



7

Reaction rate modelling of coal devolatilization

7.1 Introduction

Yield- and quality assessments of products from devolatilization provide valuable insights into the structural and molecular changes occurring during the degradation of coal to form gas, tar and char. These were the main aspects addressed in Chapter 6. Formulation of a fundamental model describing volatile evolution applicable to large coal particles requires the evaluation of the rate behaviour of coal during thermal degradation. The description of the devolatilization of large coal particles with a comprehensive mathematical model requires knowledge of both intrinsic kinetics and transport properties. This therefore necessitates an investigation of the rate behaviour of both small- and large coal particles.

The evaluation and modelling of rate loss behaviour during coal devolatilization (in particular for large coal particles) are therefore the main focus of this chapter. This chapter includes a discussion of the experimental procedures followed as well as the subsequent results obtained. An overview of the coals and materials used for the investigation is given in Section 7.2, while the experimental methodology and -program used for evaluating coal devolatilization behaviour are addressed in Sections 7.3 and 7.4, respectively. This is followed by an overview of the modelling strategies employed for both small- and large particles in Section 7.5.

Experimental- and modelling results obtained are discussed in two consecutive sections. A full account of the quantitative- and qualitative devolatilization behaviour of both small- and large coal particles is provided in Section 7.6. This includes a discussion regarding data acquisition and –normalisation of the respective mass loss results obtained for both small and large particle devolatilization. The evaluation of intrinsic kinetics and the validation of the large particle model are respectively discussed in Section 7.7, whereafter an overall summary of the important conclusions will be provided in Section 7.8.

7.2 Materials used

7.2.1 Coals

Reaction rate and modelling behaviour during coal devolatilization was assessed on the three non-caking coals from the Witbank coalfields (coals INY, UMZ and G#5) as well as the caking coal (coal TSH) from the Venda-Pafuri district. An overview of the characteristic (using both conventional- and advanced techniques) properties of these four coals was provided in Chapters 4 and 5. Powdered samples ($\sim 200\ \mu\text{m}$) as well as large coal particles (mean coal particle size of 20 mm) were used for the experiments. The particle selection methodology for the large coal particles was discussed in the previous chapter and a detailed account thereof can be found in Section 6.3.

7.2.2 Gas

An inert gas was used for the investigation of devolatilization rate loss behaviour to ensure a completely inert environment, free from any oxidative and reductive gases and to subsequently remove formed product gases from the coal particle to ensure the minimization of any possible secondary surface reactions. For this purpose, ultra pure N_2 gas (ultra high purity grade: 99.999%; product no.: 511204-SE-C), as supplied by African Oxygen (AFROX), was chosen as carrier gas.

7.3 Experimental apparatus

7.3.1 Overview

An understanding of the devolatilization rate behaviour of coal requires the measurement of mass loss as a function of operating conditions. Large coal particle devolatilization consists of a mixture of rate determining mechanisms (kinetics and transport phenomena) and therefore necessitates the need of decoupling kinetic measurements from large particle measurements. For this purpose both small particle (powder) and large particle work was conducted. An

overview of deriving intrinsic kinetics and establishing a large particle devolatilization model was given in Chapter 3. A Mettler-Toledo TGA/DSC 1 Star[®] was used for evaluating the mass loss behaviour of the powdered samples, whilst a self-fabricated thermogravimetric analyser (TGA), especially developed for large coal particles, was used to evaluate the devolatilization behaviour of the four coals. The use of TGA systems has been successfully applied by a number of authors such as Johnson (1979 & 1981), Schumacher *et al.* (1986), Mühlen and Sulima (1986), Calo and Suuberg (1999), Njapha (2003), Kajitani *et al.* (2006) and Kaitano (2007) in investigating coal conversion rates in different gaseous environments. More recently the large particle TGA (LPTGA) has been successfully used by Beukman (2009) and Van der Merwe (2010) for studying the devolatilization and CO₂ gasification behaviour of coal.

Although widely used, TGA systems can present some limitations regarding the measure of meaningful kinetic data, especially for coal devolatilization studies. One problem that arises with the use of small particle TGA systems is the shape of the sample, which is normally restricted to the design of the sample holder or pan on which coal particles are stacked (Kandiyoti *et al.*, 2006). In particular, stacked coal particles form shallow fixed beds, where the close proximity of sample particles and evolving volatile products (tars and volatile gases) can lead to the deposition of tars on the solid devolatilizing surfaces and the subsequent cracking; and re-polymerisation of the latter to form additional char. Furthermore, if no provision is made for sufficient gas flow through the sample bed, mass transfer resistances can become more apparent and derived kinetics will therefore not reflect the characteristic kinetic behaviour of the coal but rather that of the size or shape of the sample. Another limitation of TGA systems is concerned with the ranges of applicable heating rates (Kandiyoti *et al.*, 2006). In some instances, TGA systems are generally rated to work at heating rates of up to 200 °C/s, which is much lower compared to some relevant industrial applications such as devolatilization during pf-combustion or fluidized bed gasification where heating rates can exceed even 1000 °C/s. A gap therefore exists between the capabilities of TGA systems and heating rates required for effectively investigating aspects of typical industrial applications. In addition, rapid heating of coal particles (high heating rates) also provides some additional difficulties, especially for stacked coal samples. Although the outer particles of the stacked sample might experience the applied heating rate, noticeable temperature gradients could exist through the rest of the sample. This in turn can lead to the derivation of inadequate kinetic results due to the non-uniform devolatilization of the coal sample as a result of additional heat transfer resistances.

7.3.2 Small particle thermogravimetric analyser (Mettler-Toledo TGA/DSC 1 STAR^e)

7.3.2.1 Operation and limitations

Intrinsic, devolatilization rate measurements were performed on a Mettler-Toledo TGA/DSC 1 STAR^e thermogravimetric system. An illustrated schematic representation of the system is given in Figure 7.1. As in the case of any thermogravimetric system, sample mass loss is measured against temperature under specified environmental conditions and retained on an appropriate data acquisition interface.

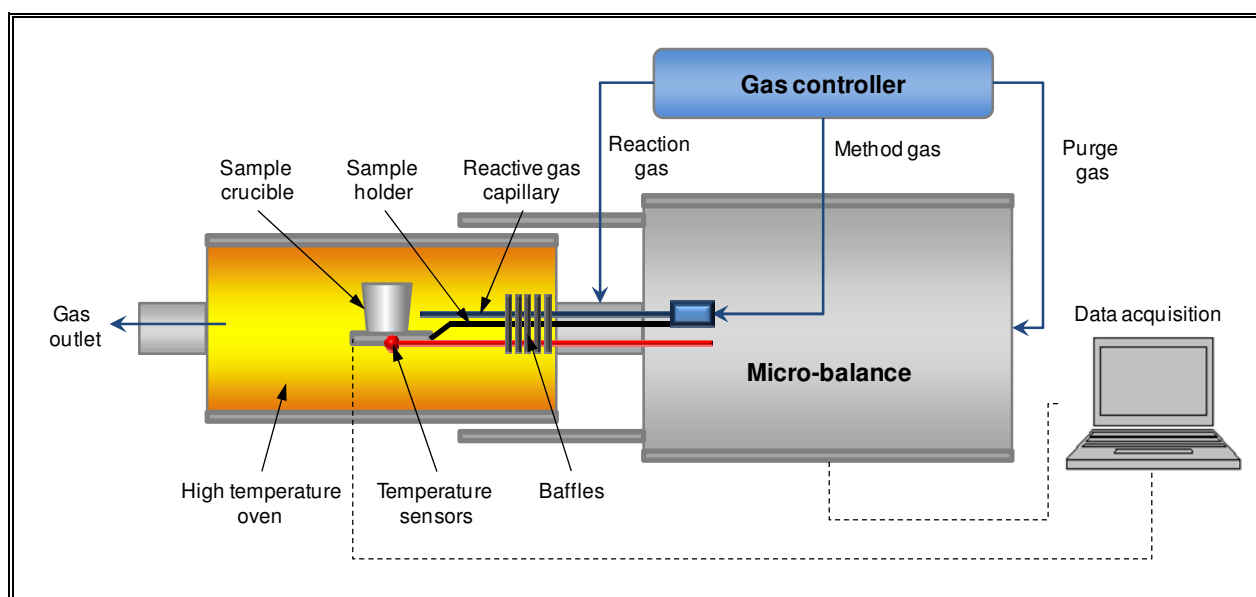


Figure 7.1 Schematic overview of the Mettler-Toledo TGA/DSC 1 STAR^e system.

Empty sample crucibles are automatically weighed and calibrated prior to analyses to ensure that the mass recorded during each analysis resembles that of the sample. Mass measurement is accomplished with the aid of a supported platinum/ceramic rod connected to a parallel-guided micro-balance, equipped with internal calibration ring weights to ensure unsurpassed accuracy. Hereafter, a sample is weighed and loaded into an appropriate sample crucible and placed on the designated space of the sample carousel. Crucibles are constructed of alumina and can be filled with sample volumes of between 20 μL and 900 μL , while the carousel has the capability of handling a total number of 34 crucibles (not shown in the schematic representation). Sample crucibles are introduced into the high temperature oven and placed on a supported platinum/ceramic rod via a universal gripper (not shown in the schematic representation). This

support contains sensors for measuring the sample temperature during each experiment. After the sample has been loaded onto the support, the necessary reaction- and purge gases are introduced; while the experimental profile sequences are initiated by the experimental method established by the user in the Mettler-Toledo software. The furnace moves over the sample and is heated to the set temperature according to the user defined method, while the necessary reaction gases are introduced. The flow of purge gas ensures that no harmful reaction gases or gaseous products accumulate in the micro-balance unit, while the baffles contained within the oven unit enhances mixing of the reaction gases. Sample mass, temperature and acquisition time is periodically recorded by the software and provides a real-time overview of the respective experiment. A summary of system constraints and limitations is provided in Table 7.1.

Table 7.1 Summary of Mettler-Toledo TGA/DSC STAR[®] constraints and limitations.

Variable	Experimental constraint or limitation
Temperature range	Room temperature up to 1600 °C
Temperature accuracy and -precision	± 0.5 K and ± 0.3 K
Heating rate	Rates of up to 100 K/min are feasible
Cooling rate	Cooling to less than 200 °C at a rate of up to -20 K/min
Sample volume	Volumes of up to 900 μ L
Balance measurement range	Masses of up to 1 g
Balance resolution	~ 1.0 μ g
Data sampling rate	Maximum of 10 values per second
Operating pressure	Atmospheric

7.3.3 Large particle thermogravimetric analyser (LPTGA)

7.3.3.1 Operating constraints and limitations

A detailed schematic representation of the LPTGA is provided in Figure 7.2. Although the LPTGA has certain operating constraints, it is unique in the sense that it can handle both high temperatures and large particles. The LPTGA under discussion is able to:

- Handle coal particles ranging from 1 mm to 45 mm and sample masses up to ± 100 g. Quartz sample baskets containing porous quartz discs are used for this purpose;

- Handle temperatures up to 1250 °C (Beukman, 2009);
- Can be operated in either isothermal or non-isothermal mode. Heating rates up to 25 °C/min are feasible in non-isothermal operation;
- Reductive (O_2 , CO_2 and steam) and inert (N_2 and Ar) gaseous atmospheres can be used. The use of steam requires the installation of a steam generating facility.

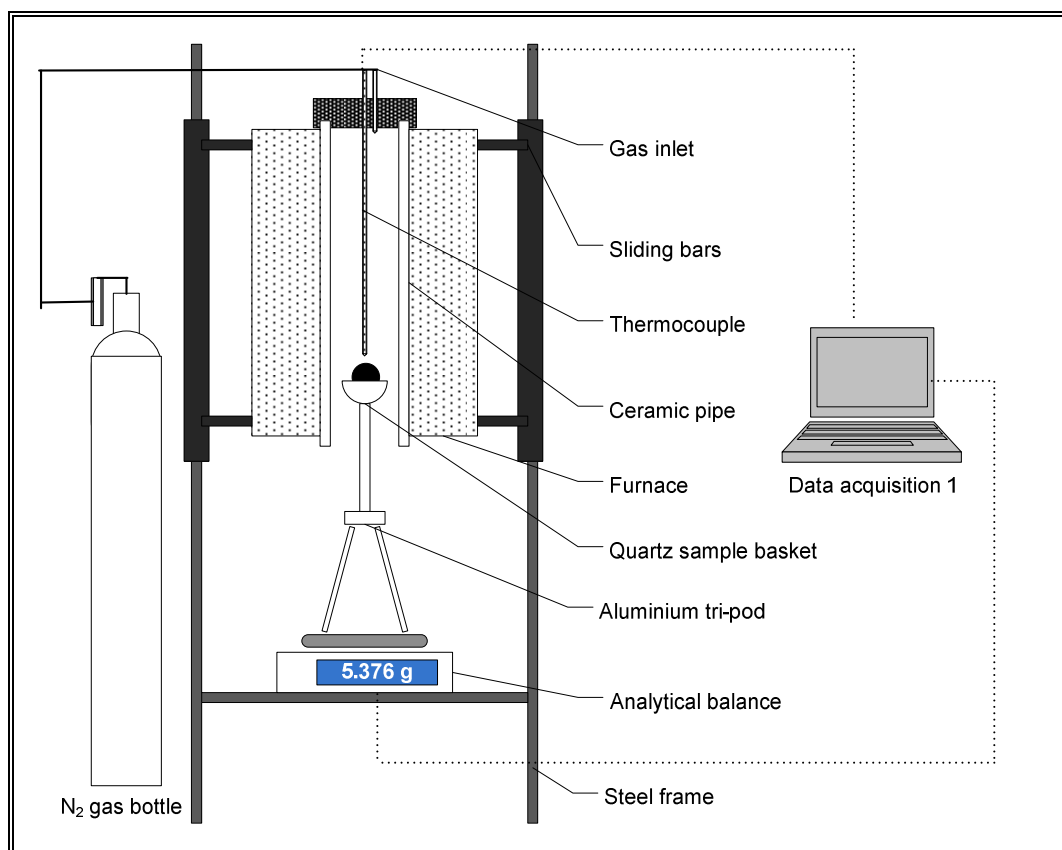


Figure 7.2 Large particle thermogravimetric analyser.

7.3.3.2 TGA operation

The apparatus consists of a Lenton[®] TSV 15/50/180 vertical tube furnace, which is mounted on steel guide rails. The addition of guide rails provides the capability to move the furnace freely up and down as required. Furthermore, supporting pins enable the furnace to be set at two different heights. A coal particle is placed in the quartz sample basket (melting point: ± 1650 °C), and subsequently mounted on an analytical balance (Sartorius[®] ED4202S, maximum weight capacity: 4200 g, accuracy of ± 0.01 g). Once the sample has been loaded, the furnace can either be lowered at room temperature and heated up to the required temperature (non-

isothermal mode), or can be heated to reaction temperature prior to sample introduction (isothermal mode). The sample is therefore subsequently introduced into the hot zone, when the furnace is lowered (lowest setting). Reaction gas is introduced from the top via a stainless steel connection flange, which ensures minimum loss of reaction gas at the top of the system. This forces the reaction/inert gas to flow downwards through the tube and discharge into the atmosphere at the bottom. The flow rate of gas to the system is controlled manually with a rotameter to ensure a high enough flow rate to prevent external gas (air) from leaking into the system. The reaction temperature is carefully monitored with the aid of a thermocouple (K-type contained within a ceramic tube sleeve), positioned directly above the coal sample/particle, while the oven is controlled via a thermocouple connected to the outer surface of the working tube. Temperature control at the particle surface is therefore ensured by over compensating for the temperature on the tube wall. Furthermore, particle mass loss with time and particle temperature is recorded to a data acquisition interface by means of Visidaq online acquisition software.

7.3.3.3 Data acquisition interfaces

Different electronic interfaces were employed in order to record mass loss and temperature data in real-time. Adam 4011 and Adam 4521 converter modules were used to convert the voltage signal from the thermocouple and the analog signal from the balance, respectively, to RS232 signals. In addition, these two converter modules were connected in parallel to a single Adam 4561 module, which converted both RS232 signals to a single USB signal. Visidaq acquisition software was used to assess the signal provided by the Adam 4561 module and to visually display the real-time data.

7.4 Experimental methodology

7.4.1 Small particle thermogravimetric analyser (Mettler-Toledo TGA/DSC 1 STAR^e)

7.4.1.1 Operating conditions

Low heating rates of conventional, small particle TGAs as well as the high devolatilization rate of powdered samples necessitates the need for running non-isothermal measurements in order

to determine intrinsic kinetic behaviour. A detailed overview of the experimental conditions used for assessing the rate behaviour of powdered coal samples is outlined in Table 7.2.

Table 7.2 Overview of experimental conditions used for kinetic rate measurements.

Variable	Experimental range or composition
Coal feed stocks	INY, UMZ, G#5 and TSH
Coal particle size	< 200 μm
Oven programme	Heat to 30°C at 1 K/min and isothermal for 5 min. Heating at specified heating rate to 950°C and isothermal for 30 min.
Heating rates	5, 10, 25 and 40 K/min
Operating pressure	Atmospheric pressure
Reactants/inerts used	Coal and N ₂
N ₂ composition	Ultra high purity grade, ~99.99 %
Total gas flow rate	1.5 NL/min
Sample mass	~20 mg
Repeatability tests (Amount of runs)	5 K/min (3 per coal), 10 K/min (2 per coal), 25 K/min (2 per coal) and 40 K/min (1 per coal)

Mass loss measurements were performed on all four coal samples at four different heating rates, by heating the samples under an inert atmosphere from 30°C to 950°C as described in the Table above. The region between the initial- and final temperature was chosen to be representative of the range of expected coal devolatilization.

Sample masses of no more than 20 mg, with a particle size distribution of less than 200 μm , were used in order to reduce the occurrence of possible secondary gas-solid reactions as well as the effects of mass- and intra particle heat transfer (Aboyade *et al.*, 2011; Antal & Várhegyi, 1995). This is in accordance with investigations conducted on the devolatilization of a large number of different solid fuels including biomass and coal (Abhari & Isaacs, 1999; Aboyade *et al.*, 2011 & 2012; Alonso *et al.*, 2001; Antal & Várhegyi, 1995; Biagini *et al.*, 2002).

7.4.2 Large particle thermogravimetric analyser (LPTGA)

7.4.2.1 Operating conditions

As temperature is one of the most important parameters affecting devolatilization, it was decided to choose operating temperatures closely resembling the main stages of devolatilization. According to Ladner (1988) and Kabe *et al.* (2004), the main stages of devolatilization occur in the temperature range between 350°C and 1100°C. Operating temperatures were thus accordingly used in this range to investigate coal devolatilization. An overview of the experimental plan is provided in Table 7.3. Single coal particles as selected according to Sections 6.3.1-6.3.3 were used for devolatilization rate studies.

Table 7.3 Experimental conditions.

Variable	Experimental range or composition
Coal feed stocks	INY, UMZ, G#5 and TSH
Coal particle size	± 20 mm (hand- and density selected)
Operating temperatures	300 °C, 450 °C, 550 °C, 600 °C, 650 °C, 750 °C and 900 °C (Isothermal furnace temperature)
Operating pressure	Atmospheric pressure
Reactants/inerts used	Coal and N ₂
N ₂ composition	Ultra high purity grade, ~99.99 %
Total gas flow rate	8 NL/min
Sample mass	Single coal particles ranging in mass from 5 g to 7 g.
Repeatability tests	At least 8 particles per coal per temperature.
Total run time per experiment	2 hours
Temperature profile estimations	450 °C and 750 °C of all four coals (5 experiments per coal per temperature)

A high N₂ flow rate was chosen to reduce the possibility of external secondary reactions taking place and to prevent atmospheric air leaking into the reactor system. A total run time of 2 hours was used to ensure that the mass loss reached a constant asymptotic value.

7.4.2.2 Experimental protocol

One coal particle at a time was weighed prior to each experimental run and the respective mass was recorded. This was followed by the pre-heating of the furnace to the desired isothermal operating temperature. Once the furnace reached the desired temperature, N_2 gas was introduced to flush out any air within the system. The empty sample holder was positioned on the balance and the furnace was lowered to the appropriate height. The balance was subsequently zeroed with respect to the empty sample holder. With the balance zeroed, the furnace was lifted to its original position (highest setting) and the sample holder was left to cool down. Once cooled the coal sample was inserted into the quartz sample holder. The data acquisition system was started prior to each experiment and the sample holder with sample was introduced into the furnace as described previously.

Each experiment was left to run for 2 hours in order for the coal/char mass value to reach a constant asymptotic value. After 2 hours run time, the data acquisition was stopped; the furnace was switched off and lifted to the intermediate setting so that the sample holder was only a few centimetres from the main heated zone. The charred particle was kept here for approximately 10 minutes, whereafter the furnace was lifted to the highest setting and another 10 minute cooling time was applied. This was done to ensure that the char particle cooled down sequentially, under the inert atmosphere, to approximately room temperature and to prevent any combustion from occurring. The char sample was then removed from the sample holder, photographed and subsequently stored under N_2 (Beukman, 2009).

Temperature profile measurements (Table 7.3) were done separately at two selected temperatures according to the same experimental protocol as outlined above, with the exception that no mass measurement was done. Temperatures were recorded at both the particle surface and the centre of the particle with the aid of two 3 mm K-type thermocouples. Measurement of the inner core temperature was achieved by following the same strategy employed by Strydom (2010), which involved drilling a 3.5 mm hole to the required depth into each respective coal particle and tension fitting the thermocouple within the drilled hole. Profile estimations were done on at least 5 particles per coal in order to obtain good reproducibility.

7.5 Modelling strategies

7.5.1 Small particle modelling and determination of intrinsic kinetics

The kinetic analysis of coal devolatilization is based on the rate equation for solid state decomposition (Brown, 2001; Várhegyi, 2007; Vyazovkin, 2000) and can be formulated as:

$$\frac{dX}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right) \cdot g(X) \quad \text{Equation (7.1)}$$

where $g(X)$ is the reaction model. For simple first order reactions the above reaction is reduced to:

$$\frac{dX}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right) \cdot (1 - X) \quad \text{Equation (7.2)}$$

The fractional conversion, X can be derived with the aid of the following equation (Aboyade *et al.*, 2011 & 2012):

$$X = \frac{m_0 - m_t}{m_0 - m_f} \quad \text{Equation (7.3)}$$

The devolatilization of the four coals was assumed to follow a pseudo-component decomposition mechanism, which could be described by multiple independent parallel reactions corresponding to the amount of pseudo-components (Aboyade *et al.*, 2012; Alonso *et al.*, 2001; Várhegyi, 2007; White *et al.*, 2011). In this respect the term pseudo-component refers to a group of reactive species exhibiting similar reactivity (Aboyade *et al.*, 2012; Várhegyi, 2007). Under this assumption the above equation takes on the form of Equation (3.13):

$$\frac{dX}{dt} = \xi_a \frac{dX_a}{dt} + \xi_b \frac{dX_b}{dt} + \xi_g \frac{dX_g}{dt} + \sum_{i=1}^3 \xi_i \frac{dX_i}{dt} = \sum_{i=1}^j \xi_i \frac{dX_i}{dt} \quad \text{Equation (3.13)}$$

or as more generally defined in Equation (3.14a):

$$\frac{dX_t}{dt} = \sum_{i=1}^j \xi_i k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i); \quad j = 1, 2, \dots, n \quad \text{Equation (3.14a)}$$

For non-isothermal TGA measurements the above equation can be re-arranged by substituting dt with dT/β (with β the heating rate applied) and integrating as follows:

$$\int_0^{X_i} \frac{dX_t}{(1 - X_t)} = \sum_{i=1}^j \xi_i \frac{k_{0,i}}{\beta} \cdot \int_{T_0}^T \exp\left(\frac{-E_{a,i}}{RT}\right) dT, \quad i = 1, 2, \dots, n \quad \text{Equation (7.4)}$$

It has been shown previously that the temperature integral on the right hand side has no exact analytical solution, but with the aid of integration by parts and substitution it can be written in the following form (Aboyade *et al.*, 2012, Caballero & Conesa, 2005):

$$\int_{T_0}^T \exp\left(\frac{-E_{a,i}}{RT}\right) dT = \frac{E_{a,i}}{R} \cdot \left[\frac{\exp(-y_i)}{y_i} - \int_y^\infty \frac{\exp(-y_i)}{y_i} dy \right] \text{ with } y_i = \frac{E_{a,i}}{RT} \quad \text{Equation (7.5)}$$

For n amount pseudo-reactions Equation (7.4) can therefore be formulated after integration as:

$$X_t = \sum_{i=1}^n \xi_i \cdot \left(1 - \exp\left\{ \frac{k_{0,i}}{\beta} \cdot \frac{E_{a,i}}{R} \cdot \left[\frac{\exp(-y_i)}{y_i} - \int_y^\infty \frac{\exp(-y_i)}{y_i} dy \right] \right\} \right) \quad \text{Equation (7.6)}$$

A large number of approximations are available for evaluating the kinetic constants in the above equation and have been discussed in Chapter 3. The evaluation of the kinetic parameters was conducted numerically with application of the direct integral method for solving the exponential integral in Equation (7.6). This was accomplished with an appropriate algorithm and the *expint* function in MATLAB[®] 7.1.1. Optimization of the kinetic parameters was performed by multidimensional non-linear regression. This involved searching for values of $k_{0,i}$, $E_{a,i}$ and ξ_i that minimised the objective function (*OBF*) as formulated in Equation (3.15).

$$OBF = \sum_{k=1}^{N_k} \sum_{m=1}^{N_m} \left[\left(\frac{dX_t}{dt} \right)_{\text{exp}} - \left(\frac{dX_t}{dt} \right)_{\text{calc}} \right]^2 \quad \text{Equation (3.15)}$$

In addition, Equations (7.6) and (3.15) were applied to the differential TG data (DTG), mainly due to the fact that small changes in the features and peaks of the corresponding TGA curves are magnified when using DTG, which eases the identification of kinetics (Aboyade *et al.*, 2012, Brazier & Nickel, 1975; Brazier & Schwartz, 1978; Caballero & Conesa, 2005; Sircar & Lamond, 1975; Yang *et al.*, 1993). Initial estimates for the kinetic parameters algorithm were scaled and based on ranges published in literature (Aboyade *et al.*, 2011 & 2012; Caballero & Conesa, 2005). Furthermore, the validity of the predicted model values on the quality of fit (*QOF*) of the experimental data was evaluated with the aid of Equation (3.16) for each heating rate as well as for the overall process:

$$QOF (\%) = 100 \times \frac{\sum_{m=1}^{N_m} \sqrt{\left[\left(\frac{dX_t}{dt} \right)_{\text{exp}} - \left(\frac{dX_t}{dt} \right)_{\text{calc}} \right]^2 / N_m}}{\max \left| \frac{dX}{dt} \right|_{\text{exp}}} \quad \text{Equation (3.16)}$$

The basic structure of the MATLAB algorithm used for solving the necessary equations and evaluating the kinetic parameters is summarised in Figure 7.3. TGA results from multiple heating rates are provided as input to the algorithm in the form of temperature (K) and mass fraction loss. The MATLAB® 7.1.1 algorithm converts the input data to the rate of devolatilization (dX_t/dt) (DTG curve) as well as fractional conversion (X_t) for each heating rate. Hereafter, the subsequent converted data is filtered with the aid of the Savitzky-Golay filter (polynomial order of 4 and frame size of between 9 and 21) in order to remove any systematic noise from the calculated DTG curves. Savitzky-Golay parameters were chosen according to the suggestions made by Caballero and Conesa (2005). Evenly spaced experimental DTG points were selected for each heating rate and used for parameter estimation. The simultaneous, multiple, non-linear regression of different heating rate DTG data has been widely used and recommended for assistance in the breakage of the kinetic compensation effect, which is achieved by the addition of an extra constraint (Aboyade *et al.*, 2011 & 2012; Caballero & Conesa, 2005; Conesa *et al.*, 1995). The Levenberg-Marquardt optimization algorithm was chosen for regression of the kinetic parameters from the DTG curve with the aid of the *lsqcurvefit* function in the MATLAB® 7.1.1 optimization toolbox (Caballero & Conesa, 2005). Curve fitting was done in two steps with a gradual decrease in the values of the solver tolerances. A for loop was included to generate a large number of different initial values from the user specified values. This was done in order to minimize the sensitive nature of solvers with respect to incorrectly scaled initial values (Caballero & Conesa, 2005).

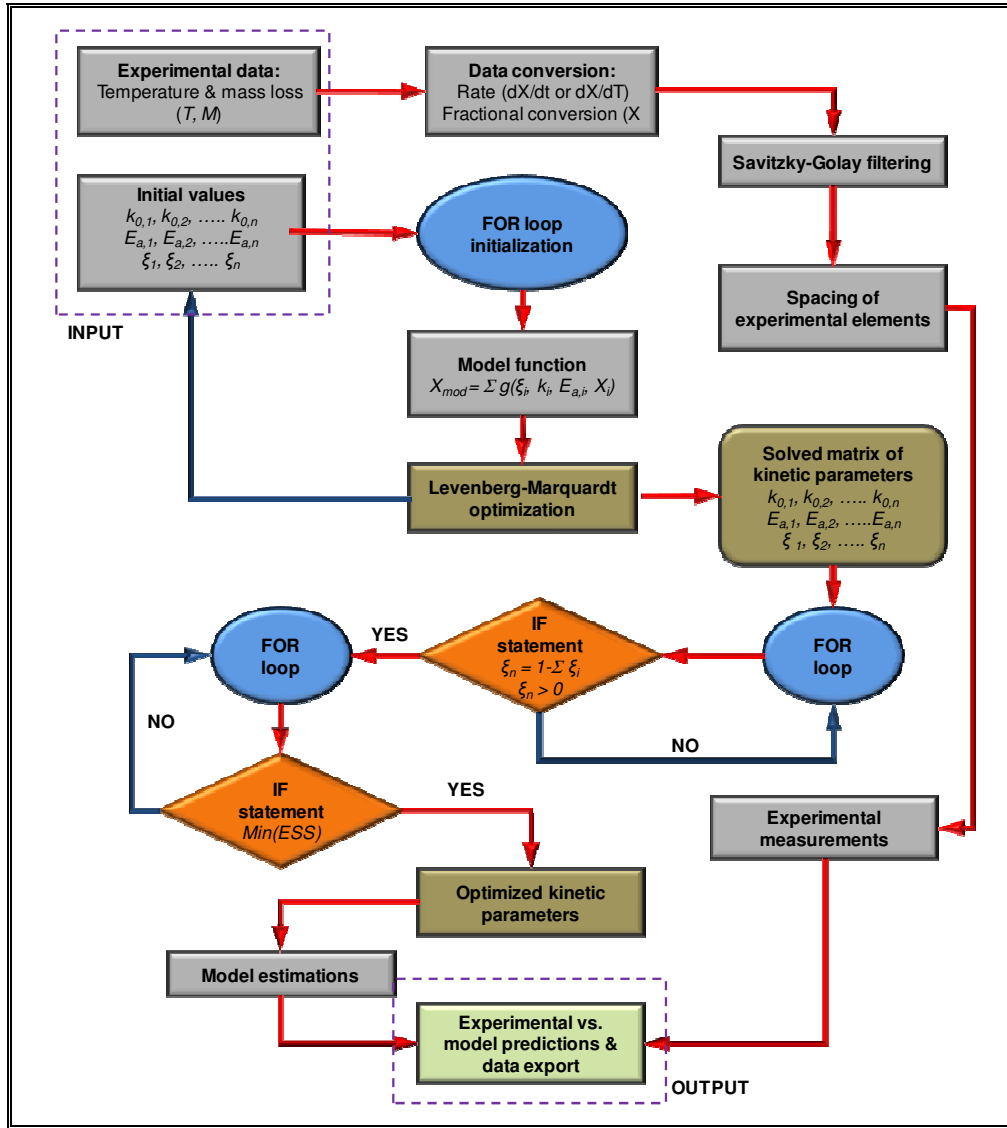


Figure 7.3 MATLAB algorithm used for solving kinetic parameters.

Solved kinetic parameters obtained from the Levenberg-Marquardt routine were stored in a solution matrix for optimization. From this matrix the optimum kinetic parameters were selected via a two-step “for loop – if statement” selection procedure. Parameters of which $\xi_n > 0$ and which yielded the lowest residual error sum of squares were selected as the optimum values for describing the kinetic behaviour. Finally, the optimum values were used for model estimations and compared to the experimental TG and DTG curves. The number of pseudo-reactions necessary to accurately describe the devolatilization behaviour of each coal was based on the improvement in the *QOF* of not only the individual heating rate data but also that of the overall process. The number of pseudo-components used was limited to eight, as larger values could

induce the risk of over fitting the experimental rate data (Aboyade *et al.*, 2012; Roduit, 2000). Additional information regarding the algorithm syntax is provided in Appendix D.1.

7.5.2 Large particle modelling

7.5.2.1 Rescaling of pseudo-component reactions

From Section 7.5.1 and Chapter 3 it was established that the intrinsic devolatilization rate of small particles can be described according to the pseudo-component approach as shown in the following equation for 8 pseudo-component reactions:

$$\frac{dX_t}{dt} = \sum_{i=j}^8 \xi_i k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i) \quad \text{Equation (3.14a)}$$

Separation of Equation (3.14a) into terms accounting for the release of moisture and volatiles, respectively, yields the following mathematical expression:

$$\frac{dX_t}{dt} = \xi_a k_{0,a} \cdot \exp\left(\frac{-E_{a,a}}{RT}\right) \cdot (1 - X_a) + \sum_{i=j}^7 \xi_i k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i) \quad \text{Equation (7.7)}$$

Multiplication of the above equation with the ultimate amount of volatile matter (moisture and volatile species) yields the more general differential equation for describing the release of volatile matter as a function of time and temperature:

$$\frac{dV_t}{dt} = V_t^* \left\{ \xi_a k_{0,a} \cdot \exp\left(\frac{-E_{a,a}}{RT}\right) \cdot (1 - X_a) + \sum_{i=j}^7 \xi_i k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i) \right\} \quad \text{Equation (7.8)}$$

The use of the above equation for describing pseudo-isothermal or isothermal devolatilization rates at different temperatures does, however, pose a problem as fractional contribution values (ξ_a and ξ_i) are determined from non-isothermal devolatilization measurements performed at different heating rates and a single, fixed, final temperature (as outlined in Section 7.4.1.1). For temperatures below the final temperature, used for evaluating the respective fractional

contributions, this leads to the following modelling constraint to become valid if sufficient time for completion of the devolatilization reactions is not provided (which can be quite extensive for lower temperatures):

$$X_a \xi_a + \sum_i X_i \xi_i < 1 \quad \text{Equation (7.9)}$$

This, combined with the knowledge that ultimate volatile matter yields (for the overall reaction and the individual pseudo-components) are strongly dependent on both reaction time and temperature, requires the rescaling of the overall conversion to be representative of the final operating conditions under investigation (as is the case for the large particle devolatilization measurements). This is accomplished by rewriting Equation (7.8) in a form accounting for both the ultimate volatile matter yield at fixed isothermal operating conditions and rescaling of the overall fractional conversion of the devolatilization process. Accordingly, Equation (7.8) can be rewritten as:

$$\frac{dV_{t,T}}{dt} = V_a^* \cdot k_{0,a} \cdot \exp\left(\frac{-E_{a,a}}{RT}\right) \cdot (1 - X_a) + \frac{(V_{t,T}^* - V_a^*)}{X_{f,v}^*} \cdot \sum_{i=j}^7 \xi_i^* k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i) \quad \text{Equation (7.10a)}$$

In Equation (7.10a), V_a^* represents the ultimate amount of moisture released, while $V_{t,T}^*$ can be defined as the ultimate amount of total volatile matter (moisture and volatiles) released at time, t and isothermal temperature T . Due to the uncertainty in the exact value of $V_{t,T}^*$, a rescaling factor ($X_{f,v}^*$) has been included in Equation (7.10a) to ensure that the final fractional conversion (at time, t) of the overall volatile release process is always normalised to a value of 1. A brief overview of the derivation for the inclusion of such a scaling factor in the volatile release term can be found in Appendix D.2. In addition, rescaled fractional contributions (ξ_i^*) were normalised on a moisture fraction free basis according to:

$$\xi_i^* = \frac{\xi_i}{1 - \xi_a} \quad \text{so that} \quad \sum_i \xi_i^* = 1 \quad \text{Equation (7.10b)}$$

Although the use of the above model requires a prior knowledge of both the final fractional conversion of volatile release ($X_{f,v}^*$), as well as the ultimate amount of volatile matter released,

the preceding developments do, however, provide a simplistic and efficient way of incorporating intrinsic devolatilization behaviour into an overall, larger rate model taking into account the effect of transport limitations. For large particle devolatilization, the particle averaged (volume averaged) moisture- and volatile release can be determined according to Equation (7.11):

$$\frac{dV_{t,T}}{dt} = \frac{3}{R_p} \int_0^{R_p} \left\{ V_a^* \cdot k_{0,a} \cdot \exp\left(\frac{-E_{a,a}}{RT}\right) \cdot (1 - X_a) + \frac{(V_{t,T}^* - V_a^*)}{X_{f,v}^*} \cdot \sum_{i=j}^7 \xi_i^* k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i) \right\} r^2 dr$$

Equation (7.11)

7.5.2.2 Accounting for contractive and/or swelling behaviour

From Section 4.6.1.3 it was concluded that all four coals displayed some form of thermophysical behaviour during heating under an inert atmosphere. Coals originating from the Witbank coalfield (UMZ, INY and G#5) were characterised mainly by contractive- or shrinking behaviour, while the devolatilization of coal TSH was found to display both particle shrinkage and swelling. Numerous thermoplastic modelling strategies (empirical, uniform swelling/shrinkage, etc.) have been proposed in order to account for the effect of swelling and/or shrinkage phenomena on the devolatilization rate of solid fuels such as biomasses and coals (Bellais *et al.*, 2003; Bharadwaj *et al.*, 2004; Gale *et al.*, 1995; Hagge & Bryden, 2002; Shurtz *et al.*, 2012).

For the sake of simplicity, but also due to the complex physical mechanism associated with particle shrinkage and/or swelling, an empirical modelling approach was followed in order to describe the thermoplastic nature of the four coals under investigation. For this purpose, empirical fitting was performed on the dilatometry results presented in Section 4.6.1.3. Shrinkage and/or swelling models consisted of expressing particle volume (v) as a function of both initial particle volume (v_0) and solid temperature (T_s) as defined in Equation (7.12):

$$v = v_0 \cdot f(T_s)$$

Equation (7.12)

Derivation of a suitable empirical model descriptive of each coal's thermoplastic nature was accomplished with the aid of the non-linear regression tool provided in the Origin 8.0 software package.

7.5.2.3 Overview of large particle modelling with COMSOL Multiphysics®

Model assumptions and -formulations:

Despite the complex nature of both chemical and physical mechanisms occurring during the thermal decomposition of solid fuels (coals and/or biomasses), numerous investigations in the past have been able to provide some modelling strategies for describing, in particular, the devolatilization process of large fuel particles (Agarwal *et al.*, 1984a & b; Bharadwaj *et al.*, 2004; Chern & Hayhurst, 2006; Heidenreich *et al.*, 1999; Janse *et al.*, 2000; Peters & Bruch, 2003; Peters, 2011; Sadhukhan *et al.*, 2009; Sadhukhan *et al.*, 2011; Stubington & Sumaryono, 1984; Tomeczek & Kowol, 1990; Wildegger-Gaissmaier & Agarwal, 1990; Zhang *et al.*, 2012). The general consensus among these investigations was that large particle devolatilization consists of a complex combination of the following chemical- and physical phenomena:

- Conductive heating of the solid fuel particle (coal or biomass) through convective and radiative heat transfer from the external surroundings (gas medium, reactor wall, etc.);
- Vaporization of inherently bound moisture as well the subsequent recondensation thereof in colder parts of the particle not being affected by the progressive movement of the temperature front;
- Transport of evolved moisture through the porous structure of the solid particle to the particle surface via convection and/or diffusion;
- Thermal degradation of the solid material at sufficiently high temperatures to produce char, tars and gases (volatile products);
- Transport of the volatile products through the porous structure of the char and/or unreacted solid layer to the particle surface via convection and/or diffusion. This is accompanied by an exchange of heat between the solid mass and the moving volatile products (convective cooling of the particle), which can substantially affect the heat profile within the solid mass;
- Secondary cracking and/or recondensation of the product vapour (tars) to produce additional product gas and char;
- Change in the physical structure of the solid particle (swelling and/or shrinkage) due to a combination of the preceding processes.

Modelling the complex chemical- and physical processes associated with single particle devolatilization therefore requires the formulation of some simplifying assumptions. For this particular investigation, assumptions made to describe the thermal conversion of single, large coal particles showed good agreement with those postulated in other investigations (Bharadwaj *et al.*, 2004; Janse *et al.*, 2000; Peters & Bruch, 2003; Peters, 2011; Sadhukhan *et al.*, 2009; Sadhukhan *et al.*, 2011) and included the following:

- Particle geometry is assumed to be spherical and symmetric in nature,
- The modelling description consists of the one-dimensional and transient formulation of the conservation of mass, species and energy;
- Gaseous, liquid, inert and solid phases within the coal particle are considered to be in a state of thermal equilibrium;
- Devolatilization kinetics are described according to the pseudo-component approach, while the evaporation of moisture is assumed to follow a first-order evolution mechanism;
- No condensation of any formed tars or liquids occurs within the coal particle;
- Product gas/vapour is considered to be a homogenous mixture of the formed tars, moisture and gases; and can be described by the ideal gas law;
- Pores of the coal particle are initially filled with air at standard ambient conditions (room temperature and atmospheric pressure);
- Secondary cracking or deposition of tar vapours in the char layer to form additional gases and char is not taken into account (for the sake of simplicity this is neglected);
- Both convection and diffusion contributes to the transport of species within the porous solid matrix. Bulk flow (or convection) is considered to be driven by pressure gradients created by the evolution of moisture and volatiles; and can be described with the aid of Darcy's law;
- The effects of Stefan flow on heat and mass transfer can be neglected;
- Dirichlet boundary conditions are used in the description of external mass transfer limitations;
- Porosity changes during coal conversion are assumed to be strongly associated with changes in particle density. For simplification purposes, skeletal density is assumed to remain constant. In all cases, a value of 2.5 was assumed for the particle tortuosity (τ).
- Swelling/shrinkage of coal particles can be described sufficiently at the hand of empirical models;

- Thermophysical properties of the coal as well as heat- and mass transfer coefficients are based on either fixed constant parameters or empirical correlations (Chapter 3);
- The latent heat of vaporization of water is considered separately from the heat of reaction of devolatilization;
- Values for the ultimate yield of moisture and volatiles (as a function of time and temperature) are directly derived from the thermogravimetric results obtained for the large coal particles

From the developments of Chapter 3 and the preceding assumptions, the governing equations describing large particle devolatilization can therefore be summarised as:

Reaction kinetics

$$\frac{dV_{t,T}}{dt} = \frac{3}{R_p} \int_0^{R_p} \left\{ V_a^* \cdot k_{0,a} \cdot \exp\left(\frac{-E_{a,a}}{RT_s}\right) \cdot (1 - X_a) + \frac{(V_{t,T}^* - V_a^*)}{X_{f,v}^*} \cdot \sum_{i=j}^7 \xi_i^* k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT_s}\right) \cdot (1 - X_i) \right\} r^2 dr$$

Equation (7.11)

Conservation of heat (Sadhukhan *et al.*, 2009; Sadhukhan *et al.*, 2011)

$$c_{p,s} \frac{\partial(\rho_s T_s)}{\partial t} = \frac{1}{r^2} \left[k_s \cdot \left(\frac{\partial}{\partial r} r^2 \frac{\partial T_s}{\partial r} \right) - \sum_{i=a,v} c_{p,i} \cdot \frac{\partial}{\partial r} (r^2 u \rho_i T_s) \right] + R_v (-\Delta H_r) + R_a (-\Delta H_{vap,a}) - \frac{c_{p,s} \rho_s T_s}{v} \frac{\partial v}{\partial t}$$

Equation (3.17e)

With the boundary and initial conditions defined as:

$$\text{At } t = 0 \text{ for } 0 \leq r \leq R_p; \quad T_s = T_i \quad \text{Equation (3.18a)}$$

$$\text{For } t > 0 \text{ at } r = 0; \quad -k_s \frac{\partial T_s}{\partial r} + u \rho_v c_{p,v} T_s + u \rho_a c_{p,a} T_s = 0 \quad \text{Equation (3.18b)}$$

$$\text{For } t > 0 \text{ at } r = R_p; \quad -k_s \frac{\partial T_s}{\partial r} + u \rho_v c_{p,v} T_s + u \rho_a c_{p,a} T_s = \sigma_b \epsilon_{rad} (T_s^4 - T_f^4) + h_{conv} (T_s - T_f) \quad \text{Equation (3.18c)}$$

Conservation of solid mass (Sadhukhan *et al.*, 2011):

$$\frac{\partial \rho_s}{\partial t} = -(R_v + R_a) - \frac{\rho_s}{v} \frac{\partial v}{\partial t} \quad \text{Equation (3.28e)}$$

Conservation of mass (Bharadwaj *et al.*, 2004; Peters, 2011; Sadhukhan *et al.*, 2011)

$$\frac{\partial(\epsilon \rho_{v,t})}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_{v,t} u) = R_v + R_a - \frac{\epsilon \rho_{v,t}}{v} \frac{\partial v}{\partial t} \quad \text{Equation (3.33b)}$$

$$\frac{\partial(\epsilon \rho_v)}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_v u) - \frac{D'_{eff,v}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \rho_v}{\partial r} \right) = R_v - \frac{\epsilon \rho_v}{v} \frac{\partial v}{\partial t} \quad \text{Equation (3.34a)}$$

$$\frac{\partial(\epsilon \rho_a)}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_a u) - \frac{D'_{eff,a}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \rho_a}{\partial r} \right) = R_a - \frac{\epsilon \rho_a}{v} \frac{\partial v}{\partial t} \quad \text{Equation (3.34b)}$$

The above equations are formulated with the following boundary- and initial conditions:

$$\text{At } t = 0 \text{ for } 0 \leq r \leq R_p; \quad p = p_0 \text{ or } \rho_{v,t} = \rho_{air,T_0} \text{ and } \rho_i = 0; \quad i = a, v \quad \text{Equation (3.35a)}$$

$$\text{For } t > 0 \text{ at } r = 0; \quad \frac{\partial \rho_{v,t}}{\partial r} = \frac{\partial \rho_i}{\partial r} = 0; \quad i = a, v \quad \text{Equation (3.35b)}$$

$$\text{For } t > 0 \text{ at } r = R_p; \quad \rho_{v,t} = \rho_{air,T_f} \text{ and } \rho_i = 0; \quad i = a, v \quad \text{Equation (3.35c)}$$

Using COMSOL Multiphysics® 4.3:

The aforementioned system of governing equations (including the auxiliary equations described in Chapter 3) was solved numerically for a 1D geometry (particle radius) according to a finite element method using a time-dependent study approach in the COMSOL Multiphysics® 4.3 simulation software package. Equations describing kinetics (Equation (7.11)) and the laws of conservation (Equations (3.17), (3.28e), (3.34a) and (3.34b)) were modelled using the ordinary differential (ODE)- and coefficient form, partial differential (PDE) modules provided by the COMSOL Multiphysics® 4.3 simulation software package, while evaluation of the gas phase continuity equation (Equation (3.33a)) and Darcy flow was achieved with the aid of the Darcy's

law module. Thermophysical, kinetic and material related constants and/or correlations were entered as either model definitions or material variables dependent on the physical properties (such as temperature) to be solved. Progressive changes in source terms, gas density/velocity and other physical properties do, however, lead to the existence of strong couplings between the different equations as depicted in Figure 7.4 (Govearts & Helsen, 2010).

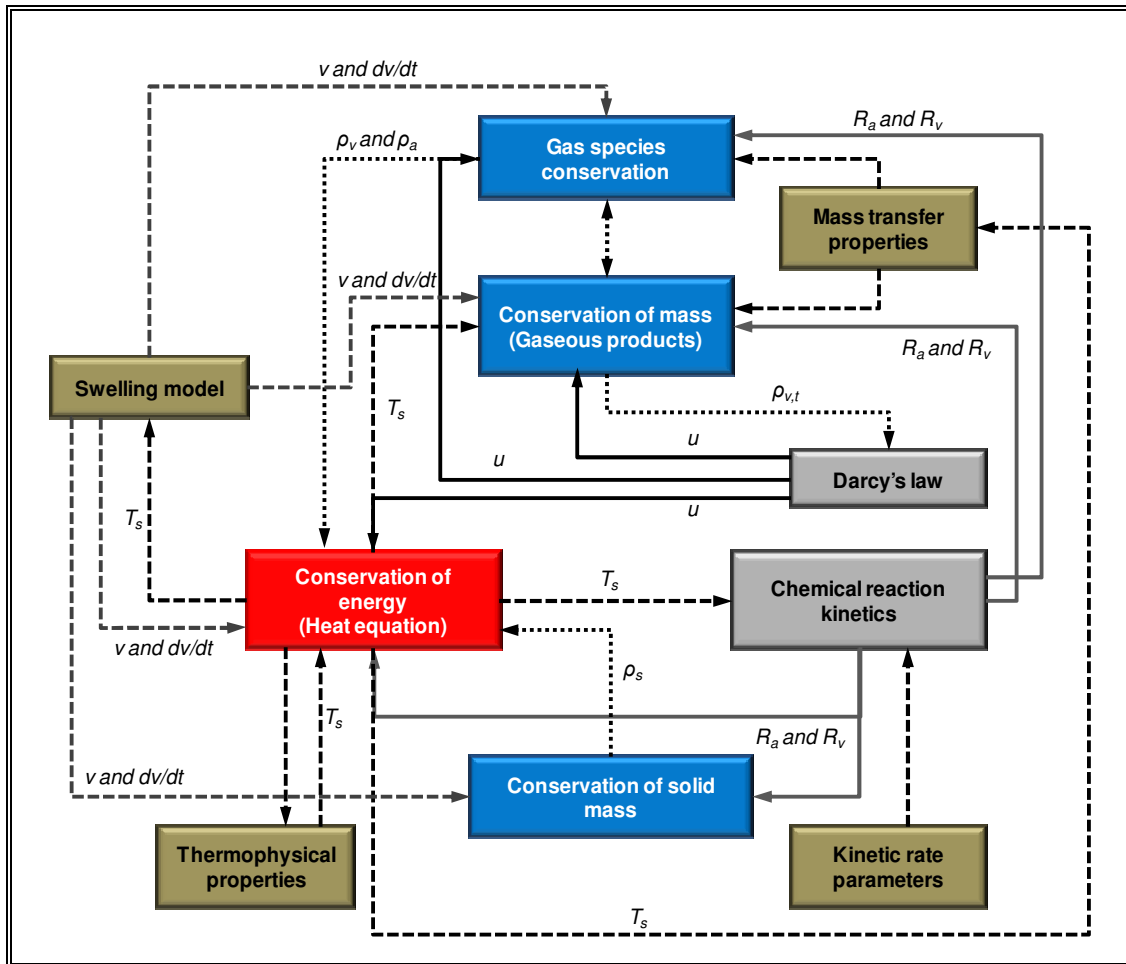


Figure 7.4 Couplings between the different descriptive equations.

This results in the formation of a very stiff system which requires the sequential solving of the different governing equations. Firstly, heat transfer and chemical reaction kinetics were solved simultaneously, followed by the inclusion of the conservation of solid mass. Secondly the Darcy's law module was added in order to evaluate the change in total product gas density, pressure and gas velocity. This was followed by the subsequent solving of the conservation equations for moisture- and volatile evolution. Finally, the empirical models accounting for shrinkage and/or swelling were incorporated and coupled with the equations describing the laws

of conservation. Discretization of the defined 1D geometry model involved the generation of a physics' controlled mesh of normal elemental size, while a time-dependent, direct MUMPS (Multifrontal Massively Parallel Sparse) solving strategy was employed to solve the complex set of non-linear equations (COMSOL, 2012). Simulation results were exported and subsequently compared against experimental results obtained from the large particle devolatilization study.

7.6 Results and discussion

7.6.1 Small particle devolatilization

Raw mass loss results, obtained from small particle thermogravimetric analyses performed on all four samples, were converted to normalised mass ratios for comparative purposes. A comparison between the normalised mass versus temperature ($^{\circ}\text{C}$) curves, at the four different heating rates is provided in Figure 7.5 for the four different coals.

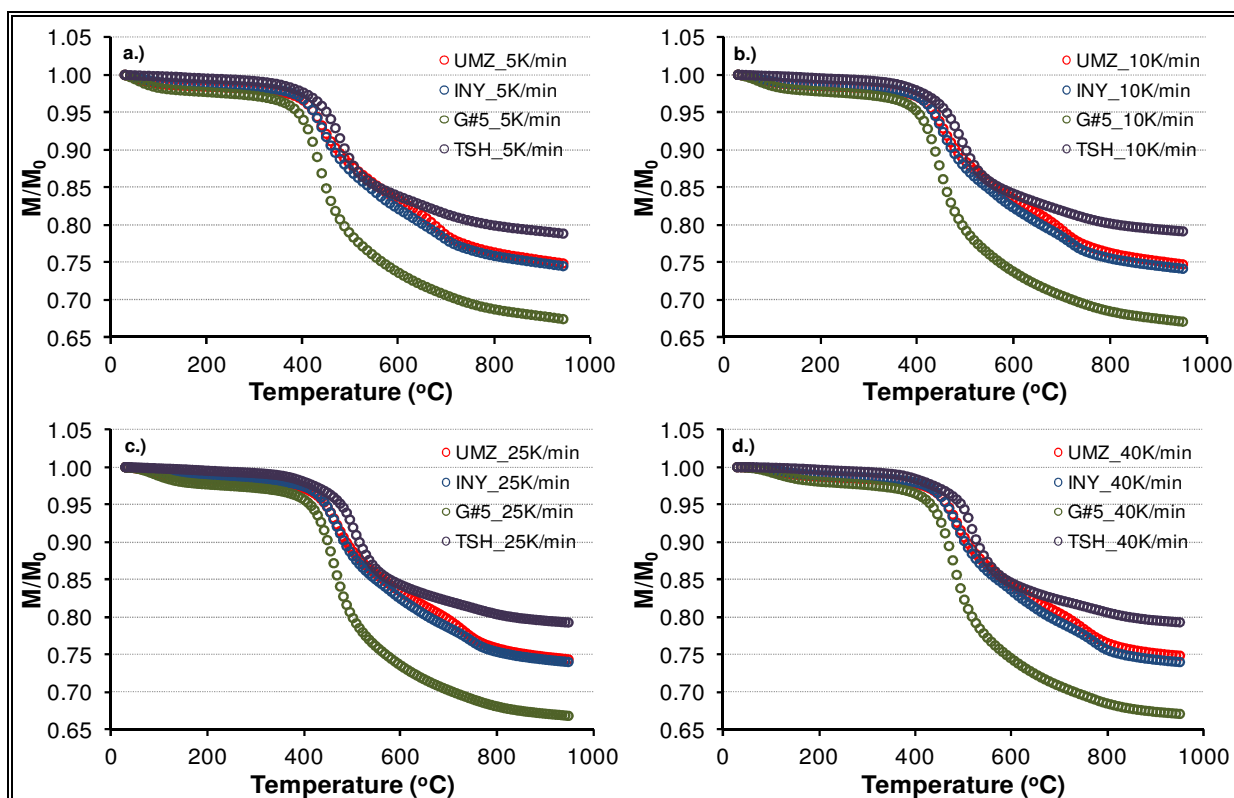


Figure 7.5 Normalised mass versus temperature (TGA) results from the devolatilization of the four coals at a.) 5 K/min, b.) 10 K/min, c.) 25 K/min and d.) 40 K/min, respectively

From the Figure it is evident that for all four heating rates the TGA profiles showed a monotonic weight decrease with increasing temperature, while the first noticeable change in mass was observed at temperatures below 150 °C. The latter has been attributed to the presumable loss of absorbed moisture and occluded gas (Alonso *et al.*, 2001; Seo *et al.*, 2011; Serio *et al.*, 1987; Solomon *et al.*, 1992; Sutcu, 2007; Wang *et al.*, 2010). For temperatures between approximately 110 °C and 350 °C, only slight changes in the loss of mass is observed and which has been found to correspond to the evolution of both colloidal bound water (110-200 °C) and secondary pyrolytic water (200-350 °C) generated from the thermal decomposition of minerals, phenolic-, carboxyl- and carbonyl groups (Moghtaderi *et al.*, 2004; Sutcu, 2007). In addition, peripheral parts of the molecular phase, which comprises mainly of polycyclic aliphatic compounds, are believed to decompose at temperatures below 350 °C (Cai *et al.*, 2008). Above 350 °C, the TGA profiles for the different samples are characterised by a significant decrease in initial coal mass (Figure 7.5), which involves the thermal decomposition of aromatic compounds of different chemical structures, present in the coal, to form tars and gases (Elder & Harris, 1984; Vuthaluru, 2004).

According to literature, this main region of thermal degradation/devolatilization can be seen as a combination of two main regimes of decomposition, i.e.: primary decomposition (formation of tars, oils and gases below 690 °C) and secondary decomposition (sharp increases in CO, CO₂, H₂ and CH₄ evolution at temperatures above 690 °C) (Cai *et al.*, 2008; Howard, 1981; Kabe *et al.*, 2004; Ladner, 1988; Serio *et al.*, 1987; Singh *et al.*, 2012). This is also supported by the conclusive evidence provided on product composition in Chapter 6. Furthermore, as previously concluded, the largest amount of volatile matter (moisture and volatiles) was generated from coal G#5 (~33.5 wt.%), followed by coals UMZ and INY (~26.5 wt.% and 26.2 wt.% respectively), while coal TSH contained the least amount of volatile matter (~21.2 wt.%). Good agreement was therefore obtained between these results and those established from proximate analyses (Section 4.6.1.1). In addition, reproducibility measurements, performed on all coals, were found to be very satisfactory with experimental errors not exceeding more than 0.2%. A schematic overview of reproducibility profiles generated at 5 K/min for all four coals can be found in Appendix D.3. For a more pronounced comparison between coals subjected to devolatilization, numerous authors (Brazier & Swartz, 1978; Brazier & Nickel, 1975; Caballero & Conesa, 2005; Sircar & Lamond, 1975; Yang *et al.*, 1993) have proposed the additional use of the time derivative of the TGA results instead of only the TGA profile. This has the advantage of amplifying small changes in the TG curves which are normally not that elucidative. Accordingly,

DTG curves were produced from the fractional conversion data (Equation 7.3) for all the respective heating rates and coal samples. The corresponding DTG curves, shown as a function of temperature, are provided in Figure 7.6. In addition, to aid in the description of the DTG results, some characteristic parameters have been derived from the respective curves and are summarised in Table 7.4. These parameters include: temperature of initial weight loss (T_o) (defined as the temperature at 5% fractional conversion), temperatures identified at occurring local maxima in the rate curve (T_P) and their corresponding weight loss rates (MR). Similar parameter strategies were reported by Cai *et al.* (2008).

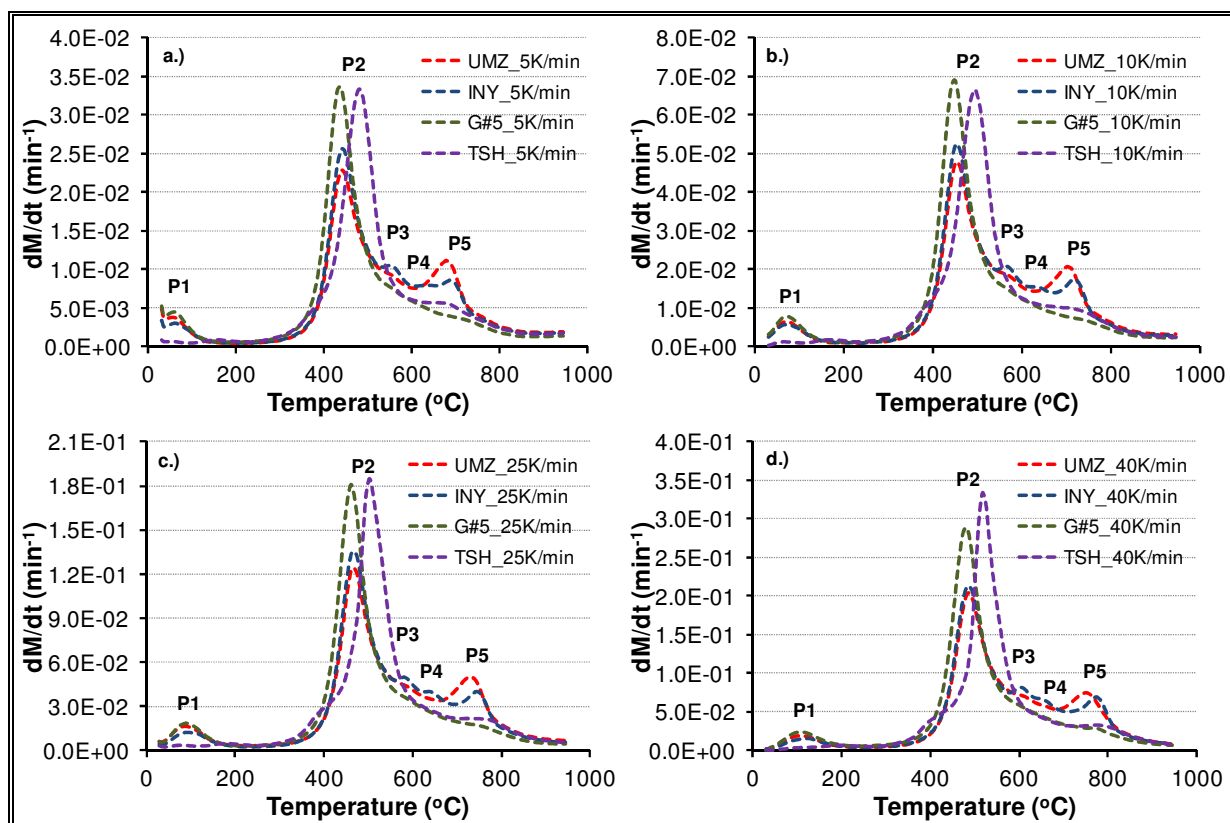


Figure 7.6 DTG profile comparison for coal devolatilization at the four different heating rates.

From a qualitative point of view, the DTG profiles given in Figure 7.6 showed striking differences for the different coals. DTG results of the four coals were characterised by two distinct peaks; one at a temperature lower than 200°C (P_1) (to a very low extent for coal TSH) and the other in the temperature range between 400°C and 500°C (P_2). These peaks were shown to be representative of the evolution of moisture and primary degradation, respectively. At temperatures exceeding 500°C, two additional peaks (P_3 and P_5) were evident for coal UMZ, while three points of local maxima could be observed for coal INY (P_3 , P_4 and P_5).

Table 7.4 Summary of characteristic parameters derived from DTG results.

Sample	T_o^a (°C)	T_{P1}^b (°C)	MR_{P1}^c (min ⁻¹)	T_{P2}^b (°C)	MR_{P2}^c (min ⁻¹)	T_{P3}^b (°C)	MR_{P3}^c (min ⁻¹)	T_{P4}^b (°C)	MR_{P4}^c (min ⁻¹)	T_{P5}^b (°C)	MR_{P5}^c (min ⁻¹)
Coal UMZ											
5 K/min	421±2	57.6	3.80×10 ⁻³	434.1	2.20 ×10 ⁻²	544.4	9.58 ×10 ⁻³	N/A	N/A	673.0	1.10 ×10 ⁻²
10 K/min	430±2	62.2	6.43 ×10 ⁻³	447.9	4.72 ×10 ⁻²	549.0	1.95 ×10 ⁻²	N/A	N/A	691.3	2.02 ×10 ⁻²
25 K/min	442±2	80.5	1.56 ×10 ⁻²	457.1	1.16 ×10 ⁻¹	571.9	4.55 ×10 ⁻²	N/A	N/A	718.9	4.83 ×10 ⁻²
40 K/min	471±2	98.9	1.91 ×10 ⁻³	480.1	1.99 ×10 ⁻¹	590.3	7.38 ×10 ⁻²	N/A	N/A	741.8	7.39 ×10 ⁻²
Coal INY											
5 K/min	421±2	57.6	2.84 ×10 ⁻³	434.1	2.46 ×10 ⁻²	544.4	1.04 ×10 ⁻²	617.9	7.87 ×10 ⁻³	682.1	8.49 ×10 ⁻³
10 K/min	430±2	62.2	5.62 ×10 ⁻³	443.3	4.95 ×10 ⁻²	553.6	2.05 ×10 ⁻²	618.0	1.55 ×10 ⁻²	709.7	1.71 ×10 ⁻²
25 K/min	442±2	85.1	1.22 ×10 ⁻²	457.1	1.26 ×10 ⁻¹	571.9	4.91 ×10 ⁻²	627.0	3.99 ×10 ⁻²	741.8	4.00 ×10 ⁻²
40 K/min	471±2	108.1	1.48 ×10 ⁻²	475.5	2.01 ×10 ⁻¹	590.3	7.80 ×10 ⁻²	640.8	6.73 ×10 ⁻²	764.8	6.71 ×10 ⁻²
Coal G#5											
5 K/min	393±2	48.4	4.32 ×10 ⁻³	429.6	3.36 ×10 ⁻²	N/A	N/A	N/A	N/A	700.5	3.79 ×10 ⁻³
10 K/min	398±2	62.2	7.57 ×10 ⁻³	438.7	6.66 ×10 ⁻²	N/A	N/A	N/A	N/A	728.1	7.16 ×10 ⁻³
25 K/min	415±2	80.5	1.76 ×10 ⁻²	457.1	1.77 ×10 ⁻¹	N/A	N/A	N/A	N/A	746.4	1.71 ×10 ⁻²
40 K/min	430±2	98.9	2.28 ×10 ⁻²	470.9	2.76 ×10 ⁻¹	N/A	N/A	N/A	N/A	755.6	2.84 ×10 ⁻²
Coal TSH											
5 K/min	449±2	144.8	8.50 ×10 ⁻⁴	475.5	3.29 ×10 ⁻²	N/A	N/A	N/A	N/A	668.4	5.67 ×10 ⁻³
10 K/min	454±2	158.6	1.76 ×10 ⁻³	484.7	6.42 ×10 ⁻²	N/A	N/A	N/A	N/A	700.5	1.00 ×10 ⁻²
25 K/min	468±2	163.2	4.33 ×10 ⁻³	498.4	1.80 ×10 ⁻¹	N/A	N/A	N/A	N/A	732.6	2.16 ×10 ⁻²
40 K/min	494±2	181.6	6.68 ×10 ⁻³	512.2	3.19 ×10 ⁻¹	N/A	N/A	N/A	N/A	760.2	3.28 ×10 ⁻²

^a Temperature observed at 5 % fractional conversion. ^b Temperatures observed at well-defined points of local maxima. ^c Corresponding weight loss rates observed at temperatures of local maxima.

In contrast, however, the DTG profiles of coals G#5 and TSH exhibited only an additional low intensity peak (P_5) in the range from 700°C to 850°C. Furthermore, it is clear from Figure 7.6 and the values reported in Table 7.4 that a significant shift in the main devolatilization zone (P_2) was observed for coal TSH in comparison to the other coals. This behaviour could possibly be attributed to the extensive thermoplastic nature of this coal (as depicted in the FSI, dilatation and Gieseler fluidity results provided in Chapter 4). According to Cai *et al.* (2008), the main reaction zone (primary devolatilization) is dominated by de-polymerisation reactions leading to the formation of tars and gases. Furthermore, these decomposition reactions are continuously in competition with re-polymerisation or cross-linking reactions controlling the formation of char. In contrast, however, the subsequent shift in the main reaction region of coal TSH could have been the result of a retarded effect on the de-polymerisation reaction mechanism due to re-polymerisation (cross-linking) reactions controlling the devolatilization rate mechanism of this coal after metaplast formation.

A closer examination of P_5 in the DTG profiles revealed that the occurrence of this peak was much more prominent for the inertinite-rich coals (UMZ and INY) than for the vitrinite-rich coals (G#5 and TSH), suggesting a substantial difference in the reaction mechanism towards the end of devolatilization. According to Cai *et al.* (2008), the diminishing presence of the last stage of devolatilization could be ascribed to a depletion of aliphatic structures, oxygen-containing functionalities as well as other thermally unstable molecular functionalities. The sharp increase in the reaction rate of P_5 for INY and UMZ could therefore have been the result of some previously thermally stable bonds being broken to form secondary char in the higher temperature regime. Comparative curves have been constructed in Figure 7.7 in order to assess the effect of heating rate on coal devolatilization. From the Figure it can be seen that the TGA profiles of each coal shifted to the right (although only slightly) with increasing heating rate. This observation is supported by the subsequent increase in peak temperature values reported in Table 7.4 for all four coals and provides evidence of the kinetic compensation effect normally observed during variable heating rate TG measurements (Aboyade *et al.*, 2012; Cabalero & Conesa, 2005; Seo *et al.*, 2011; Wang *et al.*, 2010). Investigations involving the evaluation of devolatilization kinetics of coals and/or biomasses have attributed this delay in thermal decomposition of samples to differences in heat transfer and kinetic rates (Seo *et al.*, 2010 & 2011; Williams & Besler, 1996). In addition, it can be seen from Table 7.4 that an increase in heating rate led to a subsequent increase in the mass loss rate (MR values) of each identified peak, therefore supporting the thermal lag phenomena associated with the heating rate effect.

In general, the mass loss rate was found to be the highest for peaks P₁, P₂ and P₃ of coal G#5, followed by coals INY and UMZ, while the lowest values were determined for coal TSH. At higher temperatures, mass loss rates were found to be the highest for the two inertinite-rich coals.

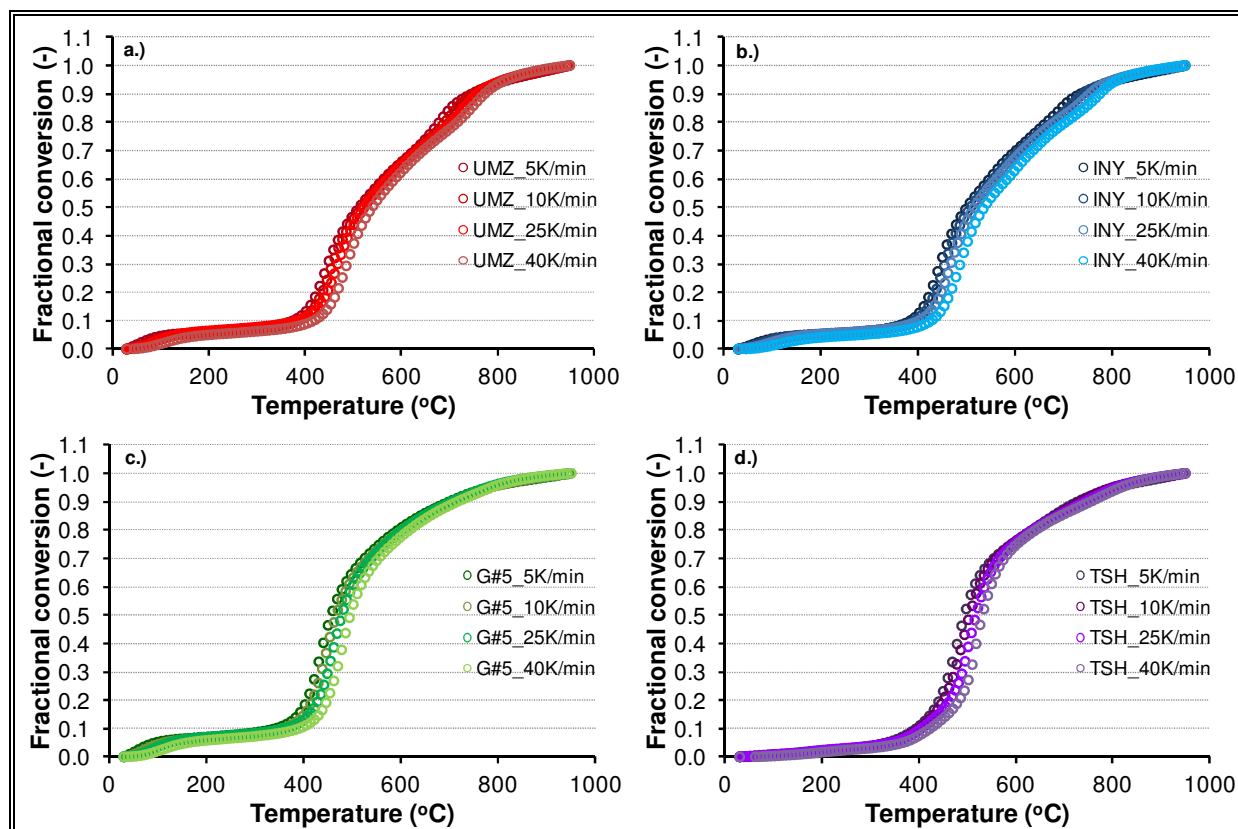


Figure 7.7 Effect of heating rate on the devolatilization rate of the different coals: a.) UMZ, b.) INY, c.) G#5 and d.) TSH.

The significant difference in mass loss reactivity (in particular for the main devolatilization zone) between the different coals can also be related to substantial differences in coal structural properties. From this perspective, the highly reactive nature of coals G#5 and TSH can be attributed to the presence of more reactive material (vitrinite and especially the substantial amount of liptinite present in coal G#5), while the slower thermal decomposition rate of the inertinite-rich coals strongly agrees with their exceptionally high amounts of inert material (inert inertodetrinite and inert semifusinite) when compared to the other two coals. Rate profiles and systematic trends observed in this investigation showed excellent agreement with findings made by Aboyade *et al.* (2011 & 2012), Seo *et al.* (2010 & 2011), Wang *et al.* (2010) and Zhang *et al.* (2007) during non-isothermal devolatilization studies on coals and/or biomasses.

7.6.2 Large particle devolatilization

7.6.2.1 Qualitative physical changes

Coal particles used for large particle devolatilization experiments were photographed before and after each experimental run, to observe any qualitative changes in the physical structure and integrity of the particles. Qualitative changes in the coal structure of selected particles are shown in Figures 7.8 and 7.9 for devolatilization temperatures of 450 °C and 900 °C respectively. Photographs of the other 4 devolatilization temperatures are provided in Appendix D.4. From the figures it is evident that no significant changes occurred externally to the inertinite-rich coal particles submitted to devolatilization temperatures below 450 °C. Minor fracture lines with accompanying larger cracks occurred when coals UMZ and INY were heated at temperatures above 450 °C. This was accompanied by slight particle shrinkage at 900 °C as shown in Figure 7.8, and is consistent with findings from Ruhr dilatometry.

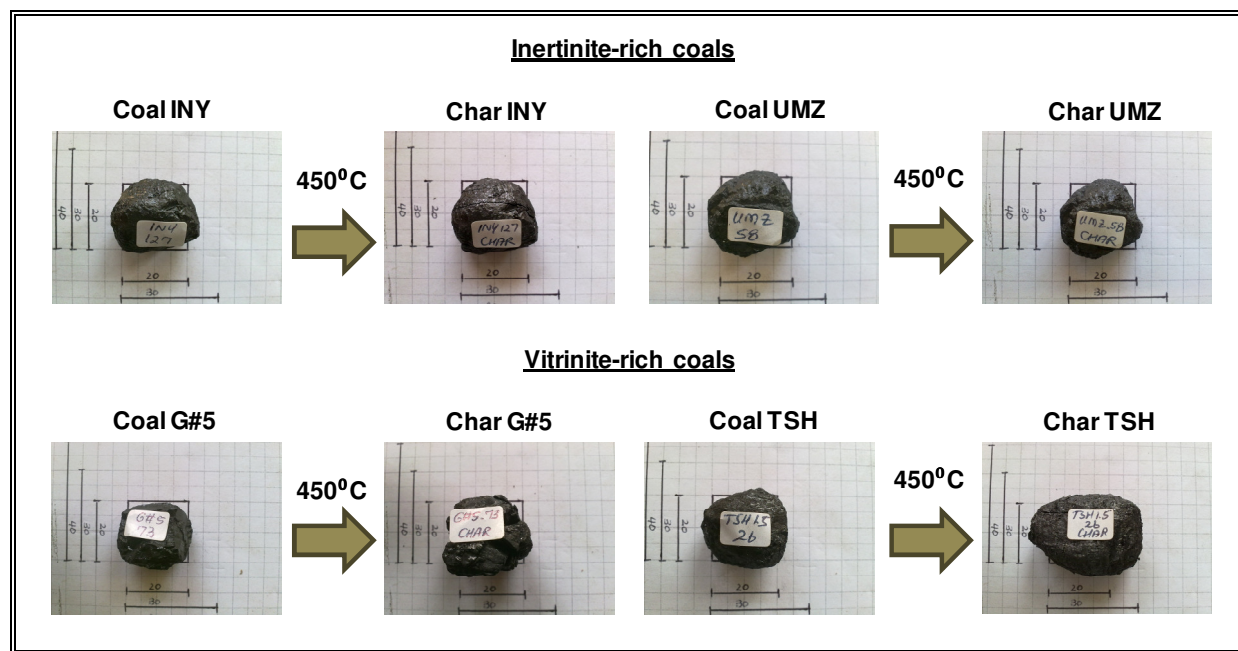


Figure 7.8 Coal particles before and after devolatilization at 450 °C.

The vitrinite-rich coals exhibited quite different behaviour compared to their inertinite-rich counterparts. Particle volume change of both coals TSH and G#5 was observed at temperatures as low as 450 °C, with particles swelling to almost twice their size for coal TSH (Figures 7.8 and 7.9), as expected for coals rich in vitrinite (Du Cann, 2002).

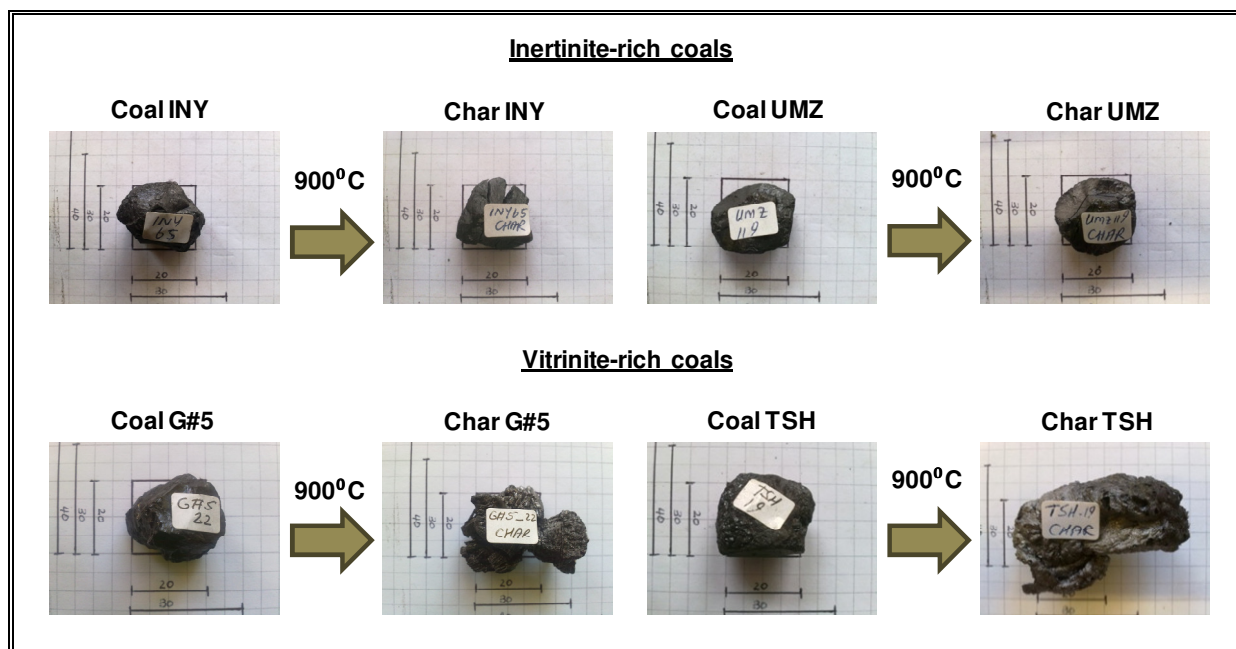


Figure 7.9 Coal particles before and after devolatilization at 900°C.

Chars produced at different temperatures from coal G#5 were characterised with extensive fissures parallel to the lithotype bands. Some vertical fissures were also visible at higher temperatures. Similar observations were made by Beukman (2009) and Minkina *et al.* (2010) during their investigation of the devolatilization of lump coal particles.

Chars produced from coal TSH at different temperatures did not display a large extent of observable external cracks or fissures as observed for coal G#5, but were characterised as containing a myriad of hollow thin-walled internal pore structures. This indicates that coal TSH most probably went through a metaplast formation stage which entailed the physical mobilization of aromatic-rich structures and the subsequent formation of “bubbles” due to the influx and saturation of tar and gas vapours in the melted coal structure (Lynch *et al.*, 1988; Oh *et al.*, 1989; Smith *et al.*, 1994).

7.6.2.2 Rates of large particle devolatilization

A typical mass loss result at isothermal LPTGA operation at 600°C is shown for coal G#5 in Figure 7.10. The temperature measured directly above the particle is also included to show that the experimental runs were indeed performed at isothermal furnace operation.

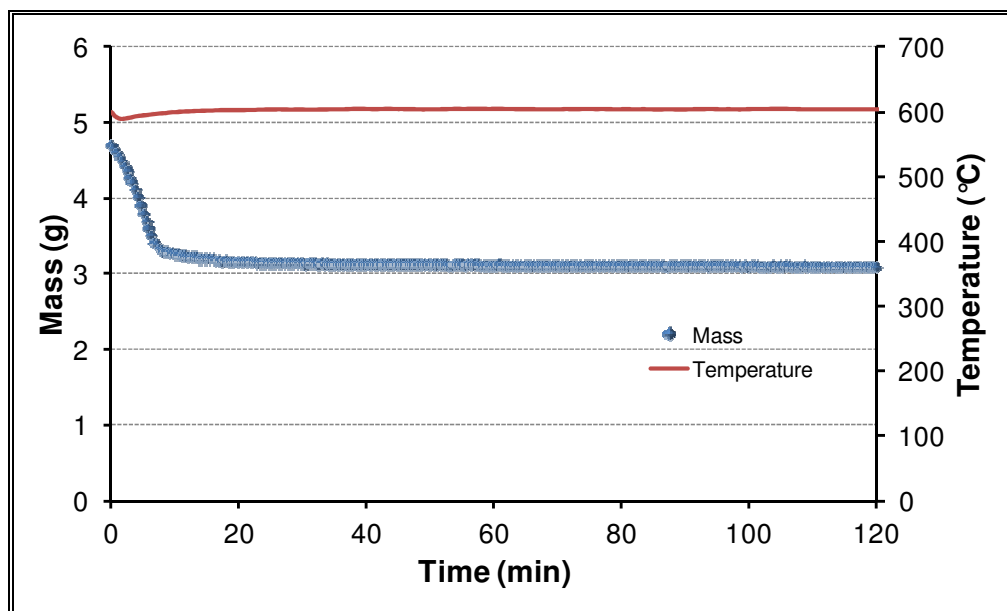


Figure 7.10 Experimental result as obtained for coal G#5 at 600°C.

The use of a single coal particle per experimental run necessitated the evaluation of approximately eight devolatilization experiments in order to obtain a representative result for each coal type. For comparison purposes, the mass results were normalised based on the initial mass (m_0) of coal prior to each experiment. Typical normalised results for coal G#5 at 600°C are shown in Figure 7.11.

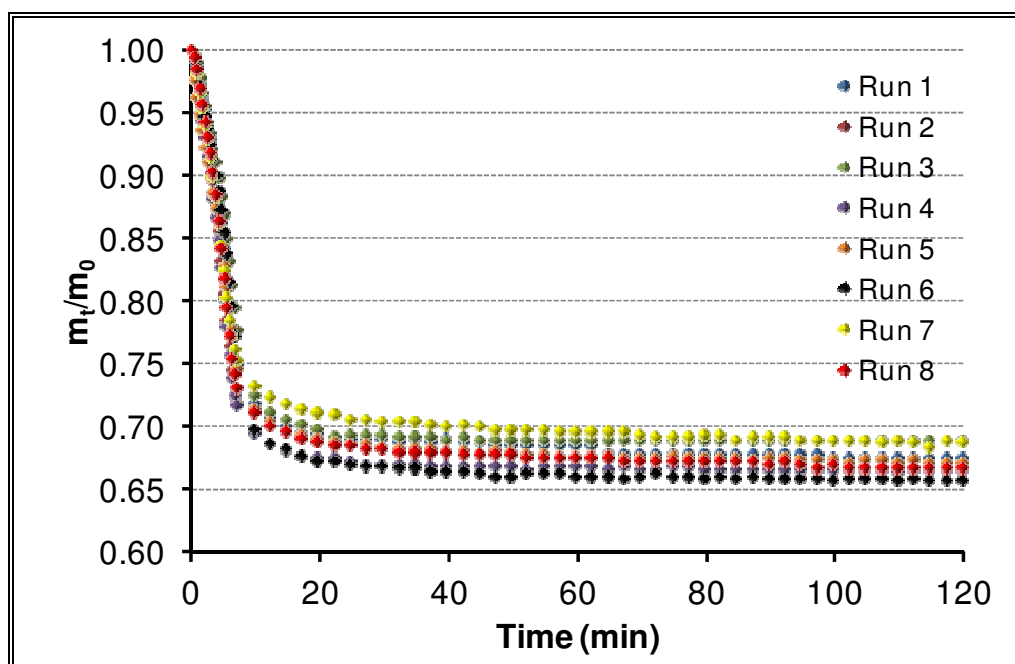


Figure 7.11 Normalised devolatilization results for coal G#5 at 600°C.

From Figure 7.11 it can be seen that the typical mass loss at 600°C from coal G#5 ranged between 31 wt.% and 34 wt.%. The discrepancy in the results of the eight different particles can, however, be attributed to the heterogeneity existing between different coal particles. Although small differences in final mass loss value occurred between the different experimental runs, overall repeatability was better in comparison to what was obtained by Beukman (2009). This can most probably be attributed to the use of mercury submersion as an additional large particle selection technique. Similar observations were made for the other three coals, which are included in Appendix D.5. The average of all eight experiments per coal was determined in order to describe the devolatilization behaviour of a particular coal at a certain temperature.

Effect of devolatilization temperature

The influence of operating temperature on the devolatilization rate of coals UMZ, INY, G#5 and TSH is provided in Figures 7.12 and 7.13. Coal devolatilization behaviour over the extent of total reaction time is shown in Figure 7.12 (a-d), whilst the devolatilization behaviour within the first 30 minutes of reaction for each coal is given in Figure 7.13 (a-d). In addition, an overview of the ultimate volatile yields generated, as a function of devolatilization temperature, is summarised for the different coals in Table 7.5.

Table 7.5 Effect of experimental temperature on the ultimate volatile yield.

Ultimate volatile yields (V*)		Inertinite-rich coals		Vitrinite-rich coals	
Devolatilization temperature	Unit	INY	UMZ	G#5	TSH
350 °C	wt. %	4.14±0.37	4.73±0.76	6.98±0.87	1.34±0.24
450 °C	wt. %	10.87±2.41	10.03±1.38	23.31±2.38	6.71±1.53
550 °C	wt. %	15.40±2.68	17.03±3.31	30.45±1.70	12.84±1.43
600 °C	wt. %	17.59±2.98	18.50±1.66	32.87±1.27	14.23±1.56
650 °C	wt. %	19.77±2.31	20.89±2.94	33.65±2.61	16.46±2.65
750 °C	wt. %	23.27±2.17	23.76±3.00	35.38±2.37	18.64±2.68
900 °C	wt. %	27.28±3.28	26.61±2.44	36.98±1.67	22.14±1.79
Proximate volatile matter + moisture	wt. %	27.1	27.3	36.9	21.1

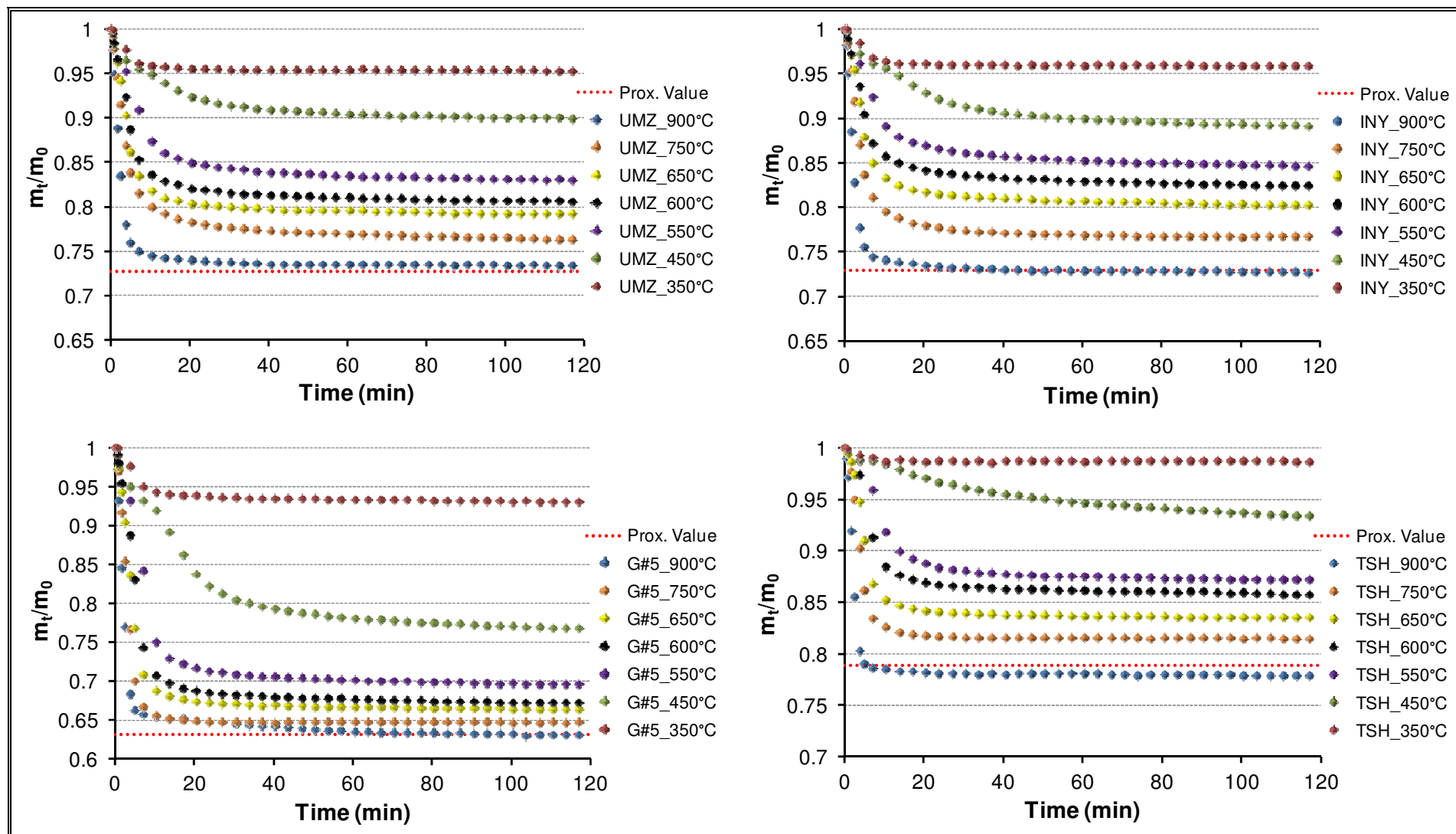


Figure 7.12 Effect of temperature on the devolatilization rate of coals a) UMZ, b) INY, c) G#5 and d) TSH for total reaction time.

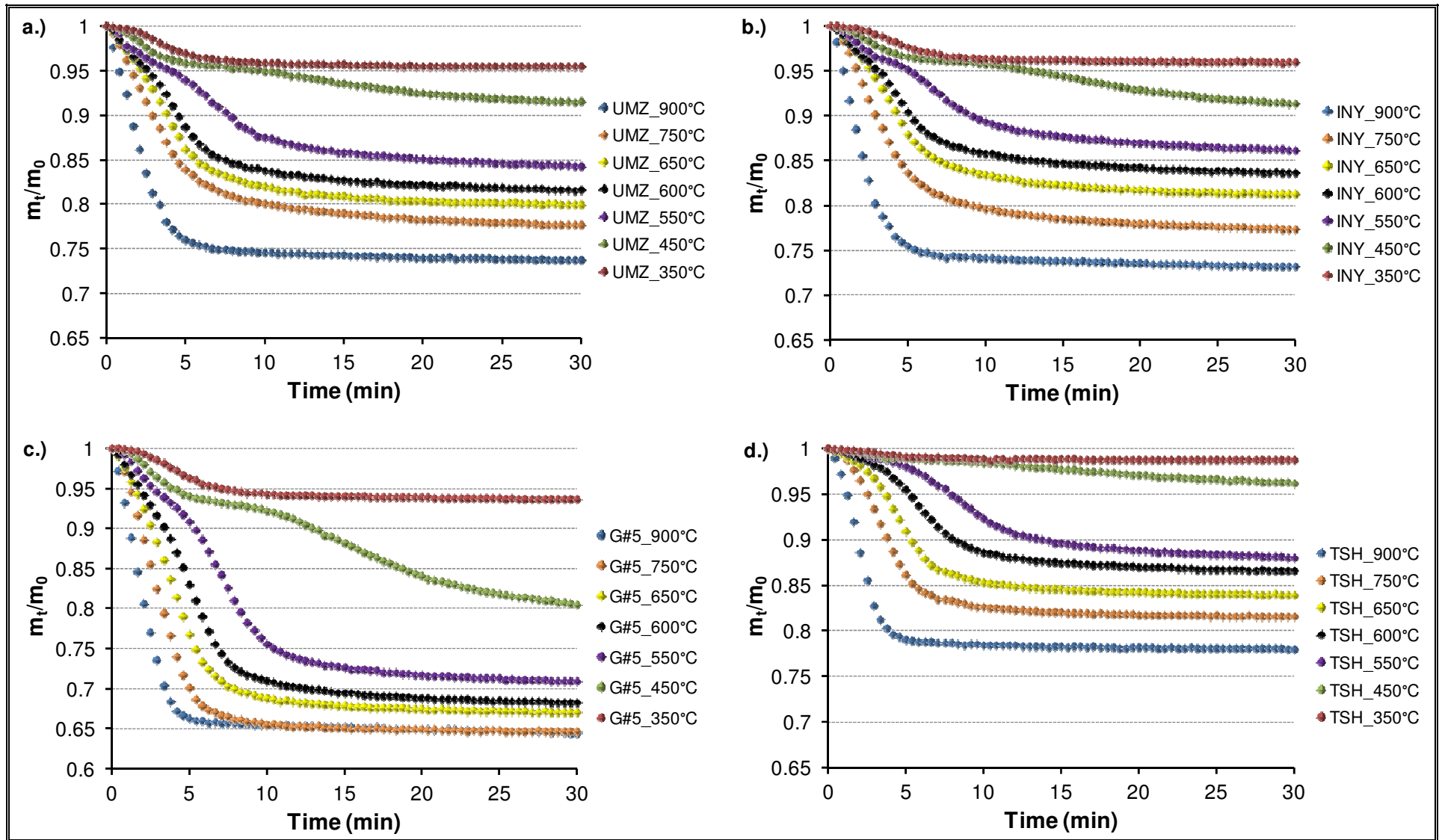


Figure 7.13 Effect of temperature on the initial devolatilization rate of coals a) UMZ, b) INY, c) G#5 and d) TSH for the first 30 minutes.

From Figures 7.12 and 7.13 it is evident that the rate of volatile release reached a maximum for each temperature during the first 20 minutes of devolatilization, whereafter the rate decreased proportionally until the volatile loss reached a nearly constant, asymptotic value in the range of 80-120 minutes. This is supported by the work of Beukman (2009), Fu *et al.* (1987), Sadhukhan *et al.* (2012), Van der Merwe (2010) and Zhang *et al.* (2012), who observed similar orders of magnitude in the rate of volatile loss as seen in this investigation. Furthermore, the mass loss curves of all four coals showed a distinct lag in the release of volatiles in the first 5 minutes of especially the lower temperature experimental runs (Figure 7.13). This can be attributed to the heating of the particle to the isothermal reaction temperature and is consistent with findings made by Beukman (2009) and Van der Merwe (2010). This stage becomes less prominent for devolatilization temperatures above 650°C. When the desired isothermal particle temperature is reached, the devolatilization process is characterised by rapid volatile release following the initial slow devolatilization.

From Table 7.5 it is clear that the maximum (ultimate yield) of volatiles released increases with increasing temperature. This was especially evident for coals UMZ, INY and TSH, with the exception of coal G#5 which showed a very rapid convergence of the total amount of volatiles at temperatures above 750°C. In addition, low volatile yields, of between 1 wt.% and 7 wt.%, and the subsequent completion of volatile release within only 10 minutes were observed for the devolatilization experiments at 350°C. This can be ascribed to the fact that primary devolatilization (which is characterised by the release of primary gases and-tars) has not yet been initiated and that the observed mass loss is mainly attributed to the release of inherent moisture, crystal water associated with inherent minerals, as well as the vaporization and transport of loosely bounded molecular species described as the so-called molecular phase (Alonso *et al.*, 2001; Boiko, 2000; Solomon *et al.*, 1992). Ultimate volatile yields at 900°C closely resembled the amount of volatiles (volatile matter plus moisture content) as measured with proximate analysis, although in all cases slightly larger values were reported. This can be explained by the longer residence times used compared to that of the proximate analysis (Beukman, 2009; Gibbins & Kandiyoti, 1989). Orders of the amount volatiles released (TSH < UMZ, INY < G#5) were also found to adhere to the significant discrepancies in coal structural properties (maceral content and aromaticity) as established from the product evolution (Chapter 6) and small particle devolatilization studies (Section 7.6.1).

7.7 Particle modelling and parameter estimation

7.7.1 Intrinsic kinetic parameter evaluation

7.7.1.1 Modelling and curve fitting results

Kinetic modelling was performed on the TGA data (all four heating rates) of all four coals by applying the strategy as outlined in Section 7.5.1. Kinetic analysis was performed by varying the number of pseudo-components between 3 and 8, with the number of pseudo-components representing the number of independent parallel reactions (Aboyade *et al.*, 2012; Alonso *et al.*, 2001). A maximum number of 200 subsets of initial values was provided as input to the Levenberg-Marquardt algorithm, in order to solve the required kinetic parameters. Table 7.6 summarises the quality of fit (*QOF*) values determined separately for each heating rate during the kinetic analyses, as well as the global *QOF* for all four heating rates (5-40 K/min) combined.

Table 7.6 Quality of fit or percentage deviation for the simulated rate curves^a.

Coal samples	Heating rate	QOF (Number of pseudo-component reactions)					
		3	4	5	6	7	8
INY	5 K/min	9.84	8.31	7.06	5.44	4.26	3.84
	10 K/min	7.02	5.54	4.81	3.45	2.52	2.33
	25 K/min	3.94	2.74	2.76	2.22	2.04	1.74
	40 K/min	3.40	2.46	2.13	1.71	1.45	1.25
	Overall	6.05	4.76	4.19	3.21	2.57	2.29
UMZ	5 K/min	14.10	10.50	8.90	6.58	5.65	4.88
	10 K/min	9.27	6.94	5.37	3.94	3.40	2.75
	25 K/min	4.81	3.20	2.46	2.25	2.16	1.85
	40 K/min	3.65	2.68	2.12	1.77	1.58	1.01
	Overall	7.97	5.82	4.72	3.63	3.20	2.62
G#5	5 K/min	8.48	6.67	4.97	4.68	4.01	3.46
	10 K/min	5.62	4.09	3.26	2.96	2.46	2.11
	25 K/min	3.10	2.12	1.92	1.67	1.54	1.50
	40 K/min	2.81	1.87	1.55	1.13	1.03	0.90
	Overall	5.00	3.68	2.93	2.61	2.26	1.99
TSH	5 K/min	7.41	6.13	4.94	4.33	4.07	4.12
	10 K/min	5.08	4.44	3.54	3.27	2.96	2.93
	25 K/min	2.91	2.25	1.95	1.90	1.63	1.49
	40 K/min	2.84	2.02	1.75	1.68	1.21	1.04
	Overall	4.56	3.71	3.05	2.80	2.47	2.40

^a Estimated from the experimental data according to Equation (3.16).

In addition, graphical comparisons between the experimental and modelled DTG/TG curves of the four coals are provided in Figure 7.14 to 7.17, respectively. Equation (3.13) was used in the construction of the modelled DTG profiles by using the derived kinetic parameters, while Equation (7.6) was employed for construction of the simulated, fractional conversion curves (TG curves). Only the model validations, assuming three, four, five and eight pseudo-components, of the 25 K/min and the 40 K/min experiments have been included for illustrative purposes in Figures 7.14 and 7.15, while comparisons of the modelled TG curves, at the four heating rates, assuming 3 and 8 pseudo-components can be found in Figures 7.16 and 7.17 for coals INY and TSH. Other comparative TG/DTG plots are included in Appendix D.6.

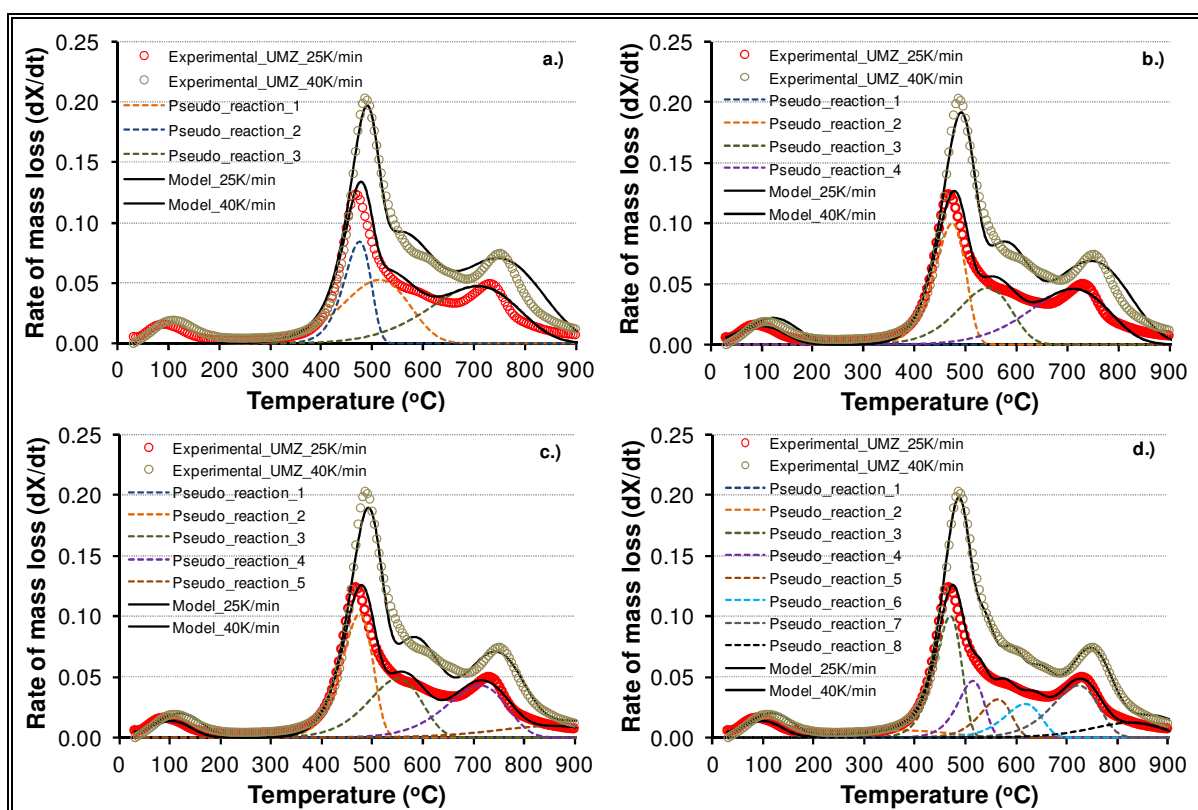


Figure 7.14 Simulated reaction rate curves for coal UMZ based on the first order model of a.) 3, b.) 4, c.) 5 and d.) 8 pseudo-components.

From the Table it is evident that the assumption of three pseudo-components yielded relatively poor global *QOF* values (4.56%-7.97%), while a further increase in the amount of assumed pseudo-components resulted in a remarkable enhancement of both the individual- and global *QOF* values from as high as 14.10% to as low as 0.90%. This is also reflected in the graphical representations provided in Figures 7.14 to 7.17, which show better reproduction of the respective experimental DTG curves for increasing amounts of assumed pseudo-components.

Simulation of higher values of pseudo-components (7 and 8) did, however, require longer computational times and provided only minor improvements in the quality of fit for some cases. The assumption of the amount of pseudo-components was therefore only restricted to 8 as larger values could have induced the risk of over fitting of the experimental rate data (Aboyade *et al.*, 2012; Roduit, 2000). Furthermore, the aforementioned results showed good agreement with the results obtained by Aboyade *et al.* (2012). Accordingly, *QOF* values of between 1.9% and 16.0% were obtained for the amount of pseudo-components ranging between 1 and 5 (Aboyade *et al.*, 2012).

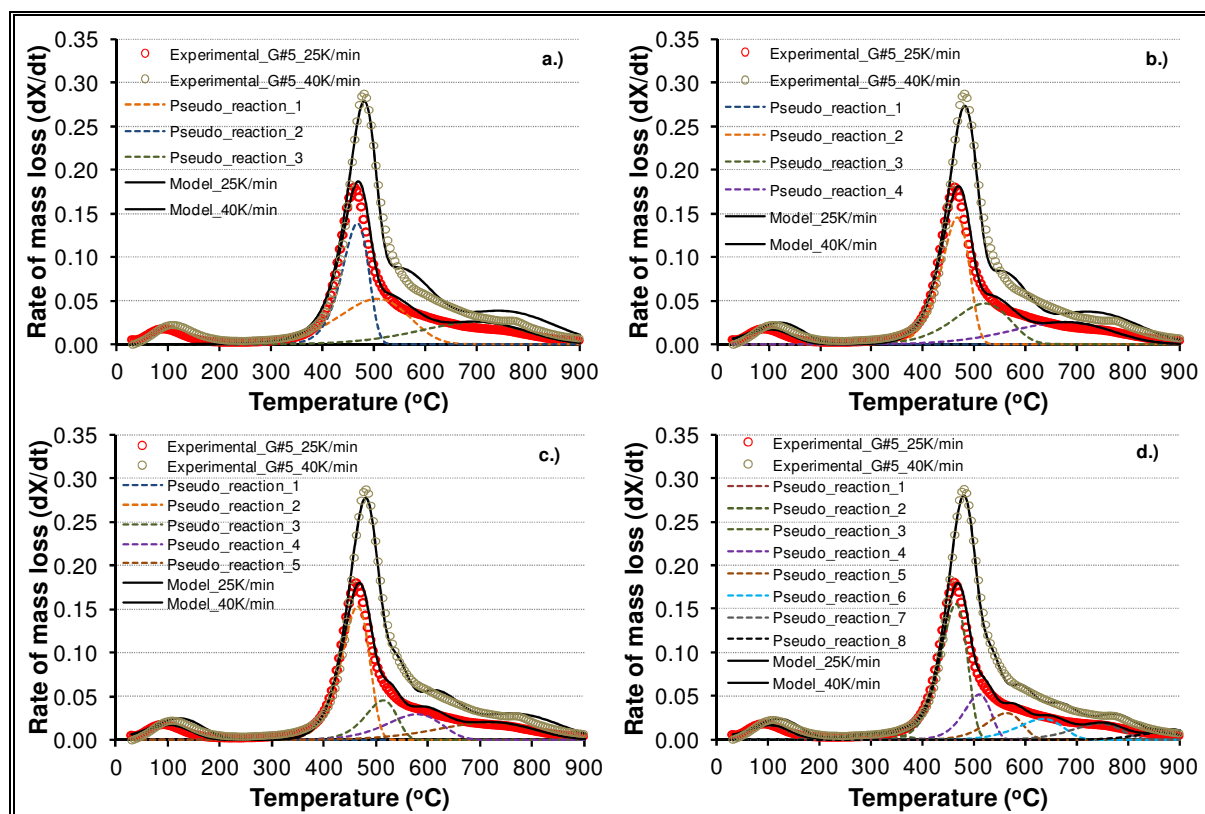


Figure 7.15 Simulated reaction rate curves for coal G#5 based on the first order model of a.) 3, b.) 4, c.) 5 and d.) 8 pseudo-components.

Examination of the modelling results provided in Table 7.6 revealed that significantly better fit qualities (global and individual) were obtained for the vitrinite-rich coals in comparison to their inertinite-rich counterparts. This can be attributed to the fact that the DTG curves of the vitrinite-rich coals are not characterised by the presence of well resolved reaction peaks confined to temperature ranges exceeding $\sim 500^{\circ}\text{C}$, which eased peak deconvolution.

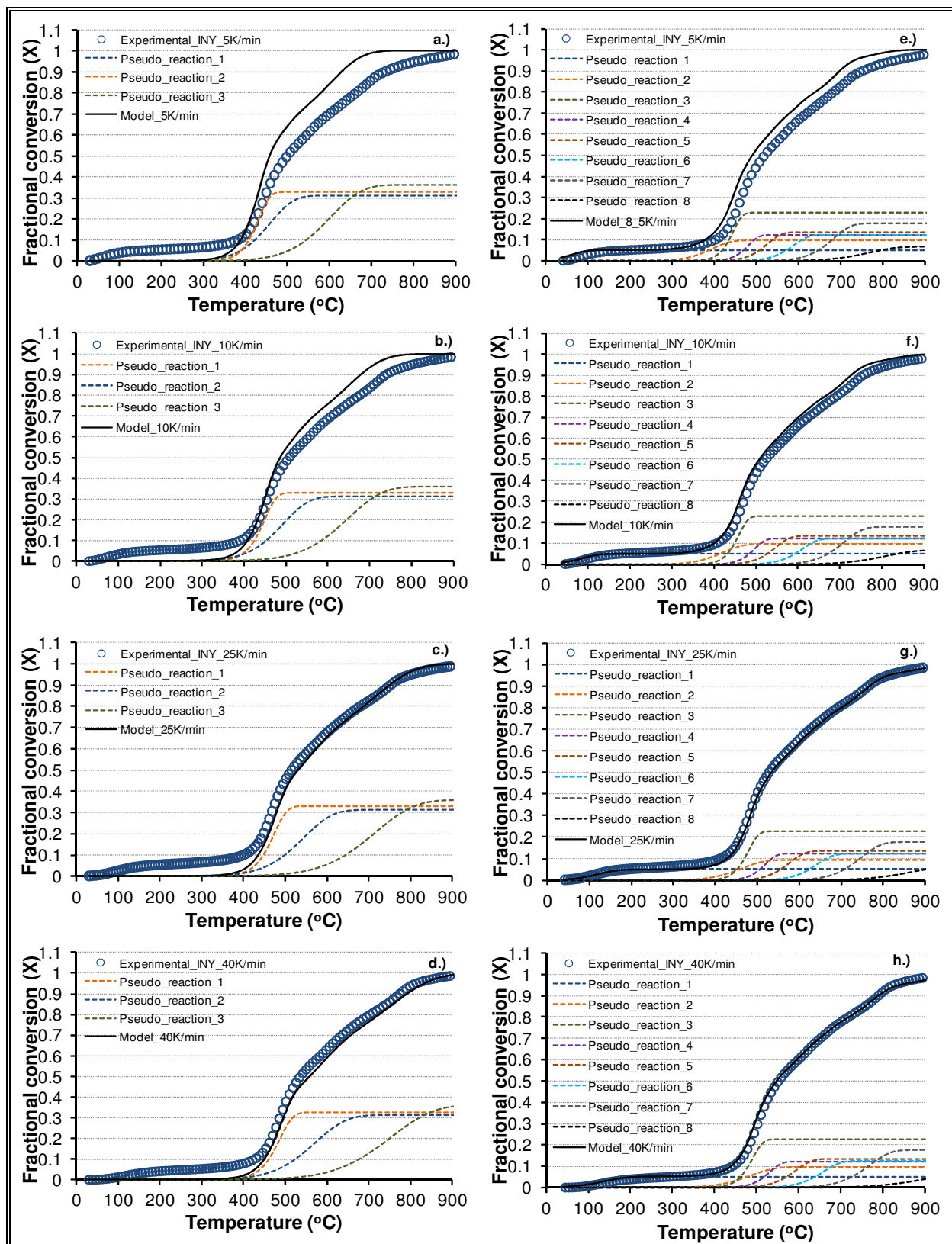


Figure 7.16 Comparison between experimental and modelled TG curves for coal INY assuming a-d.) 3 reactions and e-h.) 8 reactions.

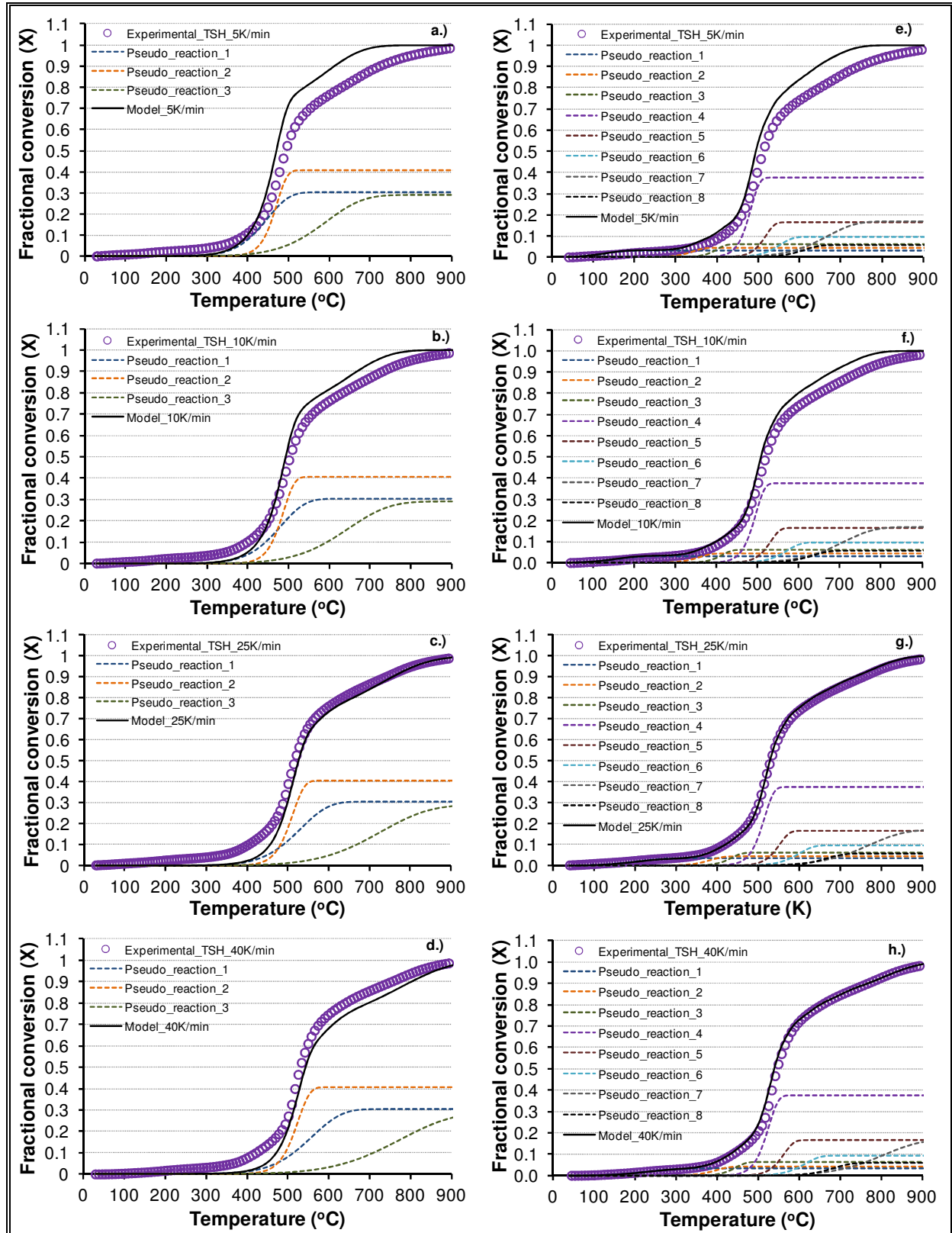


Figure 7.17 Comparison between experimental and modelled TG curves for coal TSH assuming a-d.) 3 reactions and e-h.) 8 reactions.

Although the assumption of 4 pseudo reactions produced relatively poor *QOF* values, the assumption was however consistent with generally accepted decomposition mechanisms for coal as proposed by Alonso *et al.*, (2001), Serio *et al.*, (1987); and Van Heek and Hodek (1994). Additionally, the description of inertinite-rich coal decomposition required further deconvolution of the secondary devolatilization regime (above 500°C) to obtain adequate improvements in the fit quality, while the model predictions for the vitrinite-rich coals (Figures 7.15 and 7.17) showed reasonable good fits for only 4 pseudo-components due to the less prominent nature of secondary reaction components when compared to the inertinite-rich coals (Figure 7.14 and 7.16). This postulation therefore suggests that secondary reactions play a progressively larger role in the devolatilization mechanism of inertinite-rich coals compared to that of vitrinite-rich coals where devolatilization is concentrated largely in the primary devolatilization regime as seen from the large contribution of the deconvoluted peak in the 350-550°C temperature range. Furthermore, a decrease in heating rate resulted in the deterioration of the subsequent *QOF* values as observed from Table 7.6. For all four coals it was evident that *QOF* values for the lower heating rates (5 and 10 K/min) were substantially higher than those estimated for 25 K/min and 40 K/min, which could be ascribed to the simultaneous fitting of kinetic parameters to the different heating rates. This is consistent with findings made on the devolatilization of biomasses and/or coals by Aboyade *et al.* (2012) and Branca *et al.* (2005). According to Branca *et al.* (2005), the disparity in the *QOF* values between different heating rates can be explained by the fact that the complex structure of both biomasses and coal consist of more components that can be physically envisaged by kinetic models. In other words, better fit qualities can be obtained by assuming a larger number of pseudo-components during multi-component analysis, which has been found to be particularly true for lower heating rates where the probability of better separation into individual component reactions exists (Aboyade *et al.*, 2011). Consequently, in order to achieve similar levels of fit as higher heating rates, multi-component kinetic analysis of lower heating rates necessitates the assumption of more pseudo-components.

7.7.1.2 Kinetic parameters for coal devolatilization

An overview of kinetic parameters (ξ_i , $E_{a,i}$ and $k_{0,i}$) derived from multi-component kinetic analysis of the different coals is provided respectively in Tables 7.7-7.10 for coals INY, UMZ, G#5 and TSH. The tables include the kinetic results for each assumption of the amount of pseudo-components as well as the respective values obtained for *OBF* and *QOF*.

Table 7.7 Kinetic parameters for coal INY obtained from 1st order model fitting on multiple heating rate data (5-40 K/min).

Kinetic parameter	Coal INY (Number of pseudo-component reactions)					
	3 reactions ^a	4 reactions ^a	5 reactions ^a	6 reactions ^a	7 reactions ^a	8 reactions ^a
E_{a1} (kJ/mol)	152.03±10.8	22.91±1.38	22.81±1.16	24.46±0.96	23.88±0.73	24.21±0.67
$k_{0,1}$ (s ⁻¹)	(5.84±0.42)×10 ⁸	(1.04±0.63)×10 ¹	(9.82±0.50)×10 ⁰	(1.82±0.71)×10 ¹	(1.45±0.45)×10 ¹	(1.67±0.46)×10¹
ξ_1 (-)	0.33±0.02	0.06±0.00	0.06±0.00	0.05±0.00	0.05±0.00	0.05±0.00
E_{a2} (kJ/mol)	81.32±5.78	150.45±9.03	161.56±8.23	163.98±6.44	165.71±5.10	82.36±2.28
$k_{0,2}$ (s ⁻¹)	(9.52±0.68)×10 ²	(4.42±0.27)×10 ⁸	(3.40±0.17)×10 ⁹	(5.03±0.20)×10 ⁹	(6.89±0.21)×10 ⁹	(6.42±0.18)×10³
ξ_2 (-)	0.31±0.02	0.34±0.02	0.31±0.02	0.30±0.01	0.31±0.01	0.09±0.00
E_{a3} (kJ/mol)	87.03±6.18	90.22±5.42	171.01±8.71	166.85±6.56	188.98±5.81	192.43±5.33
$k_{0,3}$ (s ⁻¹)	(1.75±0.12)×10 ²	(3.36±0.20)×10 ³	(3.03±0.15)×10 ⁹	(1.52±0.60)×10 ⁹	(5.25±0.16)×10 ¹⁰	(5.63±0.16)×10¹¹
ξ_3 (-)	0.36±0.03	0.28±0.02	0.12±0.01	0.13±0.01	0.13±0.00	0.23±0.01
E_{a4} (kJ/mol)	-	96.94±5.82	114.01±5.81	118.53±4.66	169.10±5.20	193.62±5.37
$k_{0,4}$ (s ⁻¹)	-	(6.37±0.38)×10 ²	(7.16±0.37)×10 ⁴	(1.20±0.05)×10 ⁵	(3.45±0.11)×10 ⁸	(1.25±0.04)×10¹¹
ξ_4 (-)	-	0.32±0.02	0.22±0.01	0.23±0.01	0.13±0.00	0.12±0.01
E_{a5} (kJ/mol)	-	-	109.32±5.57	147.68±5.80	178.57±5.49	163.03±4.52
$k_{0,5}$ (s ⁻¹)	-	-	(2.79±0.14)×10 ³	(3.58±0.14)×10 ⁵	(2.07±0.06)×10 ⁸	(1.51±0.04)×10⁸
ξ_5 (-)	-	-	0.29±0.01	0.21±0.01	0.12±0.00	0.13±0.00
E_{a6} (kJ/mol)	-	-	-	104.44±4.10	178.49±5.49	176.26±4.88
$k_{0,6}$ (s ⁻¹)	-	-	-	(2.07±0.08)×10 ²	(1.39±0.04)×10 ⁷	(1.52±0.04)×10⁸
ξ_6 (-)	-	-	-	0.08±0.00	0.18±0.01	0.12±0.00
E_{a7} (kJ/mol)	-	-	-	-	112.17±3.45	182.02±5.04
$k_{0,7}$ (s ⁻¹)	-	-	-	-	(5.12±0.16)×10 ²	(2.16±0.06)×10⁷
ξ_7 (-)	-	-	-	-	0.08±0.00	0.18±0.00
E_{a8} (kJ/mol)	-	-	-	-	-	140.54±3.89
$k_{0,8}$ (s ⁻¹)	-	-	-	-	-	(1.65±0.05)×10⁴
ξ_8 (-)	-	-	-	-	-	0.07±0.00
OBF^b	8.77×10⁻⁶	5.23×10⁻⁶	3.85×10⁻⁶	2.51×10⁻⁶	1.89×10⁻⁶	1.51×10⁻⁶
Overall QOF^c	6.05	4.76	4.19	3.21	2.57	2.29

^a Kinetic parameters evaluated by the Levenberg-Marquardt algorithm according to Equation (7.6). ^b Objective function (OBF) evaluated according to Equation (3.15). ^c Global/overall quality of fit evaluated according to Equation (3.16).

Table 7.8 Kinetic parameters for coal UMZ obtained from 1st order model fitting on multiple heating rate data (5-40 K/min).

Kinetic parameter	Coal UMZ (Number of pseudo-component reactions)					
	3 reactions ^a	4 reactions ^a	5 reactions ^a	6 reactions ^a	7 reactions ^a	8 reactions ^a
E_{a1} (kJ/mol)	72.53±6.61	22.33±1.51	25.06±1.44	24.37±1.03	24.97±0.91	25.63±0.81
$k_{0,1}$ (s ⁻¹)	(3.81±0.35)×10 ²	(1.03±0.07)×10 ¹	(2.79±0.16)×10 ¹	(2.18±0.09)×10 ¹	(2.68±0.09)×10 ¹	(3.58±0.11)×10¹
ξ_1 (-)	0.35±0.03	0.07±0.00	0.06±0.00	0.06±0.00	0.06±0.00	0.06±0.00
E_{a2} (kJ/mol)	173.86±15.84	148.87±10.05	148.79±8.54	159.09±6.75	159.56±5.81	33.55±1.06
$k_{0,2}$ (s ⁻¹)	(2.11±0.19)×10 ¹⁰	(3.45±0.23)×10 ⁸	(3.32±0.19)×10 ⁸	(2.14±0.09)×10 ⁹	(2.30±0.08)×10 ⁹	(1.88±0.06)×10⁹
ξ_2 (-)	0.23±0.02	0.32±0.02	0.32±0.02	0.30±0.01	0.30±0.01	0.05±0.00
E_{a3} (kJ/mol)	84.60±7.71	100.02±6.75	101.71±5.84	167.89±7.13	166.51±6.06	176.11±5.54
$k_{0,3}$ (s ⁻¹)	(1.41±0.13)×10 ²	(1.88±0.13)×10 ⁴	(2.12±0.12)×10 ⁴	(1.40±0.06)×10 ⁹	(1.10±0.04)×10 ⁹	(3.66±0.12)×10¹⁰
ξ_3 (-)	0.42±0.04	0.25±0.02	0.26±0.02	0.14±0.01	0.14±0.00	0.27±0.01
E_{a4} (kJ/mol)	-	96.89±6.54	129.53±7.44	136.94±5.81	138.79±5.06	196.85±6.19
$k_{0,4}$ (s ⁻¹)	-	(6.94±0.47)×10 ²	(4.92±0.28)×10 ⁴	(1.83±0.07)×10 ⁶	(2.25±0.08)×10 ⁶	(1.72±0.05)×10¹¹
ξ_4 (-)	-	0.36±0.02	0.26±0.01	0.17±0.01	0.17±0.01	0.13±0.00
E_{a5} (kJ/mol)	-	-	94.38±5.42	153.56±6.52	167.48±6.10	186.82±5.88
$k_{0,5}$ (s ⁻¹)	-	-	(8.57±0.49)×10 ¹	(9.22±0.39)×10 ⁵	(5.73±0.21)×10 ⁶	(5.91±0.19)×10⁹
ξ_5 (-)	-	-	0.10±0.01	0.23±0.01	0.21±0.01	0.10±0.00
E_{a6} (kJ/mol)	-	-	-	102.69±4.36	175.41±6.39	177.97±5.60
$k_{0,6}$ (s ⁻¹)	-	-	-	(2.51±0.11)×10 ²	(2.77±0.10)×10 ⁶	(2.95±0.09)×10⁸
ξ_6 (-)	-	-	-	0.10±0.00	0.06±0.00	0.10±0.00
E_{a7} (kJ/mol)	-	-	-	-	129.11±4.70	174.68±5.49
$k_{0,7}$ (s ⁻¹)	-	-	-	-	(1.81±0.07)×10 ³	(1.24±0.04)×10⁷
ξ_7 (-)	-	-	-	-	0.06±0.00	0.21±0.01
E_{a8} (kJ/mol)	-	-	-	-	-	138.32±4.35
$k_{0,8}$ (s ⁻¹)	-	-	-	-	-	(2.04±0.39)×10⁴
ξ_8 (-)	-	-	-	-	-	0.09±0.00
OBFB	1.09×10⁻⁵	5.77×10⁻⁶	4.13×10⁻⁶	2.45×10⁻⁶	2.26×10⁻⁶	1.38×10⁻⁶
Overall QOF^c	7.97	5.82	4.72	3.63	3.20	2.62

^a Kinetic parameters evaluated by the Levenberg-Marquardt algorithm according to Equation (7.6). ^b Objective function (OBF) evaluated according to Equation (3.15). ^c Global/overall quality of fit evaluated according to Equation (3.16).

Table 7.9 Kinetic parameters for coal G#5 obtained from 1st order model fitting on multiple heating rate data (5-40 K/min).

Kinetic parameter	Coal G#5 (Number of pseudo-component reactions)					
	3 reactions ^a	4 reactions ^a	5 reactions ^a	6 reactions ^a	7 reactions ^a	8 reactions ^a
E_{a1} (kJ/mol)	68.47±5.52	23.35±1.48	23.41±1.11	25.75±1.15	25.38±0.98	26.00±0.86
$k_{0,1}$ (s ⁻¹)	(2.15±0.17)×10 ²	(1.49±0.09)×10 ¹	(1.52±0.07)×10 ¹	(3.67±0.16)×10 ¹	(3.68±0.14)×10 ¹	(3.49±0.13)×10¹
ξ_1 (-)	0.36±0.03	0.08±0.00	0.08±0.00	0.07±0.00	0.07±0.00	0.07±0.00
E_{a2} (kJ/mol)	174.83±14.09	164.71±10.44	164.77±7.79	47.67±2.12	58.87±2.24	53.54±1.76
$k_{0,2}$ (s ⁻¹)	(3.24±0.26)×10 ¹⁰	(6.27±0.40)×10 ⁹	(6.98±0.33)×10 ⁹	(1.41±0.06)×10 ²	(1.29±0.05)×10 ³	(4.20±0.14)×10²
ξ_2 (-)	0.37±0.03	0.41±0.03	0.43±0.02	0.03±0.00	0.03±0.00	0.03±0.00
E_{a3} (kJ/mol)	69.63±5.61	91.09±5.78	168.39±7.97	169.30±7.54	170.16±6.48	171.40±5.64
$k_{0,3}$ (s ⁻¹)	(2.03±0.16)×10 ¹	(7.11±0.45)×10 ³	(2.02±0.10)×10 ⁹	(1.49±0.07)×10 ¹⁰	(1.74±0.06)×10 ¹⁰	(2.17±0.16)×10¹⁰
ξ_3 (-)	0.27±0.02	0.26±0.02	0.14±0.01	0.42±0.02	0.42±0.02	0.42±0.01
E_{a4} (kJ/mol)	-	70.32±4.46	108.78±5.15	171.77±7.65	178.95±6.82	190.28±6.27
$k_{0,4}$ (s ⁻¹)	-	(2.84±0.18)×10 ¹	(3.47±0.16)×10 ⁴	(3.64±0.16)×10 ⁹	(1.19±0.04)×10 ¹⁰	(7.62±0.25)×10¹⁰
ξ_4 (-)	-	0.25±0.02	0.16±0.01	0.15±0.01	0.15±0.01	0.14±0.00
E_{a5} (kJ/mol)	-	-	81.89±3.87	114.61±5.10	135.28±5.15	163.71±5.39
$k_{0,5}$ (s ⁻¹)	-	-	(8.61±0.41)×10 ¹	(8.39±0.37)×10 ⁴	(2.20±0.08)×10 ⁶	(1.96±0.06)×10⁸
ξ_5 (-)	-	-	0.19±0.01	0.15±0.01	0.13±0.00	0.11±0.00
E_{a6} (kJ/mol)	-	-	-	84.76±3.78	109.90±4.19	150.65±4.96
$k_{0,6}$ (s ⁻¹)	-	-	-	(1.34±0.06)×10 ²	(8.61±0.33)×10 ³	(4.27±0.14)×10⁶
ξ_6 (-)	-	-	-	0.18±0.01	0.12±0.00	0.11±0.00
E_{a7} (kJ/mol)	-	-	-	-	109.18±4.16	175.34±5.77
$k_{0,7}$ (s ⁻¹)	-	-	-	-	(1.21±0.05)×10 ³	(8.42±0.27)×10⁶
ξ_7 (-)	-	-	-	-	0.09±0.00	0.09±0.00
E_{a8} (kJ/mol)	-	-	-	-	-	244.28±8.04
$k_{0,8}$ (s ⁻¹)	-	-	-	-	-	(1.65±0.05)×10⁹
ξ_8 (-)	-	-	-	-	-	0.03±0.00
OBF^b	1.19×10⁻⁵	5.59×10⁻⁶	3.84×10⁻⁶	2.97×10⁻⁶	2.48×10⁻⁶	2.15×10⁻⁶
Overall QOF^c	5.00	3.68	2.93	2.61	2.26	1.99

^a Kinetic parameters evaluated by the Levenberg-Marquardt algorithm according to Equation (7.6). ^b Objective function (OBF) evaluated according to Equation (3.15). ^c Global/overall quality of fit evaluated according to Equation (3.16).

Table 7.10 Kinetic parameters for coal TSH obtained from 1st order model fitting on multiple heating rate data (5-40 K/min).

Kinetic parameter	Coal TSH (Number of pseudo-component reactions)					
	3 reactions ^a	4 reactions ^a	5 reactions ^a	6 reactions ^a	7 reactions ^a	8 reactions ^a
E_{a1} (kJ/mol)	80.19±5.60	100.11±5.79	111.68±5.20	63.17±2.58	28.75±1.10	26.74±1.04
$k_{0,1}$ (s ⁻¹)	(9.87±0.69)×10 ²	(7.04±0.41)×10 ⁵	(5.13±0.24)×10 ⁶	(4.85±0.20)×10 ²	(3.44±0.13)×10 ⁰	(6.02±0.23)×10⁰
ξ_1 (-)	0.30±0.02	0.10±0.01	0.10±0.00	0.14±0.01	0.04±0.00	0.03±0.00
E_{a2} (kJ/mol)	181.62±12.69	201.17±11.64	201.78±9.40	212.93±8.70	134.79±5.17	114.52±4.46
$k_{0,2}$ (s ⁻¹)	(1.76±0.12)×10 ¹⁰	(4.39±0.25)×10 ¹¹	(4.95±0.23)×10 ¹¹	(2.76±0.11)×10 ¹²	(2.72±0.11)×10 ⁸	(2.26±0.09)×10⁷
ξ_2 (-)	0.41±0.03	0.42±0.02	0.42±0.02	0.39±0.02	0.08±0.00	0.04±0.00
E_{a3} (kJ/mol)	70.96±4.96	151.54±8.77	192.20±8.95	199.51±8.16	214.85±8.25	169.70±6.60
$k_{0,3}$ (s ⁻¹)	(1.77±0.12)×10 ¹	(3.77±0.22)×10 ⁷	(1.97±0.09)×10 ¹⁰	(6.66±0.27)×10 ¹⁰	(4.25±0.16)×10 ¹²	(8.02±0.31)×10¹⁰
ξ_3 (-)	0.29±0.02	0.20±0.01	0.16±0.01	0.18±0.01	0.39±0.02	0.06±0.00
E_{a4} (kJ/mol)	-	71.36±4.13	105.73±4.92	153.80±6.29	227.70±8.74	222.54±8.66
$k_{0,4}$ (s ⁻¹)	-	(2.30±0.13)×10 ¹	(1.04±0.05)×10 ⁴	(9.10±0.37)×10 ⁶	(5.29±0.20)×10 ¹²	(1.46±0.05)×10¹³
ξ_4 (-)	-	0.28±0.02	0.13±0.01	0.12±0.00	0.16±0.01	0.37±0.01
E_{a5} (kJ/mol)	-	-	89.97±4.19	143.35±5.86	156.82±6.02	236.05±9.18
$k_{0,5}$ (s ⁻¹)	-	-	(1.43±0.07)×10 ²	(1.53±0.06)×10 ⁵	(2.13±0.08)×10 ⁷	(2.18±0.08)×10¹³
ξ_5 (-)	-	-	0.20±0.01	0.14±0.01	0.11±0.00	0.17±0.01
E_{a6} (kJ/mol)	-	-	-	265.29±10.84	116.25±4.46	184.26±7.17
$k_{0,6}$ (s ⁻¹)	-	-	-	(1.19±0.05)×10 ¹⁰	(6.28±0.24)×10 ³	(1.64±0.06)×10⁹
ξ_6 (-)	-	-	-	0.05±0.00	0.17±0.01	0.09±0.00
E_{a7} (kJ/mol)	-	-	-	-	255.82±9.82	106.54±4.14
$k_{0,7}$ (s ⁻¹)	-	-	-	-	(3.09±0.12)×10 ⁹	(1.15±0.05)×10³
ξ_7 (-)	-	-	-	-	0.04±0.00	0.17±0.01
E_{a8} (kJ/mol)	-	-	-	-	-	180.49±7.02
$k_{0,8}$ (s ⁻¹)	-	-	-	-	-	(1.34±0.05)×10⁸
ξ_8 (-)	-	-	-	-	-	0.06±0.00
OB^b	1.62×10⁻⁵	8.92×10⁻⁶	7.11×10⁻⁶	6.89×10⁻⁶	4.96×10⁻⁶	4.40×10⁻⁶
Overall QOF^c	4.56	3.71	3.05	2.80	2.47	2.40

^a Kinetic parameters evaluated by the Levenberg-Marquardt algorithm according to Equation (7.6). ^b Objective function (OBF) evaluated according to Equation (3.15). ^c Global/overall quality of fit evaluated according to Equation (3.16).

A comparison between the results presented in Tables 7.7-7.10 revealed that activation energies typically ranged between 22.33 and 244.28 kJ/mol for the different coals, with the lowest activation energies (22.33-28.75 kJ/mol) confined to the deconvoluted peak (for 4 pseudo-components and higher), which has been previously attributed to the formation of moisture and the evolution of the so-called molecular phase (Alonso *et al.*, 2001; Seo *et al.*, 2011; Serio *et al.*, 1987; Solomon *et al.*, 1992; Sutcu, 2007; Wang *et al.*, 2010). Although the assumption of describing water evolution as a first order chemical reaction is questionable, the reported activation energies showed good agreement with the molar heat for water vaporization (~40-45 kJ/mol) as reported in literature (Incropera *et al.*, 2007). Furthermore, from Tables 7.7-7.10 it is evident that reported activation energies showed similar orders of magnitude for the different coals and number of pseudo-components, although substantial differences in fractional contributions were found. Therefore, reaction processes requiring lower activation energies showed higher fractional contributions to the overall rate of coals TSH and G#5 (0.37 and 0.42, respectively) compared to those of coals INY and UMZ (0.23 and 0.27 respectively).

Researchers have often questioned the relatively low orders of magnitude for reported activation energies of coal devolatilization (lower than approximately 209 kJ/mol) due to the fact that typical energies for the cleavage of single carbon bonds normally range between 335 kJ/mol and 420 kJ/mol (Yue, 1995). Authors such as Yue (1995) have attributed this discrepancy to the fact that activation energies for the thermal decomposition/devolatilization of organic heterogeneous material, such as coal, cannot be interpreted in terms of specific bond-breaking processes, but should rather be seen as a unique set of kinetic parameters representative or descriptive of a set of reactive species exhibiting similar reactivity (Aboyade *et al.*, 2012). This is in accordance with findings by Anthony and Howard (1976) and Jüntgen and Van Heek (1979), which showed that both the computed activation energy as well as the pre-exponential constant was substantially smaller when a single first order expression is used to describe a set of overlapping, parallel, independent first order reactions. In addition, it has been proposed by Suuberg (1977) that the factor largely responsible for the observation of low apparent activation energies could be attributed to the possible existence of a set of concerted and/or radical reactions. From this perspective, it has been established that activation energies may be reduced to as low as 21-42 kJ/mol when a radical reaction mechanism is adopted (Fitzer *et al.*, 1991; Yue, 1995). Furthermore, it can be seen from Tables 7.7-7.10 that the derived kinetic parameters ($E_{a,i}$ and $k_{0,i}$) for all four coals could be linearly correlated via the well known isokinetic effect, which suggests that high $E_{a,i}$ values generally correspond to high $k_{0,i}$

values (Aboyade *et al.*, 2012; Alonso *et al.*, 2001). Table 7.11 summarises the ranges of kinetic parameter values as obtained from this investigation as well as those reported in literature for the devolatilization of typical solid fuels such as coal and wood.

Table 7.11 Comparison of evaluated kinetic parameters with those reported in literature.

Reference	Type of solid fuel	Model used ^a	Kinetic parameters		
			E_a (kJ/mol)	k_0 (s ⁻¹)	n (-)
This investigation	Coal	MPRM	22.3-244.3	1.9×10^0-2.2×10^{13}	1.0
Aboyade <i>et al.</i> (2012)	Coal and biomass	MPRM	37.6-360.2	7.1×10^2 - 3.5×10^{17}	1.0-6.0
Ahmaruzzaman & Sharma (2005)	Vacuum residue, coal, plastics, Petrocrop	MPRM	11.1-152.8	1.1×10^0 - 6.5×10^7	0.0-4.0
Alonso <i>et al.</i> (2001)	Coal	MPRM	26.5-223.7	1.0×10^0 - 1.2×10^{16}	1.0
Antal <i>et al.</i> (1998)	Cellulose	SRM	230.0-245.0	2.95×10^7 - 1.8×10^8	1.0
Cai <i>et al.</i> (2008)	Coal and plastic	MPRM	35.7-558.8	1.6×10^3 - 1.0×10^{40}	1.0
Cordero <i>et al.</i> (1989)	Holm oak	SRM	72.4-73.2	3.0×10^5 - 4.3×10^5	1.0-2.0
Dhumal & Saha (2006)	Coal	DAEM	119.6-294.9	1.0×10^5 - 5.7×10^{16}	1.0
Grieco & Baldi (2011)	Wood	MPRM	45.0-251.0	1.2×10^0 - 2.0×10^{11}	1.0
Grønli <i>et al.</i> (2002)	Wood	MPRM	46.9-236.0	1.2×10^0 - 6.7×10^7	1.0
Gürüz <i>et al.</i> (2004)	Coal	SRM	13.5-20.7	6.0×10^0 - 5.1×10^5	2.1-30.6
Lázaro <i>et al.</i> (1998)	Coal	MPRM & DAEM*	188.8-264.2	N/A	1.0
Sadhukhan <i>et al.</i> (2011)	Coal	DAEM	194.4-206.2	5.1×10^{10} - 6.0×10^{11}	1.0
Seo <i>et al.</i> (2010)	Biomass	MPRM*	37.6-128.4	2.1×10^3 - 1.1×10^{12}	1.0
Singh <i>et al.</i> (2012)	Waste material	MSRM	27.4-294.8	N/A	1.0
Skodras <i>et al.</i> (2007)	Animal waste	MPRM	46.7-199.5	6.1×10^4 - 1.7×10^{17}	1.0
Sutcu (2007)	Peat/Coal	MSRM	11.2-108.6	5.2×10^{-2} - 1.1×10^2	1.0
Vlaev <i>et al.</i> (2003)	Rice husk	MPRM	5.3-228.3	3.2×10^{-1} - 2.1×10^{16}	1.0
Wiktorsson & Wanzl (2000)	Coal	MPRM*	26.1-239.0	3.8×10^1 - 5.1×10^7	1.0-2.0
Yongjiang <i>et al.</i> (2011)	Oil shale	SRM	123.6-137.4	2.5×10^6 - 3.3×10^8	1.0
Zhang <i>et al.</i> (2007)	Coal	MPRM	154.9-245.1	3.8×10^6 - 3.9×10^7	N/A
Zhang <i>et al.</i> (2012)	Lignite	DAEM	99.5-827.1	3.79×10^7 - 1.6×10^{28}	1.0

* Kinetic parameters evaluated based on gaseous and liquid components. ^aModel abbreviations- DAEM: Distributed activation energy model, MPRM: Multiple, parallel reaction model, MSRM: Multiple stage reaction model and SRM: Single reaction model.

From the Table it is therefore evident that the kinetic parameters obtained from this investigation showed excellent agreement with values established for not only the devolatilization of other coals but also for the devolatilization of biomasses, wood, oil shales, etc. The remainder of the chapter (Section 7.7.2), which focuses on the description of large particle devolatilization, will henceforth utilize the kinetic parameters as determined for 8 pseudo-components, as the lowest *QOF* values were yielded from the assumption of the latter.

7.7.1.3 Trends of modelling results

This section addresses the relationships obtained between coal characteristic properties and the kinetic parameters (fractional contribution and peak temperatures) as obtained from the deconvolution procedure assuming 8 pseudo-components. Only the modelling results of the first- and the main peak were taken into consideration, as they are assumed to represent the evolution of moisture and the process of primary devolatilization according to the model of Serio *et al.* (1987). Fractional contributions of the moisture- and main peak were expressed in terms of the ultimate amount of volatile matter (volatiles and moisture) (wt.%) yielded for each coal at 950 °C, by using the following equation:

$$F_{VM,i} = \xi_i \cdot VM_{TGA,ult}; \quad i = \text{moisture, main peak} \quad \text{Equation (7.13)}$$

Values obtained from the above equation were compared with the amount of inherent moisture as determined through proximate analysis (Chapter 4) as well as the amount of tar yielded from both the Fischer-assay (Chapter 4) and the 450 °C product assessment discussed in Chapter 6 (5 and 20 mm particles). A qualitative overview of the relationship between proximate moisture and the fraction of moisture estimated from the modelling results, as well tar yield versus estimated amount of volatile matter confined to the main peak are given, respectively, in Figure 7.18 a.) and b.). A strong linear relationship could be deduced from Figure 7.18 a.), suggesting that the amount of moisture evolved showed values of similar order as was obtained from the proximate analysis. Further examination of the Figure revealed that the contribution of moisture to the volatile fraction increased in the order TSH < INY < UMZ < G#5, therefore mimicking what was observed for inherent moisture levels reported in Chapter 4.

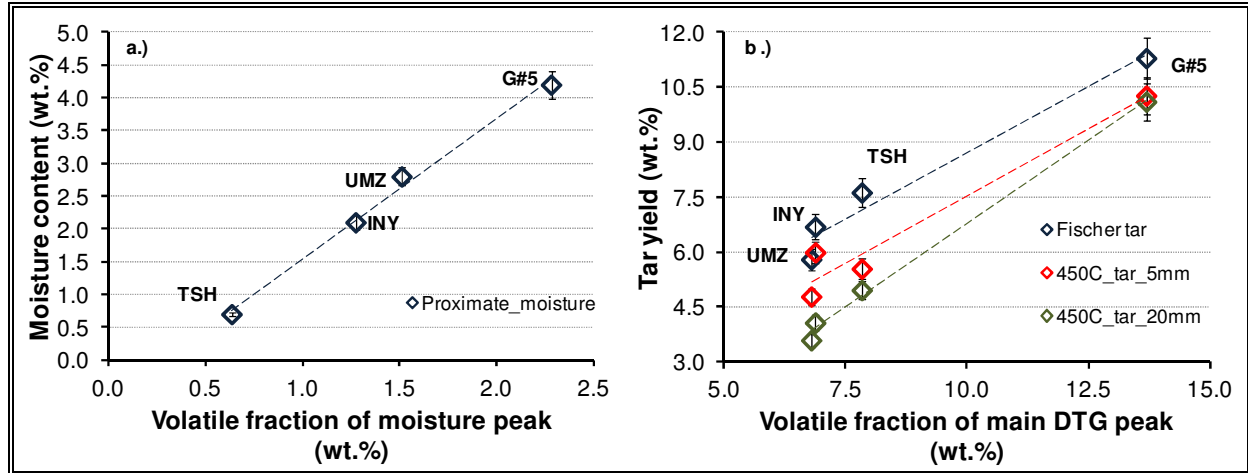


Figure 7.18 Comparison between a.) proximate moisture content and fractional contribution of peak 1 to the volatile matter and b.) tar yield and the fractional contribution of the main DTG peak to the volatile matter.

It should, however, be noted that the values determined from the modelling results were slightly lower than those determined by the proximate analysis, especially for coals INY, UMZ and G#5. This discrepancy could possibly be attributed to the thermal lag problem associated with non-isothermal TG measurements, therefore leading to slightly lower yields observed for the first peak. Similar linear relationships were also found between the experimental tar yields from the different methods and the estimated amount of volatiles attributed to the main pyrolysis regime (primary devolatilization peak). It is clear that the values estimated from the fractional contributions of the primary devolatilization peak were of similar order, although slightly higher values were found in comparison to the experimental tar yields obtained from the different tar assessment techniques. This therefore supports the findings of Serio *et al.* (1987) that the primary devolatilization peak cannot be solely attributed to the formation of tars, but also the formation of some additional devolatilization gases.

According to Alonso *et al.* (2001), the temperature of maximum global reactivity ($Tm_{1,calc}$) provides an additional means of assessing devolatilization behaviour of different coals and has been shown to be almost coincident with the temperature of maximum reactivity of the primary devolatilization peak. After evaluating a number of coal samples, Alonso *et al.* (2001) proposed the following parametric equation for directly estimating $Tm_{1,calc}$ from coal characteristic properties:

$$Tm_{1,calc} = Tm_1(R_r) + \Delta Tm_1(I_{main\ peak}) + \Delta Tm_1(L_{main\ peak}) \quad \text{Equation (7.14)}$$

The above equation has been shown to be a function of rank and maceral content and requires the evaluation and estimation of additional parameters in order to determine $Tm_{1,calc}$. A summary of the required parameters used to evaluate Equation (7.14) are listed in Table 7.12 (Alonso *et al.*, 2001; Borrego *et al.*, 2000).

Table 7.12 Parametric equations used to relate $Tm_{1,calc}$ to coal rank and maceral content.

Variable	Parametric expression	Fitting parameters
$\xi_{main\ peak}$	$\alpha_{iV}\phi_{vitrinite} + \alpha_{iL}\phi_{liptinite} + \alpha_{iI}\phi_{inertinite}$ Equation (7.15)	$\alpha_{iV}, \alpha_{iL}, \alpha_{iI}$
$I_{main\ peak}$ and $L_{main\ peak}$	$I_{main\ peak} = \frac{\alpha_{iI}\phi_{inertinite}}{\xi_{main\ peak}}$ and $L_{main\ peak} = \frac{\alpha_{iL}\phi_{liptinite}}{\xi_{main\ peak}}$ Equation (7.16) and Equation (7.17)	N/A
$Tm_1(R_r)$	$Tm_{1,0} + r_1R_r + r_2R_r^2 + r_3R_r^3$ Equation (7.18)	$Tm_{1,0} = 423.39;$ $r_1 = -19.04; r_2 = 78.94;$ $r_3 = -19.27$
$\Delta Tm_1(I_{main\ peak})$	$i_{m,i} \cdot \left(1 - \left(1 - I_{main\ peak}^{i_{m,2}}\right)^{i_{m,3}}\right)$ Equation (7.19)	$i_{m,1} = 448.97; i_{m,2} = 19.70;$ $i_{m,3} = 0.096$
$\Delta Tm_1(L_{main\ peak})$	$l_{m,i} \cdot \left(1 - \left(1 - L_{main\ peak}^{l_{m,2}}\right)^{l_{m,3}}\right)$ Equation (7.20)	$l_{m,1} = -6.36; l_{m,2} = 2.22;$ $l_{m,3} = 153.34$

In the above table ϕ_j represents the fractional volatile matter content of maceral j (as determined in Section 4.6.1.2 for all four coals), while α_{iV} , α_{iI} and α_{iL} are defined as the rank-dependent fractional contributions of vitrinite, inertinite and liptinite to the main devolatilization peak ($f_{main\ peak}$). The value of $f_{main\ peak}$ is taken as the fractional peak contribution value determined from the multi-component kinetic analysis of the four coals, while the values of α_{iV} , α_{iI} and α_{iL} were solved numerically by adhering to the following constraint (Alonso *et al.*, 2001):

$$\alpha_{iV} + \alpha_{iL} + \alpha_{iI} = 1 \quad \text{Equation (7.21)}$$

Values estimated according to the above parametric analysis are summarised in Table 7.13 and compared graphically to the experimentally determined temperatures of global maximum reactivity ($Tm_{1,exp}$) in the parity plot provided in Figure 7.19 a.).

Table 7.13 Values determined according to Alonso *et al.* (2001) and Borrego *et al.* (2000).

PEAK TEMPERATURE PREDICTION					
Parameter	Unit	INY	UMZ	G#5	TSH
$\phi_{\text{vitrinite}}^a$	-	0.39	0.39	0.42	0.29
$\phi_{\text{liptinite}}^a$	-	0.58	0.58	0.65	0.31
$\phi_{\text{inertinite}}^a$	-	0.23	0.23	0.24	0.20
$\xi_{\text{main peak}}^b$	-	0.23	0.27	0.42	0.37
α_{iV}^c	-	0.00	0.25	0.52	0.00
α_{iL}^c	-	0.00	0.00	0.26	0.00
α_{iI}^c	-	1.00	0.75	0.22	1.00
$Tm_{1,calc}$	°C	443.2	443.2	433.3	477.2
$Tm_{1,exp}^d$	°C	421-471	421-471	393-430	449-494

^aFractional volatile contents of macerals as determined in Section 4.6.1.2 according to Borrego *et al.* (2000). ^bFractional contribution of main peak determined from the multi-component kinetic analysis. ^cRank dependent maceral contributions determined numerically. ^dRanges of $Tm_{1,exp}$ estimated from the experimental DTG curves at the four different heating rates.

Values determined experimentally for the temperature at maximum global reactivity ($Tm_{1,exp}$) were taken from the DTG curves produced for the different heating rates of each coal and reported as an applicable temperature range in Table 7.13.

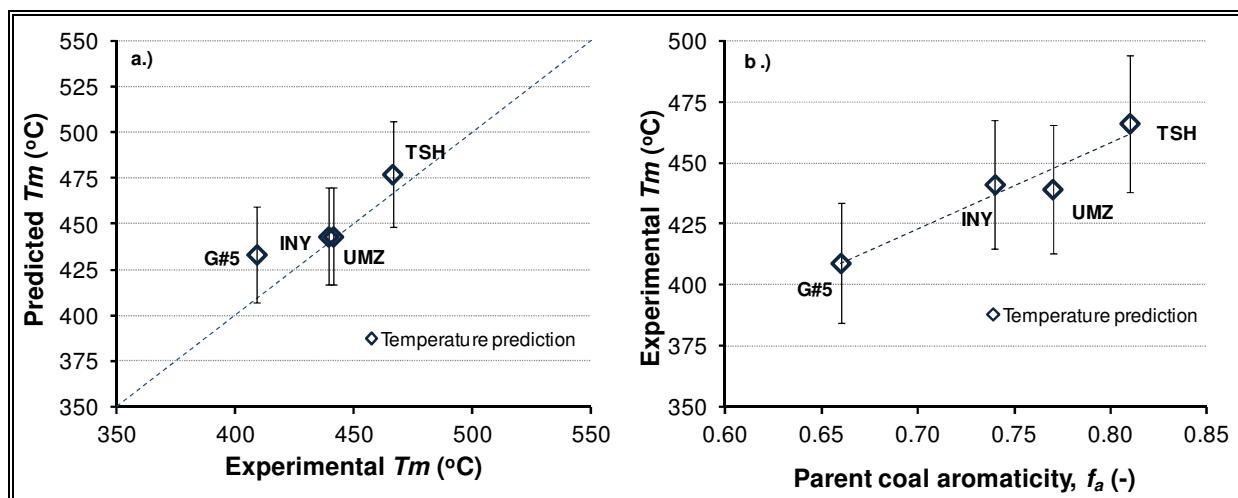


Figure 7.19 Comparison of $Tm_{1,exp}$ to a.) $Tm_{1,calc}$ and b.) parent coal aromaticity.

Average $Tm_{1,exp}$ values, applicable over the whole heating rate range, were used for each coal to compare to the estimated $Tm_{1,calc}$ value. From Table 7.13 and Figure 7.19 a.), it can be seen that the experimentally determined Tm_1 values could be predicted satisfactorily with the parametric equation developed by Alonso *et al.* (2001) and provide supportive evidence that the temperature of maximum reactivity of the main devolatilization peak is almost coincident with that of the temperature of maximum global reactivity. Error bars have been included in Figure 7.19 a.) to indicate the region of applicable $Tm_{1,exp}$ values, characteristic of each heating rate, and therefore show good correlation with temperature values calculated theoretically. According to Alonso *et al.* (2001), $Tm_{1,calc}$ shows a strong linear relationship with coal rank, while increasing contents of liptinite have been found to slightly decrease the value of $Tm_{1,calc}$. In contrast, however, increasing amounts of inertinite have shown to lead to significant increases in $Tm_{1,calc}$ for $I_{main\ peak}$ values greater than 0.8. The lower $Tm_{1,exp}$ values for coal G#5 could therefore have been a direct result of the higher liptinite content found in this coal, while the slightly higher rank of coal TSH was predominantly responsible for the elevated values of $Tm_{1,exp}$ observed. Experimentally determined Tm_1 values were also compared to parent coal aromaticity determined from ^{13}C NMR as depicted graphically in Figure 7.19 b.). A strong linear relationship could also be observed between $Tm_{1,exp}$ and f_a , which can be explained by the strong interrelationship existing between aromaticity and coal rank (Smith *et al.*, 1994; Solum *et al.*, 1989).

7.7.2 Modelling the devolatilization behaviour of large coal particles

7.7.2.1 Modelling particle swelling and/or shrinkage

Dilatometry data for each coal was converted from percentage contraction/swelling to shrinkage/swelling ratio (v/v_0) in order to derive empirical shrinkage/swelling models of the form proposed in Equation (7.12):

$$v = v_0 \cdot f(T_s) \text{ with } v_0 = \frac{4}{3}\pi R_p^3 \quad \text{Equation (7.12)}$$

Non-linear/linear regression (in Origin 8.0) of the converted dilatometry data involved the subdivision of the experimental results into several temperature intervals (in K) in order to

evaluate the piecewise functionality of each experimental data set. The temperature dependence ($f(T_s)$) term defined in Equation (7.12) was chosen to be of either linear, power or exponential form in a similar fashion to what was reported by (Bellais *et al.*, 2003). Furthermore, it was assumed that no further change in particle volume occurred for temperatures exceeding 773 K (500°C), due to limitations in the applicable temperature range of Ruhr dilatometry. A comparison between the derived empirical models and the experimental data is presented in Figure 7.20 for all four coals, while Table 7.14 provides a summary of the adjusted coefficients of determination (R^2 values) obtained from the fitting procedure.

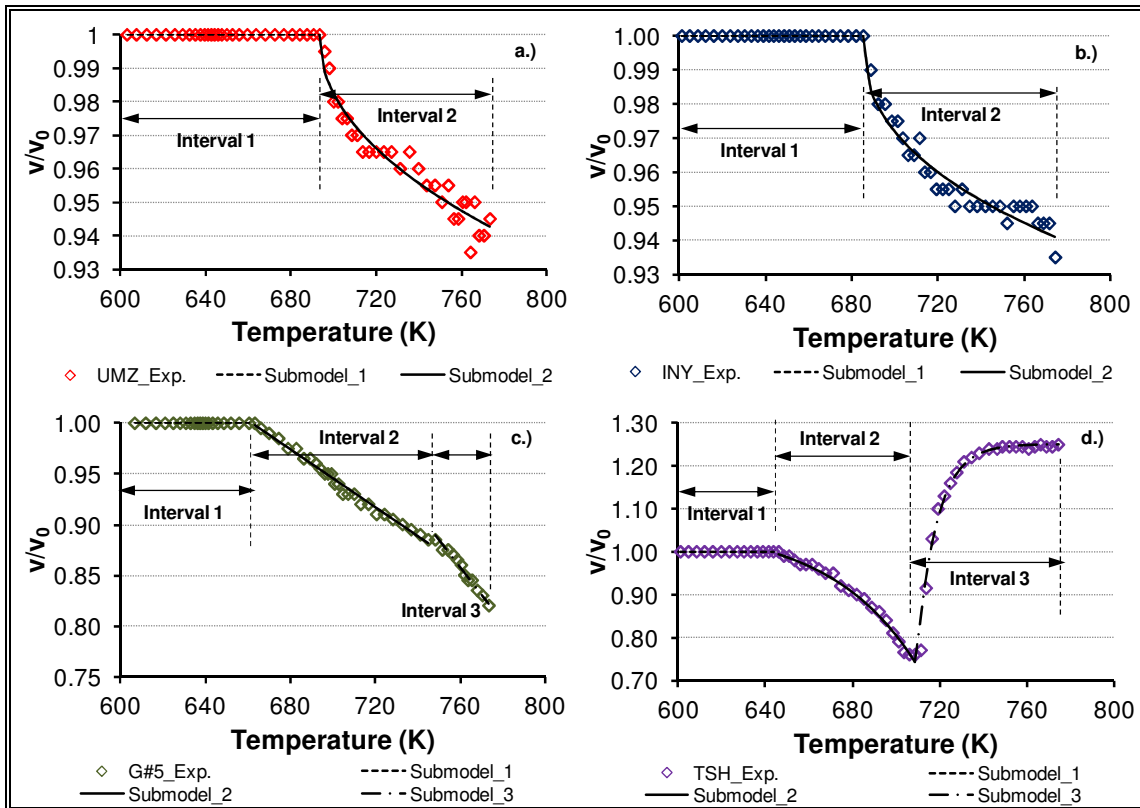


Figure 7.20 Empirical model fitting to the dilatometry results of coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH.

Table 7.14 Summary of adjusted R^2 values obtained from the empirical model fitting analyses.

Adjusted R^2 values					
Sub model	Unit	INY	UMZ	G#5	TSH
Interval 1 ^a	-	1.00	1.00	1.00	1.00
Interval 2	-	0.94	0.94	0.99	0.99
Interval 3	-	N/A	N/A	0.97	1.00

^a Values are assumed to be 1 due to the fact that no change occurs in particle volume during temperature interval 1.

From Figure 7.20 and Table 7.14 it is clear that the derived empirical correlations provide suitable approximations for the shrinkage and/or swelling behaviour of each coal and can be described mathematically by the following equations:

Contraction model for coal UMZ:

$$v = v_0 \text{ and } \frac{dv}{dt} = 0; \quad T_s \leq 693.6 \text{ K} \quad \text{Equation (7.22a)}$$

$$v = v_0 \cdot \left[1 - 7.13 \times 10^{-3} \cdot (T_s - 693.6)^{0.48} \right]; \quad 693.6 \text{ K} < T_s \leq 773 \text{ K} \quad \text{Equation (7.22b)}$$

$$v = 0.943 \cdot v_0 \text{ and } \frac{dv}{dt} = 0; \quad T_s > 773 \text{ K} \quad \text{Equation (7.22c)}$$

Contraction model for coal INY:

$$v = v_0 \text{ and } \frac{dv}{dt} = 0; \quad T_s \leq 685.4 \text{ K} \quad \text{Equation (7.23a)}$$

$$v = v_0 \cdot \left[1 - 9.3 \times 10^{-3} \cdot (T_s - 685.4)^{0.41} \right]; \quad 685.4 \text{ K} < T_s \leq 774 \text{ K} \quad \text{Equation (7.23b)}$$

$$v = 0.941 \cdot v_0 \text{ and } \frac{dv}{dt} = 0; \quad T_s > 773 \text{ K} \quad \text{Equation (7.23c)}$$

Contraction model for coal G#5:

$$v = v_0 \text{ and } \frac{dv}{dt} = 0; \quad T_s \leq 661.9 \text{ K} \quad \text{Equation (7.24a)}$$

$$v = v_0 \cdot \left[1 - 1.42 \times 10^{-3} \cdot (T_s - 661.9) \right]; \quad 661.9 \text{ K} < T_s \leq 748 \text{ K} \quad \text{Equation (7.24b)}$$

$$v = v_0 \cdot \left[1 - 2.71 \times 10^{-3} \cdot (T_s - 707.6) \right]; \quad 748 \text{ K} < T_s \leq 773 \text{ K} \quad \text{Equation (7.24c)}$$

$$v = 0.822 \cdot v_0 \text{ and } \frac{dv}{dt} = 0; \quad T_s > 773 \text{ K} \quad \text{Equation (7.24d)}$$

Contraction and swelling model for coal TSH:

$$v = v_0 \text{ and } \frac{dv}{dt} = 0; \quad T_s \leq 646 \text{ K} \quad \text{Equation (7.25a)}$$

$$v = v_0 \cdot \left[1.06 - 6.36 \times 10^{-9} \cdot \exp(0.03 \cdot T_s) \right]; \quad 646 \text{ K} < T_s \leq 711 \text{ K} \quad \text{Equation (7.25b)}$$

$$v = v_0 \cdot \left[1.251 - 7.934 \times 10^{32} \cdot (-0.11 \cdot T_s) \right]; \quad 711 \text{ K} < T_s \leq 774 \text{ K} \quad \text{Equation (7.25c)}$$

$$v = 1.251 \cdot v_0 \text{ and } \frac{dv}{dt} = 0; \quad T_s > 774 \text{ K} \quad \text{Equation (7.25d)}$$

7.7.2.2 Validation of the devolatilization model for single, large coal particles

The comprehensive large particle model, proposed in Chapter 3, was evaluated according to the methodology outlined in Section 7.5.2 and subsequently validated against experimental findings made from the large particle devolatilization study (Section 7.6.2.2). Auxiliary constants and equations needed for inclusion into the large particle model and descriptive of the thermoplastic-, thermophysical-, diffusive- and/or transfer properties of each coal were provided in Chapter 3 and Section 7.7.2.1. Model predictions for the fractional loss of volatiles as well as the core and surface temperature profiles (450 °C and 750 °C) were compared respectively to the experimental results and are presented in the text to follow.

Fractional volatile-loss profiles:

Comparison of experimental profiles to that obtained from model simulations required the conversion of the raw mass loss data (m_t/m_0) as presented in Figures 7.12 and 7.13 to fraction or percentage of volatiles released/evolved ($V_{t,T}$) after time t :

$$V_{t,T} = 1 - \frac{m_t}{m_0} \quad \text{Equation (7.26)}$$

Model values needed for V_a^* (ultimate value of moisture released) were assumed to be equal to the asymptotic mass loss value observed for the 350 °C experiments of each coal as it has been shown previously that moisture and secondary water release (due to the decomposition of minerals) dominates the devolatilization behaviour at temperatures below 350 °C (Moghtaderi *et al.*, 2004; Sutcu, 2007). Values for $V_{t,T}^*$ were, however, directly derived from the ultimate total mass loss value of each individual experiment. A comparison between experimentally derived fractional volatile-loss profiles and those predicted using two different thermal conductivity models proposed in Chapter 3 is presented graphically in Figure 7.21 for all seven devolatilization temperatures (350 °C, 450 °C, 550 °C, 600 °C, 650 °C, 750 °C and 900 °C) of coals INY and G#5. Thermal conductivity models used for the simulation of the respective evolution

profiles were taken from the work of Badzioch and Hawksley (1970) and Heidenreich *et al.* (1999) and can be mathematically expressed as:

Thermal conductivity model (1) (Heidenreich *et al.*, 1999):

$$k_s = 0.19; \quad T_s \leq 573 \text{ K} \quad \text{Equation (3.19a)}$$

$$k_s = 0.19 + 2.5 \times 10^{-4} \cdot (T_s - 573); \quad T_s > 573 \text{ K} \quad \text{Equation (3.19b)}$$

Thermal conductivity model (2) (Badzioch & Hawksley, 1970):

$$k_s = 0.23; \quad T_s \leq 673 \text{ K} \quad \text{Equation (3.20a)}$$

$$k_s = 0.23 + 2.24 \times 10^{-5} \cdot (T_s - 673)^{1.8}; \quad T_s > 673 \text{ K} \quad \text{Equation (3.20b)}$$

Furthermore, the validity and suitability of each of these conductivity models were assessed with the aid of a reformulated equation for the *QOF* parameter as provided in Equation (7.27):

$$QOF (\%) = 100 \times \sum_{m=1}^{N_m} \sqrt{\frac{\{(V_{t,T})_{\text{exp}} - (V_{t,T})_{\text{calc}}\}^2}{N_m}} \quad \text{Equation (7.27)}$$

Table 7.15 summarises the quality of fit (*QOF*) values determined separately for each temperature, as well as the average *QOF* taken over the entire temperature range.

Table 7.15 Quality of fit or percentage deviation for the simulated rate curves

Quality of fit (QOF %)								
Experimental temperature	INY		UMZ		G#5		TSH	
	CM1^a	CM2^b	CM1^a	CM2^b	CM1^a	CM2^b	CM1^a	CM2^b
350 °C	2.35	2.66	3.11	3.15	4.07	4.39	0.74	0.77
450 °C	6.16	9.25	3.24	4.84	9.04	10.60	5.03	5.75
550 °C	4.21	7.27	7.08	4.57	4.99	8.55	5.84	8.92
600 °C	10.80	8.75	12.20	11.40	5.71	7.09	3.63	4.50
650 °C	7.38	5.49	4.67	3.46	2.89	4.68	2.47	3.47
750 °C	3.65	7.35	11.1	13.80	3.60	5.26	1.65	4.35
900 °C	5.36	6.26	5.76	5.31	13.3	14.80	5.28	5.79
Average	5.70	6.72	6.74	6.65	6.23	7.91	3.52	4.79

^a Conductivity model (1) of Heidenreich *et al.* (1999). ^b Conductivity model (2) of Badzioch and Hawksley (1970).

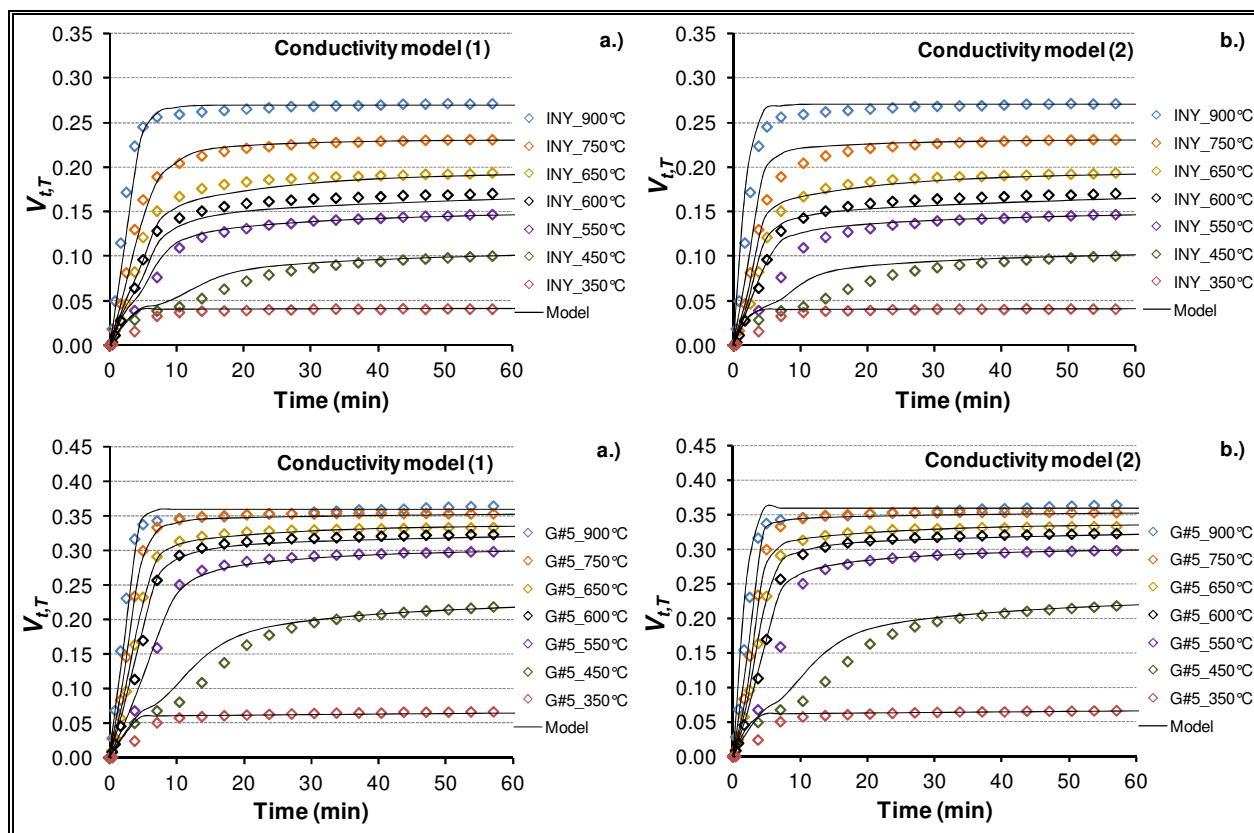


Figure 7.21 Comparison between model predictions for coals INY and G#5 using a.) thermal conductivity model (1) and b.) thermal conductivity model (2).

From Figure 7.21 it could be observed that both thermal conductivity models provided satisfactory descriptions of the experimental data of coals INY and G#5, while similar observations were made for the other two coals (Appendix D.7). This is also reflected in the *QOF* values presented in Table 7.15, which showed values of less than 15% for each coal. A comparison between *QOF* values presented in Table 7.15 revealed that the profiles simulated with the aid of thermal conductivity model (1) provided better fit qualities compared to those simulated with thermal conductivity model (2). Some discrepancies were, however, observed in the *QOF* values determined for coals INY and UMZ, especially in the temperature range between 550°C and 650°C where the use of conductivity model (2) provided better results. In contrast, profiles determined with the use of conductivity model (1) provided better fit qualities for all cases of coals G#5 and TSH. Based on the better overall fit (average *QOF*) qualities for CM1, it was therefore decided to adopt the modelling strategy of the first conductivity model in order to model the devolatilization behaviour of the four different coals. Profiles of predicted and experimental fractional volatile loss following this strategy are presented for all four coals in Figure 7.22 and 7.23 for two different time intervals.

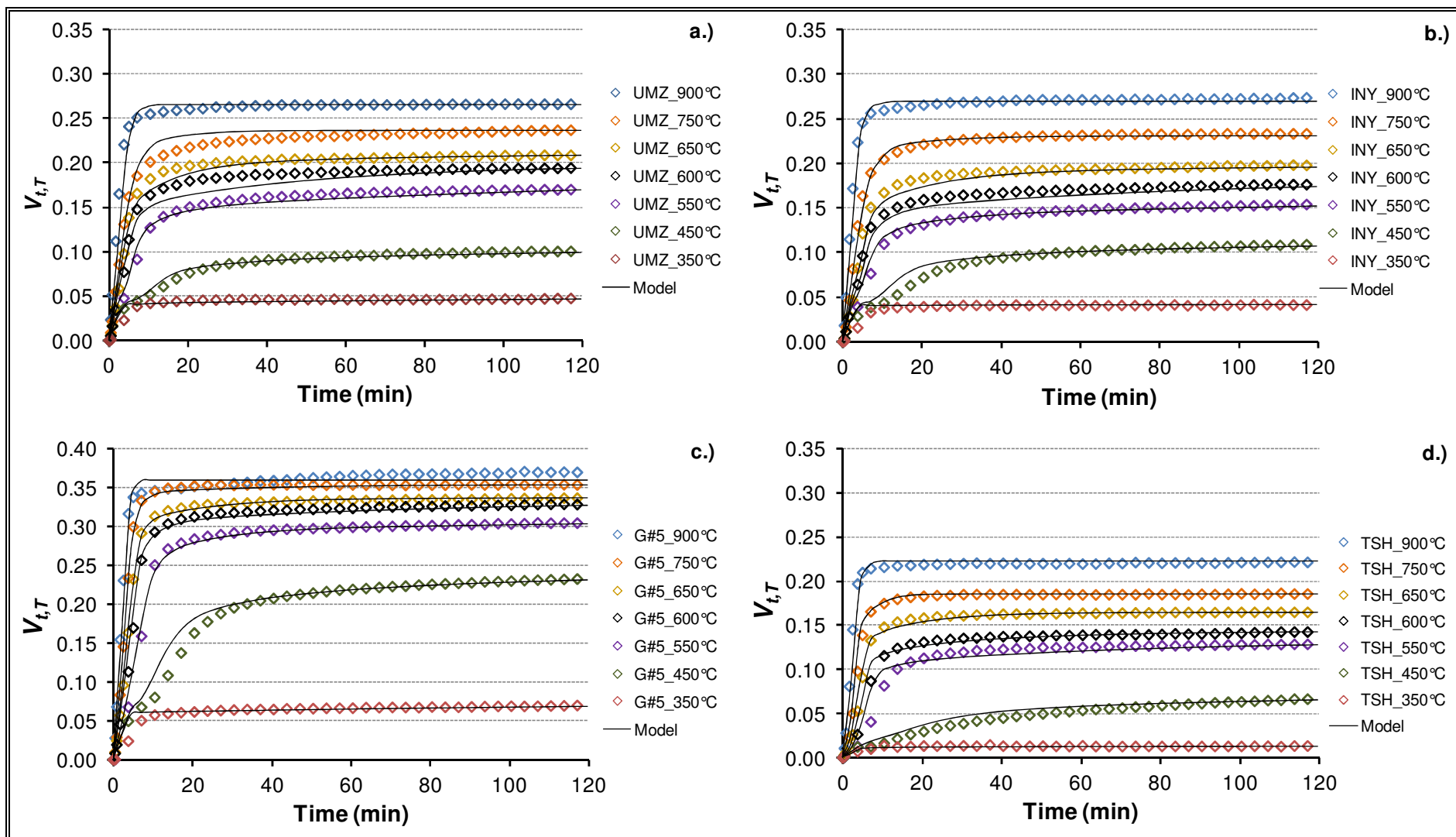


Figure 7.22 Comparison of experimental, fractional volatile release from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH with model predictions (full reaction time).

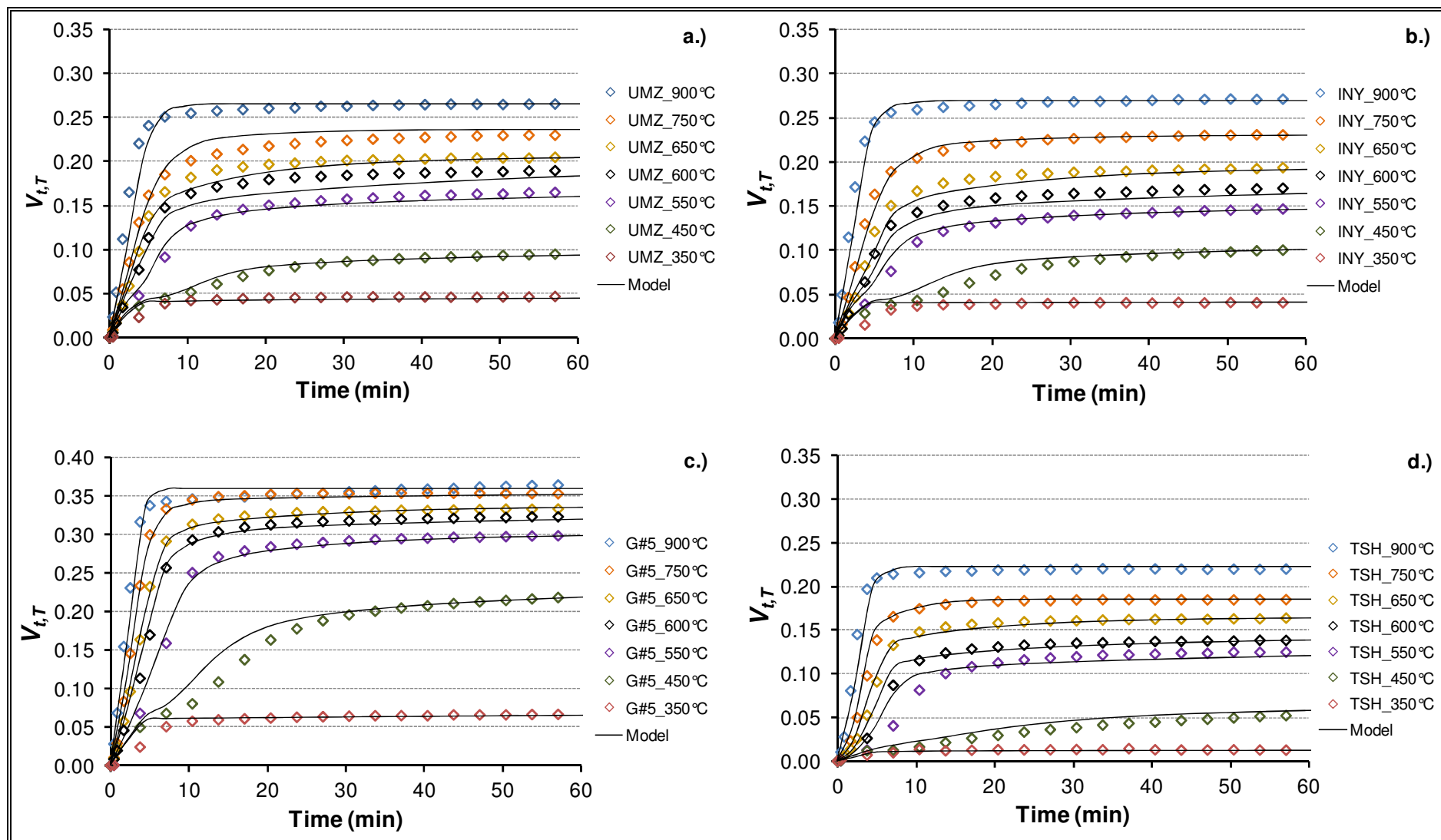


Figure 7.23 Comparison of experimental, fractional volatile release from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH with model predictions (half the reaction time).

From both figures it is evident that for all cases, the experimental results showed excellent agreement with the predicted trend, therefore verifying that the mathematical model provides an adequate description of the devolatilization performance of each coal. In addition, predicted profiles displayed a similar two-zone devolatilization behaviour, characteristic of the experimental volatile-loss profiles of each coal at the lower devolatilization temperatures (450°C to 600°C), which can be attributed to the separate inclusion of moisture- and volatile loss kinetics in the overall large particle model. In each case, the evolution of moisture was found to be slightly over predicted for the first few time instances, which could have been the result of assuming first order kinetics. Improvements in the prediction can, however, be achieved by following more fundamental modelling strategies involving particle drying, as proposed by Bellais (2007) and Grønli (1996). A comparison between the evolution profiles of the four coals revealed that model predictions of the experimental data of coal TSH were much more accurate than those obtained for the other three coals. This is also subsequently supported by the lower *QOF* values presented in Table 7.15 for this coal (0.74%-5.84%). Although small discrepancies existed between modelled- and experimental results, especially for the lower devolatilization temperatures, the determined *QOF* values of the different coals were found to be within the experimental error range determined for the devolatilization of the different coals (Table 7.5), therefore suggesting that the model still provides an excellent description of experimental data even in the determined experimental error range. The success of the proposed model showed good agreement with investigations following a similar modelling approach, as presented in the work of Blik *et al.* (1985), Heidenreich *et al.* (1999), Sadhukhan *et al.* (2009 & 2011) and Zhang *et al.* (2012).

Particle temperature profiles and heat transfer investigation:

The rate at which coal devolatilization occurs is not only dependent on the characteristic properties of each coal, but also on the particle temperature distribution, which in turn is significantly influenced by both internal- and external convective, conductive and radiative processes. Model validity was further evaluated against experimentally determined profiles for the surface- and core temperature of the 20 mm coal particles. A brief overview of the experimental methodology used for assessing the surface- and core temperatures of each coal particle was presented in Section 7.4.2.1. Experimentally determined core- and surface temperature profiles are presented respectively for 450°C and 750°C in Figure 7.24 and 7.25.

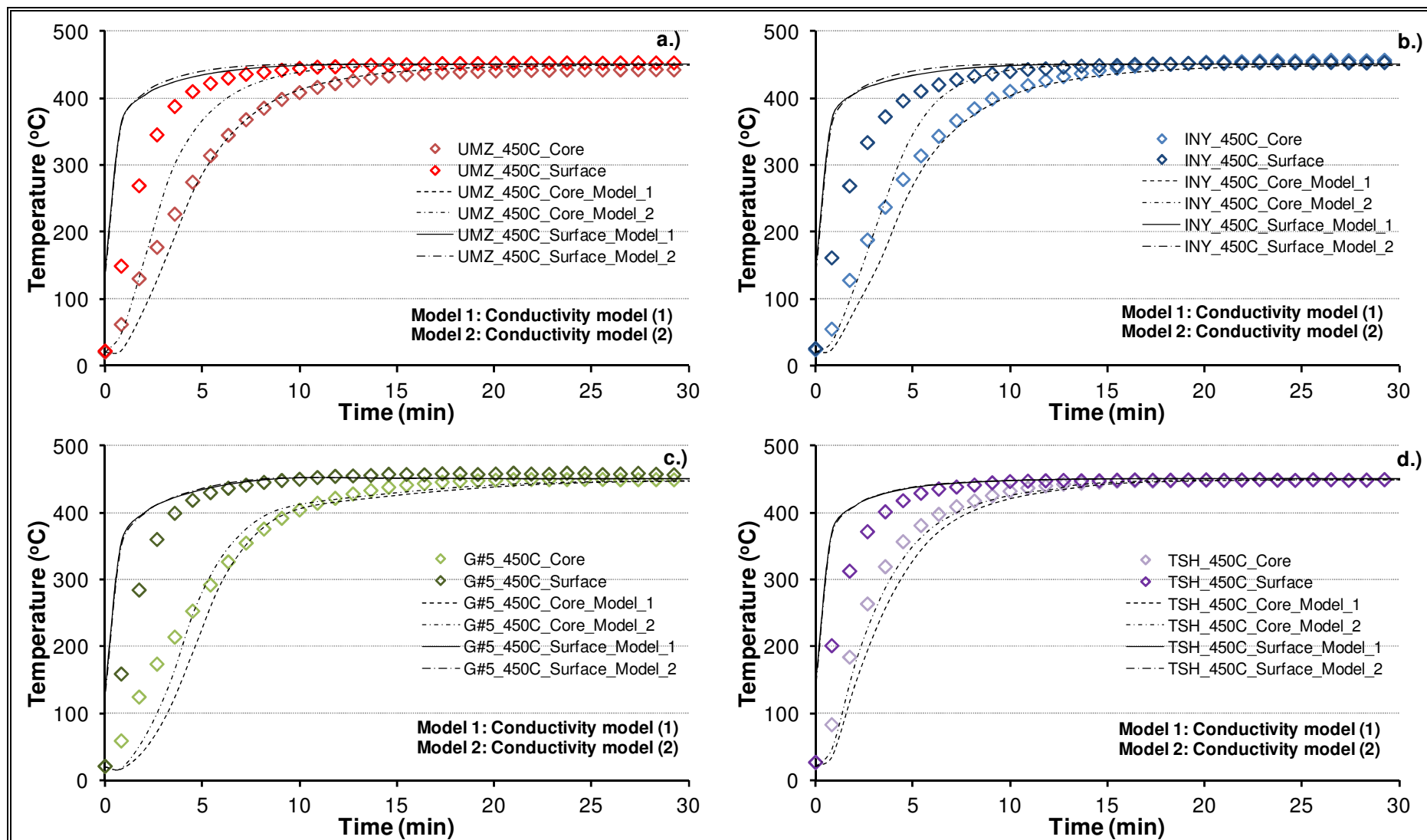


Figure 7.24 Comparison of experimental temperature profiles with model predictions at 450 °C for coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH.

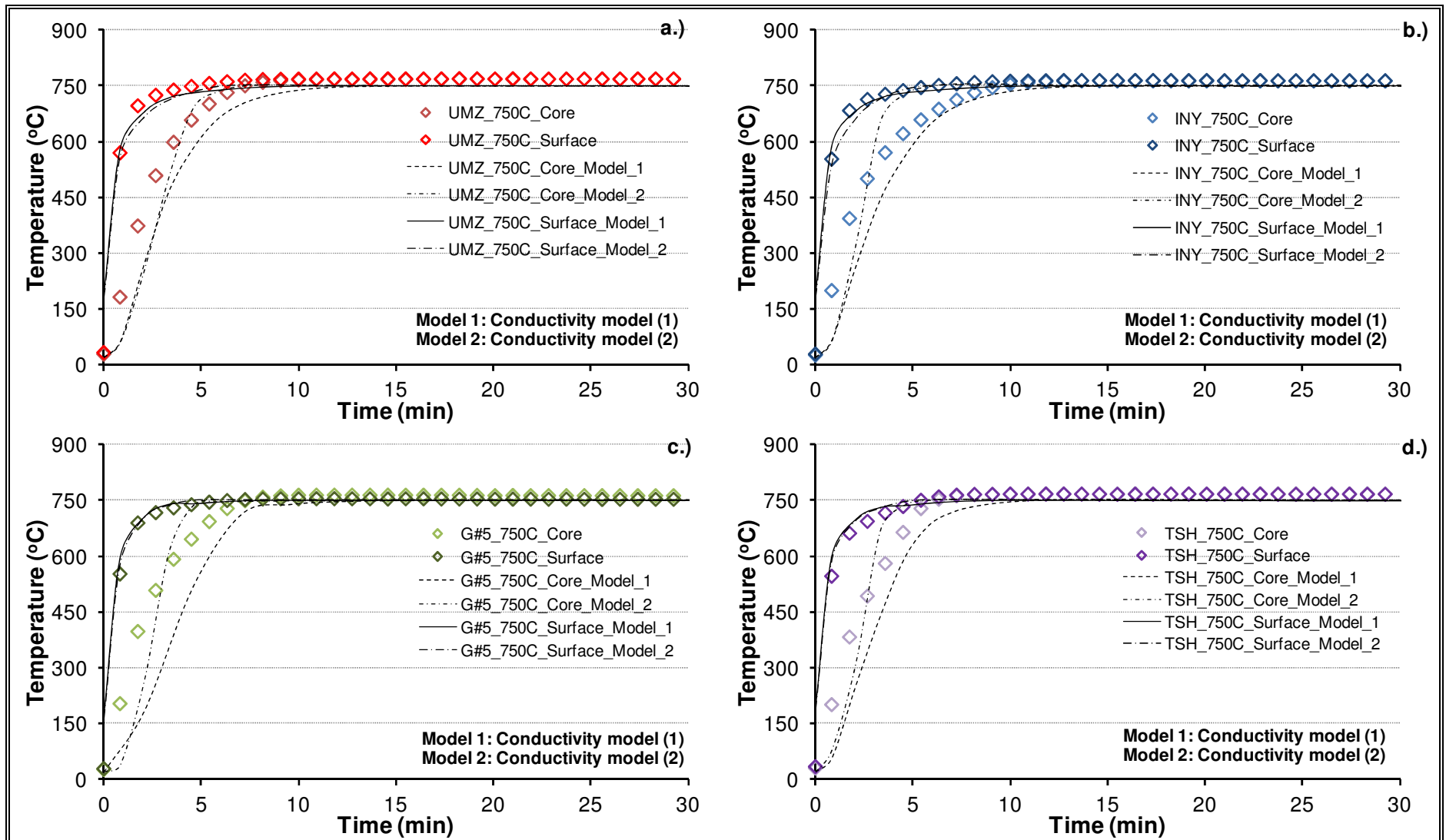


Figure 7.25 Comparison of experimental temperature profiles with model predictions at 750°C for coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH.

For comparative purposes, model predictions using the two different proposed conductivity models have also been included in both Figures 7.24 and 7.25. Experimental temperature profiles presented in the above two figures (determined respectively for 450°C and 750°C) represent temperature values derived from the average of all 5 repeatability experiments performed per coal and per temperature. Furthermore, experimental reproducibility was found to be very satisfactory with experimental errors ranging between 0.95% and 1.77% for the core temperature measurements, while errors were found to be confined between 0.62% and 1.52% for the surface temperature measurements. A schematic overview of reproducibility profiles generated at 450°C and 750°C, for all four coals (surface and core temperature profiles) can be found in Appendix D.8.

From the figures it is clear that during heating, large temperature gradients exist within the particle leading to the almost instantaneous heating of the particle surface to the thermal equilibrium state, while the core of the particle heats up with a much slower rate. This can be attributed to not only the conduction of the coal particle itself, which causes an internal transfer resistance but also the subsequent difference in heating rate experience respectively by the surface and core of the particle due to external heating processes such as convection and radiation dictating the heating behaviour of the external surface of the particle. A rough estimate of heating times needed to reach isothermal conditions indicated that approximately 15 min to 20 min are needed to reach the 450°C isothermal state, while the heating period for the 750°C experiments were determined as between 5 min and 10 min. The decrease in heating time needed for thermal equilibrium at higher temperatures can therefore be attributed to the fact that at higher temperatures, heat is conducted much more rapidly relative to the volumetric heat capacity of the coal particle, i.e.; due to the higher thermal diffusivity of the coal particle (Incropera *et al.* 2006; Sadhukhan *et al.*, 2011). A comparison between the temperature profiles of the different coals revealed that the core temperatures measured for coal TSH showed much faster heating rates than those obtained for the three Witbank coals (UMZ, INY and G#5), although the effect was much less profound for the higher temperature experiments. This can be attributed to the highly plastic nature of this coal which leads to the formation of highly porous and low density chars. From this perspective it can be reasoned that heat transfer occurs much faster as a result of the higher thermal diffusivity ($k_s/c_{p,s}\rho_s$) of this coal in comparison to the other three coals (Incropera *et al.*, 2006). Similar heat distributions were, however, observed for coals UMZ, INY and G#5. Temperature profiles obtained from this investigation showed good agreement with results obtained by Heidenreich *et al.* (1999), Peters

(2011), Sadhukhan *et al.* (2009 & 2011), Strydom (2010) and Zhang *et al.* (2012). Furthermore, from the model predictions presented in Figures 7.24 and 7.25, it is evident that the use of both types of conductivity models led to reasonably good descriptions of the experimental data with relative mean errors ranging between 3.21% and 9.18%. In some cases, however, the use of thermal conductivity model (2) provided slight improvements in the prediction of the core temperature profiles obtained for the devolatilization of coals G#5 and TSH at 450°C, but also devolatilization of coals at the higher devolatilization temperature. This is also reflected in the relative mean errors provided in Table 7.16.

Table 7.16 Relative mean error for the simulated temperature profiles.

Relative mean error (%)								
Experimental temperature	INY		UMZ		G#5		TSH	
	CM1^a	CM2^b	CM1^a	CM2^b	CM1^a	CM2^b	CM1^a	CM2^b
450°C (Core)	6.13	4.41	4.95	4.86	9.08	6.75	5.21	3.12
450°C (Surface)	6.72	6.74	6.44	6.61	6.27	6.25	5.18	5.15
750°C (Core)	6.18	5.68	6.86	6.06	9.18	6.69	5.37	8.19
750°C (Surface)	4.13	3.95	4.46	4.34	3.28	3.21	6.38	6.37

^a Conductivity model (1) of Heidenreich *et al.* (1999). ^b Conductivity model (2) of Badzioch and Hawksley (1970).

It should, however, be noted that although the use of CM2 yielded lower fitting errors, temperature profiles determined with the use of CM1 did provide better descriptions of the trend of experimental temperature profiles. This was also the case for the description of the volatile release profiles, where CM1 provided better fit qualities to the experimental data. The apparent discrepancy in the use of an appropriate empirical thermal conductivity model therefore necessitates the need for developing a more coal specific empirical model with the aid of either direct measurement of thermal conductivity or numerical optimization of an existing thermal conductivity model. Although this was not attempted in this investigation, it should be considered for future studies regarding the modelling of large particle devolatilization.

7.7.3 Simulation studies

Numerical simulation provides an efficient way of assessing more detailed information regarding the internal behaviour of large coal particles during devolatilization. In some cases, this is helpful as difficulties may exist in measuring important properties such as radial temperature and -product evolution profiles. It should, however, be noted that numerical simulation of a

physical variable only provides a theoretical description of the process and should be confirmed by experimental data where possible. A simulation study was therefore undertaken as the proposed model provided a suitable description of the experimental results obtained in this investigation. This section will elaborate on some important process parameters affecting the devolatilization behaviour of large coal particles, which include: (1) radial volatile-loss and – temperature profiles, (2) effect of particle size, (3) effect of heat losses due to volatile transport and heats of reaction and –vaporization; (4) and the effect of thermoplastic behaviour.

7.7.3.1 Radial profiles of fractional volatile-loss and particle temperature

Detailed information regarding the radial distribution of volatiles and -temperature within a 20 mm coal particle was evaluated using the proposed numerical model. Figure 7.26 shows the time-dependent, simulated product evolution and temperature profiles at 450°C and 750°C for the devolatilization of a typical 20 mm UMZ coal particle.

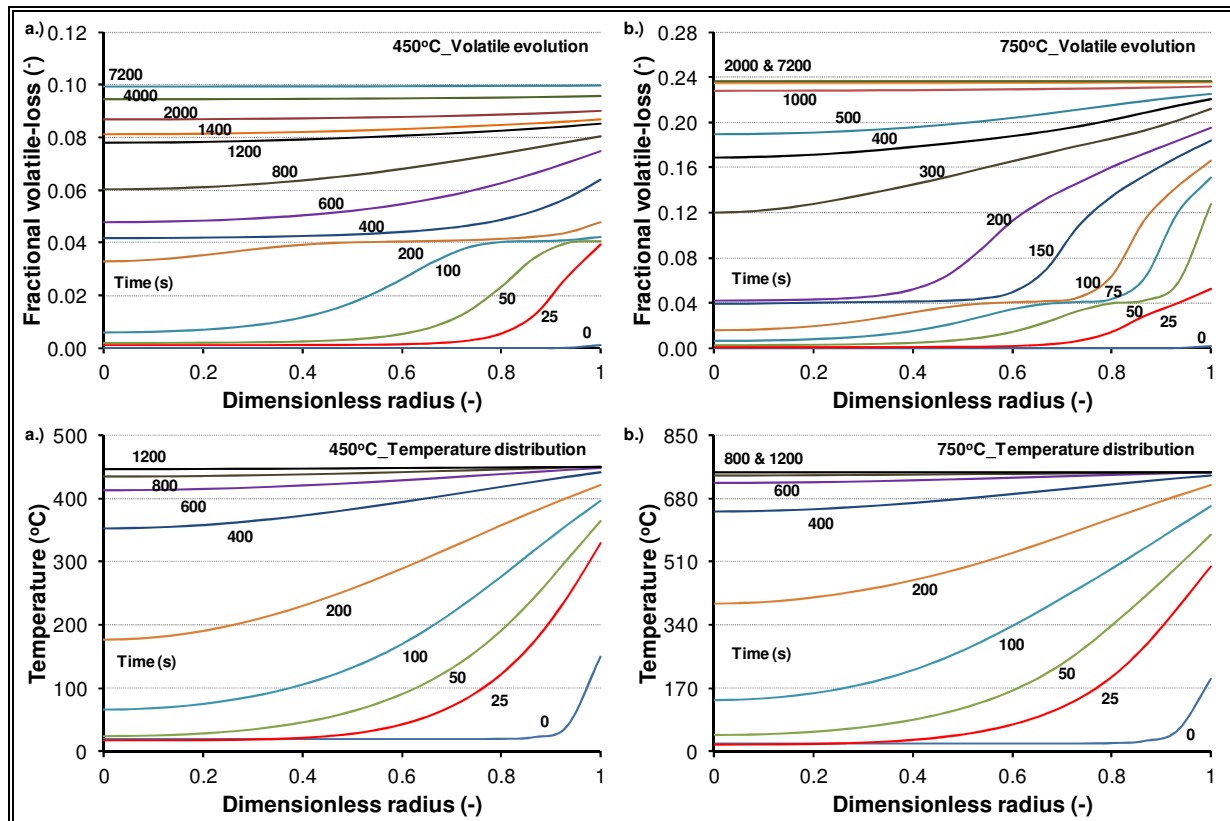


Figure 7.26 Model-predicted radial volatile loss- and temperature profiles at different time instances for the devolatilization of coal UMZ at a.) 450°C and b.) 750°C respectively.

From the Figure it is evident that the radial temperature distribution predominantly dictates the fractional product evolution within the solid particle. For both 450°C and 750°C, the product evolution profiles are characterised by two distinct regions of mass loss, which can be attributed to the initial rapid loss of moisture and secondary water in the first few minutes of devolatilization, followed by the initiation of the main devolatilization process leading to the formation of tars and gases. Furthermore, it can be observed from the 450°C simulation that the volatile-loss profiles (main devolatilization zone) exhibit a slow release of volatiles mainly due to the gradual heating of the coal particle, while the evolution profile is nearly flat near the end of devolatilization reaction. The latter also holds true for the product evolution profile simulated for the 750°C devolatilization of coal UMZ. In addition, volatile-loss profiles for 450°C are characterised by a significant time lag in comparison to volatile evolution at higher temperatures. In all cases, volatile evolution at the particle surface is always higher in comparison to the particle centre, which can be attributed to the existence of a higher temperature gradient in the vicinity of the particle surface (Sadhukhan *et al.*, 2011). It is, however, noteworthy to mention that, although thermal equilibrium at 450°C is only reached by the entire particle within about 13 min to 20 min (800 s to 1200 s), devolatilization still continues beyond this time leading to the evolution of an additional 20% to 30% of the total volatile product.

At higher devolatilization temperatures (750°C), the volatile-loss profile near the particle surface exhibits no significant time lag with respect to the initiation of primary devolatilization, while much steeper evolution gradients can be observed for the rest of the particle volume. According to Sadhukhan *et al.* (2009 & 2011), radial, volatile evolution profiles at high temperatures are characterised by three distinct zones of devolatilization, as can be inferred from the theoretical volatile evolution profile of coal UMZ after about 100 s. In the outermost zone (zone 1) (near the particle surface) the particle has already devolatilized and attained close to 95% conversion to char. This is subsequently followed by a more gradual and delayed release of volatiles within the second devolatilization zone (zone 2), while the coal remains almost unreacted within the inner core of the particle (zone 3) (Sadhukhan *et al.*, 2009; Sadhukhan *et al.*, 2011). From this perspective, the devolatilization process, in its limit, exhibits similar behaviour to what is observed for a typical shrinking core reaction mechanism. In comparison to the lower temperatures, the devolatilization mechanism approaches almost shrinking core behaviour at higher temperatures, while at lower temperatures devolatilization reactions tend to take place mainly throughout the entire particle volume (volume reaction mechanism) (Sadhukhan *et al.*,

2009; Sadhukhan *et al.*, 2011). Similar observations were made from the simulated curves of the other three coals (not shown here) at the different temperatures. Simulated radial profiles of volatile-loss and temperature showed good agreement with what was simulated by Bharadwaj *et al.* (2004), Sadhukhan *et al.* (2009 & 2011) and Zhang *et al.* (2012).

7.7.3.2 Effect of particle size

Figure 7.27 provides a graphic illustration of simulated product evolution and temperature profiles as a function of particle size for the devolatilization of coal INY at 450°C and 750°C, respectively.

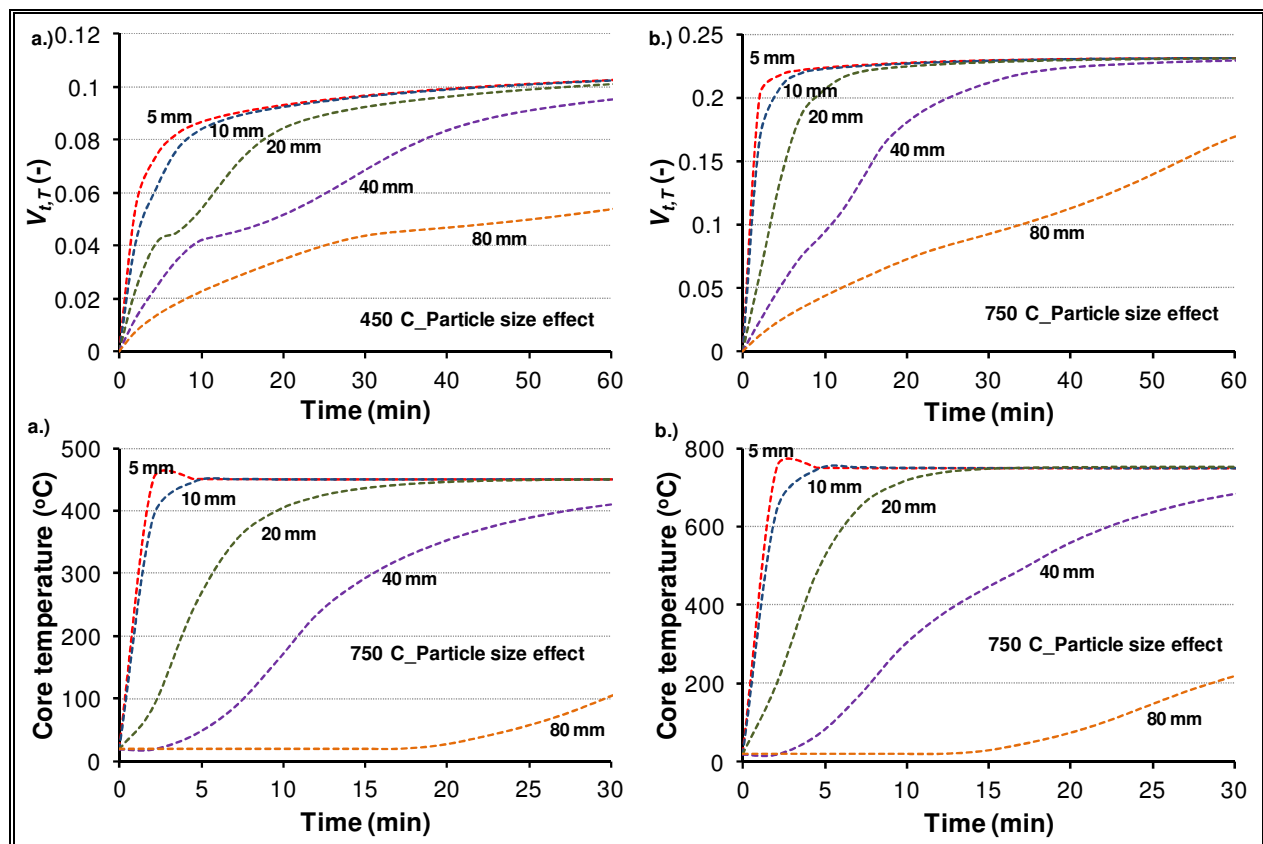


Figure 7.27 Profiles simulating the effect of particle size on total volatile loss and core temperature for the devolatilization of coal INY at a.) 450°C and b.) 750°C, respectively.

Illustrated volatile-loss profiles have been determined with the assumption that ultimate volatile yield ($V_{t,T}^*$) stays relatively unchanged for a change in particle size. This is supported by the findings of Sadhukhan *et al.* (2009) and Zhang *et al.* (2012), who showed relatively little change

in the final amount of volatile matter for an increase in particle size, if a sufficient amount of time is allowed for all devolatilization reactions to reach completion. From Figure 7.27 it is, however, evident for both temperatures that particle size influences the temporal profiles of volatile-loss and devolatilization time significantly due to significant differences in heat transfer resistances (neglecting any secondary decomposition reactions) between the different particle sizes. A comparison between the different particle sizes (5, 10, 20, 40 and 80 mm) indicates that for 450°C devolatilization, 50% theoretical fractional evolution of volatiles is attained after 2.1, 3.5, 9.6, 19.6 and 52.1 min for the respective particle sizes, while for 750°C, 50% evolution is attained after only 0.6, 0.85, 3.75, 12.1 and 37.1 min respectively. This phenomenon is also reflected in the longer times needed for larger particles to reach the final equilibrium temperature as depicted for the core temperature profiles presented in Figure 7.27. In other words, a smaller particle requires less time to reach thermal equilibrium and to attain full volatile evolution than a larger particle. The effect of particle size on both volatile-loss and core temperature can be mainly attributed to the fact that larger particles are characterised by smaller specific surface areas, i.e.: surface area per unit volume ($3/r$), and larger conduction resistances, which result in lower rates of heating. It is therefore evident that the rate at which a particle is heated (due to its internal resistance of conduction) significantly influences the time-resolved evolution of products during devolatilization. Similar conclusions were made by Heidenreich *et al.* (1999), Janse *et al.* (2000), Peters (2011), Sadhukhan *et al.* (2009 & 2011) and Zhang *et al.* (2012).

7.7.3.3 Effect of convective transport of volatile species and heats of reaction and -vaporization

Simulation studies were further performed, using the proposed model, in order to assess the effects of heat losses due to the internal transport of volatile products and moisture; as well as the heat of reaction and vaporization. For this purpose, simulations were performed at 450°C and 750°C using the model of 20 mm G#5 coal particles, as it yielded the highest amount of devolatilization products (moisture and volatiles), therefore providing a good illustration of not only the effect of internal transport but also heat of reaction. Similar observations, although to a lesser extent, were made for simulations of the other three coals. Figure 7.28 provides a overview of simulated temperature profiles (surface and core temperature) (1) neglecting heat losses due to the internal transport of volatiles and (2) assuming heat losses due to convective

cooling (proposed modelling strategy), while the effect of heat of reaction and -vaporization is depicted graphically in Figure 7.29.

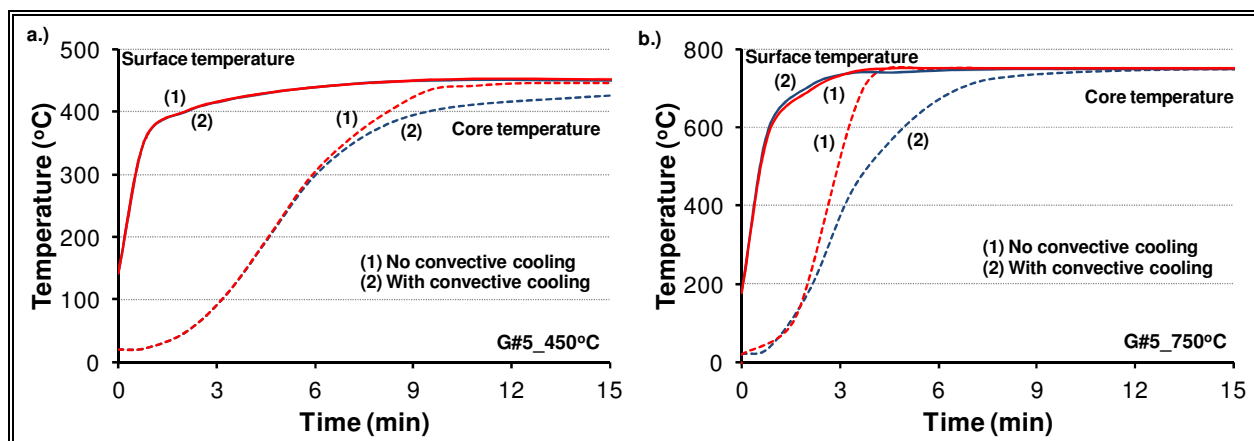


Figure 7.28 Effect of heat losses due to the internal transport of volatiles as depicted for the temperature profiles of coal G#5 at a.) 450°C and b.) 750°C.

From the above Figure it is clear that convective cooling has no significant influence on the external surface temperature, whilst core (centre) temperatures at a specific time were found to be significantly lower in the presence of internal convection. A comparison between the different simulated temperature profiles indicated that the time to final isothermal core temperature decreases with approximately 55% and 67%, respectively, for 450°C and 750°C if the convective term is neglected. The subsequent decrease in time to final isothermal temperature (as well as a decrease in volatile evolution rate), in the presence of convective cooling, can therefore be attributed to the transport of additional enthalpy out of the coal particle due to the convective flux of volatile products through the internal pore structure of the devolatilizing solid. Furthermore, it can also be seen that this effect becomes much more profound for the higher temperatures, due to the release of more volatiles and the presence of larger convective transport resistances (larger mass fluxes of volatile products).

Similar observations were made from the simulation results obtained during the assessment of the influence of heat of reaction and heat of vaporization as depicted in Figure 7.29. According to Janse *et al.* (2000), the endothermicity of devolatilization reactions can create a heat sink, which in turn can result in both extended conversion times but also in longer times to reach thermal equilibrium. This is seen clearly in Figure 7.29 where the time to 90% of the final isothermal temperature decreases from 10 min to 8 min for 450°C and from 6.5 to 5.5 min for 750°C if heat of reaction and -vaporization is neglected

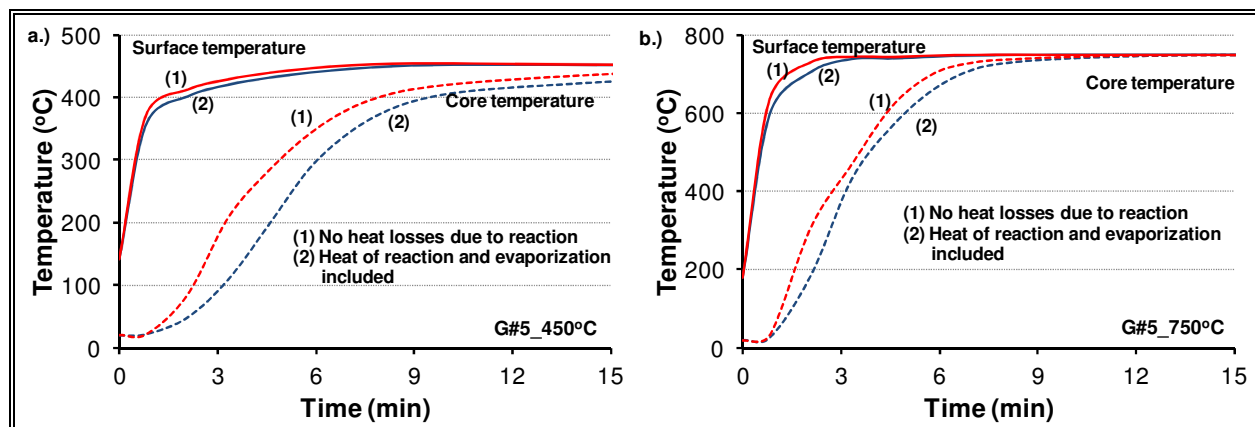


Figure 7.29 Effect of heat losses due to heat of reaction and heat of vaporization as depicted for the temperature profiles of coal G#5 at a.) 450°C and b.) 750°C.

In all cases, the predicted core temperature will be lower in the presence of heat of reaction and- vaporization as heat is absorbed to fuel both the initiation of moisture vaporization as well as the endothermic devolatilization reactions. The effect does, however, seem to be less prominent for the higher temperatures, due to higher external heat fluxes satisfying the energy demand, which evidently results in slightly faster heat penetration into the coal particle (Janse *et al.*, 2000). The success of prediction of the experimental data with the aid of the proposed model (as presented in Section 7.7.2) therefore stresses the importance of incorporating both the convective and heat of reaction-and vaporization terms in the overall governing energy equation. The relative importance of including these terms have also been stressed in the work of authors such as Janse *et al.* (2000), Sadhukhan *et al.* (2009 & 2011) and Zhang *et al.* (2012).

7.7.3.4 Effect of volume change during devolatilization

The effect of volume change can be described in a similar fashion to what is observed for the effect of particle size. Simulation studies were performed using both the proposed models for coals INY and TSH in order to provide an illustration of the effect of shrinkage and/or swelling on the simulated temperature profiles of a typical inertinite-rich coal (INY) and a typical vitrinite-rich coal. Profiles simulated with and without the inclusion of coal-related thermoplastic effects are provided respectively for coal INY in Figure 7.30 a.) and b.), while Figure 7.30 c.) and d.) shows the effects of particle swelling and/or shrinkage on the devolatilization behaviour of coal TSH.

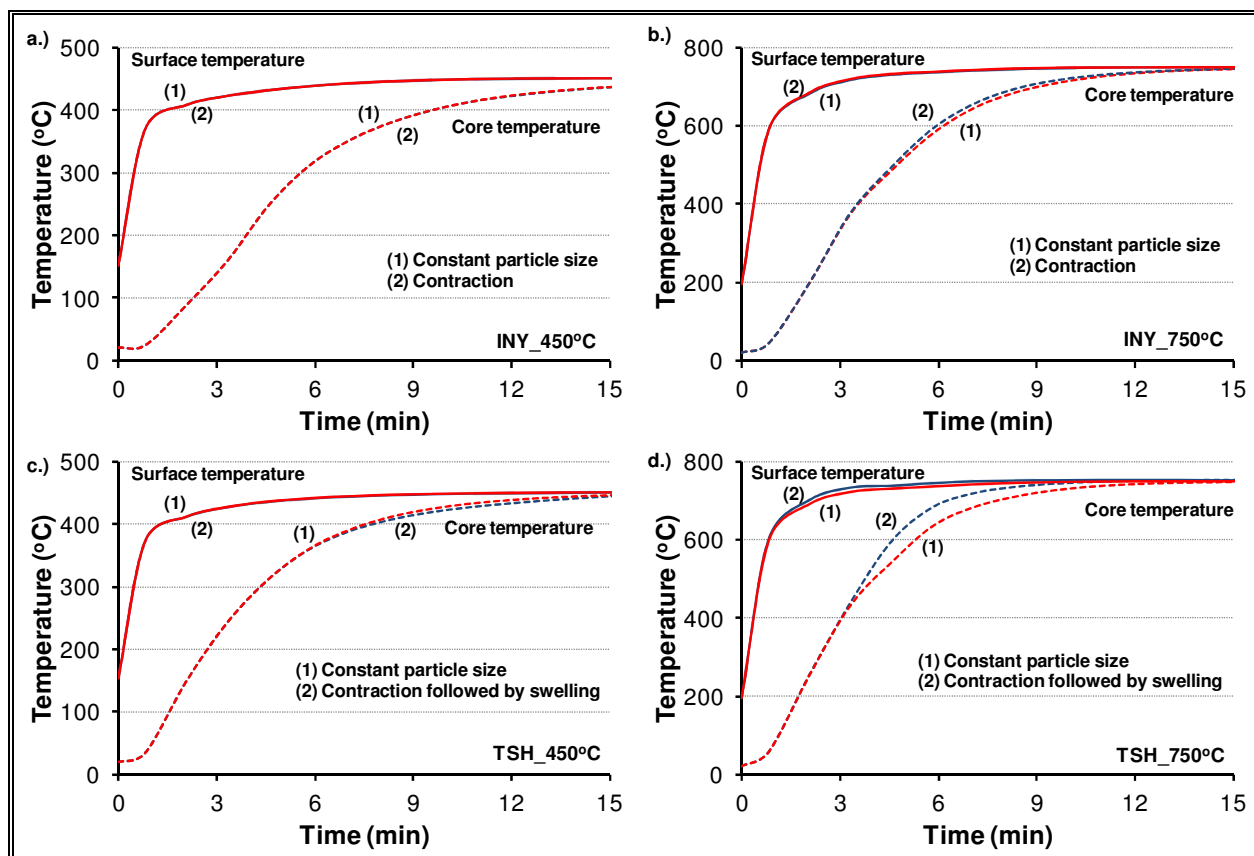


Figure 7.30 Effect of swelling/shrinkage on the temperature profile of a typical inertinite-rich coal (a.) and (b.) and a typical vitrinite-rich coal (c.) and (d.) for devolatilization at 450°C and 750°C.

In general, shrinkage leads to an increase in the specific surface area ($3/r$) of the coal particle, therefore resulting in smaller conductive resistances and faster rates of particle heating, while the opposite is true for particles undergoing extensive swelling (Sadhukhan *et al.*, 2011). From the Figure it is, however, evident that particle swelling and/or shrinkage were found to have no remarkable effect on the temperature profiles of both coals INY and TSH at the lower devolatilization temperature, which suggests that the propagation of the temperature distribution within the particle is mainly controlled by heat transfer mechanisms rather than the thermoplastic mechanism. At the higher temperatures, some differences can, however, be inferred, where only a slight decrease in heating time could be observed for coal INY. This slight deviation in core temperature can be attributed to the fact that the inertinite-rich coals were only observed to exhibit particle shrinkages of no more than 6%, thus indicating that the effect of volume change could be neglected for all practical purposes in the description of the devolatilization behaviour of inertinite-rich coals. For coal TSH, characterised by significant shrinkage and swelling behaviour (as high as 25%), core temperatures were found to be slightly higher when volume change was included. This is, however, contradictory to what should be

observed for coal samples characterised by shrinkage followed by subsequent particle swelling, as in the case of coal TSH. Theoretically the core temperature profile of coal TSH should therefore exhibit lower values due to the extensive increase of particle size during swelling. It is believed that the reason for the opposite trend could be partly explained by the fact that, during devolatilization of this coal, the temperature gradient is also significantly influenced by the formation of highly porous, low density char as observed in a separate study done by Hattingh (2012) (char densities were found to range between 600 kg/m³ and 900 kg/m³ in comparison to densities determined for the inertinite-rich chars which ranged between 1115 kg/m³ and 1300 kg/m³). Accordingly, lower density chars lead to higher thermal diffusivities, which in turn result in increased heating fluxes into the particle.

7.8 Summary

Assessment of the intrinsic kinetics of devolatilization involved the evaluation of small particle rate behaviour (-200 µm) with the aid of non-isothermal thermogravimetry using four different heating rates (5, 10, 25 and 40 K/min), and a final isothermal temperature of 950°C. Large particle rate measurements were conducted in a self-fabricated thermogravimetric analyser at seven different isothermal reactor temperatures ranging between 350°C and 900°C, using a total residence time of 2 hours. Experiments consisted of heating the TG system to the desired reaction temperature (isothermal reaction temperature) prior to the introduction of the coal sample to be analysed. Non-isothermal TG results obtained at the different heating rates indicated that an increase in temperature led to a subsequent decrease in sample mass, while ultimate volatile yields at 950°C were found to decrease in the order G#5 > UMZ > INY > TSH. Further investigation of the respective TG results of each coal revealed the division of the overall TG profile into clear regions of mass loss i.e.: the release of moisture, occluded gases and secondary pyrolytic water at temperatures below 350°C and a main devolatilization regime where the parent coal structure decomposes to form tars, gases and char at temperatures exceeding 350°C. From DTG results it was evident that all four coals exhibited a clear, primary peak of devolatilization confined to the temperature range between 350°C and 600°C, while a subsequent shift in peak temperature occurred for the maximum evolution rate of the main peak of coal TSH. This subsequent shift in peak temperature for coal TSH could be attributed to both its higher aromaticity (rank) as well as its extensive thermoplasticity, which could have resulted in re-polymerisation reactions becoming more favourable in the first stages of metaplast

formation. In addition, mass loss rate in the main region of devolatilization was found to be significantly larger for coals G#5 and TSH in comparison to the other two coals and could be related to the presence of more reactive material (vitrinite and especially the substantial amount of liptinite present in coal G#5) within the organic structures of coals G#5 and TSH. Large particle chars derived from the two inertinite-rich coals showed only minor fracture lines and larger cracks for temperatures exceeding 450°C, while substantial structural deformation could be observed for chars produced from coals TSH and G#5. From the time-resolved rate profiles of each coal it could be concluded that an increase in reaction temperature leads to a subsequent increase in both mass loss rate and the ultimate amount of volatiles released.

Evaluation of the intrinsic kinetic parameters describing the devolatilization behaviour of each coal involved the simultaneous, non-linear regression of non-isothermal reaction rate data (DTG data) in MATLAB® 7.1.1, according to the pseudo-component reaction modelling approach. From the modelling results it was evident that an increase in the amount of pseudo-components led to substantial decreases in the *QOF* parameter, with modelling predictions assuming a total of eight pseudo-components providing the best description of the experimental DTG curves. Estimated activation energies were found to range between 22.3 kJ/mol and 244.3 kJ/mol for the different coals, with the lowest activation energies (22.3-28.8 kJ/mol) confined to the deconvoluted peak (for 4 pseudo-components and higher) describing the release of moisture during devolatilization.

Kinetic parameters were further used in the evaluation of a comprehensive, large particle model allowing for the effects of particle thermoplasticity as well as heat- and mass transfer. Evaluation of the proposed model required the use of the COMSOL Multiphysics® 4.3 simulation software package to numerically solve the governing set of equations, according to a finite element method. For all four coals, experimentally derived profiles of fractional volatile yield, particle surface temperature and particle core temperature showed excellent agreement with predicted trends obtained from model simulation, therefore suggesting that the proposed mathematical model provides a suitable description of the devolatilization performance of each coal. This is also reflected in the *QOF* values obtained from volatile-loss predictions, which showed values of less than 15% for each coal, while relative mean errors for the particle temperature predictions ranged between 3.21% and 9.18%. Simulation studies also underlined the relative importance of operational parameters such as particle size, swelling and heat losses due to convective transport on the total volatile evolution and particle temperature history.

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