
Oil Shale Pyrolysis Reaction Model by Solving Ordinary Differential Equation

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Abstract

A mathematical model was developed to represent kerogen and bitumen decomposition reactions occurring during oil shale pyrolysis. To predict the weight loss over temperature for the given shale sample, the Runge Kutta method is used to solve the ordinary differential equations (ODE). The ODE method applied in this paper is compared with the ODE linearisation method used in a previous paper and with experimental data obtained on an oil shale sample from the Moroccan Timahdit oil shale at different heating rates.

This paper also introduces the concept of separating the oil, gas and water into individual components by differentiation between the substances composing in the vapour phase. Cracking and coking reactions of the oil produced from kerogen and bitumen decomposition are also taken into account in this concept.

Introduction

The study on the modeling of oil shale decomposition has been limited. Understanding of the oil shale decomposition process through the application of heat termed pyrolysis represents an important aspect in the oil shale development.

A previous study by the authors focused on characterising the oil shale decomposition by solving the ordinary differential equations through the linearisation method (Zainal Abidin et al, 2006). This solution method has yet to be compared with other mathematical models and numerical solutions that can be used effectively to solve the differential equations system. This paper focuses on solving the ordinary differential equations for the pyrolysis of an oil shale sample by utilizing the iterative fourth order Runge-Kutta Method. The differential equations in this study were derived from correlations representing the kinetics of the reaction from the thermogravimetric analyser (TGA) results obtained from previous lab-scale study using Moroccan Timahdit oil shale samples.

A Brief Overview on Solution of Differential Equations System

Depending on the nature of the differential equations system, various methods can be employed to solve these equations. As the analytical method is restricted in its application most problems resort to the application of various numerical methods such as the Runge-Kutta and orthogonal collocation. The selection of a numerical method will in turn depend on the nature of the boundary conditions for the equations system. The initial value problem (IVP) for the ordinary differential equations (ODE) system can be posed in the following generic form:

$$\frac{dy_i(x)}{dx} = f_i(x, y_1, \dots, y_N) \quad (1)$$

$$y_i(x_o) = y_{i_o} \quad i = 1, \dots, N$$

where y_{i_o} is the value of y_i at some starting value of x_o .

Generally, the Runge-Kutta method is the most widely used method to generate the solution for this ODE system. The following equations are the generic form used to obtain the approximate solution of (1):

$$y_{n+1} = y_n + \frac{h}{6}(k_1 + 2k_2 + 2k_3 + k_4) + O(h^5)$$

where

$$k_1 = f(x_n, y_n)$$

$$k_2 = f\left(x_n + \frac{h}{2}, y_n + \frac{h}{2}k_1\right)$$

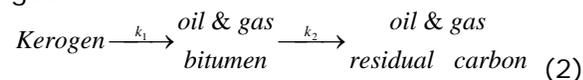
$$k_3 = f\left(x_n + \frac{h}{2}, y_n + \frac{h}{2}k_2\right)$$

$$k_4 = f(x_n + h, y_n + hk_3)$$

This is an iterative procedure where each subsequent k value utilizes the k value calculated in the previous step. The procedure is repeated to integer n until a convergence criterion for the solution has been achieved. Software tools are most commonly utilized to solve such repetitive procedures as performed in this study.

Methodology

A simplified representation for the decomposition of oil shale is represented in the following reaction. Continuous heating of the oil shale will further decompose the kerogen into bitumen as well as oil and gas.



Where:

$$k_1 = k_{10}e^{-E_1/RT}$$

$$k_2 = k_{20}e^{-E_2/RT}$$

The mathematical model aims to quantify the values as represented in the reaction constants above. The numerical analysis allows the parameters in Table 1 to be determined.

Experimental Methodology

This model relied on data from previous TGA analysis of the Timahdit oil shale sample. TGA is conducted by using equipment that measures the weight loss of a sample as a function of time under temperature control.

This model utilized the non-isothermal analyses hence having the heating rate as

Table 1: The model parameters with their associated symbols and units

Model parameters	Symbol	Unit
Activation energy for kerogen decomposition	E_1	J/mol
Frequency factor for kerogen decomposition	k_{10}	s^{-1}
Activation energy for bitumen decomposition	E_2	J/mol
Frequency factor for bitumen decomposition	k_{20}	s^{-1}
Fraction of kerogen decomposition into oil and gas at each heating rate	f_1	

a dependant variable in the numerical analysis.

From the TGA experiments on the M1 layer of Timahdit shale sample, the chart in Figure 1 was devised and used in solving the ordinary differential equations. This chart represents the sample weight loss in percentage versus temperature for the oil shale sample at three different heating rates (1°C/min, 5°C/min and 20°C/min). The corresponding derivative curves for the experimental plot are shown in Figure 2. The derivation of the chart was achieved by means of the curve-fitting procedure and analytical evaluations of the derivatives.

These charts provide the typical decomposition temperature ranges for the main oil shale components shown in Table 2. The modeling also requires several parameters to solve the ordinary differential equations. This was determined in the previous study on the oil shale decomposition. The organic matter content is a determinant of the amount of kerogen and bitumen that could be produced. The Timahdit oil shale sample used in this study contains 15.28% of organic matter (Bekri, O, 1996).

Mathematical Modeling

The decomposition reaction equations are ordinary differential equations (ODE) that can be solved through numerical methods. The fourth order Runge- Kutta method was used in this study.

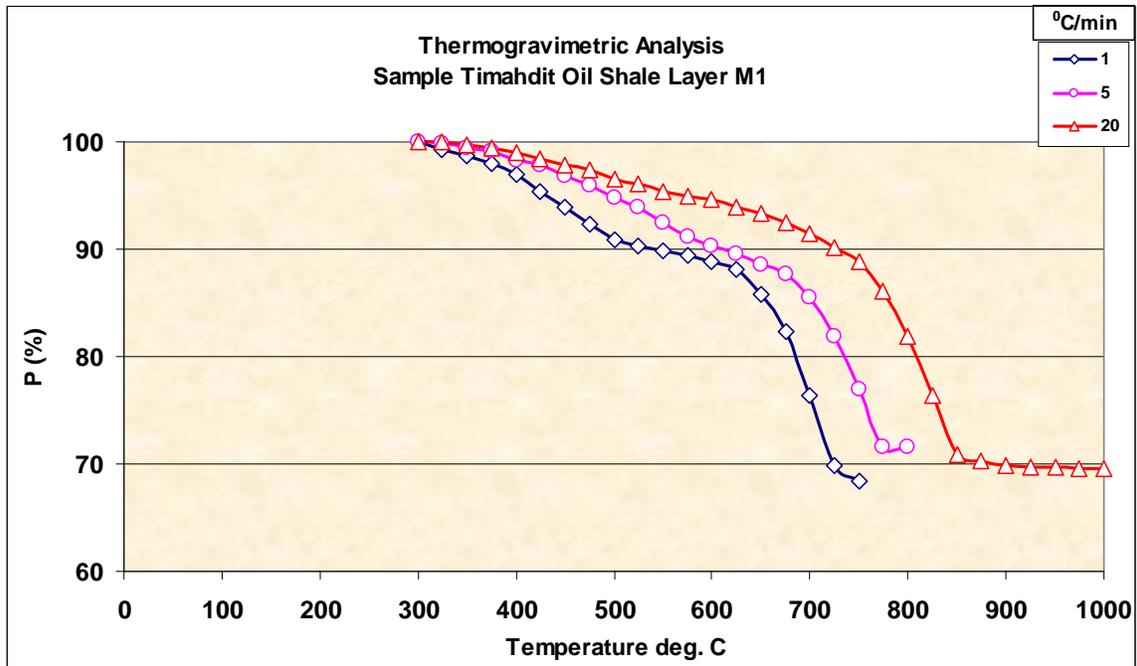


Figure 1: Weight loss versus temperature profile at several heating rates from Bekri, 1996

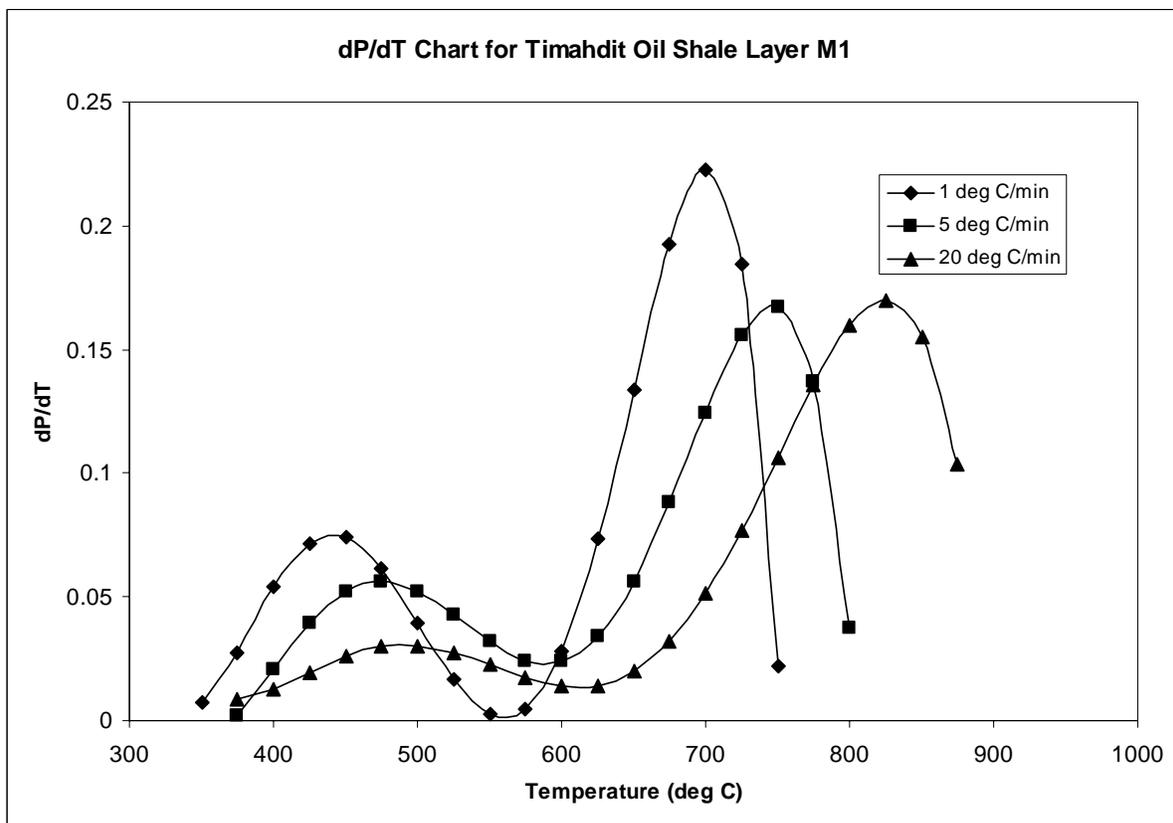


Figure 2: Derivative Curves (dP/dT) of the TGA curves

Table 2: Decomposition temperature range

Component	Temperature Range (°C)
Kerogen	300-500
Bitumen	440-650
Dolomite	650-750
Calcite	720-850

The TGA analysis provided the data needed to provide the boundary conditions and initial values to solve the following ordinary differential equations. The following equations were derived based on the decomposition reaction of the kerogen (Eq. 3) and bitumen (Eq 6).

$$\frac{dP}{dT} = \frac{\exp\left(-\frac{E_1}{RT} + \ln(Mo.f_1.k_{10}) - \left(\frac{k_{10}.RT^2}{E_1} . e^{-E_1/RT}\right) \cdot \frac{1}{V}\right)}{-V} \quad (3)$$

$$\text{Where } k_{10} = (E_1.A1(T)/RT^2) e^{E_1/RT} \quad (4)$$

$$f_1 = \frac{1 - P - \left(V \cdot \frac{dP}{dT} \cdot \frac{e^{E_1/RT}}{k_{10}}\right)}{Mo} \quad (5)$$

$$\frac{dP}{dT} = \frac{1}{V} k_{20} . e^{-E_2/RT} . (P - P_o) \quad (6)$$

$$f_2 = \frac{1 - P_o - Mo.f_1}{Mo.(1 - f_1)} \quad (7)$$

Equations 5 and 7 allow the calculation of the fraction of kerogen and bitumen converted to oil and gas (f_1 & f_2 respectively) at different heating rates. It must be noted that an important assumption in the above decomposition reactions is that bitumen concentration is neglected in the reaction for kerogen and likewise kerogen concentration is neglected for the decomposition of bitumen.

Solution Approach Using the Fourth Order Runge Kutta Method

The solver was based on the fourth-order Runge-Kutta implementation with fixed step size control. The output from the solver will be the tabulated values of sample mass fraction (weight loss) versus temperature at particular heating rates. Meanwhile, the parameter estimation pro-

cedure was based on the minimization of residual error between model calculations and experimental data (weight loss, P, versus temperature, T, data).

Ideally, this can be posed as an optimization problem where the objective function will be the accumulated residual error between experimental data and model prediction. Additionally the manipulated variables (MVs) for this optimization problem will be the parameters for the model as tabulated in Table 1 above.

As the fraction of kerogen and bitumen decomposition into oil and gas must be constrained between 0% and 100%, the constrained non-linear multivariable optimization method was used in this work. Microsoft Excel Solver®, a spreadsheet optimization tool was adopted as the optimization routine to determine the model parameters.

This optimization package was based on the Generalized Reduced Gradient (GRG2) implementation that can handle the non-linear model as well as variable constraints. The execution flow of this parameter estimation procedure involving the information flow between the Excel Solver and the numerical ODE solver is outlined in Figure 3.

To complete the degree-of-freedom of the model for parameter estimation purpose, several model parameter values were independently determined (see Table 3). The temperature ranges for kerogen and bitumen decomposition were determined by analysing the corresponding dP/dT curve (see Fig. 2). The final values from the iteration procedure were then tabulated and plotted on a separate worksheet where the results could be analysed.

Reaction Model

The reaction model is illustrated in Figure 4, showing the experimental data entry screen, and in Figure 5, which shows tabular and graphical presentations of various results.

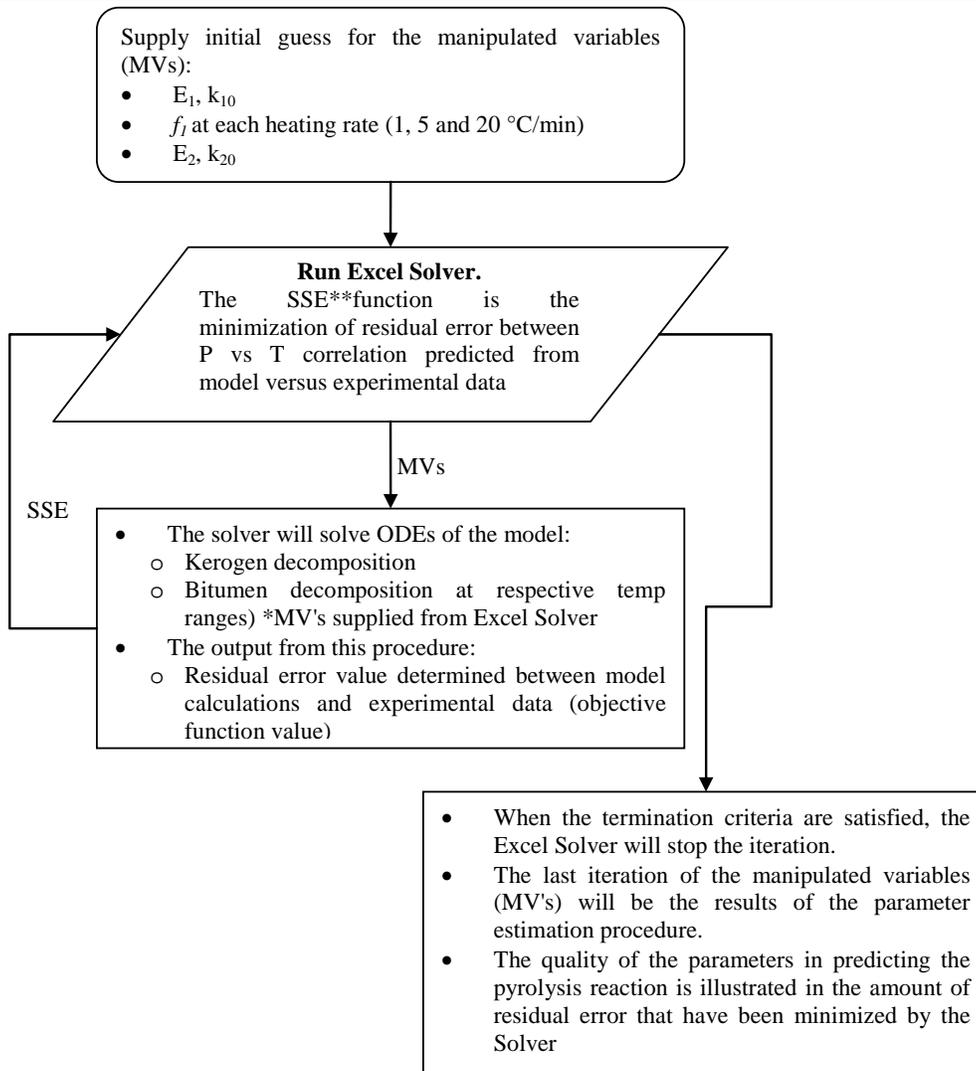


Figure 3: Flow Diagram of the Model Solution Approach

Table 3: Model parameters independently determined in this work for the purpose of model solution

Fixed parameters for the model	Value
Initial fraction of organic material in the shale, Mo (%)	15.28
Kerogen decomposition temperature range	300 – 441.07 °C at 1 °C/min 300 – 474.17 °C at 5 °C/min 325 – 489.20 °C at 20 °C/min
Bitumen decomposition temperature range	441.07 – 560.20 °C at 1 °C/min 474.17 – 588.53 °C at 5 °C/min 489.20 – 611.23 °C at 20 °C/min
Sample mass fraction where organic matter decomposition terminates, Po (%)	68.5 at 1 °C/min 71.5 at 5 °C/min 69.6 at 20 °C/min

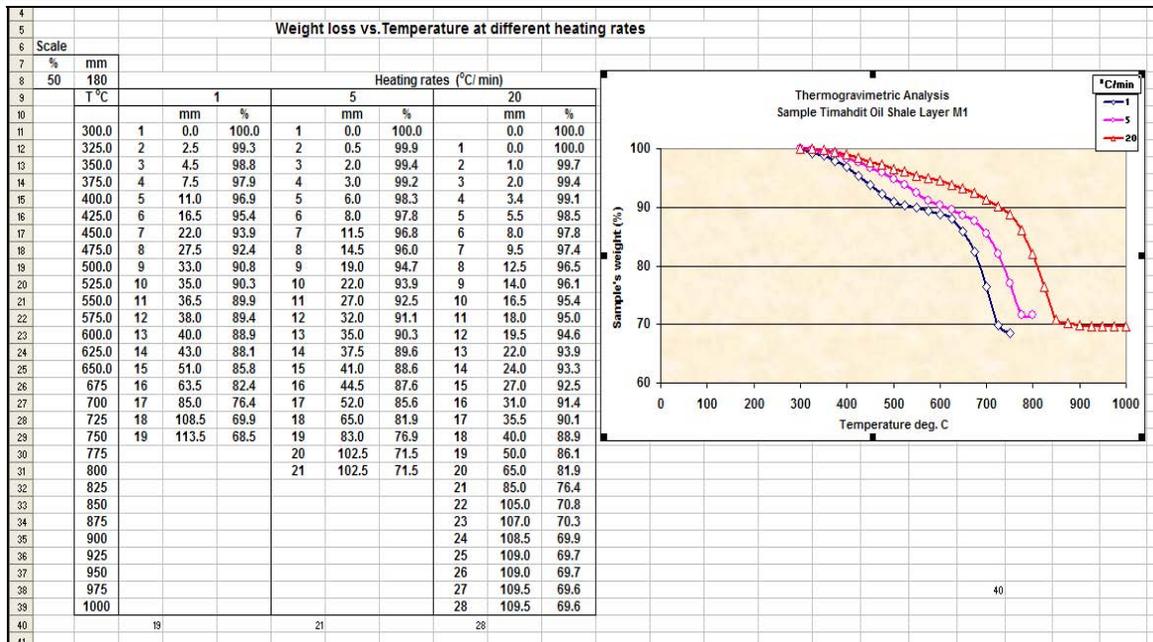


Figure 5: Experimental Data Entry into Solver

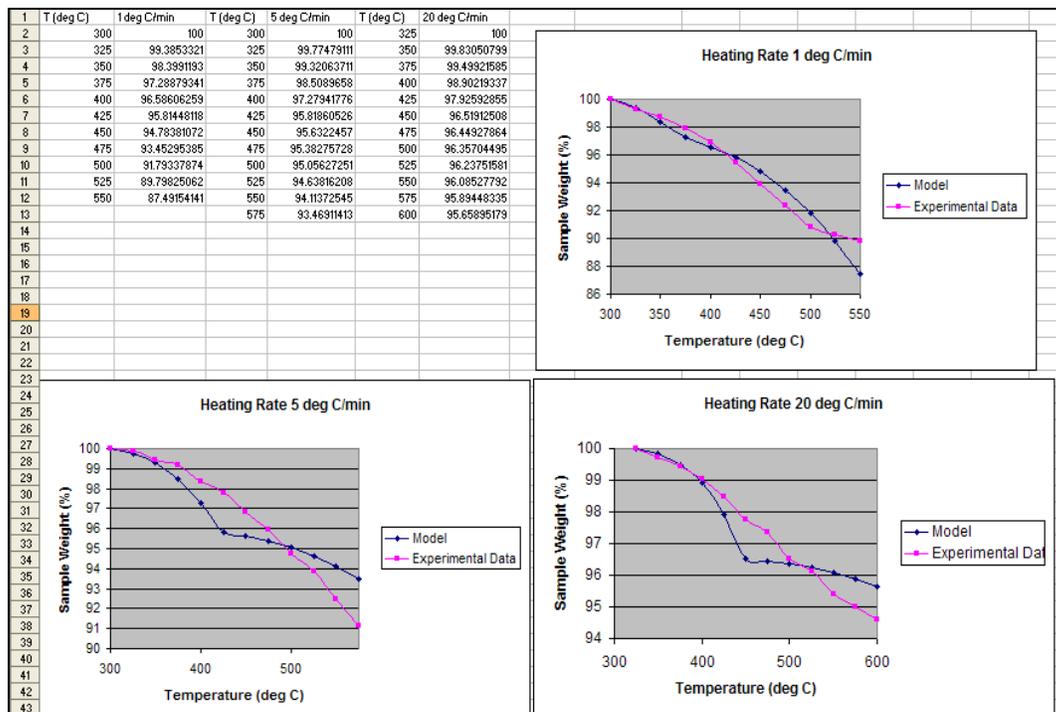


Figure 4: Tabulated and graphical representation of results at various heating rates for evaluation

Results and Discussion

The values of the parameters determined from the above method are tabulated in Table 4.

The comparison between model estimation and the corresponding experimental observation obtained from the TGA analysis is shown in several of the figures below (Figures 6 – 8).

Table 4: Initial guess and final values for the model parameters that were determined by applying the above methodology

<i>Model parameters</i>	<i>Initial guess</i>	<i>Final value</i>
E_1 (J/mol)	77.70×10^3	9.08×10^4
k_{10}	2.80×10^4	8.19×10^5
E_2 (J/mol)	116.20×10^3	4.63×10^5
k_{20}	4.80×10^5	1.08×10^6
f_7 @ 1 °C/min	0.21	0.36
f_7 @ 5 °C/min	0.24	0.39
f_7 @ 20 °C/min	0.32	0.41
Sum of residual error (SSE)	2.41×10^{-2}	3.57×10^{-3}

Generally, it can be seen that by solving the decomposition model equations via numerical ODE solver algorithm, the general trend of the sample's weight loss along the retorting temperature can be predicted and this matches reasonably well with the trend observed from the non-isothermal TGA experiment. However from the examination of Figure 9, we can see that there always exist deviations in model prediction from the experimental results. This error can be attributed to several factors ranging from the accuracy of the experimental results as well as the model that was used to estimate the decomposition process itself. Moreover as the methodology adopted to determine the model parameters was a nonlinear optimization problem, the presence of many local solutions to the given problem will make the effort to determine the most accurate value of the model parameters difficult. Thus, the initial starting values for the manipulated variables (model parameters) to start off the calculations that will minimize the residual error were critical. In this work, the starting values of the manipulated variables were taken from the previous study on oil shale

decomposition (Zainal Abidin, S.A. et al, 2006).

There are various methods that can be implemented in order to improve the overall results from this analysis. From the modeling point of view, including additional terms in the model formulation that can increase the capability of the model to predict the decomposition process of the oil shale sample can enhance the model accuracy. However, the accuracy and the complexity of the model must reflect on the ability of the model to make good prediction that agrees with experimental observations.

Utilizing more accurate apparatus and improving the experimental procedure can enhance the accuracy of the experimental results. Improvisation of the overall methodology would also be possible by validating the results using various sets of oil shale sample data and improving the experimental data estimation which in this work was only based on the graphical interpretation of the Timahdit M shale sample from previous studies.

Numerical data from more extensive TGA analysis or other experimental analyses, which could provide sufficient and accurate data, would be valuable in this analysis

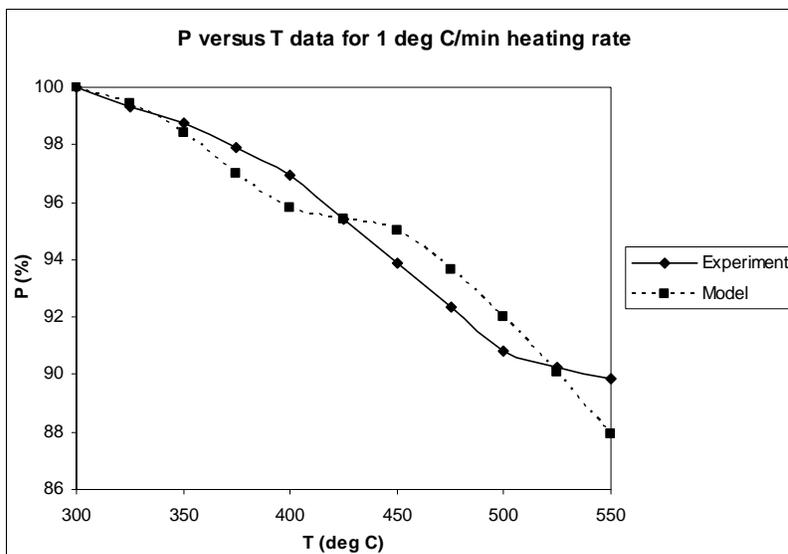


Figure 6: Weight Loss versus Temperature for 1 °C/min Heating Rate - Model Prediction and Experimental Results

study. As with the previous study that utilized the linearization method in solving the differential equations of the model (Zainal Abidin, S.A. et al, 2006), the numerical analysis on this sample maintains the prediction of oil and gas formation on the basis of heating regardless of the retorting technique used.

A limitation in the TGA analysis is the inability to characterize the oil and gas into detailed chemical composition (Bekri, O. et al, 1983). However, the quick results from the non-isothermal TGA analysis and simple equipment setup as compared to other methods makes this method favourable. However, this limitation in TGA, which can seem over-simplified, should be improved to include the presence of hydro-cracking and hydro-coking reactions. Moreover TGA results are unable to determine detailed compositional analysis of final or intermediate products, which are mostly due to the small sized samples, used for the analysis.

Conclusions

The oil shale decomposition reaction based on the simplified reaction pathway that derives a set of ordinary differential equations can be solved using numerical methods. This paper aims to study the modeling for oil shale decomposition using particularly the iterative fourth order Runge-Kutta method of numerical solutions. These solutions will provide the parameters of the reaction kinetics.

The result of the model using the Runge-Kutta method as compared to experimental data from previous studies was reasonably accurate with

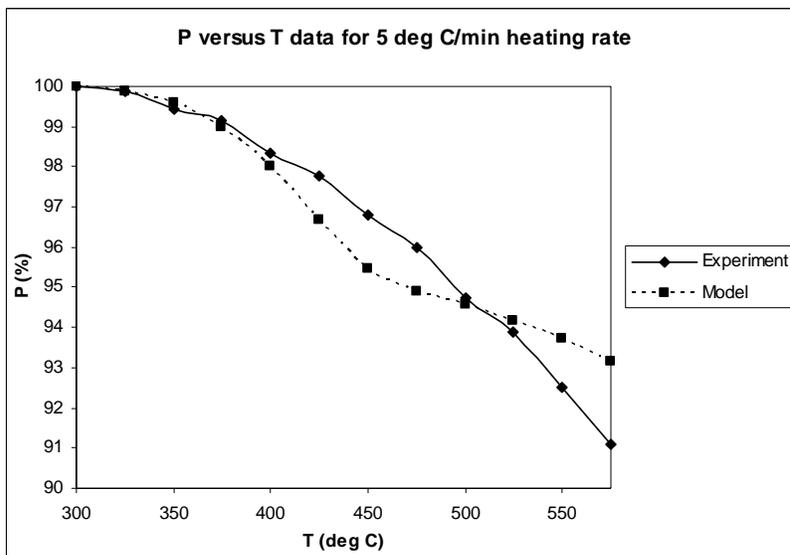


Figure 7: Weight Loss versus Temperature for 5 °C/min Heating Rate - Model Prediction and Experimental Results

a maximum deviation of 2.3%.

However the oil cracking and coking reactions occurring along with the oil shale decomposition were not included in this kinetics study, which utilized the thermogravimetric analysis (TGA) only.

Future studies will include variations to the experimental methodology to ensure increased accuracy to better represent the oil shale decomposition process. This will assist in providing a better understanding

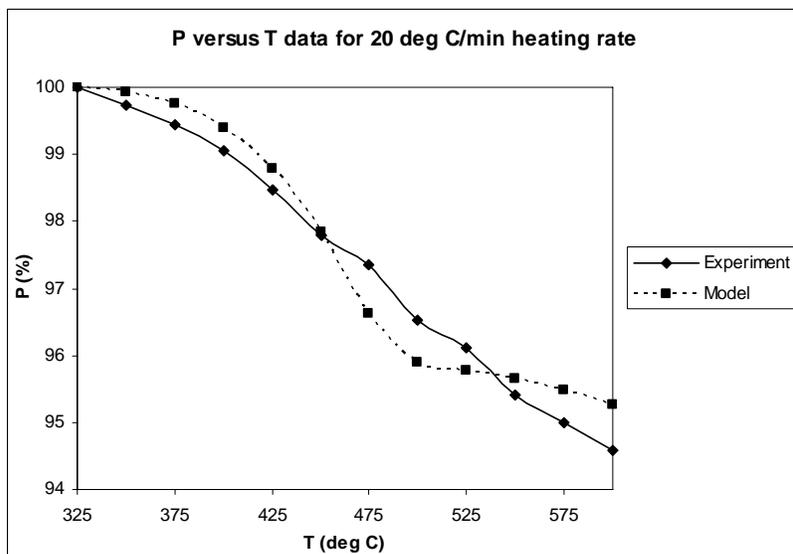


Figure 8: Weight Loss versus Temperature for 20 °C/min Heating Rate - Model Prediction and Experimental Results

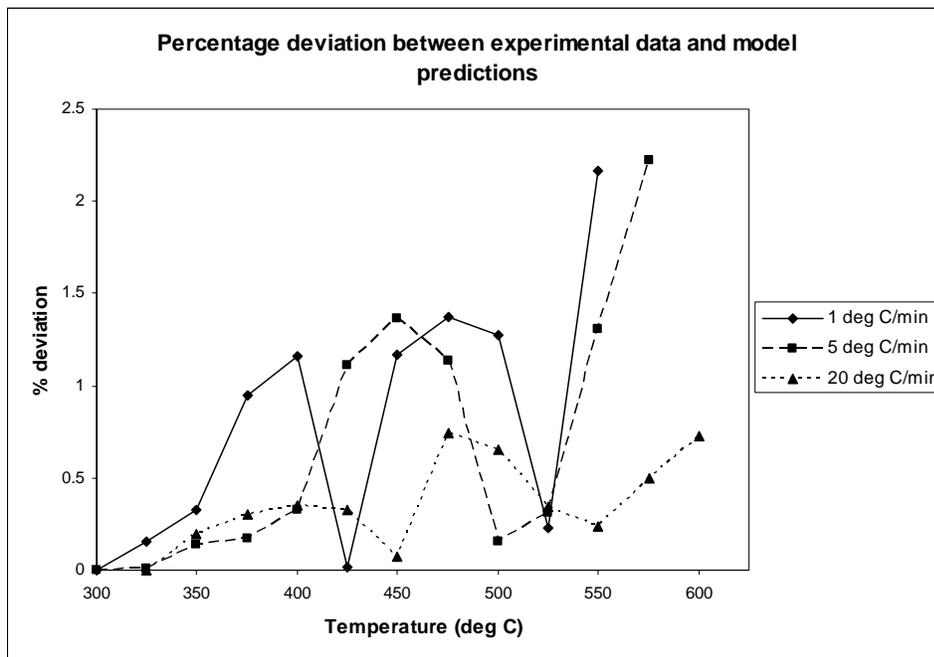


Figure 9: Percentage Deviation in Model Predictions and Experimental Results for the Oil Shale Decomposition Process - Model Prediction and Experimental Results

of the oil shale decomposition kinetics from any source and potentially improve productivity in the areas of oil shale production.

Limitations of Study and Future Work

This paper also intends to introduce the concept of oil upgrading for future studies in improving the model and to better understand the upgrading requirements of the oil shale products. This is because the simplistic approach to the model is a limiting factor in the accuracy of the developed model.

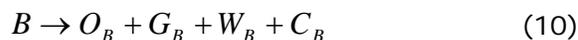
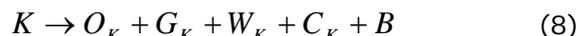
The model would have to be based on the reaction pathway as in Equation 2 mentioned previously. The first aspect would be the differentiation between the substances composing the vapour phase product (oil, gas and water).

The equation in Figure 10 represents a slightly detailed composition differentiation of the kerogen and bitumen decomposition products. The solid kerogen would decompose into oil, gas and water which are in vapour phase whilst the residual carbon

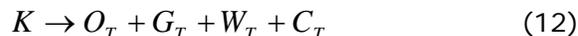
and bitumen would be in solid form with the bitumen as a highly viscous liquid. Further heating would result in the bitumen decomposing into oil, gas and water components also in vapour form and will leave solid carbon residues. The ability to consistently quantify these substances in an experiment would allow a more comprehensive and detailed modeling for the decomposition reactions.

The other aspect would be the mod-

eling of the cracking and coking reactions of the oil produced from the kerogen and bitumen decomposition. This reaction set can be described in four generalized reactions:



This can be simplified into the following correlation:



Where

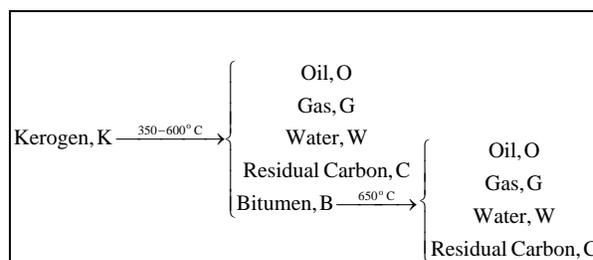


Figure 10: Compositional differentiation of kerogen and bitumen decomposition products

$$O_T = O_{O_K} + O_{O_B}$$

$$G_T = G_K + G_{O_K} + G_B + G_{O_B}$$

$$W_T = W_K + W_B$$

$$C_T = C_K + C_{O_K} + C_B + C_{O_B}$$

The K subscript denotes that the components oil (O), gas (G), water (W) and residual carbon (C) are derived from the kerogen component and likewise a B subscript denotes the components originating from the bitumen composition.

T represents the total of the components (oil, gas, water) produced by kerogen and bitumen decomposition. It must also be noted that each of these components can be further characterized into detailed chemical substances with more comprehensive experimental methodologies such as IR spectroscopy and gas chromatography.

Acquiring these data in future studies through detailed experimentation would allow a more rigorous and detailed analysis to be utilized in the model. This would provide a more accurate representation of the oil shale decomposition process.

Future works would also include studying the kinetics of the detailed reactions to be incorporated into the model as well as justifying the model with other numerical methods in determining the solutions to the ordinary differential equations.

Nomenclature

dP/dT: weight loss over temperature for sample

V: heating rates (°C/min)

Mo: initial fraction of organic material in the shale

P: mass fraction of sample at temperature T

P_o: mass fraction of sample at the temperature where organic matter decomposition terminates

T: selected temperatures for kerogen or bitumen decomposition (K)

R: Universal Gas Constant taken as 8.314 J/gmol.K

E₁: activation energy for the rate of decomposition of kerogen

k₁: reaction rate constants following the Arrhenius equation for kerogen decomposition

k₁₀: frequency factors in the Arrhenius equation where $k_1 = k_{10}e^{-E_1/RT}$

f₁: fraction of kerogen decomposition into oil & gas

k₂: reaction rate constants following the Arrhenius equation for bitumen decomposition

k₂₀: frequency factors in the Arrhenius equation where $k_2 = k_{20}e^{-E_2/RT}$

f₂: fraction of bitumen decomposition into oil and gas

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