CHAR-CO_2 KINETICS DETERMINATION USING THERMOGRAVIMETRY AND THE DISTRIBUTED ACTIVATION ENERGY MODEL

ABSTRACT

An established DAEM-based algorithm was modified to determine the reaction behaviour of materials reacting in CO_2 by means of incorporating the Random Pore Model (RPM).

The novelty in this research was the determination of multiple reaction mechanisms occurring in RPM systems. Despite specifying multiple reactions, a single RPM structural parameter ($\varphi=12.2$) was still suitable, and produced accurate data fits. Charred Coal-CO_2 reactivity data was processed with the algorithm and activation energy values of E_1=261.7kJ/mol, E_2=246.4kJ/mol and E_3=227.6kJ/mol were found. Grouped pre-exponential factor values were found to be A_1^*=1.60E+07$s^{-1}.m^{-1}$, A_2^*=2.08E+06$s^{-1}.m^{-1}$ and A_3^*=2.75E+06$s^{-1}.m^{-1}$. The corresponding mass fractions were $f_{0,1}$=0.31, $f_{0,2}$=0.32, $f_{0,3}$=0.37. These proved to predict the reaction behaviour better than the conventional single reaction approach which found activation energy and grouped pre-exponential factor of E=254.5kJ/mol and A^*=1.0E+07 $s^{-1}.m^{-1}$ respectively.

The findings show that the algorithm can be successfully adapted to process RPM data and produce accurate and reliable results.

INTRODUCTION

Fossil fuels are currently the world's primary energy source. Coal is one of the more abundant low-cost fossil fuels, but the high carbon to hydrogen ratio results in high production of CO_2 which, given the concern over global warming, is an unfavourable trait of the use of this fuel (Irfan et al., 2011). Coal gasification is however one of the most versatile and cleanest ways to convert coal to fuel and energy (Research and Markets, 2006). The ability of the gasification process to eliminate and/or contain air pollutants and green house gases (GHG's) also makes this process highly favourable. Hence, it is vital that this process be thoroughly understood.

One particular aspect of the gasification process which is being considered in this research is the determination of the kinetics of the reactions occurring when chars are gasified. A comprehensive review of the many factors affecting the kinetics of gasification in CO_2 is covered in Irfan et. al. (2011). Of particular interest is collection of methods which are commonly known as model-free isoconversion methods (Starink, 2003). While the model-dependent methods (Irfan et al., 2011) are based mainly on the Langmuir-Hinshelwood model, the isoconversion methods are based on the premise that reaction rate is a product of two functions; one depending solely on temperature, and the other depending solely on the fraction transformed. The temperature function is usually expressed as an Arrhenius type dependency, in which the pre-exponential factor (A) and activation energy (E) are the desired kinetic parameters. Most

isoconversion methods make an approximation to the “temperature integral” (those which do not are known as “algorithmic methods but are generally considered too calculation intensive) and then find *E*, without needing a reaction model. A reaction model is further required to find *A*. The results are however presented as a range rather than discrete values since the solution method requires the parameters to be determined at specified conversions.

However, a recent algorithm based on the Distributed Activation Energy Model (DAEM) has been developed to determine the pyrolysis kinetics of complex solid fuels. The algorithm provides a way of inverting the DAEM which results in the determination of discreet mass-fraction values which accurately identify the activation energy and pre-exponential factor for each parallel step participating in the thermal decomposition of the fuel. This research will focuses on extending this method to CO_2 reactivity, which is best described by the Random Pore Model (RPM) (Irfan et al., 2011).

THEORY: ALGORITHM DEVELOPMENT

The original DAEM-based algorithm was derived and shown to be effective in determining pyrolysis kinetics (Scott, Dennis, Davidson, and Hayhurst, 2006a, 2006b). The algorithm is applied in three main steps, where the activation energy, E_i , pre-exponential factor, A_i and mass fraction, f_i, (The Arrhenius kinetic triplet) are calculated. The original algorithm is presented as follows:

$$\frac{M(t)}{M_0} = w + \sum_{All\ reactions,i} f_{i,0} \exp\left[-A_i \int_0^t \exp\left(\frac{-E_i}{RT}\right) dt\right] \quad 1$$

Where $M(t)$ is the mass of the sample at time t, M_0 is the initial mass of the fuel, w is the fraction of inert material and $f_{i,0}$ is the fraction of M_0 which decomposes with activation energy E_i and pre-exponential factor A_i. The double-exponential term can be expressed as Ψ_i. Note that f_i represents the discrete fractional density function, or remaining mass fraction as a function of conversion. The full derivation of the algorithm can be found in Scott et al., (2006a).

The double exponential term in equation 1 is identified as:

$$\Psi(\mathrm{E}, \mathrm{t}) = \exp\left[-A(E) \int_0^t \exp\left(\frac{-E}{RT}\right) dt\right] \quad 2$$

And if it is multiplied by a constant heating rate, can be expressed as:

$$\Psi_i(t) = \Psi_i(T) = \exp\left[-\frac{A_i}{B} \int_{T_0}^T \exp\left(\frac{-E_i}{RT}\right) dT\right] \quad 3$$

Like the DAEM, this algorithm proposes that the reactions occurring in a complex solid fuel occur in series rather than parallel and assumes that at each fractional conversion, a single reaction is dominating. The algorithm uses this assumption and the expression in equation 3 to calculate the activation energy without the use of a proposed reaction model. At this station, the method is akin to an isoconversion method; significant differences between this method and isoconversion versions appear later.

The first step of the algorithm considers the conversion at 2 different heating rates, say B_1 and B_2. It is then assumed that the ith reaction is the only reaction taking place at this conversion, then $f_i(B_1,T_1)=f_i(B_2,T_2)$. It then follows, since Ψ is also a function of heating rate, that:

$$\Psi_i(B_1,T_1) = \Psi_i(B_2,T_2) \qquad 4$$

Then, substituting the heating rate and taking natural logarithms on both sides results yields:

$$\frac{1}{B_1}\left[T_0 \exp\left(\frac{-E_i}{RT_0}\right) - \frac{-E_i}{R}\int_{E/RT_0}^{\infty}\frac{\exp(-u)}{u}du - T_1 \exp\left(\frac{-E_i}{RT_1}\right) + \frac{E_i}{R}\int_{E/RT_1}^{\infty}\frac{\exp(-u)}{u}du\right] = \frac{1}{B_2}\left[T_0 \exp\left(\frac{-E_i}{RT_0}\right) - \frac{-E_i}{R}\int_{E/RT_0}^{\infty}\frac{\exp(-u)}{u}du - T_1 \exp\left(\frac{-E_i}{RT_1}\right) + \frac{E_i}{R}\int_{E/RT_1}^{\infty}\frac{\exp(-u)}{u}du\right] \qquad 5$$

From this, the activation energy can be determined using thermogravimetric data alone i.e. temperature-conversion data and the known heating rate are sufficient to determine activation energy. This result is presented as a conversion range with corresponding activation energy values. Since this step is model independent (Saloojee, 2011), no modification is required in the first step.

Once the activation energy for component *i* has been found using equation 5, A_i can be found (Scott, Dennis, Davidson, and Hayhurst, 2006a). This is done by assuming that the dominating reaction is at some conversion. It is assumed that the reaction of component *i* (not the overall reaction) is at its maximum rate of decomposition. This assumption follows from how the approach is posed, i.e. that the reactions occur in series and that at each fractional conversion, only one reaction is dominating. For one reaction to be dominating, it is safe to assume that its reaction rate is at or near its maximum value. Based on this assumption, the value of conversion *x* that results in this maximum decomposition rate is used in calculation, i.e. where:

$$\frac{d^2 f_i}{dt^2} = 0 \qquad 6$$

The determined conversion value (called x_{max}) is used to specify the value of the left hand side of equation 7.

$$\ln(\Psi_{\mathrm{i}}(T)) = \frac{A_i}{B_1}\left[T_0 \exp\left(\frac{-E_i}{RT_0}\right) - \frac{E_i}{R}\int_{E/RT_0}^{\infty} \frac{\exp(-u)}{u} du - T_1 \exp\left(\frac{-E_i}{RT_1}\right) + \frac{E_i}{R}\int_{E/RT_1}^{\infty} \frac{\exp(-u)}{u} du\right] \quad 7$$

To demonstrate, for a first order reaction, a value of x=1-e^{-1} ratifies equation 6. Then, if the first-order reaction model is expressed in terms of *Ψ*:

$$\Psi_{\mathrm{i}}(T) = 1 - x \quad 8$$

Hence

$$\ln(\Psi_{\mathrm{i}}(T)) = -1 \quad 9$$

To apply this algorithm to CO_2 reactivity using the RPM, This value of conversion, *x,* and corresponding value of *ln[(Ψ$_i$ (T)]* must be modified. Hence, following the same approach, equation 6 was applied to the RPM. The result is presented in equation 10:

$$\frac{\varphi A^{*2} \exp\left(\frac{-2E}{RT}\right)(1-x)}{2\beta^2} - \frac{A^{*2} \exp\left(\frac{-2E}{RT}\right)(1-x)(1-\varphi \ln(1-x))}{\beta^2} - \frac{A^* E \exp\left(\frac{-E}{RT}\right)(x-1)\sqrt{1-\varphi \ln(1-x)}}{\beta R T^2} = 0 \quad 10$$

Where *φ* is a dimensionless structural parameter in the RPM, A*(s^{-1}.m^{-1}) is the grouped pre-exponential factor and *β* is the constant heating rate (*K/sec*).

Equation 10 cannot be expressed explicitly in terms of *x*. An error minimisation method can be applied, with a series of proposed values of E, A* and *φ* values to determine *x* at which the *ith* reaction (not the overall material reaction) reaches a maximum rate of decomposition. This value is substituted into the manipulated RPM expression in order to determine *ln[(Ψ$_i$ (T)]*. The expression and determined values are presented in Table 1.

Table 1: Modified RPM expression and corresponding values for Algorithm modification

Reaction Model	$\int_{x_0 \approx 0}^{x} \frac{dx}{f(x)} = g(x)$	x_{max}	$g(x_{max}) = \ln(\Psi_i)$ For Equation 7
Random Pore Model (RPM)	$\frac{2}{\varphi}\left(\sqrt[2]{1-\varphi \ln(1-x)} - 1\right)$	$x_{max} = 0.6502$	$\ln(\Psi_i) = -0.8801$

Now for each fractional conversion, a set of activation energy and pre-exponential factor values have been determined. At this stage the algorithm has departed from isoconversion methods in that it has determined the pre-exponential factor values without the need for an entirely separate method.

Lastly, the mass fractions must be determined. This step is vital since it further distinguishes the algorithm from other common methods. The mass fraction values allocated to each fractional conversion help identify which reactions are actually happening, and which reactions are spurious (Scott, Dennis, Davidson, and Hayhurst, 2006a). this result will produce discreet kinetic parameter values rather than a range of values which would otherwise have to averaged, which would compromise accuracy.

Now equation 1 can be written in matrix form as $\underline{M} = \underline{\Psi}.\underline{f}$ such that:

$$\frac{1}{M_0}\begin{bmatrix} M(t_0) \\ \vdots \\ M(t_\mathrm{n}) \end{bmatrix} = \begin{bmatrix} \Psi_1(t_0) & \Psi_2(t_0) \cdots \Psi_n(t_0) & 1 \\ \vdots & \vdots \quad \cdots \Psi_n(t_1) & 1 \\ \Psi_1(t_\mathrm{n}) & \Psi_2(t_\mathrm{n}) \cdots \Psi_n(t_\mathrm{n}) & 1 \end{bmatrix} \times \begin{bmatrix} f_{1,0} \\ \vdots \\ f_{\mathrm{n},0} \end{bmatrix} \qquad \textbf{11}$$

This form is used in the final step. The f_0 values for each component *i*, are calculated using linear least squares. Equation 11 is used by specifying an *E* and A^* value and generating the candidate reactions to populate the matrix $\underline{\Psi}$. The $\underline{M}$ vector is the predetermined mass loss profile of the simulated or experimental reaction. Note that resulting matrix $\underline{\Psi}$ is not a square matrix. Therefore when the $\underline{f}$ vector is calculated using matrix inversion such that $\underline{M}.\ \underline{\Psi}^{-1}=\underline{f}$, there is no exact solution. The least squares (non-negative constraint) function in Matlab (*lsqnonneg*) is therefore used to numerically determine the f_0 elements in the $\underline{f}$ vector that satisfy $\underline{M}.\ \underline{\Psi}^{-1}=\underline{f}$.

The modification of the original algorithm (Scott, Dennis, Davidson, and Hayhurst, 2006a) is needed in the generation of the $\underline{\Psi}$ matrix. In calculation of the matrix $\underline{\Psi}$, the RPM specific equivalent of the Ψ expression must be used. Equation 12 equates *g(x)* to the temperature integral such that:

$$g(x) = \ln(\Psi) \qquad \textbf{12}$$

Therefore,

$$\Psi = \mathrm{e}^{\mathrm{g(x)}} = \exp\left(\frac{2}{\varphi}\left(\sqrt{1-\varphi\, ln(1-x)}-1\right)\right) \qquad \textbf{13}$$

Whereas, for first-order:

$$\Psi = e^{g(x)} = \exp\,(1-x) \qquad \textbf{14}$$

Equation 13 is used to calculate the matrix $\underline{\Psi}$ which is then used in the *lsqnonneg* algorithm in Matlab® to do the matrix inversion and generate the vector $\underline{f}$. The activation energy and pre-exponential values corresponding to non-zero fi value(s) are the kinetics considered to represent the reaction(s) occurring in the fuel mass.

EXPERIMENTAL

The modified algorithm was then tested on two different sets of data. First, the algorithm is applied to simulated TGA data. The data was simulated using the RPM where data was generated at two different heating rates. The algorithm is then applied to experimental data. This was generated by reacting coal char in CO_2 at various heating rates and fixed initial partial pressure.

APPLICATION TO SIMULATED DATA

The basic form of the RPM must be manipulated in order to simulate reaction data that would be obtained from a TGA. Based on the integrated expression given in equation 13, the variables must be separated so that conversion can be expressed explicitly in terms of temperature. The resulting expression is as follows (which holds for $f_0=1$):

$$f_i = 1 - x_i = exp\left(\frac{1}{\varphi}\left(1 - \left(\frac{\varphi}{2}\left(\ln \Psi_i + \frac{2}{\varphi}\right)\right)^2\right)\right) \qquad \textbf{15}$$

The value for the structural parameter used in simulation one proposed for common porous solids (Bhatia and Perlmutter, 1980). The value is given as ***φ=0.88.*** Then, to simulate the reaction, an activation energy value, grouped pre-exponential factor value, and corresponding mass fraction must be specified, along with at least 2 heating rates. It must be noted that the way the algorithm has been developed and the way it has been coded into Matlab®, it is possible to simulate multiple reactions, although the single reaction case is considered here. The simulated data is presented in Figure 1. Although numerical integration techniques are used to simulate the data (since no analytical solution exists for the temperature integral), the data produced is a good representation of behaviour that would be observed from using a TGA. The parameters specified are $E=200kJ/mol$ and $A^*=10E+10s^{-1}.m^{-1}$. Since a single reaction is being simulated, the mass fraction is $f_i=1$. To run the algorithm, an arbitrary number of candidate reactions must be specified, which is merely the number of points that the entire conversion space is split into. This was set at 50 candidate reactions.

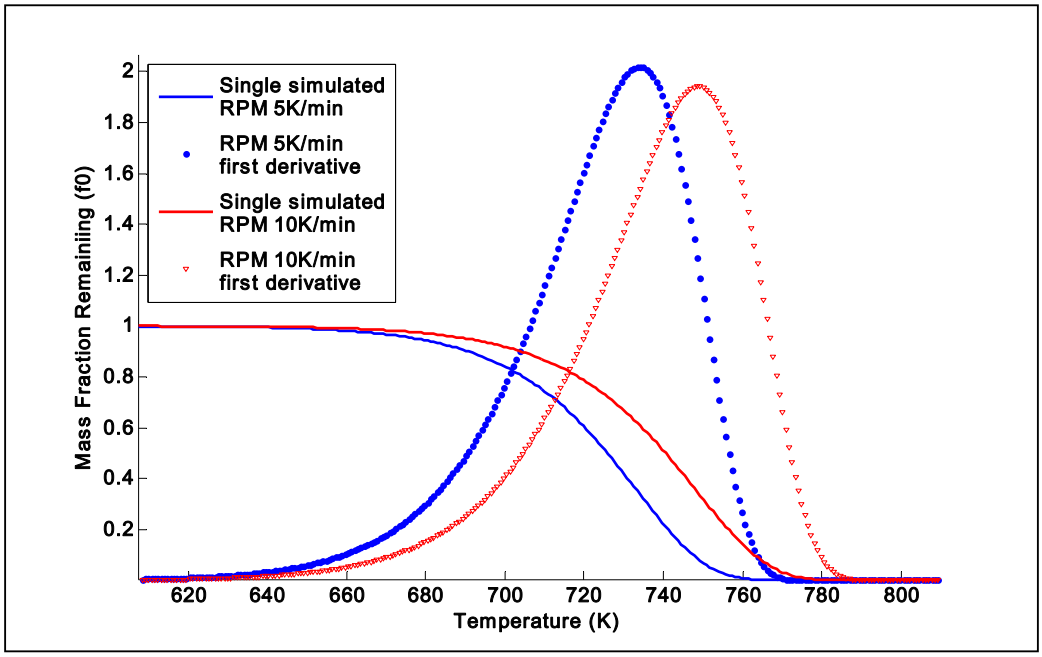

Figure 1: Single simulated RPM reaction at 5Kpm and 10Kpm

The data produced by the algorithm for all the candidate reactions is presented in Figure 2:

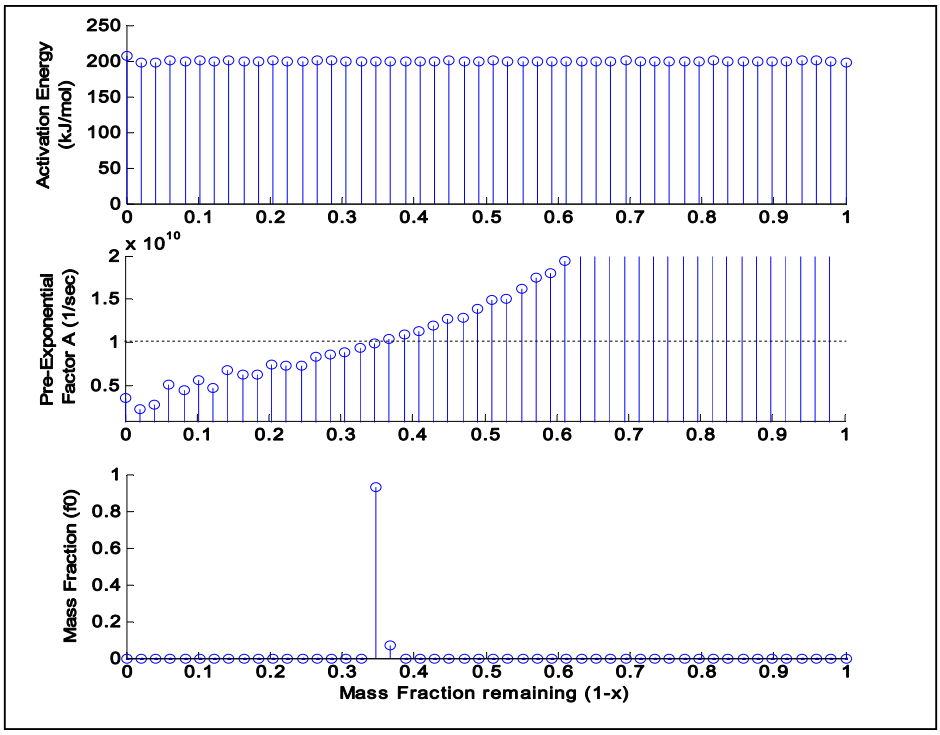

Figure 2: Stem plot of kinetic parameter results determined from simulated single RPM reaction data

It is evident that even though 50 candidate reactions were specified, only one complete kinetic triplet has been produced. The values determined by the algorithm can then be compared to those specified during simulation to determine the accuracy of the algorithm results. This comparison is presented in Table 2:

Table 2: Comparison between Specified and Algorithm Derived Kinetic Parameters for a single simulated RPM reaction

	Activation Energy *E* (kJ/mol)	Pre-Exponential Factor A^* (sec^{-1})	Initial Mass Fraction *f0*
Specified Value	200	1E+10	1
Algorithm Derived Value	200.05	1. 02E+10	0.9995
Relative Error (%)	<1%	2%	<1%

Further assessment of the accuracy of the algorithm results was conducted by comparing the data simulation plots produced using the specified kinetics and the algorithm determined kinetics. This comparison is given in Figure 3:

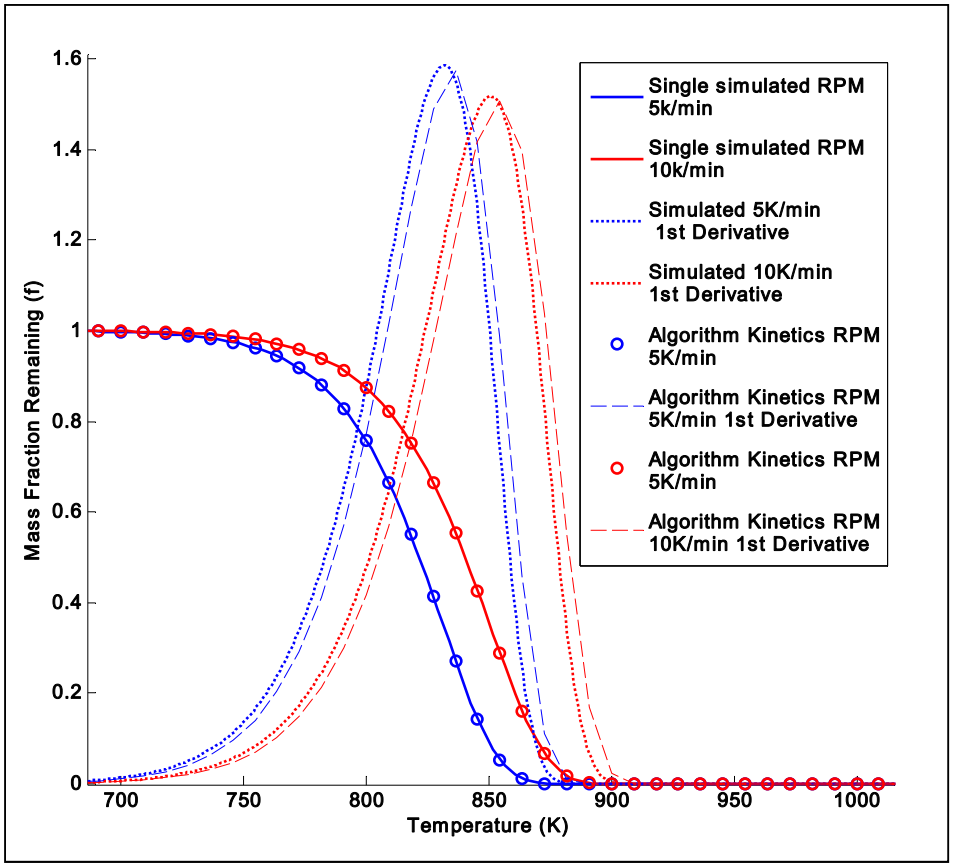

Figure 3: Single Simulated RPM reactions and 1st Derivatives at 5K/min and 10K/min With RPM Algorithm-derived Kinetics Simulations Overlaid

Table 1 and Figure 3 both illustrate that the algorithm is capable of determining highly accurate kinetic parameter values. The low relative error percentages are evident when the plots are compared. While there is slight deviation in the derivative data, (which is very sensitive to parameter values) the reaction datasets correlate very well, overlapping almost completely.

APPLICATION TO EXPERIMENTAL DATA

Given the success of the application to simulated data, the algorithm was applied to experimental data. An inertinite rich South African coal was used. The proximate analysis results are provided in Table 3:

Table 3: Coal proximate analysis results

Component	Weight Percentage
moisture	2.44
Volatile matter	18.93
fixed carbon	44.80
Ash Content	33.83
total	**100**

The coal was pulverized into particles with a nominal diameter up to 150 microns and charred before being reacted in CO_2. The charring and reaction processes were conducted using a modified TA Instruments SDT-Q600 TGA. The pulverized coal was charred by being heated in pure N_2 at rate of 20Kpm up to 1250ºC. It was then cooled to 700ºC and held for 15 minutes to ensure any residual volatiles were driven off before gasification. The char produced was then reacted in CO_2 at three different heating rates, 12Kpm, 15Kpm and 20Kpm. The CO_2 was introduced at a rate of 60ml/min, along with a small purge gas fraction of 5ml/min N_2.

The data presented in Figure 4 is normalised data for the three heating rates and does not include the mass-loss data recorded during the charring phase.

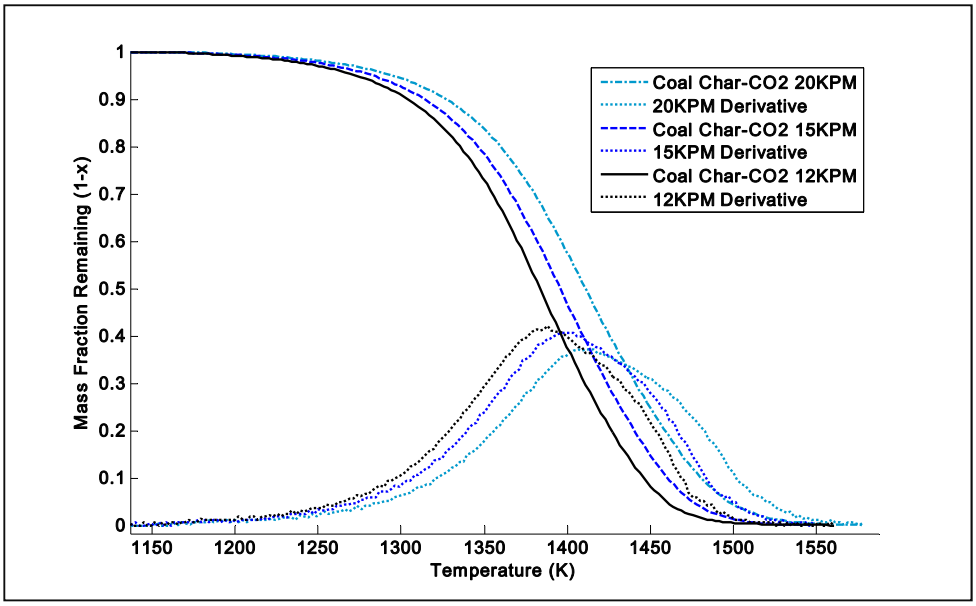

Figure 4:Coal Char Decomposition in CO2 and Derivatives

It is important to note that the derivative curves presented in Figure 4 do not resemble single reaction simulations presented in Figure 1. While the simulations' derivative curves resemble a smooth uniform almost Gaussian form, the experimental derivative data has a fairly distinct inflection as the derivative decreases, indicating the likelihood of a multiple reaction system.

With experimental data, the structural parameter is not known. While it can be measured experimentally (Su and Perlmutter, 1985), other studies (Bhatia and Vartak, 1996; Everson et al., 2006) suggest that it is best to find the structural parameter via regression analysis to avoid the need for lengthy experimental procedures, as well to ensure improved accuracy and reliability of the kinetics results. This can be done using a regression method (Sangtong-Ngam and Narasingha, 2008).

This approach is characterised by equation 16:

$$\sigma = \sqrt{\frac{err_1^2 + \cdots + err_n^2}{n}} \qquad 16$$

Where err_1 is the error between the calculated and experimental data at point *1*, and err_n is the error between the calculated and experimental data at point *n*, and *n* is the number of points in the data set. The *fminbnd* algorithm in Matlab (Matlab R14, The Mathworks Inc.) is used to vary the value of φ within a predetermined range until σ is minimised. This was a further modification applied to the original algorithm which was necessary for processing RPM data.

Having prepared the algorithm and produced the reaction data, the algorithm was applied to determine the reaction kinetics. Since the algorithm only uses 2 heating rates to complete all

calculations, the 12Kpm and 15Kpm data were used. The third heating rate will be used to assess the accuracy of the predicted reaction behaviour. The predictions will be produced by using the kinetic parameter values determined.

As suspected from the initial data inspection, the algorithm results presented in Table 4 show that the total reactive mass has been split across a number of reactions.

Table 4: Coal-Char/CO_2 Multiple Reaction Kinetics Determined by DAEM-Based Algorithm

	Mass Fraction (f_0)	Activation Energy E (kJ/mol)	Grouped Pre-exponential Factor A^* ($s^{-1}.m^{-1}$)
Reaction 1	0.060	262.0	1.69E+07
Reaction 2	0.254	261.7	1.57E+07
Reaction 3	0.075	248.9	2.71E+06
Reaction 4	0.240	245.6	1.89E+06
Reaction 5	0.366	227.6	2.75E+05
Reaction 6	0.007	305.6	5.04E+07

Table 4 presents all non-zero mass-fraction results. Reactions 1-2 and 3-4 both have similar activation energy and grouped pre-exponential factor values; they also occur at adjacent conversion values and can hence be combined and considered as single reactions. Reaction 6 does not correspond with reaction 5 in terms of kinetic parameter values and represents an almost negligible fraction of the reactive mass. For simulation of other heating rates, this reaction should be included, but will not be discussed at length when comparing actual kinetic values. For kinetic comparison, the summed and averaged reactions are given in Table 5.

Table 5: Summed/ Averaged Coal Char/CO_2 Kinetics Determined by DAEM-Based Algorithm

	Mass Fraction (f_0)	Activation Energy E (kJ/mol)	Grouped Pre-exponential Factor A^* ($s^{-1}.m^{-1}$)	Structural parameter φ
Reaction 1-2	0.313	261.8	1.60E+07	12.2
Reaction 3-4	0.315	246.4	2.08E+06	
Reaction 5	0.366	227.6	2.75E+05	

The kinetic parameter values found are of the order of those found for coal chars described by the RPM (Fermoso et al., 2010). The structural parameter value found in the regression analysis is φ=12.2.

Multiple reaction systems are seldom reported for RPM reactions; single reaction systems are far more common. Sangtong-Ngam and Narasingha (2008) applied Arrhenius plots to coal gasification data using the RPM and produced single reaction results. The same approach was applied to this data and the kinetics results are presented in Table 6. Note that unlike the algorithm, Arrhenius plots require a minimum of 3 heating rates to determine a kinetic parameter set.

Table 6: Single Reaction Kinetics Determined by Arrhenius Plot

	Mass Fraction (f_0)	Activation Energy E (kJ/mol)	Grouped Pre-exponential Factor A^* ($s^{-1}.m^{-1}$)	Structural parameter φ
Reaction 1	1	254.45	1E+07	0.30

Both sets of kinetic parameters were used to predict the reaction behaviour at 20K/min. The experimental data, as well as the predictions produced using a conventional single-reaction approach and the algorithm's multiple reaction approach is presented in Figure 5.

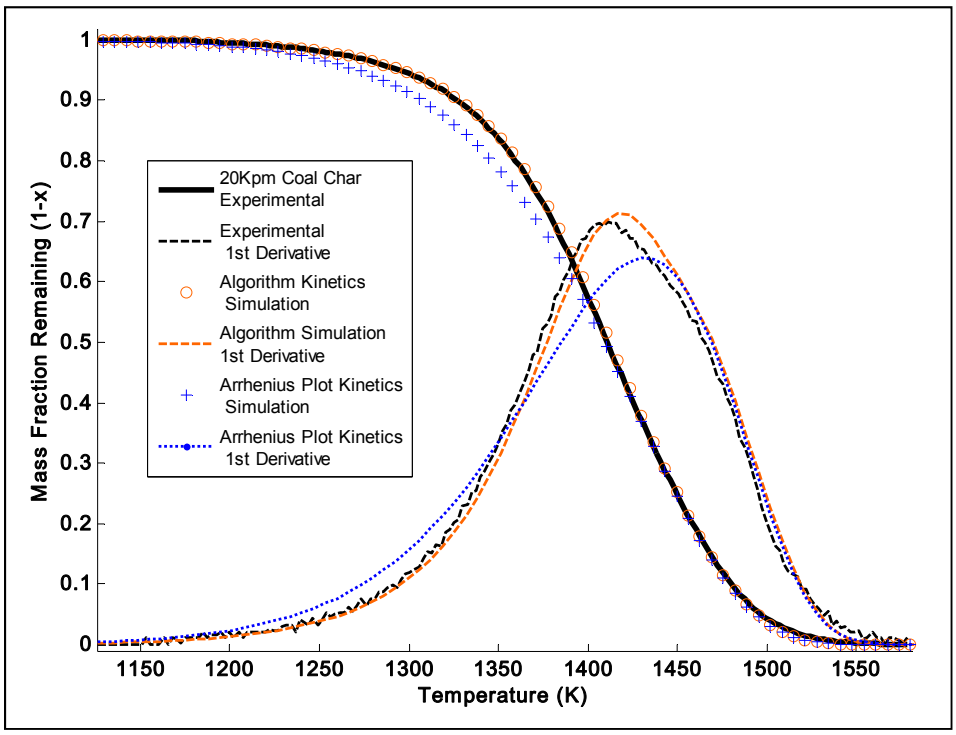

Figure 5: DAEM-based Algorithm Fit of 20Kpm Experimental Data Compared to Arrhenius Plot Fit

It is evident that while a single reaction approach can make a fair prediction of experimental reaction behaviour, a far more accurate prediction can be achieved by applying the DAEM-based algorithm. The multiple reaction approach produces significantly closer correlation between the reaction data of the algorithm kinetics prediction and the experimental data. The same observation can be made regarding the derivative data. The sensitivity of the derivative is high, thus a good derivative correlation is clear indicator that the experimental behaviour has been accurately simulated. This is not the case for the single reaction simulation, which shows very little correlation with the experimental data derivative. It must also be noted that this quality of fit was achieved without finding a unique structural parameter for each of the multiple reactions identified by the algorithm. An overall φ value produces a desirable quality of fit.

CONCLUSIONS

A number of significant conclusions can be drawn from the results presented in this research:

- The DAEM-based algorithm has again been shown to be model independent in the determination of activation energy
- The model has been adapted to process RPM data, despite its derivation being based upon first-order reaction kinetics. Further, a general method to adapt the algorithm to other reaction models has been outlined.
- The algorithm adapted to process RPM data successfully predicted the reaction kinetics for simulated RPM data
- The multiple reaction approach characteristic to this algorithm proved significantly more accurate in predicting CO_2 gasification reactivity as compared to the single reaction approach of more common methods, given the use of the same structural reaction model (RPM)

REFERENCES

Bhatia, S.K., Perlmutter, D.D., 1980. AIChE Journal 26, 379-386.

Bhatia, S.K., Vartak, B.J., 1996. Carbon 34, 1383–1391.

Everson, R.C., Neomagus, H.W.J.P., Njapha, D., 2006. Fuel 85, 418-422.

Fermoso, J., Gil, M.V., Pevida, C., Pis, J.J., Rubiera, F., 2010. Chemical Engineering Journal 161, 276-284.

Irfan, M.F., Usman, M.R., Kusakabe, K., 2011. Energy 36, 12-40.

Research and Markets, 2006. Market Analysis - Gasification of Coal and its Importance in the Power Sector [WWW Document]Synergist. URL http://www.researchandmarkets.com/reports/352283/market_analysis_gasification_of_coal_and_its

Saloojee, F., 2011. Kinetics of pyrolysis and combustion of a south african coal using the distributed activation energy modelScience.

Sangtong-Ngam, K., Narasingha, M.H., 2008. Thammasat Int. J. Sc. Tech. 13, 16-26.

Scott, S., Dennis, J., Davidson, J., Hayhurst, a, 2006a. Chemical Engineering Science 61, 2339-2348.

Scott, S., Dennis, J., Davidson, J., Hayhurst, a, 2006b. Fuel 85, 1248-1253.

Starink, M., 2003. Thermochimica Acta 404, 163-176.

Su, J.L., Perlmutter, D., 1985. AIChE journal 31, 973–981.