Oil Shale Pyrolysis Reaction Model by Solving Ordinary Differential Equation Approach

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PRESENTATION OUTLINE

- **Introduction**
- Methodology
- Results & Future Studies
- Questions

INTRODUCTION

- Previous study focused on linearization method in solving the ordinary differential equation representing oil shale decomposition reaction
- Results are to be compared to other mathematical models
- Maintains the following representation for oil shale decomposition:

$$Kerogen \xrightarrow{k_1} \begin{matrix} oil\ \&\ gas \\ bitumen \end{matrix} \xrightarrow{k_2} \begin{matrix} oil\ \&\ gas \\ residual\quad carbon \end{matrix}$$

- Aim is to obtain conversion parameters for the decomposition reaction.
- Current study is to compare with fourth order Runge-Kutta method

INTRODUCTION: Runge-Kutta Method

- One of the methods in solving ordinary differential equations
- Solution of Initial Value Problem of ODE in the form of:
  - $y_i(x_o) = y_{io} \qquad i = 1, ..., N$
  - $\frac{dy_i(x)}{dx} = f_i(x, y_1, ..., y_N)$
  - $y_{n+1} = y_n + \frac{h}{6}(k_1 + 2k_2 + 2k_3 + k_4) + O(h^5)$

    where

    $k_1 = f(x_n, y_n)$

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

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

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

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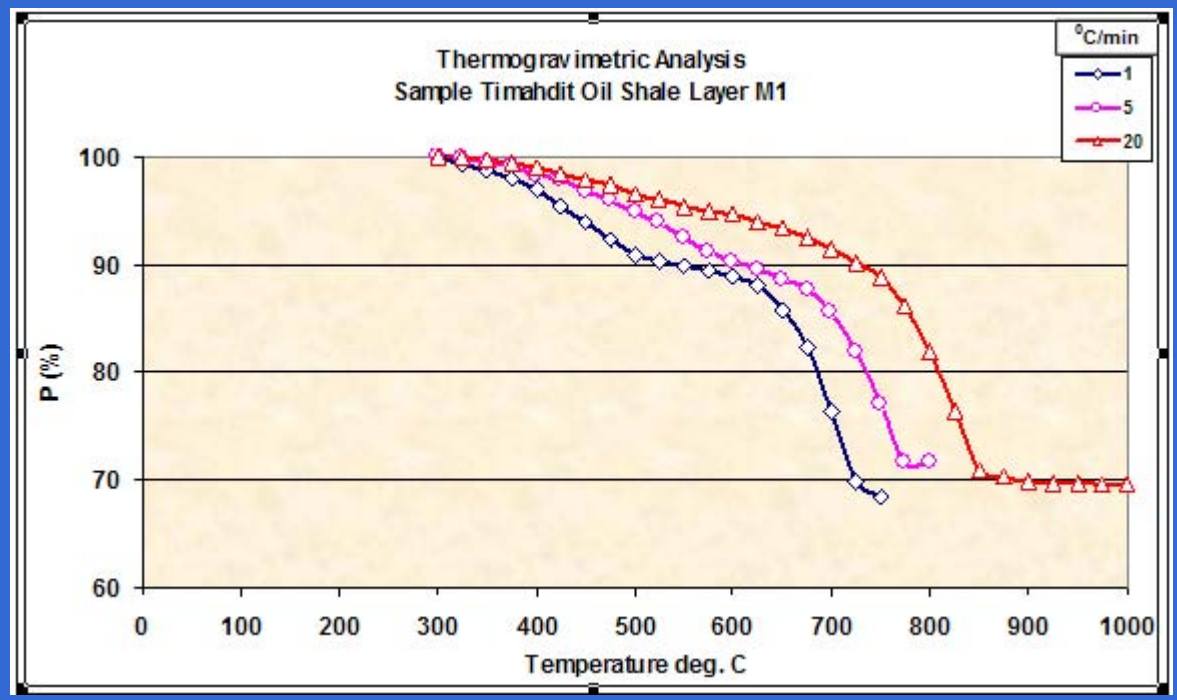
EXPERIMENTAL METHODOLOGY

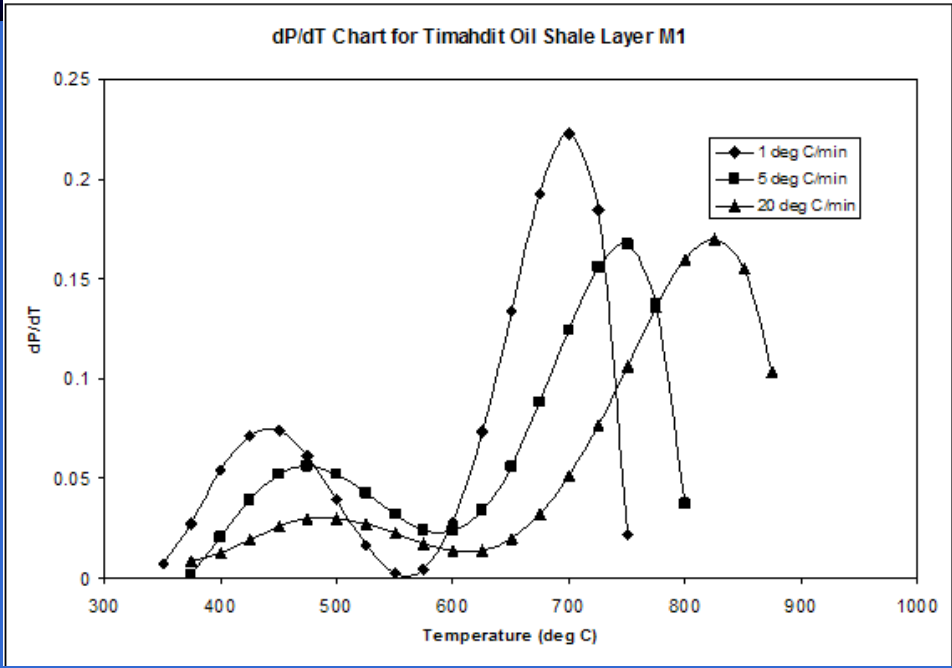
The following parameters are to be determined from the model:

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	

The TGA results at three different heating rates:



EXPERIMENTAL METHODOLOGY



The differential curve of the weight loss over temperature graph at three different heating rates. This curve will provide the estimates for the boundary conditions and initial value to solve the ODE. The table below shows the typical decomposition ranges for different components based on differential curves

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

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.

MATHEMATICAL MODELLING

- The two ODEs in this study are for kerogen decomposition and:

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

- Bitumen decomposition:

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

- The TGA results provided the data for boundary conditions and initial values to solve the ODE representing the decomposition reaction
- Developed solver based on the fourth-order Runge-Kutta implementation with fixed step size control.
- Output from the solver will tabulate values of sample mass fraction (weight loss) versus temperature at particular heating rates.

MATHEMATICAL MODELLING

The following table represents the values that were independently determined to provide initial values to solve the ODEs. The temperature ranges for kerogen and bitumen decomposition were determined by analysing the corresponding dP/dT curve

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

MATHEMATICAL MODELLING

- The parameter estimation procedure was based on the minimization of residual error between model calculations and experimental data (weight loss, P, versus temperature, T, data).
- An objective function which is the accumulated residual error between experimental data and model prediction is introduced and is the optimisation aim.
- The manipulated variables (MVs) for this optimization problem will be the parameters that the model aims to determine.
- The constrained non-linear multivariable optimization method was used to set the boundary conditions for conversion factors f to be between 0% and 100%. Microsoft Excel Solver® was used as the optimization routine to determine the model parameters.
- This optimization package was based on the Generalized Reduced Gradient (GRG2) implementation that can handle non-linear models as well as variable constraints.

MATHEMATICAL MODELLING – Solver Flowchart

Supply initial guess for the manipulated variables (MVs):
- E_1, k_{10}
- f_1 at each heating rate (1, 5 and 20 °C/min)
- E_2, k_{20}

Run Excel Solver.
The SSE**function is the minimization of residual error between P vs T correlation predicted from model versus experimental data

MVs

The solver will solve ODEs of the model:
oKerogen decomposition
oBitumen decomposition at respective temp ranges)
*MV's supplied from Excel Solver
•The output from this procedure:
oResidual error value determined between model calculations and experimental data (objective function value)

SSE

The residual error function, SSE:

$$SSE = \sum_{j=1}^{N_r} \sum_{i=1}^{N_p} \left(P_{i,j}^{\exp} - P_{i,j}^{calc} \right)^2$$

- When the termination criteria are satisfied, the Excel Solver will stop the iteration.
- The last iteration of the manipulated variables (MV's) will be the results of the parameter estimation procedure.
- The quality of the parameters in predicting the pyrolysis reaction is illustrated in the amount of residual error that have been minimized by the Solver

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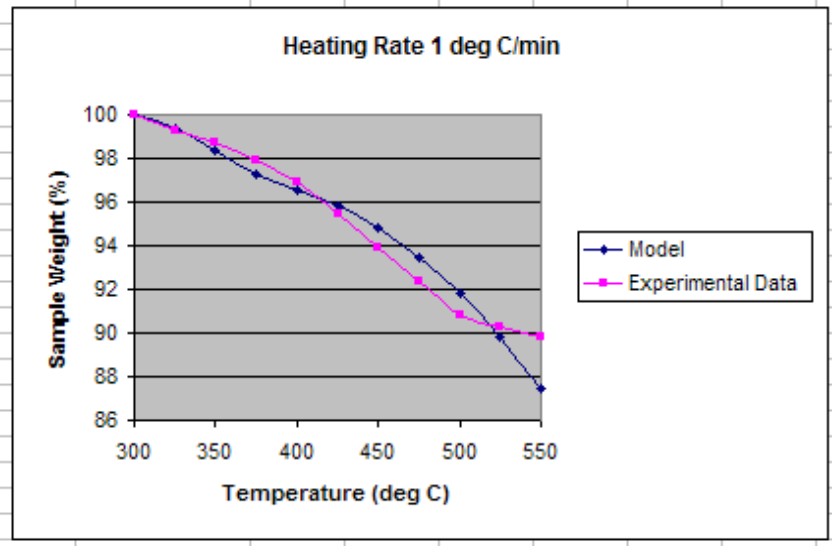
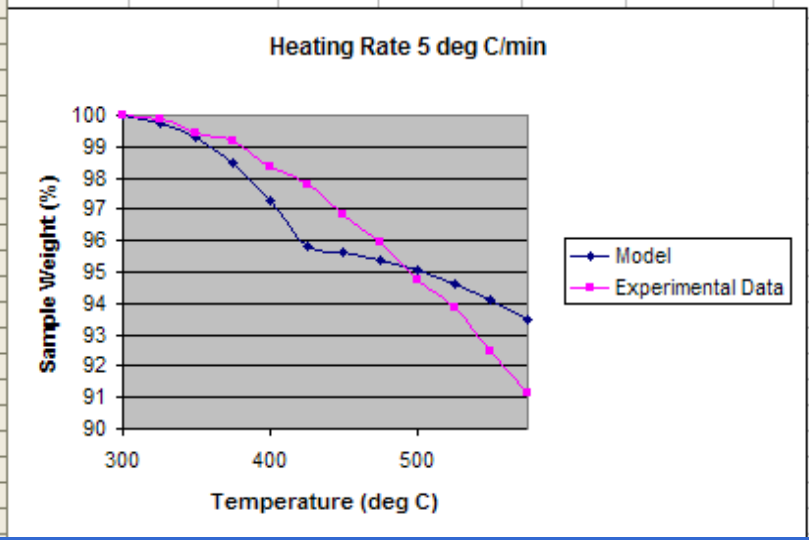
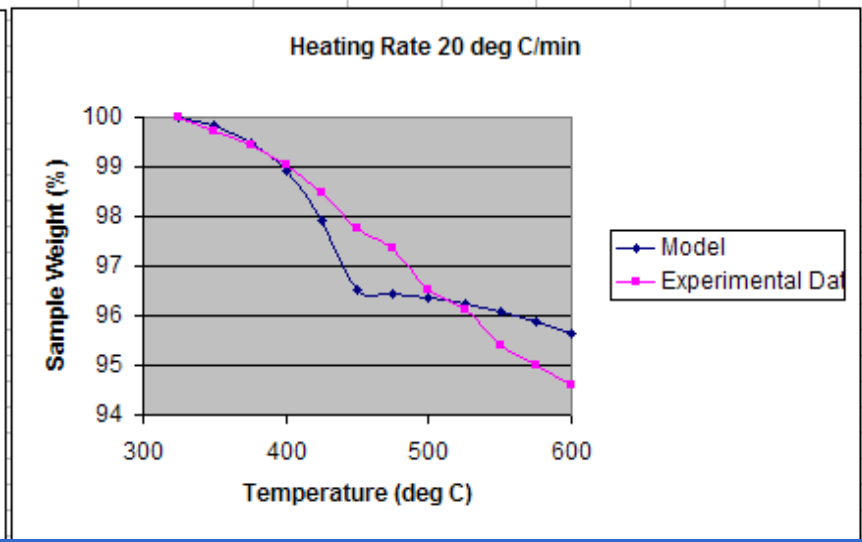
RESULTS

	T (deg C)	1 deg C/min	T (deg C)	5 deg C/min	T (deg C)	20 deg C/min
2	300	100	300	100	325	100
3	325	99.3853321	325	99.77479111	350	99.83050799
4	350	98.3991193	350	99.32063711	375	99.49921585
5	375	97.28879341	375	98.5089658	400	98.90219337
6	400	96.58606259	400	97.27941776	425	97.92592855
7	425	95.81448118	425	95.81860526	450	96.51912508
8	450	94.78381072	450	95.6322457	475	96.44927864
9	475	93.45295385	475	95.38275728	500	96.35704495
10	500	91.79337874	500	95.05627251	525	96.23751581
11	525	89.79825062	525	94.63816208	550	96.08527792
12	550	87.49154141	550	94.11372545	575	95.89448335
13			575	93.46911413	600	95.65895179





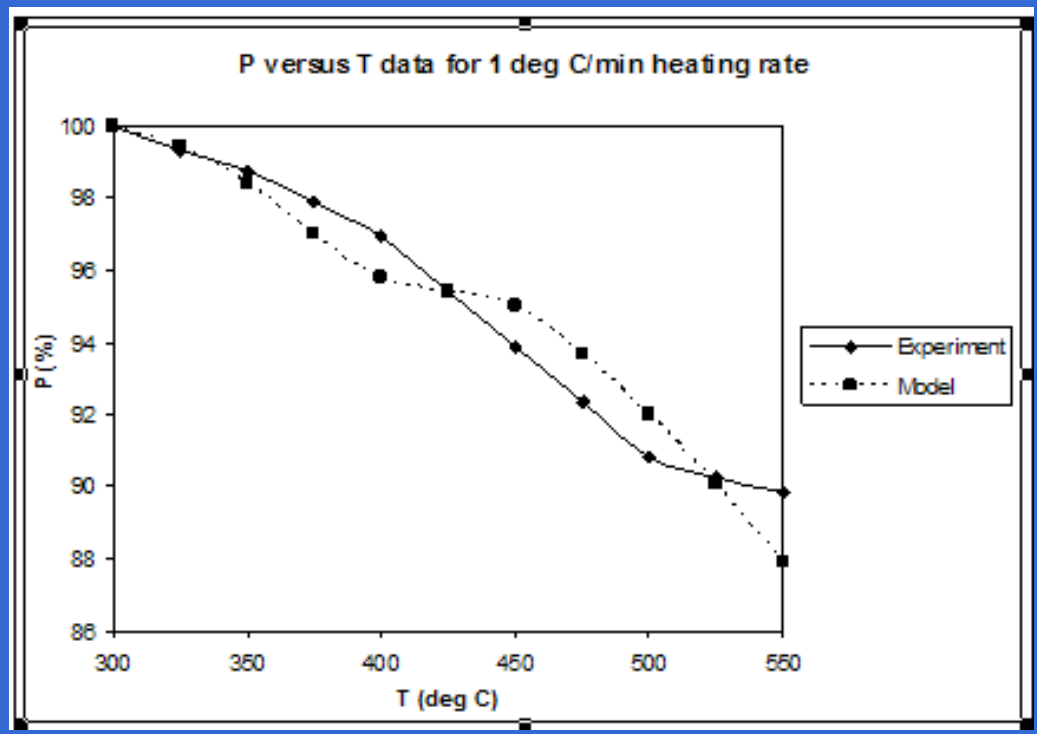


Results Summary

Model parameters	*Initial guess*	*Final value*
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_1 @ 1 °C/min	0.21	0.36
f_1 @ 5 °C/min	0.24	0.39
f_1 @ 20 °C/min	0.32	0.41
Sum of residual error (SSE)	2.41×10^{-2}	3.57×10^{-3}

Summary of initial value provided compared to final value obtained

Chart comparing experimental results versus model results for heating rate of 1°C/min



Results Summary

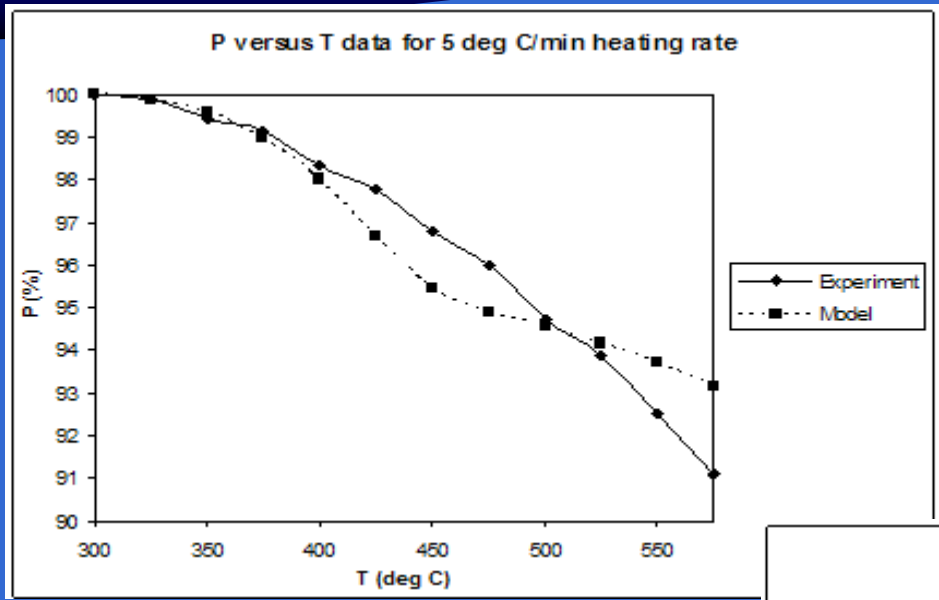
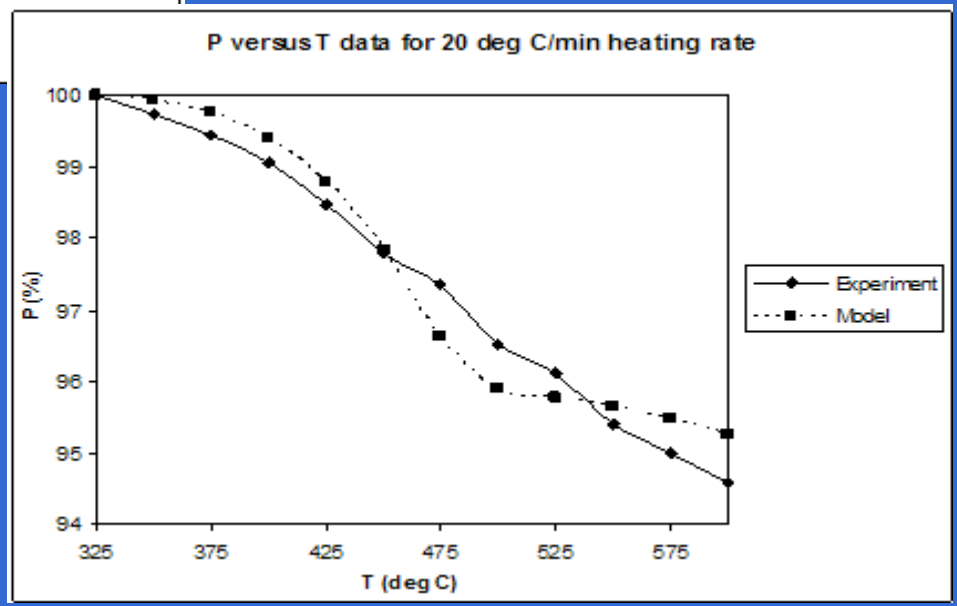
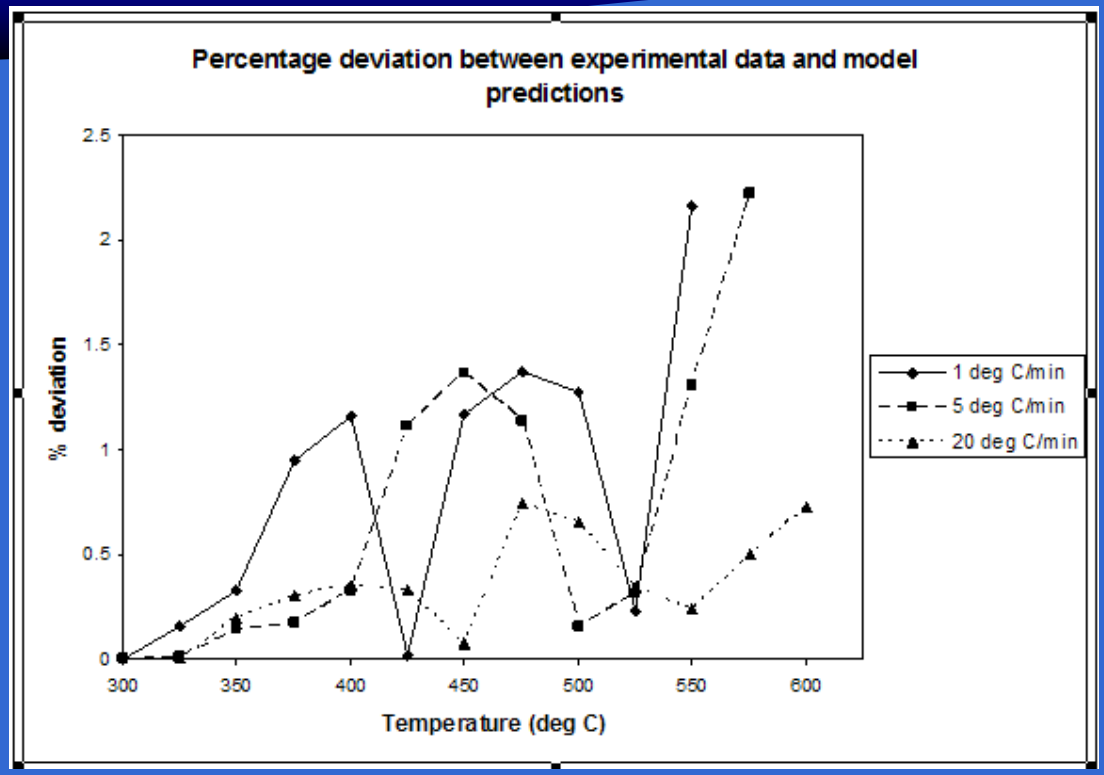


Chart comparing experimental results versus model results for heating rate of 5°C/min

Chart comparing experimental results versus model results for heating rate of 20°C/min



Results Summary



- Predicted P vs T curve matches reasonably well with the trend observed from the non-isothermal TGA experiment.
- However error is consistent.

- Possible sources of errors:
  - Accuracy of the experimental results
  - 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 as the methodology adopted to determine the model parameters was a nonlinear optimization problem

Model Results Summary

- Methods that can be applied to improve results:
  - Including additional terms in the model formulation can increase the capability of the model to predict the decomposition process of the oil shale sample and enhance model accuracy. (Model accuracy is reflected in the ability to make good predictions that agree with experimental observations)
  - Utilizing more accurate apparatus and improving the experimental procedure.
  - Validate results using various sets of oil shale sample data and improving the experimental data estimation
  - Numerical data from more extensive TGA analysis or other experimental analyses, which could provide sufficient and accurate data
  - Numerical analysis of this sample maintains the prediction of oil and gas formation on the basis of heating regardless of the retorting technique used.
- TGA analysis limitation:
  - The inability to characterize the oil and gas into detailed chemical composition
  - Should be improved to include the presence of hydro-cracking and hydro-coking reactions.
  - Unable to determine detailed compositional analysis of final or intermediate products

CONCLUSION

- The oil shale decomposition reaction that derives a set of ODEs can be solved using numerical methods. Focus on fourth order Runge-Kutta method which 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 a maximum deviation of 2.3%.
- Oil cracking and coking reactions occurring along with the oil shale decomposition were not included in this kinetics study due to TGA limitations
- The model can be used as a tool to predict oil and gas production capacity for given shale sample.
- Future studies will include variations to the experimental methodology to:
  - ensure increased accuracy
  - better represent the oil shale decomposition process
  - assist in better understanding oil shale decomposition kinetics from any source and potentially improve productivity in the areas of oil shale production

WAY FORWARD

- Introduce the concept of oil upgrading for future studies to:
- Better understand the upgrading requirements of the oil shale products.
- The first aspect would be the differentiation between the substances composing the vapor phase product (oil, gas and water).

$$\text{Kerogen, K} \xrightarrow{350-600^{\circ}\text{C}} \begin{cases} \text{Oil, O} \\ \text{Gas, G} \\ \text{Water, W} \\ \text{Residual Carbon, C} \\ \text{Bitumen, B} \xrightarrow{650^{\circ}\text{C}} \begin{cases} \text{Oil, O} \\ \text{Gas, G} \\ \text{Water, W} \\ \text{Residual Carbon, C} \end{cases} \end{cases}$$

- The above equation represents a slightly detailed composition differentiation of the kerogen and bitumen decomposition products.
- The ability to consistently quantify these substances in an experiment would allow a more comprehensive and detailed modeling for the decomposition reactions.

WAY FORWARD

- The other aspect would be modeling of cracking and coking reactions. This reaction set can be described in four generalized reactions:

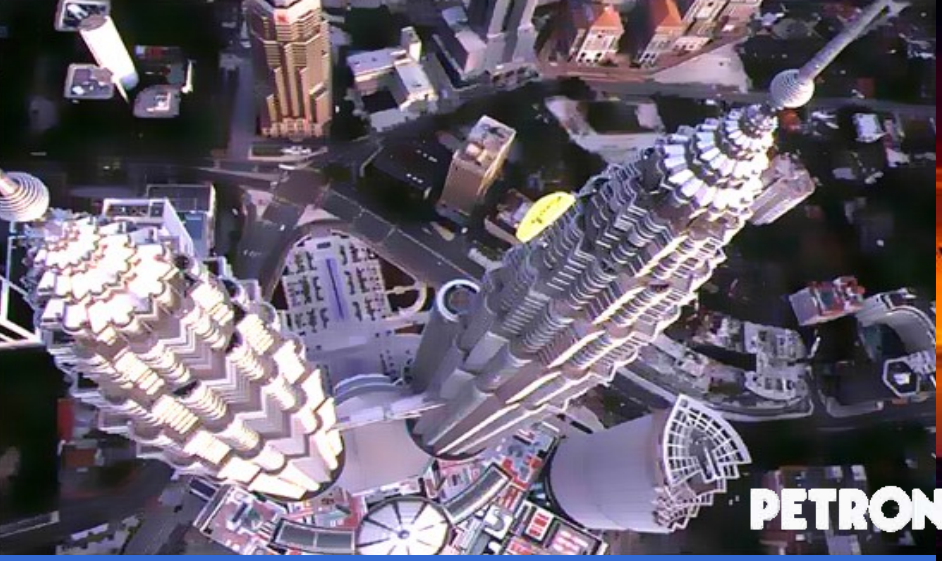
$$K \rightarrow O_K + G_K + W_K + C_K + B$$

$$O_K \rightarrow O_{O_K} + G_{O_K} + C_{O_K}$$

$$B \rightarrow O_B + G_B + W_B + C_B$$

$$O_B \rightarrow O_{O_B} + G_{O_B} + C_{O_B}$$

- Note 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 modeled.
- Future work would also include studying kinetics of the detailed reactions to be incorporated into the model as well as justifying the model with other numerical methods to determine solutions to the ODEs



Thank You

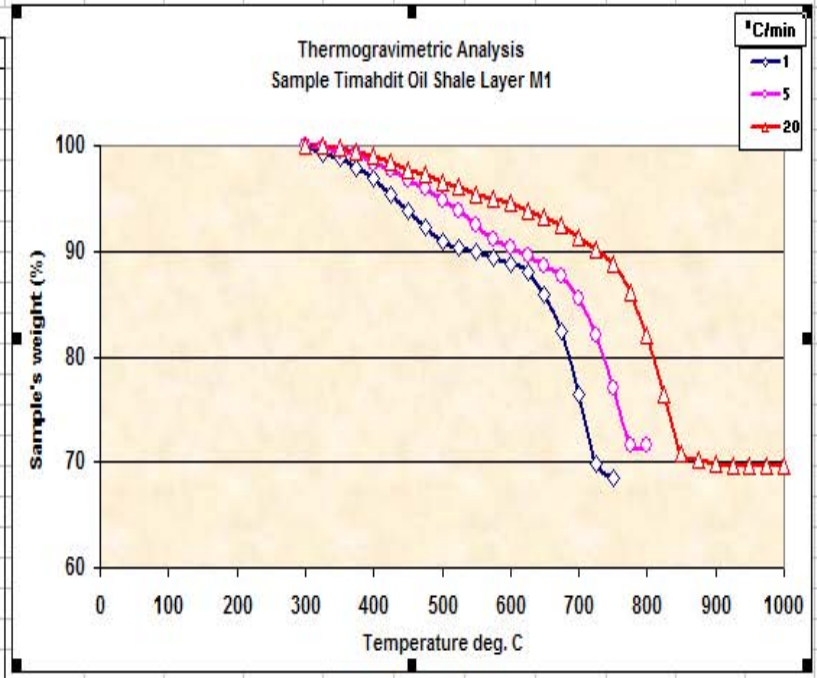
PRESENTATION OUTLINE

- Introduction to Malaysia
- PETRONAS – An Overview
- Shale Oil Modeling
- **Questions**

TGA DATA

Weight loss vs.Temperature at different heating rates

Scale											
%	mm										
50	180	Heating rates (°C/ min)									
	T °C		1			5			20		
			mm	%		mm	%		mm	%
	300.0	1	0.0	100.0	1	0.0	100.0		0.0	100.0
	325.0	2	2.5	99.3	2	0.5	99.9	1	0.0	100.0
	350.0	3	4.5	98.8	3	2.0	99.4	2	1.0	99.7
	375.0	4	7.5	97.9	4	3.0	99.2	3	2.0	99.4
	400.0	5	11.0	96.9	5	6.0	98.3	4	3.4	99.1
	425.0	6	16.5	95.4	6	8.0	97.8	5	5.5	98.5
	450.0	7	22.0	93.9	7	11.5	96.8	6	8.0	97.8
	475.0	8	27.5	92.4	8	14.5	96.0	7	9.5	97.4
	500.0	9	33.0	90.8	9	19.0	94.7	8	12.5	96.5
	525.0	10	35.0	90.3	10	22.0	93.9	9	14.0	96.1
	550.0	11	36.5	89.9	11	27.0	92.5	10	16.5	95.4
	575.0	12	38.0	89.4	12	32.0	91.1	11	18.0	95.0
	600.0	13	40.0	88.9	13	35.0	90.3	12	19.5	94.6
	625.0	14	43.0	88.1	14	37.5	89.6	13	22.0	93.9
	650.0	15	51.0	85.8	15	41.0	88.6	14	24.0	93.3
	675	16	63.5	82.4	16	44.5	87.6	15	27.0	92.5
	700	17	85.0	76.4	17	52.0	85.6	16	31.0	91.4
	725	18	108.5	69.9	18	65.0	81.9	17	35.5	90.1
	750	19	113.5	68.5	19	83.0	76.9	18	40.0	88.9
	775				20	102.5	71.5	19	50.0	86.1
	800				21	102.5	71.5	20	65.0	81.9
	825							21	85.0	76.4
	850							22	105.0	70.8
	875							23	107.0	70.3
	900							24	108.5	69.9
	925							25	109.0	69.7
	950							26	109.0	69.7
	975							27	109.5	69.6
	1000							28	109.5	69.6
		19			21			28		



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