at which energy is being conducted away from the particle surface and toward the centre of the particle. At latter stages, however, the surface temperature tends to exceed that of the reference surface temperature. This arises due to a reduction in the rate at which heat is transferred away from the particle
Figure 5.5 Comparison between the model predictions obtained for the particle surface in the HTF at 800°C assuming $k_c = 0.67$ W m$^{-1}$ K$^{-1}$ and those of the corresponding reference model predictions. (A) refers to the reference model predictions. (B) refers to the predictions assuming $k_c = 0.67$ W m$^{-1}$ K$^{-1}$.

Figure 5.6 Comparison between the model predictions obtained for the centre of the particle in the HTF at 800°C assuming $k_c = 0.67$ W m$^{-1}$ K$^{-1}$ and those of the corresponding reference model predictions. (A) refers to the reference model predictions. (B) refers to the predictions assuming $k_c = 0.67$ W m$^{-1}$ K$^{-1}$.
surface. This is a result of the reduction in the temperature gradient existing between the surface and the centre of the particle when a higher thermal conductivity is assumed, which is apparent from Figures 5.5 and 5.6. The reduction in the temperature gradient results from the greater heating rate at the centre of the particle during the earlier stages.

This reduction in the apparent temperature gradient across the radius of the particle is consistent with the theory which suggests that the assumption of an isothermal particle is valid when the heat transfer Biot number \((Bi = h d_p / k_c)\) is in the range \(Bi < 0.1\) (Holman, 1990). Hence increasing the thermal conductivity results in a reduction in the Biot number and the particle behaviour tends to become increasingly isothermal, as observed.

Ultimately, varying the thermal conductivity has been shown to have only a marginal effect on the model predictions at the particle surface. Conversely, the model predictions at the centre of the particle can be significantly effected by changes in the coal thermal conductivity. Increasing the thermal conductivity has the effect of increasing the heating rate at the centre of the particle and thus creating a more even temperature profile over the radius of the particle during heating, ie the particle behaviour becomes increasingly isothermal. At present there is no specific reason for selecting a thermal conductivity in the range of that reported by James and Mills (1976), given that the correlation of Agroskin (1957) predicts thermal conductivity values consistent with several other researchers (Perry and Green, 1984; Yang and Wang, 1990; and Wang et al., 1994). Therefore the correlation of Agroskin (1957) will be maintained for predicting the coal thermal conductivity for the remainder of the sensitivity analysis.
5.3.1.2 Specific Heat Capacity

The correlation of Agroskin et al. (1970) was employed in the reference model predictions to estimate the coal specific heat capacity. Tomeczek and Palugniok (1996) performed a rigorous experimental investigation into the specific heat capacity of several coals and observed that the effective specific heat capacity increased initially with temperature until a maximum was reached at a temperature of approximately 700°C, after which the specific heat capacity decreased. The coal with composition most similar to that of Bowmans coal, used in the study of Tomeczek and Palugniok (1970) was Czeczot coal. Figure 5.7 compares the specific heat capacity predicted by the correlation of Agroskin et al. (1970) with that of Tomeczek and Palugniok (1996) for Czeczot coal. Also shown are various correlations/constant values used to characterise the specific heat capacity of coal in various literature sources, as reported in Table 2.3 (Chapter 2). It can be seen that the specific heat capacity predicted by the correlation of Tomeczek and Palugniok (1996) is significantly greater than the remaining heat capacities, while that of Agroskin et al. (1970) predicts specific heat capacity values which are almost identical to the average specific heat capacity determined based on all the reported data in Figure 5.7.

In order to investigate the influence of the specific heat capacity on the model predictions, the reference model predictions were compared to those obtained by assuming the maximum and minimum specific heat capacity correlations observed in Figure 5.7. Figure 5.8 displays the model predictions obtained assuming the specific heat capacity correlation of Tomeczek and Palugniok (1996) for Czeczot coal, while Figure 5.9 shows the model predictions generated using the specific heat capacity of Borghi et al. (1985). In both cases the reference model predictions are included for comparison.

Figure 5.8 Comparison between the model predictions obtained for the HTF at 800°C assuming the specific heat capacity of Tomeczek and Palugniok (1996) for Czeczot coal, and those of the corresponding reference model predictions. (A) refers to the reference model predictions. (B) refers to the predictions assuming the specific heat capacity of Tomeczek and Palugniok (1996).
Figure 5.9 Comparison between the model predictions obtained for the HTF at 800°C assuming the specific heat capacity of Borghi et al. (1985), and those of the corresponding reference model predictions. (A) refers to the reference model predictions. (B) refers to the predictions assuming the specific heat capacity of Borghi et al. (1985).

Figure 5.8 indicates that increasing the specific heat capacity results in a general reduction of the particle heating rate, while the reverse is apparent in Figure 5.9. This is the expected result given that the specific heat capacity is a measure of the amount of energy required to heat the coal substance. As the heat transfer environment has not been altered, the rate of heat transfer to the particle is unchanged. Therefore, increasing the amount of energy required to heat the substance decreases the rate at which the particle can be heated, and vice versa. In both figures it is clear that the initial heating rate at the particle surface is only marginally effected by the change in the specific heat capacity. However, once devolatilization commences the respective temperature responses begin to deviate dramatically. This is due to the additional effect of the changing particle density as a result of devolatilization. When the specific heat capacity is higher, the particle heating rate is subsequently reduced. This then results in devolatilization commencing later as it takes longer to reach the minimum devolatilization temperature. As the density is directly related to the mass loss, at any point in time the effective particle density will be greater when a higher
specific heat capacity is assumed. This further reduces the comparative particle heating rate as the effective mass of coal to be heated remains larger. Therefore the influence of increasing the specific heat capacity is compounded by the subsequent effect on the particle density. The reverse also applies when the specific heat capacity is reduced.

The magnitude of the deviation in the model predictions which results from a change in the specific heat capacity of the coal was found to be directly proportional to the magnitude of the change. Assuming the specific heat capacity of Tomoczek and Palugniok (1996) as opposed to that of the reference model predictions (Agroskin et al., 1970) represents an average increase in the specific heat capacity of around 50%. The corresponding reduction in the particle temperature response at any time is, on average, 28%. Alternatively, the specific heat capacity of Borghi et al. (1985) represents on average a 36% reduction in the specific heat capacity and corresponds to a 20% increase in the predicted temperature response.

Once again it is difficult to deduce conclusively which of the aforementioned correlations/constant values for the specific heat capacity should be employed in the current model. However, given that Figure 5.7 shows the specific heat capacity predicted by Agroskin et al. (1970) is approximately equivalent to the average of all of the specific heat capacity values presented, it is acceptable that the correlation of Agroskin et al. (1970) be employed throughout the remaining sensitivity analysis. Generally, it can be concluded that the specific heat capacity has a greater impact on the model predictions than the thermal conductivity, particularly at the particle surface.

5.3.2 EMISSIVITY

The investigation by Linjewile (1993) into the emissivity of a petroleum coke particle represents a comprehensive experimental study into coal emissivity and as such, has been employed to generate the reference model predictions. This correlation predicts that the emissivity varies between $\varepsilon_c = 0.493$ and $\varepsilon_c = 0.795$ over a temperature range
between 25°C and 800°C. Various other researchers have reported values for coal emissivity of $\varepsilon_c = 0.8$ (Perry and Green, 1984), $\varepsilon_c = 0.9$ (Fu et al., 1987; and Wang et al., 1994), $\varepsilon_c = 0.93$ (Kilic et al., 1993), and $\varepsilon_c = 1$ (Sandhu and Hashemi, 1985; and Tia et al., 1991). In order to investigate the sensitivity of the model predictions to the coal emissivity, the maximum range of the values reported by the aforementioned researchers has been employed to generate alternate model predictions. Figure 5.10 exhibits the model predictions obtained by assuming an emissivity of $\varepsilon_c = 0.8$, while Figure 5.11 shows similar model results when an emissivity of $\varepsilon_c = 1.0$ is applied.

Figure 5.10 shows that the model predictions are influenced to some extent by the coal emissivity. This is expected given that radiation heat transfer is the dominant heat transfer mechanism in the horizontal tube furnace. In the case of Figure 5.10, the emissivity has been increased by an average of 35% with the effect being an increase in the particle heating rate and subsequent volatile matter release. The particle temperature response has increased on average by 5% with a maximum deviation of approximately 18% occurring at around 20-25 seconds. For the case in which an emissivity of $\varepsilon_c = 1.0$ has been assumed, the emissivity has effectively been increased by an average of 65%. The result has been a maximum increase in the particle temperature response of 29% at approximately 20-25 seconds, with an average of 9.5%. Note that for the heat transfer environment prevalent in the horizontal tube furnace, radiation heat transfer represents approximately 75% of the total heat transfer to the particle surface.

It is unreasonable to assume that an emissivity of $\varepsilon_c = 1.0$ can be assumed to be applicable to coal particles as they cannot be reasonably considered to be black bodies (Holman, 1992). The effect on the model predictions arising from assuming an emissivity of $\varepsilon_c = 0.8$ is not as significant as a similar variation in the coal specific heat capacity, as discussed in Section 5.3.1.2. It was found that reducing the specific heat capacity by 36% resulted in a 20% increase in the particle temperature response. A change in the emissivity of similar magnitude occurs in
Figure 5.10 Comparison between the model predictions obtained for the HTF at 800°C assuming a coal emissivity of $\varepsilon_c = 0.8$, and those of the corresponding reference model predictions. (A) refers to the reference model predictions. (B) refers to the predictions assuming a coal emissivity of $\varepsilon_c = 0.8$.

Figure 5.11 Comparison between the model predictions obtained for the HTF at 800°C assuming a coal emissivity of $\varepsilon_c = 1.0$, and those of the corresponding reference model predictions. (A) refers to the reference model predictions. (B) refers to the predictions assuming a coal emissivity of $\varepsilon_c = 1.0$. 
Figure 5.10, however the deviation in the predicted temperature response was found to be equivalent to just 5%. Considering that radiation heat transfer contributes only 65% to the total heat transfer, the estimated influence on the model predictions under purely radiation heat transfer is expected to be limited to 10%. This indicates that the model predictions are more sensitive to variations in the specific heat capacity than to the coal emissivity. It is reasonable then to assume that the emissivity correlation reported by Linjewile (1993) can be applied in further modelling applications, in light of the lack of coal specific data.

5.3.3 Fluidised Bed Convective Heat Transfer Coefficient

The convective heat transfer coefficient under fluidised bed conditions is dependent on a number of operational parameters within the fluidised bed reactor. These parameters include the superficial gas velocity, the size of the inert bed material, the bed temperature, the static bed height, and the active particle size. During the course of the fluidised bed reactor experiments, the size of the inert bed material employed was $d_i = -180 + 250 \ \mu m$, the superficial gas velocity employed was 1.5 times the minimum fluidisation velocity (0.81 cm s$^{-1}$ @ 25°C, 1 atm at 600°C, 0.56 cm s$^{-1}$ @ 25°C, 1 atm at 800°C), and the static bed height was 15 cm. In order for the sensitivity analysis to be conducted, comparisons will be made assuming an active particle size of -10 + 11 mm and bed temperatures of 600°C and 800°C. The correlation of Linjewile (1993) will be used to estimate the convective heat transfer coefficient for the reference model predictions under fluidised bed conditions. These model predictions will subsequently be compared with those generated from alternate heat transfer coefficient correlations.

At a bed temperature of 600°C, the correlation of Linjewile (1993) predicts a heat transfer coefficient of $h_{\text{conv,fb}} = 659 \ \text{W m}^{-2} \ \text{K}^{-1}$. Alternatively, the correlation of Baskakov et al. (1987) predicts an average heat transfer coefficient of $h_{\text{conv,fb}} = 498 \ \text{W m}^{-2} \ \text{K}^{-1}$ which represents a 25% reduction in the heat transfer coefficient predicted by Linjewile (1993). The model predictions generated at a bed temperature of 600°C using the correlation of Baskakov et al. (1987) are compared to those generated using
the correlation of Linjewile (1993) in Figure 5.12. The heat transfer coefficients predicted by the correlations of Linjewile (1993) and Baskakov (1987) at 800°C are \( h_{\text{conv,fb}} = 735 \text{ W m}^{-2} \text{ K}^{-1} \) and \( h_{\text{conv,fb}} = 526 \text{ W m}^{-2} \text{ K}^{-1} \), respectively. This represents a 28% reduction in the heat transfer coefficient. The subsequent model predictions under these conditions are seen in Figure 5.13.

It can be seen from Figures 5.12 and 5.13 that the effect of a 25% to 28% reduction in the heat transfer coefficient is relatively minimal. The model predictions generally exhibit a slower heating rate, and subsequently a slower rate of volatile matter release, which is expected given that the rate of heat transfer to the particle surface has been reduced. The average absolute deviation in the temperature response predicted at the particle surface is in the order of 2.6% in Figure 5.12 and 2.7% in Figure 5.13, while the corresponding deviation in the fraction of volatile matter evolved is 5.9% in Figure 5.12 and 5.1% in Figure 5.13.

![Graph](image)

**Figure 5.12** Comparison between the model predictions obtained for the fluidised bed reactor at 600°C. (A) refers to the model predictions generated using the correlation of Linjewile (1993). (B) refers to the predictions generated assuming the correlation of Baskakov (1987).
Figure 5.13 Comparison between the model predictions obtained for the fluidised bed reactor at 800°C. (A) refers to the model predictions generated using the correlation of Linjewile (1993). (B) refers to the predictions generated assuming the correlation of Baskakov (1987).

At the centre of the particle, the reduction in the heat transfer coefficient results in an average absolute reduction in the temperature response of 1.2% in Figures 5.12 and 5.13, and an average absolute reduction in the fraction of volatile matter evolved of 4.2% in Figure 5.12 and 2.1% in Figure 5.13. These values represent fairly minimal reduction given the magnitude in the reduction in the heat transfer coefficient. Furthermore, the deviation in the model predictions in this case are lower then for similar changes in the specific heat capacity and the coal emissivity as observed in Sections 5.3.1.2 and 5.3.2, respectively.

The fact that large variations in the convective heat transfer coefficient under fluidised bed conditions has little effect on the model predictions tends to indicate that the particle heating process is internal rather than external heat transfer controlled. Consider Equation 5.1 (Holman, 1990) which can be employed to estimate the overall resistance to heat transfer due to internal and external heat transfer.
\[ U_{\text{overall}} = \left( \frac{1}{h_{\text{conv,fb}}} + \frac{\Delta r}{k_e} \right) \]  \hspace{1cm} (5.1)

where \( U_{\text{overall}} \) is the overall heat transfer coefficient between the surroundings and the centre of the particle, and \( \Delta r \) is the particle radius. Based on the heat transfer coefficient of Linjewile (1993) and the temperature averaged thermal conductivity at 600°C, Equation 5.1 predicts an overall heat transfer coefficient of \( U_{\text{overall}} = 50.4 \text{ W m}^{-2} \text{ K}^{-1} \). Employing the convective heat transfer coefficient of Baskakov et al. (1987) results in an overall heat transfer coefficient of 49.2 \text{ W m}^{-2} \text{ K}^{-1} \). The corresponding values at 600°C are 50.8 \text{ W m}^{-2} \text{ K}^{-1} \) and 49.5 \text{ W m}^{-2} \text{ K}^{-1} \). Therefore it can be seen that varying the external heat transfer coefficient under fluidised bed conditions has minimal effect on the overall model predictions due to the particle heating process being internal heat transfer controlled in the fluidised bed reactor.

It can be concluded, therefore, that the model predictions are relatively insensitive to the heat transfer coefficient under fluidised bed operating conditions. Therefore the correlation of Linjewile (1993) can be employed in future modelling work given that the error in the convective heat transfer coefficient which may arise from the use of this correlation has minimal impact on the model predictions.

### 5.3.4 ENTHALPY OF DEVOLATILIZATION

The reference model predictions generated in Section 5.2.3 assumed a negligible enthalpy of devolatilization (ie. \( \Delta H_{\text{dev}} = 0 \)). Figure 5.14 compares the reference model predictions with those obtained when a constant endothermic enthalpy of devolatilization equivalent to \( \Delta H_{\text{dev}} = 300 \text{ kJ kg}^{-1} \) (as reported by Adesanya and Pham, 1995) is assumed. The result of considering an endothermic enthalpy of devolatilization can be observed to be a reduction in the particle heating rate upon initiation of devolatilization. Considering the temperature response at the particle surface it can be seen that the model predictions begin to deviate from the reference model predictions at approximately 250°C which corresponds to the commencement of devolatilization. As the particle is further heated, the predicted temperature
response begins to deviate further from the reference model prediction until the latter stages where both temperature responses approach the maximum furnace temperature. The fraction of volatile matter evolved shows slightly larger deviation than the temperature response and is due to the dependence of the fraction of volatile matter evolved on the entire time-temperature history of the particle.

The magnitude of the deviation of the particle temperature response predictions are 11.0% on average at the centre of the particle, and 9.4% on average at the particle surface. The corresponding degree of deviation in the fraction of volatile matter released amounts to 16.9% on average at the centre of the particle, and 15.5% on average at the particle surface. It seems, therefore, that the enthalpy of devolatilization may have a significant effect on the model predictions given the magnitude of these figures.

![Graph showing particle temperature and volatile matter release over time](image)

**Figure 5.14** Comparison between the model predictions obtained for the fluidised bed reactor at 600°C. (A) refers to the reference model predictions. (B) refers to the predictions generated when $\Delta H_{dev} = 300$ kJ kg\(^{-1}\).

However, the assumption of a constant endothermic enthalpy of devolatilization may not necessarily be valid, and various other trends in the enthalpy of devolatilization with devolatilization temperature have been reported (Lopez-Peinado et al., 1989; Tomeczek and Palugniok, 1996). Thus the trend in the enthalpy of devolatilization displayed in Figure 4.2 (Chapter 4) will be employed to characterise the enthalpy of...
devolatilization. According to this figure, two critical temperatures \((T_1\) and \(T_2\)) along with two maximum enthalpy of devolatilization values \(\Delta H_{\text{max,1}}\) and \(\Delta H_{\text{max,2}}\) must be defined. Figure 5.15 compares the reference model predictions with those obtained using the following values:

\[
\begin{align*}
T_1 &= 450 \text{ K} \\
T_2 &= 750 \text{ K} \\
\Delta H_{\text{max,1}} &= 300 \text{ kJ kg}^{-1} \\
\Delta H_{\text{max,2}} &= 450 \text{ kJ kg}^{-1}
\end{align*}
\]

**Figure 5.15** Comparison between the model predictions obtained for the fluidised bed reactor at 600°C. (A) refers to the reference model predictions. (B) refers to the predictions generated when \(\Delta H_{\text{dev}}\) is assumed to vary with temperature according to Lopez-Peinado et al. (1989), as per Figure 4.2.

The deviation which is apparent between the model predictions and the reference model predictions in Figure 5.15 appears to be marginally less than that in Figure 5.14. Also, the model predictions in Figure 5.15 are generally greater than the reference model predictions whereas in Figure 5.14 the model predictions are lower than the reference model predictions. This is confirmed when examining the average absolute deviation from the reference model predictions in each case. In Figure 5.15 the magnitude of the deviation for the particle temperature response predictions are
9.5% on average at the centre of the particle, and 8.4% on average at the particle surface. Average absolute deviations of 14.9% and 11.5% were obtained for the fraction of volatile matter evolved at the centre and surface of the particle respectively.

In Figure 5.15 it was assumed that the enthalpy of devolatilization is endothermic for temperatures less than 450 K (177°C), while it is exothermic for temperatures between 450 K and 750 K (477°C). Note that for temperatures above 750 K it was assumed that the enthalpy of devolatilization was equivalent to \( \Delta H_{dev} = 300 \text{ kJ kg}^{-1} \). It is evident from the model predictions that devolatilization is not significant for particle temperatures below as the enthalpy of devolatilization is only capable of affecting the model predictions when devolatilization is prominent. Furthermore, Figures 5.14 and 5.15 show that devolatilization is not complete at 600°C therefore the influence of the enthalpy of devolatilization on the model predictions may be limited. Figures 5.16 and 5.17 show model predictions obtained using identical assumptions as Figures 5.14 and 5.15, respectively, however a maximum temperature of 800°C is assumed in order to obtain complete devolatilization.

The model predictions in Figures 5.16 and 5.17 tend to show less deviation from the reference model predictions than those in Figures 5.14 and 5.15 despite the fact that the volatile matter is completely evolved. This is reflected in the average absolute deviation values determined from Figures 5.16 and 5.17. In Figure 5.16 the magnitude of the deviation for the particle temperature response predictions are 3.7% on average at the centre of the particle, and 1.5% on average at the particle surface. Average absolute deviations of 7.1% and 2.0% were obtained for the fraction of volatile matter evolved at the centre and surface of the particle, respectively. The average absolute deviation in the particle temperature response predictions in Figure 5.17 were found to be 2.1% and 0.98% at the centre and surface of the particle, respectively, whilst the respective deviation in the fractional amount of
Figure 5.16 Comparison between the model predictions obtained for the fluidised bed reactor at 800°C. (A) refers to the reference model predictions. (B) refers to the predictions generated when $\Delta H_{dev} = 300 \text{ kJ kg}^{-1}$.

Figure 5.17 Comparison between the model predictions obtained for the fluidised bed reactor at 800°C. (A) refers to the reference model predictions. (B) refers to the predictions generated when $\Delta H_{dev}$ is assumed to vary with temperature according to Lopez-Peinado et al. (1989), as per Figure 4.2.
volatile matter evolved was 6.5% and 2.9%. These results suggest that the increase in the devolatilization rate which occurs at the higher temperature is not as significant as the increase in the heating rate and thus the effect of the enthalpy of devolatilization is comparatively reduced.

The results presented here suggest that the enthalpy of devolatilization is capable of influencing the model predictions to a certain extent. The magnitude of the deviation in the model predictions from the reference model predictions is lower than that observed for the thermal conductivity and emissivity, which are in turn lower than that observed for the specific heat capacity. Also, the magnitude and nature of the enthalpy of devolatilization is uncertain. It was generally observed that the enthalpy of devolatilization began to influence the model predictions significantly between temperatures of 350°C and 550°C which corresponds to the temperature region where devolatilization is intensive according to the associated volatile matter loss curves. Increasing the maximum temperature was found to reduce the relative effect of the enthalpy of devolatilization on the model predictions which is likely to be due to a larger increase in the heat transfer rate relative to the rate of devolatilization. Ultimately, given the uncertainty surrounding the magnitude of the enthalpy of devolatilization and the fact that the effect of varying the enthalpy of devolatilization on the model predictions is low with respect to the specific heat capacity, the enthalpy of devolatilization can reasonably be ignored in all subsequent modelling applications.

5.3.5 **Surface Volatile Matter Flux**

The release of volatiles from the particle, and their expulsion at the particle surface, is potentially capable of altering the boundary layer which exists around the particle. Altering the boundary layer can in turn affect the rate of heat transfer to the particle by convection. This was discussed in greater detail in Section 2.4.2.7 where the work of Kalson (1983) was presented. Kalson (1983) proposed a set of equations whereby the extent of the reduction in the external convective heat transfer coefficient could be determined based on the rate of devolatilization. In Section 4.3.7, these equations
were integrated into the model such that the effect of the surface volatile matter flux could be tested.

In the previous work presented in this chapter the effect of the surface volatile matter flux has been neglected in order to ensure it does not distort the influence of the parameter/s being tested. Also, the majority of the previous model predictions have been generated under the conditions prevalent in the horizontal tube furnace. In the HTF, the heat transfer environment is predominantly radiative, with some contribution from convective heat transfer. Therefore, if this environment was used as a basis for testing the effect of the surface volatile matter flux it is likely that the overall effect would be limited. To gain a greater appreciation of the extent to which the surface volatile matter flux can influence the model predictions, the model predictions will be generated by assuming a purely convective heat transfer environment. In this way the influence of the surface volatile matter flux can be directly distinguished.

Figure 5.18 shows the model predictions generated assuming a local gas velocity of 1 m s\(^{-1}\) over the particle at 800\(^\circ\)C with the absence of radiation heat transfer. Model predictions are presented for -10 + 11 mm particles under two conditions; (A) the surface volatile matter flux has been neglected, (B) the surface volatile matter flux is considered. Figure 5.18 indicates that there is some discernible effect of the surface volatile matter flux on the model predictions. As devolatilization becomes prominent, the particle heating rate is reduced as a result of the surface volatile matter flux and its effect on the external heat transfer coefficient. The Ackermann correction factor, \(A_h^x\), was found to be at its minimum after 64 s where a value of \(A_h^x = 0.76\) was observed. This corresponds to the maximum reduction in the external convective heat transfer coefficient and occurs when the overall rate of devolatilization is at a maximum. Hence this result indicates that up to a 24% reduction in the heat transfer coefficient is possible for a -10 + 11 mm particle undergoing devolatilization in a 1 m s\(^{-1}\) convective gas flow at 800\(^\circ\)C. This corresponds to a flow Reynolds number of \(Re = 62.24\) and a Nusselt number of \(Nu = 6.59\).
Figure 5.18 Comparison between the model predictions obtained for a -10 + 11 mm particle in a purely convective flow environment (1 m s\(^{-1}\)) at 800°C. (A) refers to the model predictions when the surface volatile matter flux is neglected. (B) refers to the predictions generated when the surface volatile matter flux is considered.

The study of Kalson (1983) suggested that the volatile matter flux may be significant for particles of approximately 74 μm which could experience up to a 67% reduction in the external convective heat transfer coefficient as a result of the surface volatile matter flux. While particles in this size range are not relevant to the present study, the particle size may effect the magnitude of the reduction in the heat transfer coefficient. Given that this study is dealing with particle in the mm-size range, model predictions similar to those in Figure 5.18 were generated using a particle size equivalent to 1 mm. These model predictions are presented in Figure 5.19. It can be seen that the effect of the surface volatile matter flux seems to be less distinctive for the smaller particle in Figure 5.19.
Figure 5.19 Comparison between the model predictions obtained for a 1 mm particle in a purely convective flow environment (1 m s\(^{-1}\)) at 800°C. (A) refers to the model predictions when the surface volatile matter flux is neglected. (B) refers to the predictions generated when the surface volatile matter flux is considered.

This comparatively reduced effect of the surface volatile matter flux results despite the fact that the devolatilization rate is significantly quicker. While this increased devolatilization rate would suggest that the reduction in the external heat transfer coefficient should be enhanced, it must be remembered that the smaller particle has a greater surface area to volume ratio. Therefore the volatile matter released from the particle is dispersed over a larger effective surface area which results in a lower comparative surface volatile matter flux. Consequently the reduction in the external convective heat transfer coefficient is less distinct. The Ackermann correction factors determined from the model support this. For the model predictions reported in Figure 5.19, a minimum Ackermann correction factor of \(A_h^{\text{f}} = 0.85\) was observed which is greater then the value of \(A_h^{\text{f}} = 0.76\) from the case presented in Figure 5.18. In Figure 5.19, a Reynolds number of \(\text{Re} = 6.22\) and a Nusselt number of \(\text{Nu} = 3.45\) was determined.

While the particle size has an effect on the activity of the surface volatile matter flux, it is unlikely that the particle size alone could be used to characterise whether or not
the volatile matter flux is significant, and to what extent. It is more likely that the
effect of the surface volatile matter flux depends on a number of parameters relating to
both the flow properties of the gas and the heat transfer environment surrounding the
particle. This will be discussed in greater detail later in this study.

The results presented above suggest that the surface volatile matter can have an effect
on the model predictions, however, these results are only applicable to a purely
convective heat transfer environment. The magnitude of this influence on the model
predictions is likely to be far less pronounced in the HTF where a predominantly
radiative heat transfer environment exists. Figure 5.20 displays the model predictions
generated in the horizontal tube furnace when the surface volatile matter flux is
considered, and compares them to the reference model predictions. It can be seen that
the effect of the surface volatile matter flux under the conditions prevalent in the
fluidised bed is much lower than that under purely convective flow conditions (Figure
5.18).

![Graph](image)

**Figure 5.20** Comparison between the model predictions obtained for a -11 + 10 mm
particle in the HTF at 800°C. (A) refers to the model predictions when the surface
volatile matter flux is neglected. (B) refers to the predictions generated when the
surface volatile matter flux is considered.
The model predictions estimate a minimum Ackermann correction factor of $A_h = 0.27$ for Figure 5.20, which is significantly lower than that reported for the scenario in Figure 5.18. However, the average absolute deviation in the temperature response from the reference model predictions is 1.5% and 1.2% at the particle surface and centre, respectively, in Figure 5.20 compared with values of 5.8% and 5.6% respectively, for Figure 5.18. This arises due to the contribution of radiation to the heating environment for Figure 5.20. Convective heat transfer contributes approximately 25% of the total heat transfer to the coal particle for the conditions in the HTF for Figure 5.20. The average value for the Ackermann correction factor for the case in Figure 5.18 is $A_h = 0.85$ while in Figure 5.20 an average value of $A_h = 0.79$ was observed. Hence the magnitude of the influence of the Ackermann correction factor on the model predictions can be said to be directly proportional to the contribution of convective heat transfer to the entire heat transfer environment in any particular system, when compared to an environment when purely convective heat transfer exists.

The significantly lower Ackermann correction factor observed for the case of Figure 5.20, can be explained using Equation (2.29). The heat transfer coefficient calculated when the effect of the volatile matter flux is negligible is lower in the case of Figure 5.20 than in Figure 5.18 due to the lower gas velocity (2.25 L min$^{-1}$ in the HTF corresponds to a local gas velocity of 0.28 m s$^{-1}$ at 800°C, compared to 1 m s$^{-1}$ in Figure 5.18). However, the radiation component of the external heat transfer in Figure 5.20 ensures that the particle heating rate is actually greater than that in Figure 5.18. As a result both the devolatilization rate and the surface volatile matter flux are similarly greater. Therefore in Equation (2.29), the resulting increase in the volatile matter flux and decrease in the heat transfer coefficient leads to a larger value of $C_0$. The higher value of $C_0$ in turn leads to a lower minimum Ackermann correction factor (see Equations 2.28 and 2.29).

$$C_0 = \frac{N_{R,C_{\text{p,vol}}}}{h_0}$$  \hspace{1cm} (2.29)
The model predictions presented in Figures 5.18 to 5.20 have been generated at 800°C at which temperature it is envisaged that the effect of the surface volatile matter flux will be most pronounced due to the higher devolatilization rate. In order to verify this, model predictions identical to those presented in Figure 5.20 were generated for the conditions prevailing in the HTF at 600°C. These results are presented in Figure 5.21 and indeed show that the surface volatile matter flux is less significant at lower furnace temperatures.

![Graph](image)

**Figure 5.21** Comparison between the model predictions obtained for a -11 + 10 mm particle in the HTF at 600°C. (A) refers to the model predictions when the surface volatile matter flux is neglected. (B) refers to the predictions generated when the surface volatile matter flux is considered.

These results suggest that the volatile matter flux cannot be totally discounted when attempting to model the behaviour of large coal particles during devolatilization. The influence of the volatile matter flux is highly dependent on the heat transfer environment in which the particle is undergoing heating and the contribution of convective heat transfer to the total particle heating rate. However, the effect of the surface volatile matter flux on the model predictions under the conditions prevailing in the HTF are minimal and as such the surface volatile matter flux can be considered negligible under these conditions. Note that the equations developed by Kalson (1983) to consider the surface volatile matter effect are not relevant to the fluidised
bed environment and will not be considered when dealing with such environments. Note that the conclusions made here are only relevant to the particular experimental apparatus employed in this study and cannot be generally applied.

5.3.6 MOISTURE PARAMETERS

5.3.6.1 Reference Model Predictions

The sensitivity analysis conducted to date has dealt with the parameters which are of concern when dealing with both wet and dry coal particles. Due to the complications which arise when considering both drying and devolatilization, these parameters were tested using model predictions generated assuming dry coal particle to ensure the true nature of their effect could be observed. However, there are a number of parameters which are uniquely relevant to wet coal particle and may influence the model predictions. These parameters include the enthalpy of drying and the effective drying temperature. Also, the assumptions made regarding particle shrinkage during drying may affect the model predictions. Therefore, the effect of each of these parameters must be considered with reference to the reference model conditions defined for wet coal particles.

The reference model predictions for wet coal particles were generated by assuming a constant effective drying temperature of \( T_{\text{drying}} = 100^\circ \text{C} \) as was observed during the majority of the drying time in the experimental work in Chapter 3 and by McIntosh (1976). Furthermore, an enthalpy of drying of \( \Delta H_{\text{drying}} = 2334 \text{ kJ (kg H}_2\text{O)}^{-1} \) was employed which corresponds to the enthalpy of vapourisation of free moisture. The initial moisture content of the coal was assumed to be equivalent to that determined in Section 3.3.2 (1.052 g (g dry coal)\(^{-1}\)) and no particle shrinkage was considered (i.e. the shrinkage factor is \( SF = 0 \)). Using these parameters, model predictions were generated for conditions prevailing in the horizontal tube furnace at temperatures of 600°C and 800°C. The subsequent results are displayed in Figures 5.22 and 5.23, respectively. It can be seen that the effect of the furnace temperature on the model predictions is dramatic in that increasing the furnace temperature from 600°C to 800°C results in
Figure 5.22 Reference model predictions obtained for a -11 + 10 mm wet coal particle in the HTF at 600°C

Figure 5.23 Reference model predictions obtained for a -11 + 10 mm wet coal particle in the HTF at 800°C

approximately a 50% reduction in the predicted particle drying time. In the case of Figure 5.22, the lower furnace temperature (600°C) induces a devolatilization rate at the particle surface which is much more similar to that at the centre of the particle when compared with Figure 5.23.
The model predictions also suggest that the particle heating rate and devolatilization rate at the centre of the particle is extremely rapid once drying is complete, and can be said to be greater than at the particle surface. This can be rationalised considering that when the centre of the particle is completely dry, the outer regions of the particle are likely to have undergone significant heating. Due to the relatively high thermal conductivity of coal in comparison to the surrounding gas, the rate of heat transfer to the centre of the particle is large in relation to that at the particle surface. Also, heat is being continually transferred away from the particle surface to the centre of the particle during the earlier stages which also serves to reduce the heating rate at the particle surface.

5.3.6.2 Effective Drying Temperature

In order to assess the influence of the effective drying temperature on the model predictions it was assumed that the effective drying temperature varies according to the residual moisture content. The maximum effective drying temperature was assumed to be 200°C as reported by Winter et al. (1997), and it was further assumed that the effective drying temperature increased with decreasing moisture content in each shell according to the trend displayed in Figure 5.24. This trend is similar in nature to that observed by Allardice (1991) for the isotheric heat of desorption of Yallourn coal. It should be noted that this trend is not based on any experimental investigation of the effective drying temperature and therefore can only be considered to be an arbitrary trend. This does, however, proved a means by which the effect of varying the effective drying temperature on the model predictions can be assessed.

Figure 5.25 shows the model predictions obtained using the trend in the effective drying temperature in Figure 5.24 for the temperature response and fraction of moisture released from the centre and the surface of a -11 + 10mm coal particle in the horizontal tube furnace at 800°C. Figure 5.26 displays the model predictions obtained for the temperature response and fraction of volatile matter released from the same run. The effective drying temperature has little effect on the model predictions at the surface of the particle. Conversely, there is a noticeable effect of varying the effective
Figure 5.24 Assumed trend in the effective drying temperature with the residual moisture content during drying employed to generate the model predictions in Figures 5.25 and 5.26.

drying temperature on the model predictions at the centre of the particle. The drying time is slightly increased and, as a consequence, devolatilization is similarly delayed. The magnitude of the increase in drying time is in the order of 6 seconds which represents a 7.5% increase in the total drying time.

Figures 5.27 and 5.28 show model predictions generated using identical assumptions to those employed in Figures 5.25 and 5.26, however, a furnace temperature of 600°C is assumed. These figures tend to indicate that assuming a drying temperature which increases with a decreasing moisture content has a marginally more pronounced effect on the model predictions for a furnace temperature of 600°C than for 800°C. The total drying time at 600°C has been increased by approximately 16 s which represents a 11% increase in the total drying time compared to a 7.5% increase at 800°C. Again it can be seen that the model predictions at the centre of the particle are not greatly effected. Again it can be seen that the influence on the model predictions at the surface of the particle is marginally greater at 600°C than at 800°C.
Figure 5.25 Comparison between the model predictions for the temperature response and fraction of moisture released from a -11 + 10 mm wet coal particle in the HTF at 800°C. (A) refers to the model predictions when an effective drying temperature of $T_{\text{drying}} = 100^\circ\text{C}$ is assumed. (B) refers to the predictions generated when the effective drying temperature varies according to Figure 5.24.

Figure 5.26 Comparison between the model predictions for the temperature response and fraction of volatile matter released from a -11 + 10 mm wet coal particle in the HTF at 800°C. (A) refers to the model predictions when an effective drying temperature of $T_{\text{drying}} = 100^\circ\text{C}$ is assumed. (B) refers to the predictions generated when the effective drying temperature varies according to Figure 5.24.
Figure 5.27 Comparison between the model predictions for the temperature response and fraction of moisture released from a \(-11 + 10\) mm wet coal particle in the HTF at 600°C. (A) refers to the model predictions when an effective drying temperature of \(T_{\text{drying}} = 100^\circ\text{C}\) is assumed. (B) refers to the predictions generated when the effective drying temperature varies according to Figure 5.24.

Figure 5.28 Comparison between the model predictions for the temperature response and fraction of volatile matter released from a \(-11 + 10\) mm wet coal particle in the HTF at 600°C. (A) refers to the model predictions when an effective drying temperature of \(T_{\text{drying}} = 100^\circ\text{C}\) is assumed. (B) refers to the predictions generated when the effective drying temperature varies according to Figure 5.24.
While these predictions suggest that varying the effective drying temperature can impact on the model predictions, the trend used to investigate this phenomenon could be said to be arbitrary in that it is not based on any direct experimental findings. Therefore, in order to employ this technique within further modelling applications, it would be preferable to have some experimental data on which the variation in the effective drying temperature could be based. Unfortunately, such data is not easily obtained. One means of addressing the probability of encountering drying temperatures of up to 200°C is to consider the corresponding vapour pressure within the particles. In order for moisture to vaporise at 200°C, a vapour pressure of 15.35 atm or 1555 kPa is required. This figure seems to be quite high and it is expected that such pressures would be sufficient to fragment the coal particles given their observed fragility during the experiments conducted. Given that fragmentation was not regularly observed, it would follow that such pressures are not achieved within the particle hence drying temperatures in this region are not experienced. Measuring the internal pressure within the coal particle during drying is beyond the scope of the work presented in this study. Hence the variation in the drying temperature will not be considered.

5.3.6.3 Enthalpy of Drying

In Figures 5.22 to 5.28 it has been assumed that the enthalpy of drying is equivalent to that of free moisture ie. $\Delta H_{\text{drying}} = 2334 \text{ kJ (kg H}_2\text{O)}^{-1}$ (Chen, 1994). However, Chen (1994) suggested that the enthalpy of drying increases with decreasing moisture content due to such phenomenon as hydrogen bonding etc. In order to assess the influence of the enthalpy of drying on the model predictions, it was assumed that the enthalpy of drying varies according to the trend determined by Chen (1994) for a sub-bituminous coal, as reported in Section 4.3.8. The results obtained using these assumptions are compared with the reference model predictions for wet coal particles in the horizontal tube furnace at 800°C, in Figures 5.29 and 5.30. These results indicate that, as expected, the enthalpy of drying has a significant influence on the model predictions which is particularly reflected in the model predictions at the centre of the particle. The drying time has increased from 78 s to 96 s which represents a
23% increase in the total drying time. This increase in the drying time arises from a
37% increase in the total amount of energy required to remove the moisture at 100°C.

Again it is of interest to note the significance of the enthalpy of drying at the lower
furnace temperature (600°C) and these model predictions are displayed in Figures 5.31
and 5.32. These model predictions indicate that the enthalpy of drying assumed by
Chen (1994) has a greater relative impact on the model predictions at a furnace
temperature of 600°C than at 800°C. This is indicated by a 50% increase in the total
drying time (138s to 208s) as compared to 23% increase for a similar increase in the
enthalpy of drying at 800°C. This represents an extremely significant variation in the
model predictions which cannot be ignored.

![Diagram](image)

**Figure 5.29** Comparison between the model predictions for the temperature response
and fraction of moisture released from a -11 + 10 mm wet coal particle in the HTF at
800°C. (A) refers to the model predictions when an enthalpy of drying of $\Delta H_{drying} =
2334 \text{ kJ (kg H}_2\text{O)}^{\text{-1}}$ is assumed. (B) refers to the predictions generated when the
enthalpy of drying of Chen (1994) is assumed.
Figure 5.30 Comparison between the model predictions for the temperature response and fraction of volatile matter released from a -11 + 10 mm wet coal particle in the HTF at 800°C. (A) refers to the model predictions when an enthalpy of drying of $\Delta H_{\text{drying}} = 2334 \text{ kJ (kg H}_2\text{O)}^{-1}$ is assumed. (B) refers to the predictions generated when the enthalpy of drying of Chen (1994) is assumed.

Figure 5.31 Comparison between the model predictions for the temperature response and fraction of moisture released from a -11 + 10 mm wet coal particle in the HTF at 600°C. (A) refers to the model predictions when an enthalpy of drying of $\Delta H_{\text{drying}} = 2334 \text{ kJ (kg H}_2\text{O)}^{-1}$ is assumed. (B) refers to the predictions generated when the enthalpy of drying of Chen (1994) is assumed.
**Figure 5.32** Comparison between the model predictions for the temperature response and fraction of volatile matter released from a -11 + 10 mm wet coal particle in the HTF at 600°C. (A) refers to the model predictions when an enthalpy of drying of $\Delta H_{\text{drying}} = 2334$ kJ (kg H_2O)^{-1} is assumed. (B) refers to the predictions generated when the enthalpy of drying of Chen (1994) is assumed.

The trend in the enthalpy of drying observed by Chen (1994) has been shown to have a marked impact on the model predictions. Furthermore, the effect on the model predictions is greater at lower furnace temperatures. This is reasonable considering that the total amount of energy required to free the moisture from the coal is the same, yet the heat transfer rate to the particle at lower furnace temperatures is much lower. Therefore the respective increase in the drying time is greater at lower furnace temperatures.

The data of Chen (1994) was derived from a sub-bituminous coal whereas in the present case a low-rank coal is being considered. Low-rank coals tend to have a greater oxygen content as well as increased numbers of functional groups which may increase the fractions of loosely and tightly bound moisture via the increased potential for hydrogen bonding. While the trend observed by Chen (1994) will be employed further during this study, it would be of interest to undertake a study similar to that of Chen (1994) using a low-rank coal in order to obtain coal specific data to further
improve the model predictions. This is beyond the scope of the present study. Ultimately, it can be concluded that employing a varying enthalpy of drying equivalent to that observed by Chen (1994) in place of a constant enthalpy of drying equivalent to $\Delta H_{drying} = 2334 \text{ kJ} \ (\text{kg H}_2\text{O})^{-1}$ has far greater implications with respect to the model predictions than when a varying effective drying temperature is assumed.

5.3.6.4 Particle Shrinkage

A further factor which must be considered when dealing with wet coal particles is that of shrinkage. Shrinkage can impact on the model predictions in two ways. Firstly, the reduction in particle size during drying can result in an increase in the rate of convective heat transfer to the particle surface. This is likely to decrease the overall drying time. Furthermore, the reduction in the particle size leads to an increase in the effective particle density and this would serve to increase the overall drying time. Given that convective heat transfer is not the dominant heat transfer mechanism in the horizontal tube furnace, the latter effect is likely to be more noticeable. Figure 5.33 shows the model results obtained when considering particle shrinkage and compares them to the reference model predictions for the horizontal tube furnace at 800°C. Particle shrinkage is accounted for in the model by specifying the appropriate shrinkage factor, $SF$, for use in the particle shrinkage equations developed in Section 4.3.3, according to those determined experimentally in Section 3.5.3. In these model predictions the enthalpy of drying is assumed to remain constant at $\Delta H_{dev} = 2334 \text{ kJ} \ (\text{kg H}_2\text{O})^{-1}$ and the effective drying temperature remains constant at $T_{drying} = 100^\circ\text{C}$.

From Figure 5.33 it can be seen that there is very little influence on the model predictions at the particle surface, however, the influence at the centre of the particle is marginally more significant. The total drying time is increased by approximately 6% when compared to the reference model predictions which confirms the previous hypothesis that accounting for particle shrinkage is likely to result in an increase in the drying time. This increase compares to a 7.5% increase in the drying time when the effective drying temperature is assumed to increase with a decreasing moisture content.
Figure 5.33 Comparison between the model predictions for the temperature response and fraction of moisture released from a -11 + 10 mm wet coal particle in the HTF at 800°C. (A) refers to the model predictions when shrinkage is not considered. (B) refers to the predictions generated when particle shrinkage during drying is assumed.

and a 23% increase in the drying time when the enthalpy of drying is assumed to increase with decreasing moisture content. Note that the volatile matter data is not shown in this case as the relative trends are similar in nature to those observed previously.

It is likely that the model predictions at the particle surface are not effected to any appreciable extent due to the fact that the surface has reached the furnace temperature prior to much of the drying stage being completed. Hence there is little shrinkage evident during the heating of the particle surface and this is reflected in the absence of any deviation in the model predictions. Again it is important to consider the effect the furnace temperature has on the deviations in the model predictions resulting from assuming particle shrinkage is significant. Figure 5.34 shows the model results obtained for a -11 + 10mm particle in the HTF at 600°C when particle shrinkage is considered, and compares them to the reference model predictions for a similar set of conditions. Again it is evident that the effect of accounting for shrinkage within the model is more significant at a lower furnace temperature with an 8.3% increase in the
total drying time being observed. This compares with an 11% increase in the drying time when the effective drying temperature is assumed to increase with a decreasing moisture content and a 50% increase in the drying time when the enthalpy of drying is assumed to increase with decreasing moisture content.

These results indicate that the effect of shrinkage on the model predictions less significant than considering a varying effective drying temperature which in turn is far less significant than assuming the enthalpy of drying observed by Chen (1994). However, as shrinkage is an experimentally observed phenomenon and the model predictions are affected to some extent, particle shrinkage will be considered in future modelling work.

![Graph](image-url)

**Figure 5.34** Comparison between the model predictions for the temperature response and fraction of moisture released from a -11 + 10 mm wet coal particle in the HTF at 600°C. (A) refers to the model predictions when shrinkage is not considered. (B) refers to the predictions generated when particle shrinkage during drying is assumed.

### 5.4 SUMMARY

The role of this chapter is to critically analyse the significance of a number of model parameters and assumptions in regards to the model predictions, and to elucidate the
most appropriate means of employing these parameters in the large particle coal devolatilization model. The thermal conductivity of the coal particle controls the rate of heat conduction from the surface to the centre of the particle. It has been shown that varying the thermal conductivity has a marginal effect on the model predictions at the particle surface. However, a similar change in the thermal conductivity can invoke much larger deviations in the model predictions at the centre of the particle. It was also found that increasing the thermal conductivity has the effect of producing a more even temperature gradient across the radius of the particle during heating, i.e. the particle behaviour tends to become increasingly isothermal. It was found that the correlation given by Agroskin (1957) predicts thermal conductivity values which are consistent with those of a number of authors (Perry and Green, 1984; Yang and Wang, 1990; and Wang et al., 1994) and consequently will be used in comparisons between the model predictions and the experimental data.

The specific heat capacity determines the amount of energy which is absorbed by the particle in order to raise its temperature. Therefore, increasing the specific heat capacity has the effect of lowering the particle heating rate in a constant heat transfer environment whilst lowering the specific heat capacity of the coal results in an increased particle heating rate. It was observed that the magnitude of the deviation in the model predictions was proportional to the change in the specific heat capacity with a 50% increase in the specific heat capacity resulting in a 28% reduction in the temperature at any time during heating, and a 36% reduction in the specific heat capacity results in a 20% increase in the particle temperature at any time. The correlation of Agroskin et al. (1970) was found to be almost identical to the average of all the correlations or constant values reported in Section 2.4.2.2 and as such will be employed in future modelling efforts. The specific heat capacity in general was observed to have a greater influence on the model predictions than the thermal conductivity, particularly at the particle surface.

Despite the significant role that radiation heat transfer plays in the horizontal tube furnace, the model predictions were found to relatively insensitive to variations in the assumed particle emissivity. A 35% average increase in the emissivity was found to
result in a 5% increase, on average, in the particle temperature response. Similarly, a 65% average increase in the emissivity generated a 9.5% increase, on average, in the particle temperature response. The magnitude of the effect of the emissivity on the model predictions is similar to that observed for the thermal conductivity. However, the change in the emissivity itself was greater in relation to the change in the thermal conductivity hence the effect of varying the emissivity on the model predictions is likely to be lower than that observed for changes in the thermal conductivity of similar proportions. Given that the emissivity has a minimal impact on the model predictions, it was concluded that employing the correlation of Linjewile (1993) was reasonable in light of the absence of alternate data generated from a study of such comprehensive nature.

It was found that, under fluidised bed conditions, the particle heating and devolatilization process was internal heat transfer controlled. Therefore, varying the convective heat transfer coefficient under these conditions has little impact on the model predictions. Linjewile (1993) proposed a comprehensive correlation for estimating the convective heat transfer coefficient under these conditions and this correlation can be confidently used knowing that typical errors resulting from such empirical correlations will not significantly impact on the model predictions.

In deciding on the most appropriate means of dealing with the enthalpy of devolatilization in future modelling work, two observations were employed. Firstly, the enthalpy of devolatilization was found to have a discernible influence on the model predictions when a constant endothermic enthalpy of devolatilization was employed. However when the enthalpy of devolatilization was assumed to vary with devolatilization temperature, the influence on the model predictions was substantially lower. Furthermore, there remains a certain amount of contradiction in the literature regarding magnitude of the enthalpy of devolatilization and its variation with the devolatilization temperature. It was concluded that, at this stage, the enthalpy of devolatilization would be considered negligible for the remaining modelling work in this study. However, it should be noted that more work remains to be conducted in
this area to correctly quantify the enthalpy of devolutilization such that its true impact on the model predictions can be examined.

It has previously been proposed that the emission of volatiles from the surface of the coal particle during devolutilization can act to reduce the rate of external convective heat transfer (Kalson, 1983). In a purely convective heating environment it was observed that there is indeed the opportunity for this phenomenon to occur. However, for the heat transfer conditions prevailing in the horizontal tube furnace, the effect of the surface volatile matter flux on the model predictions can be considered negligible given that convective heat transfer contributes only 25% of the total heat transfer to the particle surface. Note that this conclusion is not universal and the nature of the heat transfer environment must be carefully considered when forming similar conclusions.

Generally it is assumed that drying takes place completely at 100°C, however it has been reported that drying temperature as high as 200°C have been observed (Winter et al., 1997). It was found that allowing the effective drying temperature to increase with decreasing moisture content (to a maximum of 200°C at 0.0 kg (kg H₂O)^{-1}) resulted in an increase in the overall drying time, particularly at the centre of the particle. The influence on the model predictions at the particle surface were less pronounced. The increase in the drying time was around 11% at 600°C and 7.5% at 800°C. While the model predictions are affected by this phenomenon, it is difficult to characterise the true variation in the effective drying temperature during drying without employing diffusion equations within the model. In the absence of any supporting data on which the variation in the effective drying temperature can be based, it is reasonable to assume that drying occurs entirely at 100°C.

By far the most influential parameter in regard to the model predictions for wet coal particles is the enthalpy of drying. The trend in the enthalpy of drying observed by Chen (1994) was found to increase the overall drying time by 50% at 600°C and 23% at 800°C when compared to the situation where the reference enthalpy of drying was assumed \( \Delta H_{\text{drying}} = 2334 \text{ kJ (kg H₂O)}^{-1} \). Therefore when dealing with wet coal
particle modelling in the future, it is advisable to consider this trend observed by Chen (1994). The data of Chen (1994) was determined using a sub-bituminous coal and it would be of interest to employ a similar technique to investigate the enthalpy of drying of low-rank coals. It is possible that the nature of low-rank coals means they have a higher level of loosely and tightly bound moisture. If this is the case it is possible that the total drying time may be further increased. In the absence of such supporting data, the trend reported by Chen (1994) can be applied.

Particle shrinkage during drying was the final parameter explored and it was found that shrinkage does influence the model predictions. The drying time was found to be slightly increased as a result of shrinkage however the magnitude of this increase was found to be lower than that observed for the effective drying temperature and the enthalpy of drying. The magnitude of the deviation in the model predictions was marginally greater at 600°C than at 800°C. While particle shrinkage was found to be the least significant of the parameters influencing wet coal particles, it has been observed experimentally and quantified for the purposes of this study hence will be considered in future work.

This chapter has explored the role of various parameters within the large particle coal devolatilization model and has established reasonable techniques for their implementation within the model. Furthermore, the relative magnitude and nature of the effect of these parameters has been observed. Employing the model developed in Chapter 4 to predict the data reported in Chapter 3 can now be performed using the assumptions which have been deduced via the work presented in this chapter. Furthermore, the observations presented in this chapter form a sound basis for analysing the ability of the model to predict the experimental data, and elucidating parameters which may be limiting the predictability of the model.
Chapter 6

MODEL RESULTS

6.1 INTRODUCTION

The experimental work detailed in Chapter 3 has provided reliable data for both the temperature response and evolution of volatile matter from a typical low-rank coal under conditions prevailing in the horizontal tube furnace, as well as for the conditions in the fluidised bed reactor which are similar to the conditions in a commercial scale fluidised bed combustor/gasifier. Chapter 4 detailed the development of the coal devolatilization model with particular emphasis on predicting the particle temperature response and is complimented by the sensitivity analysis conducted in Chapter 5 which has isolated those parameters which are critical in determining the predictability of the model. The aim of this chapter is then to compare the model predictions generated based on the model developed in Chapters 4 and 5, with the experimental data generated in Chapter 3 in order to ascertain the effectiveness of the model and to further confirm the assumptions of Chapter 5.

Model predictions for dry coal particles in the horizontal tube furnace will be initially presented, followed by those for dry coal particles in the fluidised bed reactor. This will then lead to model predictions for wet coal particles in the horizontal tube furnace and the fluidised bed reactor. Ultimately, the applicability of the model developed to date will be systematically addressed in a similar way to the model development stage,
such that logical conclusions regarding the ability of the model to predict the observed behaviour of the coal particles can be formed.

6.2 DRY COAL PARTICLES

6.2.1 HORIZONTAL TUBE FURNACE

Figures 3.1 to 3.3 display the model predictions and experimental data generated for -11 + 10 mm Bowmans coal particles in the horizontal tube furnace at 600°C, 700°C, and 800°C, respectively. In each figure the temperature response measured at the centre of the particle is compared with the predicted temperature response, and the fractional mass remaining as a function of time calculated from the mass loss experiments is compared with those predicted by the model. It can be seen that the model is capable of predicting both the particle temperature response and fraction of mass remaining extremely accurately given the assumptions presented in Chapter 5. This acts to confirm that the assumptions made in Chapter 5 are indeed reasonable.

In all of the model predictions presented, the ASTM volatile matter content reported in Table 3.1 was used to characterise the ultimate volatile yield, \( V^* \). Given that the fractional mass remaining was also predicted accurately by the model there was found to be no need to consider \( V^* \) as a variable parameter in order to achieve a reasonable fit with the model predictions. The fractional mass loss at 600°C was observed experimentally to be lower than that at 700°C and 800°C and this was also predicted by the model. This is visible by comparing Figure 6.1 with Figures 6.2 and 6.3 and results due to the Distributed Activation Energy Model predicting a pseudo-asymptotic volatile yield for the particle size and temperature in Figure 6.1. This has been previously observed by Agarwal et al. (1984b) and adds further credibility to the proposed model as a reliable approach for modelling coal devolatilization.
Figure 6.1  Comparison between experimental data and model predictions for a -11 + 10 mm Bowmans coal particle in the horizontal tube furnace at 600°C.

Figure 6.2  Comparison between experimental data and model predictions for a -11 + 10 mm Bowmans coal particle in the horizontal tube furnace at 700°C.
The experimental data and model predictions presented in Figures 3.1 to 3.3 show that the model has potential with respect to predicting the devolatilization behaviour of large coal particles. However, the results shown are restricted to one particle size. If the model predictions are to be trusted, the model must be shown to be capable of generating model predictions of similar accuracy for different particle sizes. Figures 6.4 to 6.6 display the experimental data and model predictions generated from -9 + 8 mm Bowmans coal particles in the horizontal tube furnace at 600°C, 700°C, and 800°C, respectively. Again it can be seen that the model is capable of predicting the experimental data with a high degree of accuracy. Comparing all of the results presented in Figures 6.1 to 6.6, it appears that the model predictions for the particle temperature response at the centre of the particle at 700°C are the least accurate. While this was found to be consistently true for both particle sizes, it is not seen to be a reflection on the accuracy of the model. It is more likely to be a result of the experimental error which may arise from such factors as the particle size measurements etc. as well as the heterogeneous nature of the coal itself. Given this, the model predictions which have been presented to date are excellent and there is no reason at present to question the work presented in Chapters 4 and 5. Therefore the
ability of the model to represent the particle behaviour in the horizontal tube furnace provides confidence for attempting to model similar behaviour in a fluidised bed environment.

Figure 6.4 Comparison between experimental data and model predictions for a -9 + 8 mm Bowmans coal particle in the horizontal tube furnace at 600°C.

Figure 6.5 Comparison between experimental data and model predictions for a -9 + 8 mm Bowmans coal particle in the horizontal tube furnace at 700°C.
Figure 6.6  Comparison between experimental data and model predictions for a -9 + 8 mm Bowmans coal particle in the horizontal tube furnace at 800°C.

6.2.2  **Fluidised Bed Reactor**

Whilst it was possible to measure both the temperature response and mass loss from particles in the horizontal tube furnace, the measurements obtained in the fluidised bed reactor were limited to particle temperature measurements. Mass loss measurements were far more difficult to obtain in the fluidised bed reactor due to the rapid heating rate which necessitates shorter time intervals between successive mass loss measurements. As there is a lag time between the time at which the particles are removed from the bed and the time at which they are completely quenched, the shorter the time interval between measurements the greater the potential error in the measurements becomes. It was deduced therefore that only particle temperature measurements would be obtained in the fluidised bed reactor. Furthermore, it was extremely difficult to obtain reasonable measurements with the -9 + 8 mm particles in the fluidised bed reactor hence temperature data can only be presented for the -11 + 10 mm particles.

Figure 6.7 shows the particle temperature response data obtained at the centre of -11 + 10 mm Bowmans coal particles inserted into the fluidised bed reactor at bed temperatures of 650°C, 750°C, and 850°C. This figure shows that the model
predictions are again quite reasonable at all reactor temperatures. It appears that the model slightly underpredicts the particle temperature during the early stages of the heating process. This is difficult to conclusively deduce given that it has already been conceded the particle temperature measurements in the fluidised bed reactor are of lower accuracy than those in the horizontal tube furnace. Once the particle enters the devolatilization stage \( T_p > 150^\circ C\), however, the model is seen to provide quite accurate predictions.

![Graph showing particle temperature over time](image)

**Figure 6.7** Comparison between experimental data and model predictions for a -10 + 11 mm Bowmans coal particle in the fluidised bed reactor at 650°C, 750°C, and 850°C.

The results of Figure 6.7 have a number of implications in terms of the modelling work presented to date. While much of the focus of the modelling work has dealt with the horizontal tube furnace, these results show that accurate model predictions can be achieved in any environment provided that the conditions pertaining to that environment are appropriately considered. This holds true in the case of the current model provided the mechanisms driving the devolatilization process do not change. In the current model it is assumed that heat transfer and chemical kinetics are contributing significantly to the devolatilization process. If high pressure conditions were being modelled it may be necessary to consider mass transfer/diffusion within the structure of the model. Hence the current model may not be appropriate.
Also, the results suggest that the correlation of Linjeweile (1994) is of the correct magnitude for estimating the convective heat transfer coefficient under fluidised bed conditions. In general the results presented for dry coal particles in Figures 6.1 to 6.7 indicate that the model proposed in this work is extremely reliable in predicting the temperature response of dry coal particles under the conditions prevailing in both the horizontal tube furnace and the fluidised bed reactor. There has been no indication to this point that the model development, or the conclusions from the sensitivity analysis, may be flawed hence applying the model to predicting the behaviour of wet coal particles can now be considered.

6.3 WET COAL PARTICLES

6.3.1 Horizontal Tube Furnace

In Chapter 3, the horizontal tube furnace was employed to determine both the temperature at the centre of the coal particle and the total mass fraction remaining at regular time intervals for -10 + 11 mm and -8 + 9 mm wet Bowmans coal particles at furnace temperatures of 600°C, 700°C, and 800°C. Figures 6.8 to 6.10 compare the experimental data for -10 + 11 mm particles with the accompanying model predictions at the aforementioned furnace temperatures, respectively. Similarly, Figures 6.11 to 6.13 show the corresponding model predictions for -8 + 9 mm particles.

It can be seen that generally the model predictions appear to be reasonably good. Considering the particle temperature predictions at the centre of the particle there are two regions where the model predictions deviate from the experimental data. The first region occurs during the initial heating of the wet coal particle to the effective drying
Figure 6.8 Comparison between experimental data and model predictions for a -10 + 11 mm Bowmans coal particle in the horizontal tube furnace at 600°C. Both the temperature at the centre of the particle and the fraction of total mass remaining are shown. * refers to model predictions generated when a constant enthalpy of drying of $\Delta H_{\text{drying}} = 2334$ kJ (kg H$_2$O)$^{-1}$ is assumed.

Figure 6.9 Comparison between experimental data and model predictions for a -10 + 11 mm Bowmans coal particle in the horizontal tube furnace at 700°C. Both the temperature at the centre of the particle and the fraction of total mass remaining are shown.
Figure 6.10 Comparison between experimental data and model predictions for a -10 + 11 mm Bowmans coal particle in the horizontal tube furnace at 800°C. Both the temperature at the centre of the particle and the fraction of total mass remaining are shown.

Figure 6.11 Comparison between experimental data and model predictions for a -8 + 9 mm Bowmans coal particle in the horizontal tube furnace at 600°C. Both the temperature at the centre of the particle and the fraction of total mass remaining are shown.
Figure 6.12 Comparison between experimental data and model predictions for a 8 + 9 mm Bowmans coal particle in the horizontal tube furnace at 700°C. Both the temperature at the centre of the particle and the fraction of total mass remaining are shown.

Figure 6.13 Comparison between experimental data and model predictions for a 8 + 9 mm Bowmans coal particle in the horizontal tube furnace at 800°C. Both the temperature at the centre of the particle and the fraction of total mass remaining are shown.
temperature. The model tends to overpredict the particle heating rate during this time. During the model development stage in Chapter 4 it was suggested that the thermal conductivity and specific heat capacity of the wet coal particles was determined from the mass averaged value based on the thermal conductivity and specific heat capacity of the coal and the moisture fractions of the particle. As moisture has a higher thermal conductivity than coal this leads to an increase in the overall thermal conductivity of wet coal particles. Therefore energy can be conducted towards the centre of the particle more rapidly which explains the rapid increase in the predicted temperature response during this time. However, this region is of little consequence to the model predictions, particularly for large coal particle devolatilization, as no devolatilization will occur during this time.

The second region in which the model predictions differ from the experimental data is at the end of drying prior to the centre of the particle undergoing further heating and devolatilization. It can be seen that the experimental data suggests that the temperature response plateaus at 100°C for some time however begins to slowly increase until approximately 200°C, after which the heating rate is quite rapid. The model, on the other hand, predicts that the temperature response plateaus at 100°C until drying is complete, after which the particle heats up rapidly to the furnace temperature. This trend was discussed by Winter (1987) who also indicated that assuming a constant drying temperature of 100°C would result in a rapid heating rate upon the completion of drying. Generally, however, the model predictions and the experimental data tend to converge during the latter stages of heating such that the overall heating time is reasonably similar.

This gradual increase in the measured temperature response during the latter stages of drying remains difficult to rationalise. The suggestion of Winter (1987) that the effective drying temperatures as high as 200°C are possible may explain this phenomenon. This remains to be experimentally validated which is not within the scope of the present work. Alternatively, it may be that gaining an accurate indication of the actual temperature at the centre of the particle is difficult during the latter stages of heating. Once heating is complete at the particle surface and the "wet core" of
moisture begins to recede into the particle, the dry outer surface is able to undergo further heating. Thus, the thermocouple sheath adjacent to these outer regions is exposed to higher temperatures. The distance between this region and the tip of the thermocouple gradually decreases as drying continues. Consistent with the argument outlined in Section 3.4, it is possible that the tip of the thermocouple is exposed to thermal conduction towards the tip during the latter stages of drying which results in an overprediction of the actual particle temperature response during this time. Conversely, as the centre of the particle approaches the furnace temperature, the temperature gradient across the radius of the particle is reduced and there is a lower probability of thermal conduction taking place. Hence the model predictions and the experimental data gradually converge.

An indication of the ability of the model to predict the drying and devolatilization behaviour of the particles under the conditions described can be obtained from the fractional mass remaining. Figures 6.8 to 6.13 indicate the model is extremely reliable in predicting the fractional mass remaining for both particle sizes at each furnace temperature. The model is capable of predicting both the time dependent behaviour of the total mass loss as well as the ultimate mass fraction remaining without the need to adjust the ultimate volatile matter content, \( V^* \). This is useful in that a potential variable in the model has been eliminated, given that \( V^* \) has been successfully assumed to be the ASTM volatile matter content, which reduces the number of variable parameter in the model and adds further credibility to the overall model development.

A further point of interest relates to the assumption that the enthalpy of drying increases with decreasing moisture content according to the trend observed by Chen (1994) rather than employing a constant enthalpy of drying of \( \Delta H_{\text{drying}} = 2334 \) kJ (kg \( \text{H}_2\text{O} \))\(^{-1} \) (refer to Section 5.3.4.1). It was concluded in Section 5.3.4.1 that the trend observed by Chen (1994) should be utilised given that the work of Chen (1994) represents a thorough experimental and theoretical investigation into the enthalpy of drying. However, it is also useful to compare the model predictions generated using both assumptions with the corresponding experimental data to further confirm the
previous assumption. This comparison is presented in Figure 6.8. It can be seen that when the constant enthalpy of drying is assumed, the model tends to underpredict the drying time as was observed in Section 5.3.4.1. Conversely, assuming that the enthalpy of drying varies according to the trend observed by Chen (1994) appears to overpredict the drying time. However this may be due to inaccuracies in the particle temperature measurements during the latter stages of drying, as discussed above. It appears that, in general, more accurate model predictions were obtained when the trend of Chen (1994) was assumed for the enthalpy of drying.

This is confirmed when the fractional mass remaining predicted by the model under the respective assumption is considered. When compared with the experimental data, the model predictions generated when the trend of Chen (1994) is assumed compare extremely well with the experimental data. In the alternative case, when a constant enthalpy of drying is assumed, the model tends to underpredict the fractional mass remaining in Figure 6.8 which is expected considering that this scenario also underpredicts the total drying time. Ultimately, the predictions of the fractional mass remaining support the assumption in Section 5.3.4.1 and the particle temperature predictions in Figure 6.8, thus suggesting that the enthalpy of drying can be assumed to vary according to the trend of Chen (1994).

In general it can be seen that the model can predict the behaviour of wet coal particles in the horizontal tube furnace with reasonable accuracy. There is some deviation between the model predictions and the measured temperature response during the early stages of heating (prior to drying), and during the latter stages of drying. While the deviation observed during the early stages of heating is not of importance, that observed during the latter stages of drying is of greater significance. The deviation observed may be due to an increase in the effective drying temperature, which has not been considered in the final model due to a lack of supporting data, or a limitation in the experimental data during this stage, or a combination of both. It is likely that there is some limitation in the experimental data in this region and while the model predictions presented here are not of the accuracy observed for dry coal particles, the model predictions generally appear to be acceptable. Thus it is now possible to
consider modelling the behaviour of large wet coal particles under fluidised bed heating conditions.

6.3.2 FLUIDISED BED REACTOR

As mentioned in Section 6.2.2, it was difficult to obtain reliable mass loss data from wet coal particle in the fluidised bed reactor, and obtaining reasonably accurate particle temperature data was limited to the -11 + 10 mm Bowmans coal particles. Therefore, it is only possible to compare the model predictions for the temperature response of -11 + 10 mm particles in the fluidised bed reactor at the three reactor temperatures; 650°C, 750°C, and 850°C. These comparisons are presented in Figures 6.14 to 6.16, respectively.

![Graph showing particle temperature vs time](image)

**Figure 6.14** Comparison between model predictions and experimental data for the temperature response at the centre of -11 + 10 mm coal particle in the fluidised bed reactor at 650°C. The enthalpy of drying observed by Chen (1994) and a constant effective drying temperature of 100°C are assumed.

It can be seen that the model predictions again show distinct deviation from the experimental data during the latter stages of drying. Generally, however, the particle heating time is predicted quite well by the model as it was in the case of the horizontal tube furnace in Section 6.3.1. The predictions in the horizontal tube furnace do appear
to be of a higher degree of accuracy than those in the fluidised bed reactor for wet coal particles, particularly at the end of the drying period and the early stages of the devolatilization period. If the experimental data generated in the fluidised bed reactor

![Graph](image1)

**Figure 6.15** Comparison between the model predictions and experimental data for the temperature response at the centre of -11 + 10 mm coal particle in the fluidised bed reactor at 750°C. The enthalpy of drying observed by Chen (1994) and a constant effective drying temperature of 100°C are assumed.

![Graph](image2)

**Figure 6.16** Comparison between the model predictions and experimental data for the temperature response at the centre of -11 + 10 mm coal particle in the fluidised bed reactor at 850°C. The enthalpy of drying observed by Chen (1994) and a constant effective drying temperature of 100°C are assumed.
in Figures 6.14 to 6.16 is compared to that of the horizontal tube furnace in Figures 6.8 to 6.13, it can be seen that the fluidised bed reactor data has a distinctively differing trend during the latter stages of drying. It can be seen that the experimental data shows an almost linear increase in the centre temperature from 100°C during the latter stages of drying and this continues until the centre temperature reaches approximately 400 - 500°C. After this the centre temperature response is more characteristic of that observed in the horizontal tube furnace. This linear region is highlighted in Figure 6.16.

This linear region which has been observed is likely to be due to the difficulty in obtaining accurate temperature measurements, as discussed in Section 3.4. It was concluded in Section 3.4 that obtaining reliable temperature measurements was achieved only when any influence of thermal conduction towards the tip of the thermocouple along the thermocouple sheath had been minimised. This was achieved with the use of multiple particles on the tip of the thermocouple as well as a water cooled probe to insulate the remaining thermocouple from the surroundings. However, as mentioned, it was necessary to leave a portion of the thermocouple uncovered between the water cooled probe and the particles in order to avoid thermal conduction away from the thermocouple tip. Hence a portion of the thermocouple does experience the surrounding environment.

In the horizontal tube furnace, the heating environment is moderate hence the portion of thermocouple exposed to the environment undergoes similarly moderate heating. In the fluidised bed however, the heating environment is severe and this region of the thermocouple is in intimate contact with the hot sand and will heat rapidly to the surrounding temperature. This increases the driving force for thermal conduction along the thermocouple sheath thus it is expected that the experimental data is unlikely to be as accurate. The propensity for thermal conduction to be significant, especially towards the latter stages of drying, is further increased by the higher temperature at the outer surface of the particle as discussed in Section 6.3.1. Therefore obtaining highly accurate temperature measurements in the fluidised bed reactor for the entire drying period is extremely difficult. Note that it is expected that
when the particle centre approaches the surrounding temperature the driving force for thermal conduction is low and less error is expected in the temperature measurements which was also discussed in Section 6.3.1. Therefore, while the model is unable to predict the temperature response measured in the fluidised bed reactor with a high degree of accuracy, it is likely that this is more of a reflection of the potential error in the experimental data than in the modelling technique.

6.4 COMPARISON WITH LITERATURE DATA

6.4.1 PARTICLE TEMPERATURE DATA

It was concluded in Chapter 3 that the data reported in the literature for the temperature response of coal particles during devolatilization must be used with caution due to errors which arise via the use of the conventional measurement technique (as described in Chapter 3). However, some of the data can be selectively employed based on the experimental procedures reported. Adesanya and Pham (1995) measured the temperature response of 16 mm and 9.5 mm coal particles in a purely convective flow environment (N₂ @ 0.25 m s⁻¹, 650°C). An insulating tube was employed to ensure that the particle was not influenced by radiation heat transfer by maintaining a reactor wall temperature similar to that of the particle surface. Furthermore the coal used had a moisture content of 1.3 wt % (as received) thus the effect of moisture is likely to be minimal. Given the conditions of this experiment, it is considered that the data reported can be reliably used to further examine the predictability of the model.

The data reported by Adesanya and Pham (1995) is compared with the appropriate model predictions in Figure 6.17. It can be seen that during the early stages of heating, up to approximately 500°C, the model predicts the measured temperature data quite accurately. Above 500°C the data exhibits a distinctive shift in the temperature response which is particularly evident for the 16 mm particles. Adesanya and Pham (1995) visually observed a definite change in the particle shape coinciding with this deviation in the temperature response which was attributed to softening of the coal
particle. The particle softening in turn leads to the change in the particle shape and this directly influences the heat transfer behaviour of the particle. However, prior to softening occurring, the model is capable of generating accurate model predictions. This confirms that the model is suitable for purely convective flow applications and is not entirely limited to the experimental conditions in this study which were used as a basis for the model development.

![Graph](image)

**Figure 6.17** Experimental data (Adesanya and Pham, 1995) and model predictions for the temperature response at the centre of 9.5 mm and 16 mm coal particles in a convective flow of N\(_2\) at 0.25 m s\(^{-1}\) and 650\(^\circ\)C.

A second useful set of data reported in the literature is that of Dincer et al. (1996) who measured the temperature response of an inert spherical "brick" particle in a fluidised bed reactor. The size of the brick particle employed was approximately 20 mm and 0.1 mm thermocouple wires were embedded into the centre of the particle. Measurements were conducted in a 860\(^\circ\)C fluidised bed reactor filled with 0.5 + 1.0 mm sand particles with a superficial gas velocity of 0.85 m s\(^{-1}\). The thermophysical properties reported for the brick particle were; \(k_{\text{brick}} = 0.692\) W m\(^{-1}\) K\(^{-1}\), \(\varepsilon_{\text{brick}} = 0.93\), and \(\alpha_{\text{brick}} = 5.16 \times 10^{-7}\) m\(^2\) s\(^{-1}\). Due to the size of the brick particle employed relative to the size of the thermocouple employed it is likely that the depth to which the thermocouple wires protrude into the particle is sufficient to reduce any thermal
conduction effects along the thermocouple wires. Hence this data is also suitable for model testing.

Dincer et al. (1996) reported their data as the dimensionless particle centre temperature, \( \theta \), as a function of the Fourier number, \( Fo \), and the equations defining these two parameters are given in Equations 6.1 and 6.2, respectively.

\[
\theta = \frac{T_{i,r=0} - T_i}{T_a - T_i} \quad (6.1)
\]

\[
Fo = \frac{\alpha t}{R_0^2} \quad (6.2)
\]

Using these equations, the model predictions based on the experimental conditions outlined above, are plotted against the reported data in Figure 6.18. Again it can be seen that the model is capable of providing accurate predictions for the measured particle temperature response, provided the data is of a reliable nature. In this case there is no need to account for mass loss as the brick particle is inert (no devolatilization occurs). This data also confirms that the proposed model is applicable to materials other than coal provided the appropriate adjustments to the model are made and the thermophysical properties of the material are available. The fact that the model has once again been able to predict the behaviour inside a fluidised bed reactor adds further confidence to the convective heat transfer correlation of Linjewile (1993).
Figure 6.18 Experimental data (Dincer et al., 1996) and model predictions for the temperature response at the centre of a 20 mm spherical “brick” particle in a fluidised bed reactor at 860°C.

6.4.2 VOLATILE MATTER AND MOISTURE DATA

Wildegger-Gaismaier (1990) performed devolatilization experiments using Bowmans coal in a single particle furnace and measured the volatile matter content of the particles after pre-defined time intervals. The furnace operated in such a way that the particle was supported in an upward convective flow of nitrogen at the specified devolatilization temperature and was ejected from the reactor and rapidly quenched once the desired residence time was achieved. The particle was then subjected to standard testing in order to determine the residual volatile matter content. Such experiments were conducted using a range of temperatures and particle sizes. Hence this work acts as a useful source of experimental data for further model validation. Unfortunately, no corresponding particle temperature data was reported. However, based on the model predictions shown to date, it can be confidently stated that the model is capable of accurate particle temperature predictions.
Figure 6.19 shows the experimental data of Wildegger-Gaismaier (1990) for dry 10 mm and 1.8 mm Bowmans coal particles in the single particle reactor at 650°C with fluidising gas velocities of 4.2 m s⁻¹ and 0.5 m s⁻¹ for the respective particle sizes. At each specific time interval, four or five repeat runs were performed and the results reported by Wildegger-Gaismaier (1990) were used to determine the average residual volatile matter content and the 95% confidence interval (depicted by the error bars) in order to give an indication of the accuracy of the experimental technique. Also shown in Figure 6.19 are the subsequent model predictions generated using the conditions described by Wildegger-Gaismaier (1990). In both cases the model exhibits good predictions which is especially encouraging considering that particle sizes of 1.8 mm have not been previously considered at depth. Therefore the model proposed is not restricted to particles in the -9 + 8 mm to -11 + 10 mm size range as has been dealt with in this study. It is difficult to obtain particle temperature data using particle sizes as small as 1.8 mm hence the volatile matter data alone must be used for model validation.

![Graph](image.png)

**Figure 6.19** Experimental data (Wildegger-Gaismaier, 1990) and model predictions for the residual volatile matter content of 10 mm and 1.8 mm Bowmans coal particles in the single particle reactor at 650°C.
Figure 6.19 further confirms the ability of the model to predict the behaviour of dry coal particles which, to date, has been shown to be exceptional. A greater indication of the model capabilities can be gleaned from the data of Wildegger-Gaismaier (1990) for wet coal particles. Wildegger-Gaismaier (1990) performed similar experiments to those described above using wet coal particles, and determined the residual moisture and volatile matter contents of the coal particles at specific time intervals for each set of experimental conditions. For the purposes of further validating the model predictions, model predictions were generated for both 10 mm and 1.8 mm particles at temperature of 923 K (650°C) and 1023 K (650°C). The fluidising gas velocities for the particle sizes above were 4.2 m s\(^{-1}\) and 0.5 m s\(^{-1}\), respectively. These model predictions are shown in Figures 6.20 to 6.23 and included in these figures are the corresponding experimental data reported by Wildegger-Gaismaier (1990).

![Graph showing residual moisture and volatile matter content over time]

**Figure 6.20** Experimental data (Wildegger-Gaismaier, 1990) and model predictions for a 10 mm particle in a fluidising stream of N\(_2\) at 4.2 m s\(^{-1}\) and 650°C. Both the residual moisture and volatile matter contents are shown.
Figure 6.21 Experimental data (Wildegger-Gaismaier, 1990) and model predictions for a 1.8 mm particle in a fluidising stream of N₂ at 0.5 m s⁻¹ and 650°C. Both the residual moisture and volatile matter contents are shown.

Figure 6.22 Experimental data (Wildegger-Gaismaier, 1990) and model predictions for a 10 mm particle in a fluidising stream of N₂ at 4.2 m s⁻¹ and 750°C. Both the residual moisture and volatile matter contents are shown.
Figure 6.23 Experimental data (Wildegger-Gaismaier, 1990) and model predictions for a 1.8 mm particle in a fluidising stream of N\textsubscript{2} at 0.5 m s\textsuperscript{-1} and 750°C. Both the residual moisture and volatile matter contents are shown.

In each of the cases presented in Figures 6.20 to 6.23, the model is shown to be highly effective in predicting the trends in the moisture and volatile matter contents reported by Wildegger-Gaismaier (1990). These results are even more indicative of the predictability of the model with respect to the moisture and volatile matter predictions than those presented in Figures 6.8 to 6.13 where the total mass remaining is shown. In Figures 6.20 to 6.23, the residual moisture and volatile matter contents have been determined experimentally. However, the model predictions for all of the aforementioned scenarios remain exemplary.

6.5 SUMMARY

The aim of the work presented in this Chapter has been to employ the model developed in Chapters 4 and 5 to predict the experimental data generated in Chapter 3. The first stage in this testing regime for the devolatilization model developed here was to predict the data generated for dry coal particles in the horizontal tube furnace. The model was found to be extremely effective in predicting the temperature response at
the centre of both -8 + 9 mm and -10 + 11 mm coal particles in the horizontal tube furnace at temperatures of 600°C, 700°C, and 800°C. Furthermore, the model was also effective in predicting the mass loss data under identical conditions without allowing for any variation in the ultimate volatile yield $V'$. The accuracy of these model predictions confirms that the assumptions made in Chapter 5 with particular reference to dry coal particles are reasonable. Given that accurate model predictions could be obtained with a constant ultimate volatile yield$^1$, the number of variable parameters in the model is reduced which further enhances the robustness of the model.

The ability of the model to predict the behaviour of dry coal particles during devolatilization was further heightened by the model predictions under fluidised bed conditions. Using the correlation of Linjeweile (1992) to predict the convective heat transfer coefficient under fluidised bed conditions, the model was again found to predict the temperature response at the centre of dry coal particles with a high degree of accuracy. It was observed that the model predictions slightly underpredicted the measured temperature response during the early stages of heating however it is possible that this is due to limitations in the temperature measurements rather than the model predictions. However, this initial region is not significant as devolatilization does not take place until temperatures greater than approximately 150°C (refer to Section 2.2.3.1) and the model predictions were found to predict the experimental data reasonably well during this latter period.

The accuracy of the model predictions generated for dry coal particles enabled modelling of wet coal particles to proceed with confidence that the model development is not flawed to this point. As with the dry coal particles in the horizontal tube furnace, both temperature data and mass loss data was collected for -8 + 9 mm and -10 + 11 mm wet coal particles in the horizontal tube furnace at temperatures of 600°C, 700°C, and 800°C. The predicted temperature response at the centre of the particle was found to deviate somewhat from the measured temperature response during the initial heating stage, and during the latter stages of drying.

$^1 V'$ assumed to be equivalent to the ASTM volatile matter content
The deviation observed during the initial stages of heating is of little significance. However, the deviation observed during the latter stages of drying must be considered in more detail. This deviation may be due to the assumption made in Chapter 5 that drying occurs uniquely at 100°C. This may not be true in reality, however there is no definite experimental data either supporting or contradicting this assumption. Alternatively, during the latter stages of drying it is likely to be difficult to obtain highly accurate measurements for the particle temperature response at the centre of the particle due to the increased propensity for thermal conduction. Therefore the measured temperature response may represent an overprediction of the actual temperature response during this period. As the centre temperature approaches the furnace temperature, the model predictions and experimental data tend to converge which is also expected given that thermal conduction effects are gradually reducing. Ultimately the model predictions for the particle temperature response are reasonable in light of the limitations in the experimental data.

The mass loss data collected under these conditions was again found to be relatively accurate which adds further credibility to the suggestion that the particle temperature measurements may be slightly inaccurate. Overall the model predictions for wet coal particles in the horizontal tube furnace can be assumed to be reasonably accurate which leads to modelling of wet coal particle behaviour under fluidised bed conditions.

A comparison between the temperature data collected for -10 + 11 mm wet coal particles in the fluidised bed reactor (650°C, 750°C, and 850°C) again indicates that there is significant deviation in the model predictions during the latter stages of drying. This was again considered to be a result of the difficulty in obtaining highly accurate temperature measurements during this period for reasons identical to those outlined for the horizontal tube furnace above. Furthermore, the heating environment in the horizontal tube furnace is far more severe than that in the horizontal tube furnace which explains the greater deviation between the model predictions and the experimental data for the fluidised bed reactor when compared to that for the
horizontal tube furnace. In light of these limitations in the experimental data, the model predictions are again considered to be acceptable.

During the sensitivity analysis performed in Section 5.3.4.1 it was concluded that the enthalpy of drying varied with the moisture content according to the trend observed by Chen (1994). This is in contrast to the more conventional approach in which the enthalpy of drying is assumed to be constant. Using the experimental data and associated conditions to test this assumption it was concluded that assuming a constant enthalpy of drying ($\Delta H_{\text{drying}} = 2334 \text{ kJ (kg H}_2\text{O)}^{-1}$) grossly underpredicts the total drying time and the trend observed by Chen (1994) represents a reasonable assumption for the enthalpy of drying.

Further evidence of the reliability of the model to predict the temperature response at the centre of large coal particles during devolatilization was derived from the data of Adesanya and Pham (1995) and Dincer et al. (1996). The data of Adesanya and Pham (1995) was collected under purely convective flow conditions and employed both 16 mm and 9.5 mm dry coal particles. The model was again able to predict the reported data with a high degree of accuracy thus indicating that the model is not restricted to a unique coal type. The data of Dincer et al. (1996) was collected for a 20 mm spherical "brick" particle in a fluidised bed reactor at 860°C. The ability of the model to replicate this data reinforces the robustness of the model given that it is capable of reproducing data for particles up to 20 mm in diameter, can predict the temperature response in purely convective, combined convective and radiative, and fluidised bed heating environments, and is not limited to the material type of this study.

Wildegger-Gaismaier (1990) performed extensive investigations into the devolatilization and drying of Bowmans coal particles in a single particle reactor using both wet and dry coal particles. Unfortunately, no supporting particle temperature data was generated to support the aforementioned data. The data presented by Wildegger-Gaismaier (1990) for 10 mm and 1.8 mm dry coal particles at 650°C was predicted extremely well by the model which indicates the ability of the model to consider particles with diameters as low as 1.8 mm. Similar data was collected for
wet coal particles at 650°C and 750°C using both particle sizes, with the residual moisture and volatile matter contents of the coal particles determined at various time intervals. The model was shown to predict the data reported with a high degree of accuracy for all of the conditions reported.

The work presented in this chapter represents a comprehensive analysis of the ability of the large particle coal devolatilization model developed in Chapters 4 and 5 to predict the behaviour of coal particles during devolatilization. Furthermore, the extensive validation of the model undertaken, employing both particle temperature and residual volatile matter and moisture data, is the most comprehensive assessment of a large particle coal devolatilization model presented in the literature to date. The model has been shown to be capable of predicting the temperature response and the volatile matter and moisture evolution from both wet and dry coal particles (or other materials) in a variety of heat transfer environments (convective, combined convective and radiative, and fluidised bed), for temperatures ranging from 600°C to 860°C, and for particle sizes ranging from 1.8 mm to 20 mm. The procedure undertaken in the development, sensitivity analysis and testing of this model, combined with the success of the model, suggests that the predictions of this model can be confidently employed for future modelling applications provided that the heat transfer environment is correctly characterised.
Chapter 7

ESTIMATING THE KINETIC PARAMETERS FOR VOLATILES EVOLUTION

7.1 INTRODUCTION

The model developed in Chapters 4 and 5 has been rigorously tested in Chapter 6 to evaluate the ability of the model to predict the behaviour of large coal particles. The model has been successfully tested over a range of particle sizes, maximum temperatures, and heat transfer environments which confirms that the assumptions made during the model development stages in Chapters 4 and 5 are appropriate. Furthermore, the comprehensive nature of the testing carried out in Chapter 6, which included testing of the particle temperature, moisture loss, and volatile matter loss predictions of the model, represents the most thorough testing regime carried out on a large particle coal devolatilization model presently in the literature. Based on the results of Chapter 6, the large particle coal devolatilization model presented here can be confidently used in further modelling applications.

One of the implications of this work is related to determining the kinetic parameters for the evolution of individual gas species from large coal particles during
devolatilization. This work has been conducted by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) who used a model similar to that presented here in order to test proposed kinetic for the evolution of individual gas species. The appropriate kinetics were chosen based on the predicted evolution profile generated by the model using the proposed kinetics when compared with experimentally derived evolution profiles. This technique is reasonable given that it is impossible to eliminate the effects of heat and mass transfer from large particles during experiments thus no experimental data can be used to determine the devolatilization kinetics directly.

However, the large particle coal devolatilization model employed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) was much simpler then that developed in the present study in that it did not consider evolution of volatiles from individual shells within the coal particle, constant thermophysical properties were employed, the contribution of radiation to the external heat transfer rate was arbitrarily considered, and the external heat transfer rate under fluidised bed conditions was approximated by the fixed bed equation. Furthermore, no attempt was made to verify the particle temperature predictions generated by the model. Given that the devolatilization process is highly temperature dependent (refer to Section 2.2.3.1), it would seem necessary to validate the particle temperature predictions in order to ensure the appropriate kinetic parameters are selected. Given this, the kinetics proposed by the aforementioned authors remain questionable until their particle temperature model has been successfully tested.

The purpose of this section of work is to utilise the model developed in this study to investigate the kinetic parameters proposed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) and, if necessary, the method employed to generate alternate and more suitable kinetics for individual gas species evolution. In particular this section will focus on the selection of appropriate experimental data to adequately test the proposed kinetics, the technique employed to test the kinetic parameters, and the generation and testing of alternate kinetics using the experimental data selected.
7.2 SELECTION OF EXPERIMENTAL DATA FOR INDIVIDUAL GAS SPECIES EVOLUTION

The experimental data presented in Chapter 3 employed Bowmans coal which was the basis for the model testing conducted in Chapter 6. Ideally, it would be useful to have experimental data for the evolution of individual gas species from Bowmans coal under controlled conditions and for a variety of operating conditions. Wildegger-Gaismaier (1990) performed such experiments on Bowmans coal and measured the concentrations of various gas species (CO, CO\textsubscript{2}, CH\textsubscript{4}, and etc.) in the off-gas from the single particle reactor at various time intervals during devolatilization. While the experiments covered a range of particle sizes and temperatures, the evolution profiles reported were not consistent for any one gas species over the range of experimental conditions employed. Also, repeated runs were conducted and there was observed to be a large amount of error at any particular set of experimental conditions. Given this it was concluded that this data was not sufficiently accurate to enable confidant conclusions relating to the applicability of the kinetic parameters to be made. Furthermore, the construction of a facility to test the off-gas composition from the horizontal tube furnace and fluidised bed reactor employed in this study is not within the scope of the present work. Hence suitable data must be sought for an alternate coal in the literature.

Morris and Keirns (1979) performed coal devolatilization studies in a 35 mm i.d. fluidised bed reactor using nitrogen as the fluidising medium at a number of bed temperatures and for a number of particle sizes. The inert bed material was -1.4 + 1.0 mm Western Kentucky bituminous coal char and devolatilization studies were conducted using three coals; Wyoming sub-bituminous coal, Indiana high-volatile C bituminous coal and Pittsburgh high-volatile A bituminous coal. Experiments were conducted using each coal separately at a bed temperature of 872°C using an average coal particle size of 1.55 mm with a fluidising gas velocity equivalent to 50 L min\textsuperscript{-1} (@ 25°C, 1 atm). The off-gas concentration was measured as a function of time at a sampling port downstream from the fluidised bed reactor and based on this data it was
found that methane was the most abundant gas species generated during devolatilization under these conditions.

Morris and Keairns (1979) performed further experiments on Indiana high-volatile C bituminous coal at a bed temperature of 872°F employing a range of average particle sizes (0.93 mm, 1.55 mm, 1.85 mm, 2.6 mm, and 3.68 mm) as well as additional experiments on 1.55 mm particles at bed temperatures of 982°F and 760°F. In each of these experiments the concentration of methane was monitored in the off-gas and the resulting methane evolution profiles are presented in Figures 7.1 and 7.2. Note that the curves appearing in Figures 7.1 and 7.2 are not model predictions and only serve to distinguish between data sets. It can be seen that the data presented in Figure 7.1 follow the expected trends in that the smaller particles undergo more rapid devolatilization which is complete earlier than that of the larger particles. Note that in each experiment approximately 0.27 g of coal was added hence the total yield of methane in each experiment can be assumed to be almost identical. This explains the trend observed in that the smaller particles have a higher maximum off-gas concentration as a similar quantity of methane is evolved at a higher rate.

The data presented in Figure 7.2 also follow the trends expected whereby the particle heats up more rapidly at a higher bed temperature and also exhibits a higher maximum off-gas concentration. However, the data presented at 982°F and 872°F appear to have almost identical trends except for the larger maximum peak observed at 982°F. The time at which the maximum off-gas concentration occurs is identical for both of these experiments. However it would be expected that the maximum peak would appear slightly earlier at a higher bed temperature of 982°F. This would appear to be the only inconsistency in the data presented in Figures 7.1 and 7.2. Given that the data appear to follow the expected trends and that the data cover a broad range of particle sizes and bed temperatures, this data is ideally suited to testing of the kinetic parameters for methane evolution during large particle coal devolatilization.
Figure 7.1 Experimental data (Morris and Keairns, 1979) reported for the concentration of methane in the off-gas from a fluidised bed reactor at 872°C employing a range of coal particle sizes.

Figure 7.2 Experimental data (Morris and Keairns, 1979) reported for the concentration of methane in the off-gas from a fluidised bed reactor employing an average particle size of 1.55 mm at fluidised bed temperatures of 982°C, 872°C, and 760°C.
7.3 TESTING THE KINETIC PARAMETERS FOR METHANE EVOLUTION

Based on the work of Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987), the kinetic parameters proposed to predict the evolution of methane from large particles during devolatilization are presented in Table 7.1.

Table 7.1 Kinetic parameters proposed (Agarwal et al., 1984b; Agarwal, 1985; and Agarwal et al., 1987) for the evolution of methane from large coal particles during devolatilization.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
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<tbody>
<tr>
<td></td>
<td>$j = 1$</td>
</tr>
<tr>
<td>$X_{CH_4,j}$</td>
<td>0.5</td>
</tr>
<tr>
<td>$E_{0,CH_4,j}$ (kJ mol$^{-1}$)</td>
<td>250</td>
</tr>
<tr>
<td>$\sigma_{CH_4,j}$ (kJ mol$^{-1}$)</td>
<td>12.5</td>
</tr>
<tr>
<td>$\log_{10}(k_{0,CH_4,j})$</td>
<td>14.23</td>
</tr>
</tbody>
</table>

Using the kinetic parameters displayed in Table 7.1, and the particle temperature response predicted by the model according to the experimental conditions presented above and in Morris and Keairns (1979), the model is able to calculate the normalised fraction of methane evolved, \( \left( \frac{V_{CH_4}^* - V_{CH_4}}{V_{CH_4}^*} \right)_{\text{ave}} \), as a function of time in a similar fashion to the total volatile matter, ie.

\[
\left( \frac{V_{CH_4}^* - V_{CH_4}}{V_{CH_4}^*} \right)_{\text{ave}} = \frac{\sum_{m=0}^{n} V_m \left( \frac{V_{CH_4}^* - V_{CH_4}}{V_{CH_4}^*} \right)_m}{\sum_{m=1}^{n} V_m}
\]  

(7.1)
Based on these methane evolution predictions, the model subsequently evaluates the rate of methane evolution according to Equation (7.2)

$$\frac{d}{dt} \left[ \left( \frac{V_{CH_4}^* - V_{CH_4}}{V_{CH_4}^*} \right)_{avg} \right]$$

(7.2)

The overall methane yield from each experiment, $V_{CH_4}^*$, can be determined from the data presented in Figures 7.1 and 7.2 by integrating the off-gas concentration curves over the entire devolatilization time. It is assumed that the devolatilization gases do not significantly affect the total molar gas flowrate which is reasonable given that the maximum concentration in the off-gas is < 1%. Therefore the total molar yield of methane is determined according to:

$$V_{CH_4}^* = \frac{\dot{N}_{N_2}}{100} \int_0^t \left( \left[ CH_4 \right]_{off-gas} \right) dt$$

(7.3)

Here $\dot{N}_{N_2}$ is the molar flowrate of nitrogen calculated from a flowrate of 50 L min$^{-1}$ at 25°C and 1 atm, and $[CH_4]_{off-gas}$ is the off-gas concentration of methane at time $t$ according to Figures 7.1 and 7.2. Dividing by 100 converts the data from mol% to an actual molar concentration.

Using the molar yield of methane determined in Equation 7.3 and the normalised rate of methane evolution in Equation 7.2, the predicted molar rate of methane evolution from the coal in each experiment, $\frac{d}{dt} (V_{CH_4})$, can be calculated as a function of time. The predicted “in-bed” concentration of methane can therefore be calculated using Equation 7.4.

$$[CH_4]_{in-bed} = \frac{1}{\dot{N}_{N_2}} \frac{d}{dt} (V_{CH_4}) \times 100 \text{ mol%}$$

(7.4)
The data reported by Morris and Keairns (1979) and presented in Figures 7.1 and 7.2 represents the data collected at the sampling site and is therefore subject to the residence time distribution and lag-time associated with the fluidised bed reactor and sampling line. Morris and Keairns (1979) noted that a typical delay of 3.2 s was observed between injection of gas into the bed and the first appearance of the tracer gas at the sampling port. Therefore the data in Figures 7.1 and 7.2 has been adjusted to deduce this 3.2 s achieving the time scale presented. However, this data has not been adjusted to consider the residence time distribution thus the model predictions must be appropriately adjusted in order to facilitate comparison with the reported data.

Morris and Keairns (1979) performed two separate tracer studies using CO\(_2\) (9.3 mL injected) and H\(_2\) (3.35 mL injected) which were injected over a 0.2 s interval and the subsequent concentration of the gases in the off-gas at the sampling point were detected. The results of these two tests are shown in Figure 7.3. It can be seen that both tests exhibit almost identical trends in the respective off-gas concentration profile, as expected, and that the height of the curve is directly proportional to the amount of gas injected. Based on these results, the residence time distribution (RTD) function, \(E(t)\), can be calculated which, for a pulse tracer test, is given by (Perry and Green, 1984):

\[
E(t) = \frac{C(t)}{\int_0^t C(t)dt}
\]  

(7.5)

The RTD function averaged from those calculated via the two tracer studies presented in Figure 7.3 is also exhibited in Figure 7.3. Note that the lag time (3.2 s) has been deducted to yield the RTD function shown and the two tracer tests generated almost identical RTD curves. By adjusting the RTD to remove the lag-time factor, the RTD function displayed in Figure 7.3 can be used directly to adjust the predicted in-bed concentration profiles predicted by the model to give the predicted concentration profiles at the sampling point. This then enables a direct comparison with the data presented in Figure 7.1 and 7.2 to be made.
Figure 7.3 Tracer response curves obtained from the tracer tests reported by Morris and Kearns (1979) and the subsequent residence time distribution function.

In order to adjust the in-bed concentrations predicted by the model, the predicted in-bed concentration response curve, \([CH_4]_{\text{in-bed}}(t)\) vs \(t\), was divided into 0.2 s intervals which essentially represent a multitude of 0.2 s pulses of methane being emitted from the coal particle. The total amount of gas represented by these 0.2 s pulses was assumed to be equivalent to \([CH_4]_{\text{in-bed}}(t)\).\(\Delta t\). Each of these 0.2 s pulses was subsequently adjusted via the RTD function to give the concentration profile in the off-gas due to each 0.2 s pulse, \([CH_4]_{\text{off-gas,0.2s}}\), ie.

\[
[CH_4]_{\text{off-gas,0.2s}} = [CH_4]_{\text{in-bed}}(t) \cdot \Delta t \cdot E(t)
\]  \hspace{1cm} (7.6)

The actual concentration profile in the off-gas, \([CH_4]_{\text{off-gas,\Delta t}}\), is calculated by summing the contributions from each 0.2 s pulse at each time increment, ie.

\[
[CH_4]_{\text{off-gas,\Delta t}} = \sum ([CH_4]_{\text{in-bed}}(t) \cdot \Delta t \cdot E(t))
\]  \hspace{1cm} (7.7)
Morris and Keairns (1979) also reported that the Indiana high-volatile C bituminous coal used in their study underwent swelling during devolatilization and that the degree of swelling increased from 25% for particles greater than ~4 mm to 100% for particles less than ~1.5 mm. According to these ranges of swelling, the mean particle size calculated before and after devolatilization was used in the model. Also, the coal employed was reported to have an ASTM volatile matter content of 39.6 wt% (dry basis) and the thermophysical properties and emissivity were assumed to be the same as those employed previously for Bowmans coal.

The predicted methane concentration profiles achieved using the kinetics of Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) presented in Table 7.1, and the technique presented above, are compared with the data reported by Morris and Keairns (1979) in Figures 7.4 to 7.6. It can be seen that, while the kinetics are capable of predicting the time over which devolatilization occurs reasonably well, the actual off-gas concentrations predicted by the model differ significantly from those reported by Morris and Keairns (1979). Generally it appears that the model is underpredicting the evolution of methane during the early stages of devolatilization as well as predicting a higher then expected maximum off-gas concentration. Note that the methane yield in each case is based on the experimental data and thus the area under each curve, which represents the total methane yield, is identical. This may be difficult to visualise in some cases due to the tailing effect which is apparent for the predicted data.

The deviation of the predicted off-gas concentrations from the experimental data may be due to either an incorrect choice of devolatilization kinetic, or a limitation if the particle temperature predictions. As this data was collected under fluidised bed conditions, it is unlikely that the uncertainty in the external convective heat transfer coefficient may be influencing these results as this was found to have a minimal effect of the model predictions in Section 5.3.3. Similar can be said for the thermal conductivity and coal emissivity based on the conclusions of Sections 5.3.1.1 and 5.3.2, respectively. However, the results of Section 5.3.1.2 indicate that the specific heat capacity of the coal may influence these model predictions.
Figure 7.4 Experimental data (Morris and Keairns, 1979) and model predictions for the concentration of methane in the off-gas of a fluidised bed reactor at 872°C for average particle sizes of 0.93 mm and 1.85 mm. The model predictions are generated using the kinetics proposed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) in Table 7.1.

Figure 7.5 Experimental data (Morris and Keairns, 1979) and model predictions for the concentration of methane in the off-gas of a fluidised bed reactor at 872°C for average particle sizes of 2.6 mm and 3.68 mm. The model predictions are generated using the kinetics proposed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) in Table 7.1.
Figure 7.6 Experimental data (Morris and Keairns, 1979) and model predictions for the concentration of methane in the off-gas of a fluidised bed reactor using particles of average diameter 1.55 mm at temperatures of 872°C, 760°C, and 982°C. The model predictions are generated using the kinetics proposed by of Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) in Table 7.1.

It was found in Section 5.3.1.1 that a low specific heat capacity results in a more rapid rate of devolatilization with devolatilization commencing and finishing earlier. Thus decreasing the specific heat capacity would enable the model to predict higher methane concentrations during the earlier stages of devolatilization. However, even greater maximum off-gas concentrations are likely to result and the devolatilization time would be reduced. Thus while decreasing the specific heat capacity would reduce the first problem, the latter two would be enhanced. Alternatively, increasing the specific heat capacity would act to further delay devolatilization and thus further reducing the methane concentrations predicted during the early stages of devolatilization. It is unlikely therefore that varying the specific heat capacity is likely to enable more accurate model predictions to be generated. Therefore it is more likely that the kinetics proposed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) do not accurately reflect the evolution behaviour of methane during devolatilization. Therefore, an alternate set of methane devolatilization kinetics is required to enable the model to more accurately predict the observed methane evolution profiles.
7.4 ESTIMATION AND TESTING OF ALTERNATE KINETICS FOR METHANE EVOLUTION

7.4.1 ESTIMATING ALTERNATE KINETICS FOR METHANE EVOLUTION

As mentioned above, the inability of the kinetics proposed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) to accurately predict the methane evolution trends reported by Morris and Keaimbs (1979) have resulted to the need to evaluate alternate kinetics to predict methane evolution. When investigating the kinetic for methane evolution, Agarwal (1985) used data reported throughout the literature for the evolution of methane from pulverised coal particles in fluidised beds to initially investigate the kinetics proposed by a number of authors. The data presented represents the yield of methane obtained at a particular operating temperature which have been scaled to consider the maximum methane yield of each coal. According the Agarwal (1985), a 0.7 s residence time can be assumed within the fluidised bed.

Using the kinetics proposed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) in Table 7.1, and the experimental conditions reported by Agarwal (1985), the predicted methane evolution as a function of temperature was compared with the data reported by Agarwal (1985) as seen in Figure 7.7. It can be seen that the model tends to underpredict the average methane yield at low temperatures whilst slightly overpredicting the average methane yield at high temperatures. These trends are directly comparable to those seen in Figures 7.4 to 7.6. At low temperatures, or during the early stages of devolatilization, the model underpredicts the methane yield and during the latter stages of devolatilization the methane yield is slightly overpredicted. Note that in both cases, the main area of concern is early in the devolatilization process where the methane yield is being underpredicted. Given that these kinetics do not appear to represent the average methane yield as a function of temperature, and that the trends observed in Figure 7.7 are consistent with those in Figures 7.4 to 7.6, it was concluded that deriving kinetics which provide a better
average methane yield as a function of temperature may be a useful first step in deducing more appropriate kinetics for predicting methane evolution behaviour in Figures 7.4 to 7.6.

Figure 7.7 Experimental data reported by Agarwal (1985) and model predictions for the normalised yield of methane from pulverised coal particles in a fluidised bed reactor with a residence time of 0.7 s. The model predictions have been generated using the kinetics proposed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987).

Considering the general trend in the methane yield in Figure 7.7, it can be seen that the yield does not increase significantly below approximately 500°C after which there is a significant increase in the yield to a value of \((V/V^*) = 0.3\) at around 600°C. There is a slight plateau which follows in which the yield increases marginally to \((V/V^*) = 0.35 - 0.4\) at 700°C. This is followed by an increase in the yield with temperature up to 1000°C at which methane can be said to be completely evolved. During this final stage (700°C - 1000°C), the rate of increase in the methane yield with time gradually decreases until it reaches zero at 1000°C as no further methane is evolving.

In attempting to derive alternate kinetics to predict methane evolution during devolatilization., it seems appropriate for the kinetics to be based around the trends
seen in Figure 7.7. Therefore, based on the above observations the evolution of methane can be categorised into two distinct stages. The first stage occurs at a temperature of approximately 600°C and accounts for 30% of the total evolved methane. The second stage produces the remaining 70% of the methane evolution and occurs over a higher temperature range. Therefore, it is postulated that two sources exist with the fractions of the total methane evolved from each source given by $X_{\text{CH}_4,1} = 0.3$ and $X_{\text{CH}_4,2} = 0.7$. The kinetics proposed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) in Table 7.1 have employed different values for the frequency factor, $k_{0,\text{CH}_4,j}$. However, Anthony and Howard (1976) used transition theory to estimate the value of the frequency factor for coal devolatilization and obtained a value of $\log_{10}(k_0) = 13.22$. This value will be used as the frequency factor for methane evolution from both sources which is theoretically applicable as well as serves to simplify the selection of the kinetic parameters.

The kinetic parameters which remain to be specified are the mean activation energy and standard deviation in activation energy values for the two sources, respectively. The mean activation energies were first determined using a trial and error technique, based on the observations which were made from Figure 7.7. Based on these observations there exist two methane evolution sources; one which is important at low temperatures and another which is dominant at high temperatures. Accordingly, the mean activation energies should reflect this in that the source contributing 30% to the total methane evolution should have a lower mean activation energy than that of the second source. In order to eliminate any confusion between the respective sources, the standard deviation in activation energy values were set at $\sigma_{\text{CH}_4,j} = 1$ kJ mol$^{-1}$ such that the yields predicted from each source could be easily distinguished. Methane yield curves similar to those in Figure 7.7 were generated and the mean activation energy values were varied until the required trend was obtained. This trend required that the low temperature methane evolution occur at around 550°C, and that the high temperature methane evolution was predominant at approximately 850°C. Note that the mean activation energy can be seen as a reflection in the average temperature at which the devolatilization takes place. By specifying a standard deviation in activation energy of $\sigma_{\text{CH}_4,j} = 1$ kJ mol$^{-1}$, devolatilization takes place almost
immediately upon reaching the required temperature, thus enabling the required mean activation energies to be established. Using this technique, mean activation energies of $E_{0,CH_4,1} = 210$ kJ mol$^{-1}$ and $E_{0,CH_4,2} = 265$ kJ mol$^{-1}$ were obtained. This technique is displayed graphically in Figure 7.8. The mean activation energies used in the runs presented in Figure 7.8 were$^{1}$:

Run 1: \[ E_{0,CH_4,1} = 190 \text{ kJ mol}^{-1} \]
\[ E_{0,CH_4,2} = 270 \text{ kJ mol}^{-1} \]

Run 2: \[ E_{0,CH_4,1} = 210 \text{ kJ mol}^{-1} \]
\[ E_{0,CH_4,2} = 270 \text{ kJ mol}^{-1} \]

Run 3: \[ E_{0,CH_4,1} = 210 \text{ kJ mol}^{-1} \]
\[ E_{0,CH_4,2} = 265 \text{ kJ mol}^{-1} \]

![Graphical representation of the technique employed to estimate the mean activation energy values for methane evolution.](image)

**Figure 7.8** Graphical representation of the technique employed to estimate the mean activation energy values for methane evolution.

In Run 1 it can be seen that methane evolution is predicted marginally early in the low temperature region with the bulk of the evolution complete by 550°C. The opposite can be said for Run 1 in the high temperature region where devolatilization is

$^{1}$ 1 refers to the low temperature source and 2 refers to the high temperature source.
Chapter 7  Kinetic Parameters for Volatiles Evolution

occurring too late. Accordingly, in Run 2 the mean activation energy in the low temperature region has been increased to shift the devolatilization to a higher temperature. It can be seen that the temperature at which devolatilization occurs in the low temperature region is now in the range of that required. In Run 3 the mean activation energy in the low temperature region is maintained at that of Run 2, however the mean activation energy in the high temperature region is lowered in order to shift the high temperature devolatilization to lower temperatures. This again enables devolatilization to occur within the required temperature ranges.

Once the mean activation energies have been determined, the standard deviation in activation energies must now be estimated. This again requires a trial and error approach. Given that the mean activation energies are now set, it is simply a case of altering the values until the curve represents a reasonable average value for all of the data in Figure 7.7. While this was done using a trial and error approach it was also possible to use the trends in Figure 7.7 as a guide. Generally the low temperature methane evolution takes place over a smaller range of temperatures than the high temperature evolution. Accordingly the standard deviation in activation energy for the high temperature region should be greater than that of the low temperature region to reflect this trend given that the standard deviation in activation can be seen to be a measure of the range of temperatures over which devolatilization takes place. Ultimately, it was found that values of $\sigma_{CH_4,1} = 15 \text{ kJ mol}^{-1}$ $\sigma_{CH_4,2} = 35 \text{ kJ mol}^{-1}$ were appropriate which resulted in the methane evolution curve presented in Figure 7.9. The curve generated using the kinetics of Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) is included for comparison. A summary of the alternate kinetics used to generate the curve in Figure 7.9 is shown in Table 7.2.

The curve generated using the alternate kinetics proposed in this study shows a much better fit with the experimental data in the low temperature region which was found to be a problem in the kinetics of Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987). In the high temperature region the curves are similar. However, at approximately 700°C the curve generated using the alternate kinetics has a slight plateau and shows a lower rate of methane evolution around this temperature. It is
possible that this may eliminate the problems observed in Figures 7.4 to 7.6 in which
the predicted maximum off-gas concentrations using the kinetics of Agarwal et al.
(1984b), Agarwal (1985), and Agarwal et al. (1987) were too high. The reduction in
the total sum squared error (SSE) achieved between the respective model predictions
and the entire set of experimental data, as a result of employing the alternate kinetics,
is 14%.

Figure 7.9 Experimental data reported by Agarwal (1985) and model predictions for
the normalised yield of methane from pulverised coal particles in a fluidised bed
reactor at a residence time of 0.7 s. The literature kinetics refers to those proposed by
Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) while the alternate
kinetics are those proposed in this study in Table 7.2.

Table 7.2 Kinetic parameters for the evolution of methane from large coal particles
during devolatilization proposed in this study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
</tr>
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<tbody>
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<td>$X_{\text{CH}_4,j}$</td>
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<td>$E_{0,\text{CH}_4,j}$ (kJ mol$^{-1}$)</td>
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</tr>
<tr>
<td>$\sigma_{\text{CH}_4,j}$ (kJ mol$^{-1}$)</td>
<td>15</td>
</tr>
<tr>
<td>$\log_{10}(k_{0,\text{CH}_4,j})$</td>
<td>13.22</td>
</tr>
</tbody>
</table>
7.4.2 TESTING THE ALTERNATE KINETICS FOR METHANE EVOLUTION

The alternate kinetics for methane evolution developed in the previous section must now be tested via a comparison with the experimental data of Morris and Keairns (1979). Using the same technique described in Section 7.3 however employing the kinetics for methane evolution displayed in Table 7.2, the predicted off-gas concentrations were generated for the respective particle sizes and bed temperatures used by Morris and Keairns (1979). These predictions are compared with the experimental data in Figures 7.10 to 7.16 which show the model predictions generated using both the kinetics proposed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) and the alternate kinetics proposed in this study as well as the experimental data reported by Morris and Keairns (1979) for each set of experimental conditions separately. In each of these figures the model predictions generated using "literature kinetics" refers to those generated using the kinetics of Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987), while the model predictions produced using "alternate kinetics" refers to those produced using the kinetics proposed in this study.

![Graph](image-url)

**Figure 7.10** Experimental data (Morris and Keairns, 1979) and model predictions for the concentration of methane in the off-gas from a fluidised bed gasifier at 872°C using an average particle size of 0.93 mm.
Figure 7.11 Experimental data (Morris and Keairns, 1979) and model predictions for the concentration of methane in the off-gas from a fluidised bed gasifier at 872°C using an average particle size of 1.55 mm.

Figure 7.12 Experimental data (Morris and Keairns, 1979) and model predictions for the concentration of methane in the off-gas from a fluidised bed gasifier at 872°C using an average particle size of 1.85 mm.
Figure 7.13 Experimental data (Morris and Keairns, 1979) and model predictions for the concentration of methane in the off-gas from a fluidised bed gasifier at 872°C using an average particle size of 2.60 mm.

Figure 7.14 Experimental data (Morris and Keairns, 1979) and model predictions for the concentration of methane in the off-gas from a fluidised bed gasifier at 872°C using an average particle size of 3.68 mm.
Figure 7.15 Experimental data (Morris and Keairns, 1979) and model predictions for the concentration of methane in the off-gas from a fluidised bed gasifier at 760°C using an average particle size of 1.55 mm.

Figure 7.16 Experimental data (Morris and Keairns, 1979) and model predictions for the concentration of methane in the off-gas from a fluidised bed gasifier at 982°C using an average particle size of 1.55 mm.
Figures 7.10 to 7.14 exhibit the results obtained at a bed temperature of 872°C for particle sizes of 0.93 mm, 1.55 mm, 1.85 mm, 2.60 mm, and 3.68 mm, respectively, while Figures 7.15 and 7.16 show the results obtained for an average particle size of 1.55 mm at bed temperature of 760°C and 982°C, respectively. It can be seen that in each of the figures the model predictions generated using the alternate kinetics proposed in this study give much better predictions for the respective off-gas concentrations at the sampling point than the kinetics proposed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987). This is particularly true during the early stages of devolatilization which is a significant limitation of the kinetics of Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987). The model predictions are the least accurate for the 1.85 mm particles at 872°C (Figure 7.12) however the alternate kinetics still represent an improvement in the model predictions.

Figures 7.10 to 7.14 exhibit model predictions generated for a number of different particle sizes at one fluidised bed operating temperature. The fact that the model is able to give good predictions over the particle size range employed is an indication of the accuracy of the particle temperature predictions as well as the chemical kinetics. However, the major which will influence the predictions for a range of particle sizes is the ability of the model to predict the particle temperature response sufficiently accurately. Figures 7.10 to 7.14 therefore indicate that the particle temperature response predicted by the model must be reasonable which further confirms the need to replicate, as closely as possible, the heat transfer environment surrounding the particle.

The result of Figures 7.11, 7.15 and 7.16, conversely, give a greater indication of the accuracy of the chemical kinetics as these figures represent model predictions generated at different fluidised bed operating temperature for a constant particle size. Figures 7.10 to 7.14 have indicated that the model is predicted the heat transfer environment with reasonable accuracy. Varying the operating temperature will have a greater impact on the chemical kinetic. However, the model predictions in Figures 7.11, 7.15 and 7.16 remain reasonably accurate which further emphasises the applicability of the chemical kinetics proposed in this study.
The magnitude of the improvement in the model predictions can be determined by examining the total sum squared error (SSE) values for each of the scenarios in Figures 7.10 to 7.16. These values are listed in Table 7.3 along with the % reduction in the SSE values obtained by employing the alternate kinetics.

### Table 7.3 Total SSE values between the experimental data and model predictions for the concentrations of methane in the off-gas of a fluidised bed gasifier for the experimental conditions relevant to Figures 7.10 to 7.16.

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Total SSE</th>
<th>% reduction in SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alternate Kinetics</td>
<td>Literature Kinetics</td>
</tr>
<tr>
<td>7.10</td>
<td>0.038</td>
<td>0.094</td>
</tr>
<tr>
<td>7.11</td>
<td>0.038</td>
<td>0.157</td>
</tr>
<tr>
<td>7.12</td>
<td>0.249</td>
<td>0.432</td>
</tr>
<tr>
<td>7.13</td>
<td>0.019</td>
<td>0.091</td>
</tr>
<tr>
<td>7.14</td>
<td>0.004</td>
<td>0.046</td>
</tr>
<tr>
<td>7.15</td>
<td>0.045</td>
<td>0.210</td>
</tr>
<tr>
<td>7.16</td>
<td>0.029</td>
<td>0.382</td>
</tr>
<tr>
<td>Total</td>
<td>0.422</td>
<td>1.412</td>
</tr>
</tbody>
</table>

Table 7.3 shows that the minimum reduction in the total SSE value for any particular set of experimental conditions is 42% which was obtained for 1.85 mm particles in the fluidised bed operating at 872°C. As mentioned, the model predictions were least accurate for this scenario which is also reflected in the SSE values. Despite this fact, the magnitude in the reduction of the total SSE remains statistically significant.

It should be noted that the technique used to generate the alternate kinetics in Section 7.4.1 employed methane yield data derived from a large number of coal types. This is consistent with the assumption that the kinetics of evolution of individual gas species are not highly coal dependent (Agarwal et al., 1987). It is possible that this assumption arose from the use of a model which did not accurately predict the particle temperature response and that the thermophysical properties and etc. were assumed to
be equivalent for different coals. If the thermophysical properties of individual coals could be determined and the particle temperature predictions verified, and volatile species yield data was available, it would be possible to ascertain coal specific kinetics for the evolution of individual volatile species using the technique employed in this study. Using this approach it would be interesting to compare the kinetics derived from different coals to determine any characteristic trends with coal type etc. This is not within the scope of the present study however the foundation for this work has been established.

Based on the model predictions exhibited in Figures 7.10 to 7.16, as well as those in Figure 7.8, and the SSE values reported in Table 7.3, it can be confidently concluded that the alternate kinetics proposed in this study and summarised in Table 7.2 are far more effective in predicting the evolution behaviour of methane from large coal particles during devolatilization. Furthermore, given the comprehensive testing of the particle temperature predictions generated by the model conducted in Chapter 6, these kinetics can be considered to be highly reliable for the coal considered.

7.5 SUMMARY

The focus of this chapter was to investigate the techniques employed to estimate the kinetic parameters for the evolution of individual gas species from large coal particles during devolatilization. Much work has been done in this area, particularly by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987), and the technique employed has been to test the applicability of certain kinetics using predicted evolution profiles, and comparing these predictions with experimental data. This technique is appropriate given that the kinetics cannot be isolated experimentally from other complicating factors such as heat transfer during devolatilization of large coal particles.

It was identified that a limitation of the work of Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) was their use of a model which had not been comprehensively tested, particularly with reference to the particle temperature
predictions. It was considered that the kinetics proposed by Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) may be questionable in light of this fact. This was confirmed when using the model developed in this study and the kinetics of Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987) to predict the evolution of methane from large coal particles under fluidised bed conditions, and comparing these predictions to the corresponding experimental data of Morris and Keairns (1979).

Using data collected from the literature by Agarwal (1985) for the yield of methane as a function of temperature from pulverised coal particles under fluidised bed conditions at a constant residence time, alternate kinetic parameters were proposed based on the trends observed in this data. Two distinct regions of methane evolution were evident with one generating 30% of the total evolved methane at low temperatures and the other contributing 70% of the total methane evolved at higher temperatures. The frequency factor was assumed to be $\log_{10}(k_0) = 13.22$, consistent with transition theory, and the mean activation energies for the two methane evolution regions were varied to achieve devolatilization in the middle of the observed ranges, respectively, assuming a small value of the standard deviation in activation energy. Finally, the standard deviation in activation energy values were varied for the two respective methane evolution sources such that the methane yield predicted gave a reasonable average for the entire data set considered.

Once these kinetics were established, the model was again employed to predict the methane evolution behaviour under the conditions pertaining to the experiments conducted by Morris and Keairns (1979). It was found that the alternate kinetics proposed in this study provided a much better fit to the experimental data than those of Agarwal et al. (1984b), Agarwal (1985), and Agarwal et al. (1987). The reduction in the total SSE obtained for all of the experimental data considered was 70% which represents a significant improvement in the model predictions. The alternate kinetics proposed in this study are summarised in Table 7.3.
These results confirm the aforementioned hypothesis that determining the kinetic parameters for individual volatile species evolution is limited unless the particle temperature predictions of the model being employed have been thoroughly tested. Given the rigorous testing conducted on the model proposed in this study, and the accuracy of the predictions obtained with the alternate kinetics proposed, it can be concluded that these kinetics can be reliably employed to predict methane evolution during devolatilization from the specific coal used by Morris and Keirns (1979). Furthermore, provided that the necessary particle temperature and methane evolution data were available for any coal type, it would be possible to determine coal specific kinetic parameters for the evolution of individual gas species using the technique employed in this chapter, provided the model can accurately predict the particle temperature response.
Chapter 8

HEAT TRANSFER AND CHEMICAL KINETIC REGIMES OF LARGE COAL PARTICLE DEVOLATILIZATION

8.1 INTRODUCTION

It is generally acknowledged that the process of coal devolatilization may be controlled by three main factors, viz, heat transfer to and within the coal particle, the chemical kinetics of devolatilization, and mass transfer of the volatiles products within the particle. The significance of mass transfer during coal pyrolysis remains uncertain, which is particularly true for low-rank coals which tend to have a greater porosity and hence less resistance to mass transfer. Furthermore, Koch et al. (1969) suggested that the char layer which forms around the devolatilizing coal particle provides little resistance to flow due to its enhanced porosity, and it was observed by Anthony et al. (1975) that the effect of pressure on the devolatilization behaviour of a Montana lignite was negligible. Based on these factors, mass transfer will be assumed to be negligible in comparison to the effect of heat transfer and chemical kinetics. While this may not be true in high pressure devolatilization environments, it would seem to be a reasonable assumption under atmospheric conditions.
A traditional technique to characterising the devolatilization time for large coal particles has been to relate the devolatilization time to the particle size according to Equation (8.1) (Stubington et al., 1991).

\[ t_{dev} = Ad_p^n \]  

(8.1)

The parameter \( n \) can be used to distinguish between the regimes of coal devolatilization as a value of \( n = 0 \) indicates that chemical kinetics dominate the devolatilization process, while a value of \( n = 2 \) suggests that heat (or mass) transfer is controlling the devolatilization process. Van der Horing (1991) plotted the results obtained from a number of literature sources and correlated the devolatilization times reported with the particle diameter yielding Equation (8.2). The parameter \( n \) was found to have a value of \( n = 1.1 \) which indicates that devolatilization is controlled by a mixture of chemical kinetics and heat transfer.

\[ t_{dev} = 5.77d_p^{1.1} \]  

(8.2)

A significant limitation of this technique is that correlations similar to that of Equation (8.1) do not take into account the nature of the heat transfer environment and as such, any comparison between data can only be made under identical experimental conditions. The correlations derived from such data can only be applied to estimate the devolatilization time under the same conditions. Therefore it would be preferable to obtain a relationship which is applicable to a wider range of operating conditions.

Agarwal et al. (1984b) used their large coal particle devolatilization model to perform a parametric study to investigate the devolatilization time of coal particles as a function of particle size. It was found that the devolatilization time remained relatively constant up to a particle size of 0.1 mm after which it began to increase with an increasing particle size with the devolatilization time in the latter region proportional to \( d_p^2 \). For particle sizes below 0.1 mm, chemical kinetics control devolatilization which is consistent with the findings of Juntgen and van Heek (1979) who suggested that chemical kinetics no longer control devolatilization for particle
sizes greater than 0.3 mm. Above 0.1 mm the role of heat transfer in the devolatilization process becomes increasingly significant.

To investigate the effect of the heat transfer environment, Agarwal et al. (1984b) varied the assumed heat transfer Biot number, $Bi = h d_p / k_c$, in their model and investigated the effect of the particle size on the devolatilization time. It was observed that decreasing the Biot number results in the devolatilization time tending toward becoming heat transfer controlled at lower particle sizes. This confirms the aforementioned comment that the heat transfer environment must also be considered when deciding which of the mechanisms is controlling the devolatilization process. Therefore, the aim of this chapter of work is to investigate the roles of heat transfer and chemical kinetics in controlling the devolatilization of large coal particles, and to determine a relationship which can be used to quantify their respective effects. Such a relationship should account for the particle size, heat transfer environment, devolatilization temperature, chemical kinetics, and any other factor which may influence the mechanisms controlling devolatilization.

8.2 DEVELOPMENT OF THE RELATIONSHIP BETWEEN HEAT TRANSFER AND CHEMICAL KINETICS DURING DEVOLATILIZATION

As has been mentioned, it has been customary to generate plots of the devolatilization time as a function of the particle size and to speculate from such plots the respective roles of heat transfer and chemical kinetics during the devolatilization process. However, a more direct indication of the relative roles of each of these mechanisms could be obtained by considering the ratio between the time required for the evolution of volatiles, $t_{dev}$, and the time required for the particle to reach the maximum devolatilization temperature, $t_{heat}$. If chemical kinetics are controlling the process, the particle will reach the maximum devolatilization temperature prior to the volatiles being evolved and $t_{dev} > t_{heat}$. Conversely, if heat transfer is the controlling mechanism, devolatilization will take place almost instantaneously upon reaching the
devolatilization temperature and \( t_{\text{dev}} = t_{\text{heat}} \). Note that it is often more applicable to define the devolatilization and heating time parameters as the 95% devolatilization/heating times. This is due to the effect of tailing which is often apparent for volatiles realising making the 100% devolatilization time difficult to distinguish, and is also consistent with the literature (Morris and Keirns, 1979, Stubingting and Sumaryono, 1984; and Agarwal et al., 1987). Hence a direct indication of the controlling mechanism can be obtained providing that the required data is available via the dimensionless devolatilization time defined as:

\[
\theta_{\text{dev}} = \frac{t_{\text{dev}}}{t_{\text{heat}}} \quad (8.3)
\]

Thus if \( \theta_{\text{dev}} \gg 1 \) then chemical kinetics are the dominant mechanism, while if \( \theta_{\text{dev}} \sim 1 \) then devolatilization is being controlled by heat transfer.

The 95% devolatilization time can be defined as when

\[
\left( \frac{V' - V}{V'} \right)_{\text{ave}} = 0.05 \quad (8.4)
\]

The 95% heating time can be defined as when

\[
\left( \frac{T_{r=0} - T_0}{T_\infty - T_0} \right) = 0.95 \quad (8.5)
\]

In order to relate the particle size, heat transfer environment, maximum devolatilization temperature, and the chemical kinetics to the dimensionless devolatilization time, it would be ideal to utilise a second dimensionless parameter which is able to account for each of these parameters. Rather than source one unique dimensionless parameter, it is easier to employ existing dimensionless parameters typically used in heat transfer and chemical kinetic situations, and modify these dimensionless parameters to suit the existing situation.
When considering the dimensionless parameter used in heat transfer applications it must account for both the external and internal heat transfer effects. The most appropriate dimensionless parameter to describe the heat transfer mechanisms during coal devolatilization then is the heat transfer Biot number, defined as:

\[ Bi = \frac{h_0 d_p}{k_c} \]  

(8.6)

The heat transfer Biot number relates the ratio of the rate of heat transfer to the surface of the particle from the surrounding environment, to the rate of internal heat conduction to the centre of the particle from the particle surface. The heat transfer coefficient, \( h_0 \), used in the Biot number must account for both convective and radiative heat transfer which can be achieved using the following (Kilic et al., 1993):

\[ h_0 = h_{conv} + h_{rad} = h_{conv} + \sigma_{rad} \varepsilon_{rad} \left( T_g + T_{|r=R_0} \right) \left( T_g^2 + T_{|r=R_0}^2 \right) \]  

(8.7)

Note that as the particle surface temperature is constantly changing, the value of \( h_{rad} \) also changes so it is convenient to use the average surface temperature in Equation (8.7), i.e.

\[ T_{|r=R_0} = T_{ave} = \frac{T_o + T_g}{2} \]  

(8.8)

The Biot number also accounts for internal heat transfer via the thermal conductivity and takes into consideration the particle size.

When dealing with gas/solid chemical reactions, a frequently used dimensionless parameter in heterogeneous systems is the Damkhoeler number which is given by (Perry and Green, 1984):

\[ Da = \frac{r d_p^2}{D_a C_a} \]  

(8.9)
The Damkhoiler number is a ratio of the rate of the heterogeneous reaction at the surface of the solid to the rate of diffusion of the reactant to the reacting surface. In Equation (8.9), \( r \) is the surface reaction rate, \( C_a \) is the concentration of the reactant on the particle surface, and \( D_a \) is the diffusion rate of reactant \( a \) into the particle from the surrounding environment. Equation (8.7) can be modified slightly by combining the surface reaction rate and the reactant concentration term to yield Equation (8.10).

\[
Da = \frac{r'd_p^2}{D_a}
\]

The modified reaction rate term in Equation (8.8), \( r' \), must have units of \( s^{-1} \) in order for the Damkhoiler number to remain dimensionless. While traditionally the Damkhoiler number deals with heterogeneous reactions driven by the diffusion of a reactant gas species into the particle, devolatilization is unique in that it is a heterogeneous process which is driven by the transfer of heat into the particle. Hence rather then considering the gas diffusivity in Equation (8.10) the thermal diffusivity, \( D_{\text{therm}} = k_c / \rho C_{p,c} \), must be employed in place of \( D_a \), thus producing Equation (8.11).

\[
Da' = \frac{r'\rho C_{p,c} d_p^2}{k_c}
\]

In this form the modified Damkhoiler number relates the ratio of the rate of solid reaction via devolatilization to the rate of heat conduction through the particle which is the driving force for devolatilization. In Equation (8.11) the thermal conductivity and specific heat of the coal can be taken as the temperature averaged values of the range of temperatures experienced by the particle. Whilst the particle density does vary during devolatilization, it is more convenient to use the initial particle density as it is often difficult to measure the final particle density.

Hence the only parameter remaining to be quantified in Equation (8.11) is the modified reaction rate term, \( r' \), which must be applicable to the situation of coal
devolatilization. Agarwal et al. (1984a) suggested that for the case of an isothermal particle undergoing coal devolatilization, the fraction of volatiles evolved is given by:

\[
\frac{V^* - V}{V^*} = \int_0^E \exp \left[ -k_0 \int_0^E \exp \left( \frac{-E}{RT} \right) dt \right] f(E) dE
\]  \hspace{1cm} (8.12)

Therefore the modified reaction rate term can be given by the following equation:

\[
r' = -\frac{d}{dt} \left( \frac{V^* - V}{V^*} \right) = -\frac{d}{dt} \left[ \int_0^E \exp \left[ -k_0 \int_0^E \exp \left( \frac{-E}{RT} \right) dt \right] f(E) dE \right]
\]  \hspace{1cm} (8.13)

In normal circumstances it would be appropriate to employ the reaction activation energy, or in the case of devolatilization, the mean activation energy. However, the 95% devolatilization time will be better reflected by employing a value of \(E_0 + 2\sigma\) as two standard deviations from the mean reflects 95% of the span of a normal distribution. Thus at \(E_0 + 2\sigma\) it is expected that 95% of the volatiles have evolved. Therefore, rather than considering the reaction rate calculated from an integration conducted over a range of activation energies, the reaction rate when \(E = E_0 + 2\sigma\) is considered which gives:

\[
r' = \frac{d}{dt} \left[ \exp \left[ k_0 \int_0^E \exp \left( \frac{-E_0 + 2\sigma}{RT} \right) dt \right] f(E_0 + 2\sigma) \right]
\]  \hspace{1cm} (8.14)

Given that \(k_0\) and \(f(E)\) can be assumed to be constants, Equation (8.14) can be simplified to give:

\[
r' = \exp \left[ k_0 \exp \left( \frac{-E_0 + 2\sigma}{RT} \right) \right] f(E_0 + 2\sigma)
\]  \hspace{1cm} (8.15)
Now the temperature, $T$, in Equation (8.15) must also reflect the situation which is under consideration. Thus rather than using the average particle temperature it is more appropriate to consider the 95% heating temperature, $T_{95\%}$, which is given by:

$$\frac{T_{95\%} - T_0}{T_\infty - T_0} = 0.95$$  \hspace{1cm} (8.16)

Based on the analysis above, the ratio of the Biot number to the modified Damkohler number is given by:

$$\frac{Bi}{Da'} = \frac{h}{\exp\left[k_0 \exp\left(-\frac{E_0 + 2\sigma}{RT_{95\%}}\right)f(E_0 + 2\sigma)\rho_o C_{p,c} d_p\right]}$$  \hspace{1cm} (8.17)

Due to the exponential factor present in the denominator of Equation (8.17), it is convenient to consider the log of the $Bi / Da'$ ratio. It is proposed then that by plotting $\theta_{av}$ versus $\log\left(\frac{Bi}{Da'}\right)$ according to Equation (8.18), it should be possible to observe the respective chemical kinetic and heat transfer regimes during coal devolatilization.

$$\log\left(\frac{Bi}{Da'}\right) = \log\left(\frac{h}{f(E_0 + 2\sigma)\rho_o C_{p,c} d_p}\right) - \left[k_0 \exp\left(-\frac{E_0 + 2\sigma}{RT_{95\%}}\right)\right]$$  \hspace{1cm} (8.18)

### 8.3 COMPARING THE REGIMES OF COAL DEVOLATILIZATION

In order to employ the technique described in Section 8.2 to compare the regimes of coal devolatilization, the large particle coal devolatilization model developed in Chapters 4 and 5 was employed to provide the necessary data. Model runs were conducted using the following ranges of model parameters:
\[ E_0 = 180 - 280 \text{ kJ mol}^{-1} \]
\[ \sigma = 12.5 - 40 \text{ kJ mol}^{-1} \]
\[ T_{\infty} = 600 - 900^\circ\text{C} \]
\[ h = 40 - 800 \text{ W m}^{-2} \text{ K}^{-1} \]
\[ d_p = 0.05 - 10 \text{ mm} \]

For each model run, the 95% devolatilization time, \( t_{\text{dev}} \), and the 95% heating time, \( t_{\text{heat}} \), were determined from the model predictions. Using these values and inserting the parameters for each run into Equation (8.18) results in the data presented in Figure 8.1. It can be seen that there are three distinct regions within this plot. At values of \( \log\left( \frac{Bi}{Da'} \right) > 5.5 \), the dimensionless devolatilization time increases with increasing \( \log\left( \frac{Bi}{Da'} \right) \) and values of \( \theta_{\text{dev}} > 1 \) in this region suggests that chemical kinetics is the dominant mechanism. For values of \( \log\left( \frac{Bi}{Da'} \right) < 4.5 \) the dimensionless devolatilization time remains constant at \( \theta_{\text{dev}} \sim 1 \) which indicates that heat transfer is the controlling mechanisms. In the region defined by \( 4.5 < \log\left( \frac{Bi}{Da'} \right) < 5.5 \) there is an intermediate region where devolatilization is controlled by a combination of chemical kinetics and heat transfer.

The general trends observed in Figure 8.1 can be further rationalised by considering the variation in the devolatilization mechanism which results by varying the respective parameters in Equation (8.18). Increasing the heat transfer coefficient, \( h \), is expected to result in the devolatilization mechanism becoming increasingly kinetically controlled. An increase in the value of \( h \) in Equation (8.18) results in an increase in the value of \( \log\left( \frac{Bi}{Da'} \right) \) which tends toward the chemical kinetically controlled regime in Figure 1, as expected. Increasing the devolatilization temperature in Equation (8.18), assuming a constant heat transfer coefficient, decreases the value of \( \log\left( \frac{Bi}{Da'} \right) \) thus forcing devolatilization into the heat transfer controlled regime in Figure 8.1. As
the temperature increases, the devolatilization rate is expected to become far more rapid hence the dependence of the overall devolatilization mechanism on chemical kinetics is reduced and heat transfer dominates, as is indicated in Figure 8.1. When the particle size increases the centre of the particle undergoes slower heating thus the devolatilization process tends to become heat transfer controlled. This is reflected in the trend observed in Figure 8.1 where an increase in the value of $d_p$ in Equation (8.18) results in a decrease in the $\log\left(\frac{Bi}{Da'}\right)$ ratio which indicates a tendency toward heat transfer controlled devolatilization.

![Graph](image)

**Figure 8.1** Model predictions for the ratio of the 95% volatile evolution time, $t_{dev}$, to the 95% heating time, $t_{heat}$, as a function of the Biot number to modified Damkohler number ratio, $\log\left(\frac{Bi}{Da'}\right)$. Three distinct devolatilization regimes are distinguishable, viz; Regime I: purely heat transfer controlled, Regime II: combination of heat transfer and chemical kinetically controlled, and Regime 3: purely chemical kinetically controlled.

A similar comparison can be made for the situation in which the kinetic parameters are varied. Although the frequency factor, $k_0$, has been used as a constant in this study, it can be seen that by increasing the value of $k_0$ in Equation (8.18) leads to a
decrease in the \( \log\left(\frac{Bi}{Da'}\right) \) ratio and shifts the devolatilization process toward the heat transfer controlled regime. Again this is an expected trend given that increasing \( k_0 \) increases the devolatilization rate hence the process is less dependent on chemical kinetics. Conversely increasing the mean activation energy, \( E_0 \), maintaining a constant standard deviation in activation energy, \( \sigma \), suggests that the devolatilization reactions are more difficult to initiate and take place over a higher temperature range. This would indicate that there is a greater impact of the chemical kinetics on the overall devolatilization mechanism. This is reflected in the observations made in Figure 8.1. Increasing the activation energy in Equation (8.18) increases the effective value of \( \log\left(\frac{Bi}{Da'}\right) \), hence moving into the chemical kinetically controlled regime in Figure 8.1. Finally, an increase in the standard deviation in activation energies, assuming a constant mean activation energy, suggests that the devolatilization reactions take place over a wider range of activation energies therefore devolatilization extends to higher temperatures, i.e. chemical kinetics become increasingly significant. An increase in the standard deviation in activation energy, \( \sigma \), in Equation (8.18) again results in an increase in the \( \log\left(\frac{Bi}{Da'}\right) \) ratio which shifts devolatilization into the chemical kinetically controlled regime, as is expected.

It can be seen that the regimes observed in Figure 8.1 are consistent with those which are expected based on variations in the critical parameters in Equation (8.18). This adds further support to the technique proposed here for differentiating between chemical kinetically controlled and heat transfer controlled devolatilization.

To further test the applicability of this technique, the experimental data collected using dry coal particles in Chapter 3 were employed. Using the experimental data collected in the horizontal tube furnace, both the 95% devolatilization time and the 95% heating time were determined. The dimensionless devolatilization time which results was then plotted against the corresponding Biot number to modified Damkhoeler number ratio and compared with the theoretical predictions in Figure 8.2. It can be seen that devolatilization appears to be heat transfer controlled in the horizontal tube
furnace which is a reasonable conclusion given that the heating environment is moderate and the particle sizes employed are quite large.

![Diagram](image)

**Figure 8.2** Experimental data for the ratio of the 95% volatile evolution time, $t_{dev}$, to the 95% heating time, $t_{heat}$, as a function of the Biot number to modified Damkohler number ratio, $\log\left(\frac{Bi}{Da'}\right)$ as compared with the theoretical model predictions.

To further test the model predictions, the temperature data reported for dry coal particles in the fluidized bed was used to estimate the 95% heating time, $t_{heat}$ was determined based on the corresponding model predictions. The resulting dimensionless devolatilization times were again included in Figure 8.2 using the conditions pertinent to the fluidised bed to estimate $\log\left(\frac{Bi}{Da'}\right)$. These results indicate that in the fluidised bed devolatilization is tending toward becoming chemical kinetically controlled which is apparent by a shift toward higher values of $Bi / Da'$. This conclusion is also expected given that the heat transfer environment is much more severe in the fluidised bed hence the process becomes less dependant on heat transfer.

Using a similar approach to that employed in Section 5.3.3, it is possible to investigate whether external or internal heat transfer are dominating the overall heat transfer.
mechanism in the horizontal tube furnace. Equation (5.1) has been modified to consider the environment in the horizontal tube furnace giving:

\[ U_{\text{overall}} = \left( \frac{1}{h_{(\text{conv+rad}),\text{HTF}}} + \frac{R}{k_c} \right) \]  \hspace{1cm} (8.19)

where \( h_{(\text{conv+rad}),\text{HTF}} \) represents the total rate of heat transfer to the particle via convection and radiation in the HTF. For a 10 mm coal particle in the horizontal tube furnace at 600°C, the overall heat transfer coefficient is approximately 30.7 W m\(^{-2}\) K\(^{-1}\). Increasing \( h_{(\text{conv+rad}),\text{HTF}} \) by 20% results in an overall heat transfer coefficient of 32.8 W m\(^{-2}\) K\(^{-1}\). Therefore there is a 7% increase in the overall heat transfer coefficient. This compares with the same scenario in the fluidised bed where a 28% reduction in the convective heat transfer coefficient was found to yield only a 2.5% reduction in the overall heat transfer coefficient (refer to Section 5.3.3). This indicates that the heating process in the horizontal tube furnace is controlled by a combination of external and internal heat transfer, while in the fluidised bed internal heat transfer is the limiting mechanism. The elimination of external heat transfer as a limiting mechanism in the fluidised bed is the reason for the shift toward chemical kinetically controlled devolatilization. However, due to the large particle sizes employed, this shift is not sufficient to achieve purely chemical kinetically controlled conditions. This would require a decrease in the \( \frac{R}{k_c} \) component of Equation (8.19) which results from reducing the value of \( R \). This then is consistent with previous conclusions that chemical kinetically controlled devolatilization is prevalent only for smaller particle sizes.

Morris and Keairns (1979) reported 95% devolatilization times based on methane evolution profiles in a fluidised bed reactor using a range of particle sizes, as reported in Chapter 7. Using these reported values as the 95% devolatilization times, and the predictions of the model using the kinetics for methane evolution proposed in Chapter 7 to generate the 95% heating times, this data was also included in Figure 8.2. It can be seen that the data of Morris and Keairns (1979) represents a further shift toward the
purely chemical kinetically controlled regime. The particle sizes employed by Morris and Keairns (1979) ranged from 0.46 mm to 3.68 mm and it can be seen that the smallest particle size employed, 0.46 mm, appears to undergo devolatilization in the kinetically controlled regime. It would be useful to have experimental data for smaller particle sizes to further verify this technique. However it is difficult to obtain such data particularly when considering the particle temperature data. Collection of such data is not within the scope of the present work.

8.4 SUMMARY

A technique has been developed by which the heat transfer controlled and kinetically controlled regimes of coal devolatilization can be distinguished for a large range of operating conditions. A dimensionless plot has been established which compares the ratio between the time required for 95% volatiles evolution, $t_{dev}$, and the time required for the particle to heat to 95% of its final temperature, $t_{heat}$, with the Biot number ($Bi$) to modified Damkohler number ($Da'$) ratio. The Biot number accounts for the contributions of both external and internal heat transfer to the overall heating of the particle and thus represents the magnitude of the thermal resistance to devolatilization. The Damkohler number traditionally used in heterogeneous reaction kinetics has been modified to account for the unique nature of the kinetics of the Distributed Activation Energy Model. It was proposed that when $t_{dev} > t_{heat}$ then chemical kinetically controlled devolatilization is taking place, while when $t_{dev} \sim t_{heat}$ devolatilization is primarily heat transfer controlled. These trends were proposed to be reflected by a plot of $t_{dev} / t_{heat}$ versus $\log\left(\frac{Bi}{Da'}\right)$.

Such a plot was subsequently developed based on the predictions of the model using a wide range of temperatures, particle sizes, kinetic parameters, and heat transfer coefficients. The plot obtained was found to show three distinct regions. At values of $\log\left(\frac{Bi}{Da'}\right) < 4.5$, the rate of the chemical kinetics is greater than that of heat transfer and devolatilization is heat transfer controlled which was reflected by values of $t_{dev} / t_{heat}$.
\[ t_{\text{heat}} \sim 1 \text{ in this region. At higher values of } \log\left( \frac{Bi}{Da'} \right) > 5.5, \text{ devolatilization becomes kinetically controlled which was also consistent with the predicted values of } \frac{t_{\text{dev}}}{t_{\text{heat}}} \gg 1. \text{ There was an intermediate region, } 4.5 < \log\left( \frac{Bi}{Da'} \right) < 5.5, \text{ where it is proposed that devolatilization is driven by a combination of chemical kinetics and heat transfer. The trends observed in this plot are consistent with those expected from a theoretical viewpoint as well as by considering the effect of each parameter on the magnitude of } \log\left( \frac{Bi}{Da'} \right). \text{ However it was deemed necessary to compare these theoretical findings with any available experimental data.}

As has already been mentioned in this study, no comprehensive data presently exists for both temperature response and evolution of volatiles under identical conditions from large coal particles during devolatilization. However, the data collected in the horizontal tube furnace does enable a comparison between the experimentally derived \( \frac{t_{\text{dev}}}{t_{\text{heat}}} \) ratio and that proposed theoretically based on the aforementioned plot. It was found that the experimental data correlated well with the theoretical data derived from the model predictions and, furthermore, devolatilization was occurring well within the heat transfer controlled regime in the horizontal tube furnace.

Using the temperature response data collected in the fluidised bed reactor, and the predicted volatiles evolution profile under identical conditions, it was possible to compare the behaviour in the fluidised bed reactor and the horizontal tube furnace based on the plot. It was found that devolatilization was still occurring in the heat transfer controlled regime however there was a distinct shift toward the kinetically controlled regime (higher values of \( \log\left( \frac{Bi}{Da'} \right) \)) when compared with the horizontal tube furnace data. This was attributed to a shift in the heat transfer mechanism from a combination of external and internal heat transfer in the horizontal tube furnace to predominantly internal heat transfer controlled under fluidised bed conditions. Hence the process is becoming less dominated by heat transfer.
The data reported by Morris and Keairns (1979) for the 95% evolution time for methane evolution from 0.46 mm to 3.68 mm coal particles in a fluidised bed reactor were also used to further validate the proposed technique. Using the model predictions for the 95% heating time this data was compared with the theoretical predictions which again revealed a good correlation. This data exhibited a further shift toward the chemical kinetically controlled regime which is consistent with the observation that smaller particles tend toward kinetically controlled devolatilization, and the smallest particle size reported was found to lie distinctly within the mixed kinetic and heat transfer controlled devolatilization regime. Unfortunately none of the data available resulted in purely kinetically controlled devolatilization as it is likely that the particle sizes necessary are to small to collect particle temperature experiments.

The trends observed in this plot have been shown to be consistent with those expected theoretically and a good comparison has been shown between the theoretical and experimental data. Based on this analysis it can be concluded that the $t_{dev} / t_{heat}$ versus $\log \left( \frac{Bi}{Da'} \right)$ plot developed in this chapter provides a useful tool for distinguishing between kinetically controlled and heat transfer controlled devolatilization. According to the trends observed in this plot it can be concluded that devolatilization is heat transfer controlled for $\log \left( \frac{Bi}{Da'} \right) < 4.5$, while chemical kinetics is dominant for $\log \left( \frac{Bi}{Da'} \right) > 5.5$. In this intermediate region, $4.5 < \log \left( \frac{Bi}{Da'} \right) < 5.5$, devolatilization is controlled by a mixture of chemical kinetics and heat transfer.
Chapter 9

CONCLUSIONS AND IMPLICATIONS OF THE PRESENT WORK

9.1 CONCLUSIONS

The work presented in this study has been aimed at developing a model to accurately predict the behaviour of large coal particles during devolatilization. More particularly, the emphasis of this study has been to develop a model which is capable of predicting both the temperature response and evolution of volatile matter from large coal particles under a variety of operating conditions.

The aims of this study were achieved by developing a multiple particle and water cooled probe technique for gaining accurate measurements for the temperature response at the centre of large coal particles. Experimental data was subsequently collected for the temperature response of both wet and dry coal particles under conditions prevalent in both the horizontal tube furnace and the fluidised bed reactor. Mass loss data was also collected for the experiments conducted in the horizontal tube furnace. Experiments were also conducted to estimate the extent of particle shrinkage for wet coal particles in both the horizontal tube furnace and the fluidised bed reactor. A model was proposed to predict the behaviour of large coal particles during devolatilization and the model was developed such that all of the factors likely to
influence the model predictions, under the experimental conditions relevant to this study, were accounted for. Based on the results of a sensitivity analysis, a number of assumptions relating to specific model parameters were validated and the predictions generated by the model were found to agree well with both the temperature and mass loss data.

Given the success of the model above, the application of the model to estimate kinetic parameters for the evolution of individual volatile species was investigated. Kinetic parameters obtained from the literature were found to underestimate the concentration of methane\(^1\) in the off-gas from a fluidised bed, and alternate kinetics were proposed to alleviate this problem. These alternate kinetics were found to yield accurate predictions for the off-gas concentration of methane at a number of fluidised bed temperatures and particle sizes. This confirms the reliability of these kinetics as well as the applicability of the model in estimating the kinetic parameters for the evolution of individual volatile species.

Finally, the roles of heat and mass transfer in controlling the devolatilization process were investigated under a variety of operating conditions using the predictions generated by the model. It was found that the dominant mechanism during devolatilization can be estimated by considering the heat transfer environment, chemical kinetics, reactor temperature, and particle size based on the heat transfer Biot number, \(Bi\), and a modified Damkholer number, \(Da'\). This represents an improvements on previous techniques which differentiate between heat transfer controlled and chemical kinetically controlled devolatilization based purely on the particle size.

More specifically, the conclusions which can be drawn directly from the results of this study can be summarised as follows:

---
\(^1\) The evolution of methane was used as an example of the models capability.
9.1.1 PARTICLE TEMPERATURE AND MASS LOSS MEASUREMENTS

- The conventional technique for measuring the temperature response at the centre of large coal particles during devolatilization may be affected by thermal conduction along the thermocouple sheath toward the tip of the thermocouple thus leading to an overestimation of the actual temperature response.

- Using multiple particles at the end of the thermocouple, along with a water cooled probe to insulate the thermocouple sheath, more accurate measurements for the temperature response at the centre of large coal particles can be achieved.

- A distinct plateau in the temperature response at \( \sim 100^\circ C \) is apparent for wet low-rank coal particles when using the multiple particle and water cooled probe temperature measurement technique, which is not evident from the conventional technique. This is consistent with observations in the literature, hence confirming the reliability of the aforementioned technique.

- When using data presented in the literature of the temperature response from large coal particles during devolatilization for model validation purpose, care must be taken to ensure that the experimental technique employed was reliable due to the errors which can arise from the thermal conduction effect previously mentioned.

- The data presented in this study represents a comprehensive set of mass loss and temperature data for large low-rank coal particles which is essential for a rigorous validation of the model proposed.

- The results of models developed without a thorough validation of their particle temperature predictions remain doubtful until the particle temperature predictions are validated.

9.1.2 SENSITIVITY ANALYSIS

- The specific heat capacity of the coal was found to have a significant influence on the model predictions and exhibit a greater influence on the model predictions than either of the thermal conductivity or the coal emissivity.

- The convective heat transfer coefficient under fluidised bed conditions was found to have little impact on the model predictions which is due to internal conduction
being the dominant heat transfer mechanism in a fluidised bed heating environment.

- The enthalpy of devolutilization was found to have a moderate impact on the model predictions, however is less than that of the specific heat capacity. Based on this, and the uncertainty surrounding the magnitude and nature of the enthalpy of devolutilization, it can be assumed to be negligible in future modelling applications.

- The surface volatile matter flux was found to have an impact on the model predictions in a purely convective flow heating environment. The impact is reduced in the horizontal tube furnace, due to the contribution of radiation to the total rate of external heat transfer, and becomes almost negligible.

- Assuming an enthalpy of drying similar to that of Chen (1994) results in a significant increase in the total drying time when compared with assuming constant enthalpy of drying hence must be considered in future modelling applications.

- Increasing the effective drying temperature moderately increases the total drying time. However the magnitude of this increase is far less than that resulting from assuming an enthalpy of drying based on Chen (1994). Based on this, and the uncertainty surrounding the magnitude of the effective drying temperature, the effective drying temperature can be assumed to be constant at ~100°C as reported in the literature and consistent with the temperature measurements obtained in this study.

- The effect of particle shrinkage on the model predictions is moderate. As this is a phenomenon which has been confirmed experimentally, it will be included in future modelling applications.

## 9.1.3 Model Predictions

- The model has been shown to be capable of accurately predicting the temperature response and evolution of volatiles from dry coal particles during devolutilization under conditions prevailing in both the horizontal tube furnace and the fluidised bed reactor.
The predictions for the temperature response of wet coal particles in both the horizontal tube furnace and the fluidised bed reactor exhibited some deviation during the initial stage of heating and the latter stages of drying. This deviation was found to be enhanced in the fluidised bed and is likely to be due to thermal conduction effects which could not be overcome. Therefore it was concluded that the temperature measurements are reasonable.

The model was found to accurately predict the mass loss behaviour of wet coal particles during devolatilization, given the relative accuracy of the particle temperature measurements.

Comparing the measured and predicted drying times confirms that assuming an enthalpy of drying similar to that of Chen (1994) gives the most reliable predictions than assuming a constant enthalpy of drying.

The accuracy of the model predictions, and the rigorous nature of the testing using both particle temperature and mass loss data, indicate that the model developed in this study is capable of predicting large coal particle devolatilization behaviour accurately for a variety of operating conditions.

9.1.4 ESTIMATING THE KINETIC PARAMETERS FOR VOLATILES EVOLUTION

The kinetic parameters proposed in the literature for the evolution of individual volatile species remain doubtful until the particle temperature predictions generated by the model employed to estimate these kinetic parameters are verified.

The kinetic parameters for methane evolution proposed in the literature are unable to accurately predict the evolution behaviour of methane based on the predictions of the current model.

Alternate kinetic parameters for methane evolution from Indiana high-volatile C bituminous coal, as elucidated using the present model predictions, are:
Table 9.1 Kinetic parameters for the evolution of methane from Indian high-volatile C bituminous coal during devolatilization.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
<th>j = 1</th>
<th>j = 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{CH_4,j}$</td>
<td>0.3</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>$E_{0,CH_4,j}$ (kJ mol$^{-1}$)</td>
<td>210</td>
<td>265</td>
<td></td>
</tr>
<tr>
<td>$\sigma_{CH_4,j}$ (kJ mol$^{-1}$)</td>
<td>15</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>log$<em>{10}(k</em>{0,CH_4,j})$</td>
<td>13.22</td>
<td>13.22</td>
<td></td>
</tr>
</tbody>
</table>

9.1.5 **REGIMES OF COAL DEVOLATILIZATION**

- In order to assess the dominant mechanism during coal devolatilization factors such as the kinetic parameters, reactor temperature, and the heat transfer environment must be considered in conjunction with the particle size.
- The regime (chemical kinetically controlled or heat transfer controlled) in which devolatilization is occurring can be estimated by considering the ratio of the heat transfer Biot number, $Bi$, to the modified Damkholer number, $Da'$.  
- Generally it can be said that heat transfer is dominant for log$(Bi / Da') < 4.5$ while devolatilization is chemical kinetically controlled for log$(Bi / Da') > 5.5$. In the intermediate region, $4.5 < log(Bi / Da') < 5.5$, devolatilization is controlled by a combination of chemical kinetics and heat transfer.

9.2 **IMPLICATIONS OF THE PRESENT WORK**

Whilst the present work alone represents a rigorous investigation and developmental study into large coal particle devolatilization modelling, the results of this work have a number of implications in terms of the work presently being carried out within the CRC for Low Rank Coals. These implications include:
9.2.1 Fluidised Bed Gasifier Modelling

The first, and most critical, implication of the work presented in this thesis is that it represents a sound and reliable foundation for the extension of the model presented to consider all of the transformations applicable to large coal particles under fluidised bed gasification or combustion conditions. The development of models to simulate the behaviour of fluidised bed gasifiers and combustors is a major milestone for the CRC for Low Rank Coal. This project forms the basis for the continuing development of a model to predict the behaviour of a single coal particle under such conditions.

Given the success of the model presented, it is proposed that this project can proceed according to the following steps:

Step 1 Incorporate the effects of volatiles combustion at the particle surface into the model predictions. This will influence the heat transfer to the particle surface as well as consuming oxygen which otherwise may be utilised for char combustion. Note that this stage will require knowledge of the mass transfer behaviour of the volatiles once emitted from the coal particle along with the mass transfer of oxygen into the char particle boundary layer. This step is supported by experimental work currently being undertaken within the CRC for Low Rank Coal into the fate of volatile matter in fluidised bed gasifiers.

Step 2 Incorporate the char combustion or gasification reactions into the overall model. This will require knowledge of the mass transfer of the gaseous reactants to the boundary layer and into the pore structure of the char particles, as well as the reaction kinetics at the surface of the char particles. This step is supported by work currently being undertaken within the CRC for Low Rank Coal into the kinetics of low-rank coal char gasification.

Step 3 Incorporation of the single particle reaction model resulting after Step 2 above into model which consider the complex fluid dynamic behaviour of
typical fluidised bed gasifiers or combustors. This will generate a unique model for predicting the behaviour of a fluidised bed gasifiers or combustor which accounts for both the complex physio-chemical and hydrodynamic phenomenon occurring in such coal conversion systems. Such a model will be ideally suited to scale-up and design of commercial scale gasifiers and will be the most advanced model of its type presently available.

9.2.2 FOULING, AGGLOMERATION AND DEFLUIDISATION

One of the major limitations in utilising many low-rank coals for power generation is the operational problems such as fouling, agglomeration, and defluidisation which arise during coal conversion processes. The CRC for Low Rank Coals is presently undertaking research into the fate of inorganics under fluidised bed gasification conditions, and it is these inorganic species which contribute to the operational problems so mentioned. More direct research is also underway into the mechanisms leading to agglomeration and defluidisation which are similar to those which result in fouling. It is possible then that the results of this research may be combined with the predictions of the fluidised bed gasifier model to indicate the propensity of a particular coal toward agglomeration or defluidisation under specific operating conditions, thus enabling a stable range of operating conditions to be predicted.

9.2.3 FLUE-GAS EMISSIONS

As was discussed in Section 1.3.3, the flue gas emissions of fluidised bed gasifiers and combustors are typically high in NO\textsubscript{x} and SO\textsubscript{x} gases. These gases have severe environmental impacts and it is desirable to reduce their magnitude in order to minimise their effect on the environment. Historically the approach has been to eliminate these gases from the flue gas once they have been generated. However, more recently the focus has shifted toward understanding the formations of these gases during the devolutilization and gasification or combustion stages of the coal itself.
Research presently underway within the CRC for Low Rank Coals is aimed at investigating the nature of sulphur transformations and their impact on the sulphurous products generated during coal devolatilization which are pre-cursors to the SO\textsubscript{x} gases present in the flue-gas. The large particle coal devolatilization model developed in this thesis has already been employed to assist in characterising the nature and location of the specific transformations in large coal particle based on the predicted transient radial particle temperature response and the transformations observed from temperature programmed experiments. The results of this work have been highly successful and further information can be obtained from Telfer et al. (1998).

Given the success of utilising the model developed in this thesis for analysing the behaviour of sulphur during coal devolatilization, it is reasonable to suggest that similar work could be undertaken to investigate the behaviour of nitrogen present in low-rank coals using similar techniques. Therefore, the model developed in this study has applications pertinent to the release of SO\textsubscript{x} and NO\textsubscript{x} gases from low-rank coal gasifiers and combustors, and the model predictions may assist in the development of technique or selection of operating conditions under which the formation of these species can be minimised.

9.3 EVALUATION OF THE PRESENT STUDY

The focus of the present study, large coal particle devolatilization, has been the centre of much research over recent years and the published literature was thoroughly reviewed prior to undertaking this study. It was observed that considerable work has dealt with the chemical kinetics of large particle coal devolatilization. However, very little focus has been placed on the particle temperature predictions of such models. Given the link between chemical kinetics and temperature it was concluded that this gap in the present knowledge must be thoroughly investigated.

There are a number of areas in which the results of this study can be seen to improve the present status of knowledge. These include:
• The development of an improved technique for measuring the temperature response at the centre of large coal particles during heating.

• The generation of a comprehensive set of experimental data for the temperature response and evolution of volatile matter under identical operating conditions for a range of operating temperatures and particle sizes.

• A thorough investigation of the role of a number of parameters on the model predictions obtained from the large coal particle devolatilization model, thus enabling reasonable conclusions to be drawn regarding each of these parameters.

• A thorough validation of the model predictions was undertaken using experimental data for both the temperature response and evolution of volatile matter derived from various reactor types, particle sizes, reactor temperatures, and using both wet and dry coal particles. This represents the most rigorous validation of a large particle coal devolatilization model available in the literature.

• Alternate kinetic parameters for the evolution of methane were proposed, based on the model predictions, enabling accurate predictions for the methane evolution profile from various sized particles to be accurately predicted at a number of fluidised bed reactor temperatures. These kinetics represent a significant improvement over kinetics previously proposed in the literature for the methane evolution data employed.

• A technique has been developed to predict the dominant mechanism during the devolatilization of large coal particles which accounts for the particle size, reactor temperature, heat transfer environment and chemical kinetics. This represents an improvement over previous techniques which consider only the particle size.

It is considered therefore, that this thesis has made a significant contribution to the science of large low-rank coal particle devolatilization, and represents a solid foundation upon which the future work discussed in Section 9.2 can be continued.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A,B,C,D,E$</td>
<td>Constants in Equation (2.21)</td>
<td>-</td>
</tr>
<tr>
<td>$A$</td>
<td>Constant in Equation (8.1)</td>
<td>-</td>
</tr>
<tr>
<td>$A</td>
<td>_{r=r_0}$</td>
<td>Surface area of coal particle</td>
</tr>
<tr>
<td>$A^s$</td>
<td>Ackermann correction factor</td>
<td>-</td>
</tr>
<tr>
<td>$Ar$</td>
<td>Archimedes number</td>
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</tr>
<tr>
<td>$a$</td>
<td>Constant in Equation (2.6)</td>
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</tr>
<tr>
<td>$b$</td>
<td>Constant in Equation (2.6)</td>
<td>-</td>
</tr>
<tr>
<td>$Bi$</td>
<td>Biot number</td>
<td>-</td>
</tr>
<tr>
<td>$C$</td>
<td>Constant in Equation (2.3)</td>
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<tr>
<td>$C_a$</td>
<td>Concentration of reactant &quot;a&quot; at surface</td>
<td>mol m⁻²</td>
</tr>
<tr>
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<td>Dimensionless parameter in Equation (2.29)</td>
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</tr>
<tr>
<td>$C_0$</td>
<td>Initial moisture content</td>
<td>g (g dry coal)⁻¹</td>
</tr>
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<td>$C^e$</td>
<td>Dimensionless parameter in Equation (2.27)</td>
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</tr>
<tr>
<td>$C_{Da}$</td>
<td>Drag coefficient for an isolated sphere</td>
<td>-</td>
</tr>
<tr>
<td>$C_{Da_u}$</td>
<td>Porosity drag dependent drag coefficient for a sphere in a multiparticle system</td>
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</tr>
<tr>
<td>$C_p$</td>
<td>Specific heat capacity</td>
<td>J kg⁻¹ K⁻¹</td>
</tr>
<tr>
<td>$C_{p,m}$</td>
<td>Mean specific heat capacity of coal</td>
<td>J kg⁻¹ K⁻¹</td>
</tr>
<tr>
<td>$C_{p,vol}$</td>
<td>Specific heat capacity of volatiles</td>
<td>J kg⁻¹ K⁻¹</td>
</tr>
<tr>
<td>$C_t$</td>
<td>Moisture content at time, $t$</td>
<td>g (g dry coal)⁻¹</td>
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<tr>
<td>$[CH_4]_{in-bed}$</td>
<td>In-bed concentration of methane</td>
<td>mol%</td>
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<td>$[CH_4]_{off-gas}$</td>
<td>Concentration of methane in off-gas</td>
<td>mol%</td>
</tr>
<tr>
<td>$D_a$</td>
<td>Gas diffusivity</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>$D_{thermal}$</td>
<td>Thermal diffusivity (= $\alpha$)</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>$Da$</td>
<td>Damkholer number</td>
<td>-</td>
</tr>
<tr>
<td>$Da'$</td>
<td>Modified Damkholer number</td>
<td>-</td>
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### Nomenclature

<table>
<thead>
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<th>Description</th>
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<tbody>
<tr>
<td>( d )</td>
<td>Diameter</td>
</tr>
<tr>
<td>( d_p )</td>
<td>Particle diameter</td>
</tr>
<tr>
<td>( E )</td>
<td>Activation energy</td>
</tr>
<tr>
<td>( E_0 )</td>
<td>Mean activation energy</td>
</tr>
<tr>
<td>( E(t) )</td>
<td>Residence time distribution function</td>
</tr>
<tr>
<td>( F )</td>
<td>Relaxation factor in Equation (4.28)</td>
</tr>
<tr>
<td>( F_{rad} )</td>
<td>Radiation shape factor</td>
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<td>( f(E) )</td>
<td>Activation energy distribution function</td>
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<tr>
<td>( f_i )</td>
<td>Average level frequency of bubbles in freely bubbling bed</td>
</tr>
<tr>
<td>( f_T )</td>
<td>Constant in correlation of Prins (1987) in Table 2.6</td>
</tr>
<tr>
<td>( FB )</td>
<td>Fluidised bed</td>
</tr>
<tr>
<td>( F_0 )</td>
<td>Fourier number</td>
</tr>
<tr>
<td>( H )</td>
<td>Expanded bed height</td>
</tr>
<tr>
<td>( h )</td>
<td>Heat transfer coefficient</td>
</tr>
<tr>
<td>( \bar{h} )</td>
<td>Mean heat transfer coefficient in a fluidised bed</td>
</tr>
<tr>
<td>( h_{bub} )</td>
<td>Heat transfer coefficient in a bubble</td>
</tr>
<tr>
<td>( h_{kc} )</td>
<td>Gas convective heat transfer coefficient in the emulsions phase</td>
</tr>
<tr>
<td>( h_{pc,a} )</td>
<td>Particle convective heat transfer coefficient when the particle rises during circulation in the bed</td>
</tr>
<tr>
<td>( h_{pc,d} )</td>
<td>Particle convective heat transfer coefficient when the particle sinks during circulation in the bed</td>
</tr>
<tr>
<td>( h_{p,cond} )</td>
<td>Heat transfer within the coal particle via thermal conduction</td>
</tr>
<tr>
<td>( h_{p,conv-rad} )</td>
<td>Heat transfer to the coal particle via convection and radiation</td>
</tr>
<tr>
<td>( h_{p,T} )</td>
<td>Heat transfer from the particle to the</td>
</tr>
</tbody>
</table>

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**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_{T,\text{cond}}$</td>
<td>Heat transfer along the thermocouple via thermal conduction</td>
<td>-</td>
</tr>
<tr>
<td>$h_{T,\text{conv+rad}}$</td>
<td>Heat transfer to thermocouple via convection and radiation</td>
<td>-</td>
</tr>
<tr>
<td>$H_{w,1}$</td>
<td>Enthalpy of drying of free moisture</td>
<td>kJ kg$^{-1}$</td>
</tr>
<tr>
<td>$H_{w,2}$</td>
<td>Enthalpy of drying at MC$_2$</td>
<td>kJ kg$^{-1}$</td>
</tr>
<tr>
<td>$H_{w,3}$</td>
<td>Enthalpy of drying at 0 g H$_2$O / g dry coal</td>
<td>kJ kg$^{-1}$</td>
</tr>
<tr>
<td>HTF</td>
<td>Horizontal tube furnace</td>
<td>-</td>
</tr>
<tr>
<td>$K_1$</td>
<td>Constant in Equation (2.4)</td>
<td>K$^{-1}$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>Constant in Equation (2.4)</td>
<td>K</td>
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<tr>
<td>$k$</td>
<td>Rate constant</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Frequency factor</td>
<td>s$^{-1}$</td>
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<tr>
<td>$k$</td>
<td>Thermal conductivity</td>
<td>W m$^{-1}$ K$^{-1}$</td>
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<tr>
<td>$\overline{k}_m$</td>
<td>Mean thermal conductivity of coal</td>
<td>W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$k_{di}$</td>
<td>Rate of decomposition of species i</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$k_e$</td>
<td>Effective thermal conductivity of incipiently fluidised bed</td>
<td>W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$k_{vi}$</td>
<td>Rate of evolution of species i</td>
<td>s$^{-1}$</td>
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<tr>
<td>$L$</td>
<td>Distance from tip of thermocouple to $T_{TI}$</td>
<td>m</td>
</tr>
<tr>
<td>$M_{60}$</td>
<td>Mass remaining after 60 minutes</td>
<td>g</td>
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<tr>
<td>$M_{\text{crucible}}$</td>
<td>Crucible mass</td>
<td>g</td>
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<tr>
<td>$M_{0,m}$</td>
<td>Original mass remaining in shell m</td>
<td>g</td>
</tr>
<tr>
<td>$M_{t,m}$</td>
<td>Mass remaining in shell m after time, t</td>
<td>g</td>
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<td>$\dot{M}_{\text{dev}}$</td>
<td>Rate of mass loss via devolatilization</td>
<td>kg s$^{-1}$</td>
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<tr>
<td>$m$</td>
<td>Shell number</td>
<td>-</td>
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<tr>
<td>$m_i$</td>
<td>Total yield of species i</td>
<td>g</td>
</tr>
<tr>
<td>MC</td>
<td>Original moisture content of coal</td>
<td>g (g dry coal)$^{-1}$</td>
</tr>
<tr>
<td>MC$_1$</td>
<td>Critical moisture content defining free and loosely bound moisture</td>
<td>g (g dry coal)$^{-1}$</td>
</tr>
<tr>
<td>MC$_2$</td>
<td>Critical moisture content defining loosely bound and tightly bound moisture</td>
<td>g (g dry coal)$^{-1}$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>$N$</td>
<td>Number of sample points in Equation (3.4)</td>
<td></td>
</tr>
<tr>
<td>$N_R$</td>
<td>Volatile matter flux at particle surface kg m$^{-2}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$\dot{N}_{N_2}$</td>
<td>Molar nitrogen flowrate gmol s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>Reaction order -</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>Constant in correlation of Prins (1987) in Table 2.6 -</td>
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</tr>
<tr>
<td>$n$</td>
<td>Constant in Equation (8.1) -</td>
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</tr>
<tr>
<td>$Nu$</td>
<td>Nusselt number -</td>
<td></td>
</tr>
<tr>
<td>$p$</td>
<td>Probability of the active particle residing in the dense phase during one circulation in the bed -</td>
<td></td>
</tr>
<tr>
<td>$p'$</td>
<td>Probability of the active particle residing in the dense phase while it rises during one circulation in the bed -</td>
<td></td>
</tr>
<tr>
<td>$Pr$</td>
<td>Prandtl number -</td>
<td></td>
</tr>
<tr>
<td>$Q_{dev}$</td>
<td>Energy required to drive devolatilization reactions J m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$Q_{drying}$</td>
<td>Energy required for moistur removal J m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$q$</td>
<td>Tortuosity of fluidised bed -</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant J gmol$^{-1}$ K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>Coal particle radius m</td>
<td></td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number -</td>
<td></td>
</tr>
<tr>
<td>$r$</td>
<td>Radial position within coal particle m</td>
<td></td>
</tr>
<tr>
<td>$r$</td>
<td>Surface reaction rate mol m$^{-2}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$r'$</td>
<td>Modified reaction rate s$^{-1}$</td>
<td></td>
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<tr>
<td>$SF$</td>
<td>Shrinkage factor -</td>
<td></td>
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<tr>
<td>$SF_{t,m}$</td>
<td>Degree of shrinkage in shell $m$ after time, $t$ -</td>
<td></td>
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<tr>
<td>$T$</td>
<td>Temperature K</td>
<td></td>
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<tr>
<td>$T_{drying}$</td>
<td>Effective drying temperature K</td>
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<tr>
<td>$T_M$</td>
<td>Temperature at tip of thermocouple K</td>
<td></td>
</tr>
<tr>
<td>$T_P$</td>
<td>Temperature at centre of coal particle K</td>
<td></td>
</tr>
<tr>
<td>$T_{TI}$</td>
<td>Temperature of thermocouple sheath b/w</td>
<td></td>
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{T2}$</td>
<td>Temperature of thermocouple sheath inside of water-cooled probe</td>
<td>K</td>
</tr>
<tr>
<td>$T_{95%}$</td>
<td>Particle temperature after 95% of heating is complete</td>
<td>K</td>
</tr>
<tr>
<td>$T(r,t)$</td>
<td>Temperature at radial position $r$ at time $t$</td>
<td>K</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>$t_c$</td>
<td>Contact time</td>
<td>s</td>
</tr>
<tr>
<td>$t_{dev}$</td>
<td>Devolutilization time</td>
<td>s</td>
</tr>
<tr>
<td>$t_{heat}$</td>
<td>Particle heating time</td>
<td>s</td>
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<td>$U_0$</td>
<td>Superficial gas velocity</td>
<td>m s$^{-1}$</td>
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<td>$U_R$</td>
<td>Bubble rise velocity</td>
<td>m s$^{-1}$</td>
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<tr>
<td>$U_D$</td>
<td>Dense phase velocity</td>
<td>m s$^{-1}$</td>
</tr>
<tr>
<td>$U_R$</td>
<td>Average rise velocity of active particles</td>
<td>m s$^{-1}$</td>
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<tr>
<td>$U_{mf}$</td>
<td>Minimum fluidisation velocity</td>
<td>m s$^{-1}$</td>
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<tr>
<td>$V$</td>
<td>Volaties yield</td>
<td>g (g dry/wet coal)$^{-1}$</td>
</tr>
<tr>
<td>$V^*$</td>
<td>Ultimate volaties yield</td>
<td>g (g dry/wet coal)$^{-1}$</td>
</tr>
<tr>
<td>$V_{M0}$</td>
<td>Original volatile matter content</td>
<td>g (g dry/wet coal)$^{-1}$</td>
</tr>
<tr>
<td>$V_{o,m}$</td>
<td>Original volume of shell $m$</td>
<td>m$^3$</td>
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<tr>
<td>$V_{l,m}$</td>
<td>Volume of shell $m$ after time $t$</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$W^*$</td>
<td>Original moisture content</td>
<td>g (g wet coal)$^{-1}$</td>
</tr>
<tr>
<td>$X$</td>
<td>Penetration depth of active particle in fluidised bed</td>
<td>m</td>
</tr>
<tr>
<td>$X_{H_2O}$</td>
<td>Mass fraction of moisture</td>
<td>g (g wet coal)$^{-1}$</td>
</tr>
<tr>
<td>$X_{H_2O}'$</td>
<td>Fracicion of original moisture removed</td>
<td>g (g wet coal)$^{-1}$</td>
</tr>
<tr>
<td>$X_j$</td>
<td>Fraction of voatiles derived from source $j$</td>
<td>-</td>
</tr>
<tr>
<td>$\bar{x}$</td>
<td>Population mean in Equation (3.4)</td>
<td>-</td>
</tr>
<tr>
<td>$z$</td>
<td>Test parameter in Equation (3.4)</td>
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### Greek Symbols

<table>
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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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</thead>
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<tr>
<td>α</td>
<td>Constant in Equation (2.11)</td>
<td>s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>α</td>
<td>Thermal diffusivity</td>
<td>m&lt;sup&gt;2&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>β</td>
<td>Constant in Equation (2.11)</td>
<td>g mol kJ&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>β&lt;sub&gt;f&lt;/sub&gt;</td>
<td>Constant in Equation (2.13)</td>
<td>-</td>
</tr>
<tr>
<td>ΔH&lt;sub&gt;dev&lt;/sub&gt;</td>
<td>Enthalpy of devolatilization</td>
<td>kJ kg&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>ΔH&lt;sub&gt;drying&lt;/sub&gt;</td>
<td>Enthalpy of drying</td>
<td>kJ kg&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>ΔH&lt;sub&gt;max,1&lt;/sub&gt;</td>
<td>Maximum value of enthalpy of devolatilization for 300 &lt; T &lt; T&lt;sub&gt;1&lt;/sub&gt;</td>
<td>kJ kg&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>ΔH&lt;sub&gt;max,2&lt;/sub&gt;</td>
<td>Maximum value of enthalpy of devolatilization for T&lt;sub&gt;1&lt;/sub&gt; &lt; T &lt; T&lt;sub&gt;2&lt;/sub&gt;</td>
<td>kJ kg&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>ΔM&lt;sub&gt;60&lt;/sub&gt;</td>
<td>Mass loss after 60 minutes</td>
<td>g</td>
</tr>
<tr>
<td>ΔM&lt;sub&gt;t&lt;/sub&gt;</td>
<td>Mass loss after t minutes</td>
<td>g</td>
</tr>
<tr>
<td>Δr</td>
<td>Shell thickness</td>
<td>m</td>
</tr>
<tr>
<td>Δt</td>
<td>Time increment</td>
<td>s</td>
</tr>
<tr>
<td>δ&lt;sub&gt;p&lt;/sub&gt;</td>
<td>Conduction thickness parameter</td>
<td>-</td>
</tr>
<tr>
<td>δX&lt;sub&gt;H&lt;sub&gt;2&lt;/sub&gt;O&lt;/sub&gt;</td>
<td>Moisture content correction factor</td>
<td>-</td>
</tr>
<tr>
<td>ε</td>
<td>Emissivity</td>
<td>-</td>
</tr>
<tr>
<td>ε&lt;sub&gt;rad&lt;/sub&gt;</td>
<td>Overall emissivity</td>
<td>-</td>
</tr>
<tr>
<td>ε&lt;sub&gt;mf&lt;/sub&gt;</td>
<td>Voidage at minimum fluidisation</td>
<td>-</td>
</tr>
<tr>
<td>λ</td>
<td>Parameter in Equation (2.31)</td>
<td>-</td>
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<tr>
<td>μ&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Proposed population mean in Equation (3.4)</td>
<td>-</td>
</tr>
<tr>
<td>θ</td>
<td>Dimensionless particle temperature</td>
<td>K</td>
</tr>
<tr>
<td>θ&lt;sub&gt;dev&lt;/sub&gt;</td>
<td>Dimensionless devolatilization time</td>
<td>-</td>
</tr>
<tr>
<td>ρ</td>
<td>Density</td>
<td>kg m&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Original particle density</td>
<td>kg m&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;o,m&lt;/sub&gt;</td>
<td>Original density of coal in shell m</td>
<td>kg m&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;t,m&lt;/sub&gt;</td>
<td>Density of coal in shell m after time t</td>
<td>kg m&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Density of dense phase in incipiently fluidised bed</td>
<td>kg m&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
Nomenclature

$\sigma$  Standard deviation in activation energy  kJ g mol$^{-1}$
$\sigma_{\text{rad}}$  Stephan-Boltzmann constant  W m$^{-2}$ K$^{-4}$
$\nu_m$  Fraction of total volatile matter remaining  -

Super/Sub-scripts

0  Initial conditions
1  Position 1
2  Position 2
$a$  Surrounding temperature
$a$  Active particle
$b$  Bubble phase
$b$  Fluidised bed
$c$  Coal
$\text{conv}$  Convection
CH$_4$  Methane
dev  Devolatilization
e  Emulsion phase
$fb$  Fluidised bed
g  Gas
H$_2$O  Moisture
$i$  Volatile species
$i$  Inert bed material
$j$  Volatile matter or volatile species Source
$k$  Source of species i during devolatilization
$m$  Shell number
$p$  Particle
$\text{rad}$  Radiation
$wb$  Wet-bulb temperature
$w/d$  Wet/dry interface
$\infty$  After infinite time
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APPENDIX A

Fluidised Bed Convective Heat Transfer
Model Parameters

The tables in this Appendix detail the correlations used to determine the parameters required to estimate the convective heat transfer coefficient according to Equations (2.25), and (4.12) to (4.17).

Table A1 lists the parameters and associated correlations required to calculate the conduction film thickness, $\delta_p$, in Equations (4.12) and (4.13).

Table A2 lists the parameters and associated correlations required to calculate the thermophysical parameters, $k_e$ and $\rho_e$, in Equations (4.12) and (4.13).

Table A3 lists the parameters and associated correlations required to calculate the porosity dependent drag coefficient for a sphere in a multiparticle system, $C_{D_ea}$, and the bed tortuosity, $q$, in Equation (4.14).

Table A4 lists the parameters and associated correlations required to calculate the isolated sphere drag coefficient, $C_{Da}$, in Equation (4.15), along with the hydrodynamic parameters required to calculate the probability parameters in Equations (4.16) and (4.17).
Table A1 Parameters and associated correlations used to calculate the conduction film thickness, $\delta_p$, in Equations (4.12) and (4.13).

<table>
<thead>
<tr>
<th>$\delta_p$</th>
<th>$4\Psi_a \left{ (\Omega + 1) \ln \Omega - 1 \right} + 2\left( 1 - \Psi_a \right) \left{ \sqrt{2} + \Omega \right}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Psi_a$</td>
<td>$(1 - \varepsilon_{mf})^{2/3}$</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>$2\Theta / d_i$</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>$2\Lambda \frac{2 - \gamma}{\gamma}$</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>$10^{-2} \left( \frac{T_b}{T_b + 132.5} \right) \frac{1}{P}$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$8.3T_b^{-0.42}$</td>
</tr>
</tbody>
</table>

Table A2 Parameters and associated correlations required to calculate the thermophysical parameters, $k_e$ and $\rho_e$, in Equations (4.12) and (4.13).

<table>
<thead>
<tr>
<th>$k_e$</th>
<th>$k_e = k_e^0 + 0.1\rho_g C_{p,g} d_i U_{mf}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_e^0$</td>
<td>$k_e^0 \left{ 1 + (1 - \varepsilon_{mf}) \left( 1 - \frac{k_e}{k_i} \right) \left[ \frac{k_e}{k_i} + 0.28 \varepsilon_{mf} \right] \right}^{-1}$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>$0.63 \left( \frac{k_i}{k_e} \right)^{0.18}$</td>
</tr>
<tr>
<td>$\rho_e$</td>
<td>$\rho_i \left( 1 - \varepsilon_{mf} \right) + \varepsilon_{mf} \rho_g$</td>
</tr>
</tbody>
</table>
Table A3 Parameters and associated correlations required to calculate the porosity dependent drag coefficient for a sphere in a multiparticle system, $C_{Dea}$, and the bed tortuosity, $q$, in Equation (4.14).

| $C_{Dea}$ | \[
\frac{24}{\text{Re}_e} \left\{ \frac{2\varepsilon (1 - \varepsilon_m)}{q} + (10^w - 1) \right\} \]
| $\text{Re}_e$ | \[
\frac{d_a U_m \rho_f}{\mu_f} \]
| $q$ | \[
\left\{ 1 - 0.9 \left( 1 - \varepsilon_m \right)^{2/3} \left( \varepsilon_m - 0.25 \right)^{1/3} \right\}^{-1} \]
| $z$ | \[
5.3 \left( \frac{\varepsilon_m}{1 - \varepsilon_m} \right)^{0.3} \frac{q^2}{\mu_f} \]
| $w$ | \[
0.261 \text{Re}_e^{0.369} - 0.105 \text{Re}_e^{0.431} - 0.124 \left( 1 + \left[ \log_{10} \text{Re}_e \right]^2 \right)^{-1} \]

Table A4 Parameters and associated correlations required to calculate the isolated sphere drag coefficient, $C_{Du}$, in Equation (4.15), along with the hydrodynamic parameters required to calculate the probability parameters in Equations (4.16) and (4.17).

| $C_{Du}$ | \[
\frac{24}{\text{Re}_b} \cdot 10^w \]
| $\text{Re}_b$ | \[
\frac{3d_s U_m \rho_f}{\mu_f} \]
| $w$ | \[
0.261 \text{Re}_b^{0.369} - 0.105 \text{Re}_b^{0.431} - 0.124 \left( 1 + \left[ \log_{10} \text{Re}_b \right]^2 \right)^{-1} \]
| $U_B$ | \[
\left( U_v - U_m \right) + 0.711 \sqrt{g d_B} \]
| $d_B$ | \[
0.3 \left( \frac{U_v - U_m}{g^{1/5} X} \right)^{0.4} \left\{ \left( H + 4 \sqrt{A_0} \right)^{1.8} - \left( H - X + 4 \sqrt{A_0} \right)^{1.8} \right\} \]
| $U_D$ | \[
\frac{\alpha_v \varepsilon_b U_B}{1 - \varepsilon_b - \alpha_w \varepsilon_b} \]

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<table>
<thead>
<tr>
<th>$\varepsilon_b$</th>
<th>$\frac{U_0 - U_{mf}}{U_b + 2U_{mf}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_r$</td>
<td>$0.19(U_0 - U_{mf})^{1/2}$</td>
</tr>
<tr>
<td>$f_l$</td>
<td>$\left{ \frac{0.0195(2H - X) + 0.57}{(0.039H + 0.57)^2[0.039(H - X) + 0.57]^2} \right}^{10^4}$</td>
</tr>
</tbody>
</table>