Oil Shale Pyrolysis Reaction Model by Solving Ordinary Differential Equation Approach

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PRESENTATION OUTLINE

Introduction

Methodology

Results & Future Studies

Questions
• 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:

\[ \text{Kerogen} \xrightarrow{k_1} \text{oil} \& \text{gas} \xrightarrow{k_2} \text{residual carbon} \]

- \[ \text{bitumen} \]

• 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:
  \[ y_i(x_o) = y_{i_o} \quad i = 1, \ldots, N \]
  \[ \frac{dy_i(x)}{dx} = f_i(x, y_1, \ldots, y_N) \]
  \[ y_{n+1} = y_n + \frac{h}{6} \left( k_1 + 2k_2 + 2k_3 + k_4 \right) + O(h^5) \]

where
  \[ k_1 = f(x_n, y_n) \]
  \[ k_2 = f \left( x_n + \frac{h}{2}, y_n + \frac{h}{2}k_1 \right) \]
  \[ k_3 = f \left( x_n + \frac{h}{2}, y_n + \frac{h}{2}k_2 \right) \]
  \[ k_4 = f \left( x_n + h, y_n + hk_3 \right) \]

– Iterative procedure
EXPERIMENTAL METHODOLOGY

The following parameters are to be determined from the model:

<table>
<thead>
<tr>
<th>Model parameters</th>
<th>Symbol</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy for kerogen decomposition</td>
<td>$E_1$</td>
<td>J/mol</td>
</tr>
<tr>
<td>Frequency factor for kerogen decomposition</td>
<td>$k_{10}$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>Activation energy for bitumen decomposition</td>
<td>$E_2$</td>
<td>J/mol</td>
</tr>
<tr>
<td>Frequency factor for bitumen decomposition</td>
<td>$k_{20}$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>Fraction of kerogen decomposition into oil and gas at each heating rate</td>
<td>$f_i$</td>
<td></td>
</tr>
</tbody>
</table>

The TGA results at three different heating rates:
EXPERIMENTAL METHODOLOGY

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.

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.

<table>
<thead>
<tr>
<th>Component</th>
<th>Temperature Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kerogen</td>
<td>300-500</td>
</tr>
<tr>
<td>Bitumen</td>
<td>440-650</td>
</tr>
<tr>
<td>Dolomite</td>
<td>650-750</td>
</tr>
<tr>
<td>Calcite</td>
<td>720-850</td>
</tr>
</tbody>
</table>
MATHEMATICAL MODELLING

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

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

- 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.
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.
**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.
Run Excel Solver.

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

The solver will solve ODEs of the model:
- Kerogen decomposition
- Bitumen decomposition at respective temp ranges)

* MV's supplied from Excel Solver

The output from this procedure:
- Residual error value determined between model calculations and experimental data (objective function value)
- 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

The residual error function, SSE:

\[ SSE = \sum_{j=1}^{N_j} \sum_{i=1}^{N_i} \left( P_{i,j}^{\text{exp}} - P_{i,j}^{\text{calc}} \right)^2 \]
PRESENTATION OUTLINE

Introduction to Malaysia

Methodology

Results & Future Studies

Questions
# Results Summary

Summary of initial value provided compared to final value obtained.

<table>
<thead>
<tr>
<th>Model parameters</th>
<th>Initial guess</th>
<th>Final value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$ (J/mol)</td>
<td>$7.77 \times 10^2$</td>
<td>$9.08 \times 10^6$</td>
</tr>
<tr>
<td>$k_{10}$</td>
<td>$2.80 \times 10^4$</td>
<td>$8.19 \times 10^2$</td>
</tr>
<tr>
<td>$E_2$ (J/mol)</td>
<td>$116.20 \times 10^2$</td>
<td>$4.63 \times 10^2$</td>
</tr>
<tr>
<td>$k_{20}$</td>
<td>$4.80 \times 10^5$</td>
<td>$1.08 \times 10^6$</td>
</tr>
<tr>
<td>$f_i$ @ 1°C/min</td>
<td>0.21</td>
<td>0.36</td>
</tr>
<tr>
<td>$f_i$ @ 5°C/min</td>
<td>0.24</td>
<td>0.39</td>
</tr>
<tr>
<td>$f_i$ @ 20°C/min</td>
<td>0.32</td>
<td>0.41</td>
</tr>
<tr>
<td>Sum of residual error (SSE)</td>
<td>$2.41 \times 10^{-2}$</td>
<td>$3.57 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

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).

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

- 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.
• 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

<table>
<thead>
<tr>
<th>Scale</th>
<th>Heating rates (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>T°C</td>
</tr>
<tr>
<td>11</td>
<td>300.0</td>
</tr>
<tr>
<td>12</td>
<td>325.0</td>
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<td>13</td>
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<tr>
<td>14</td>
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<td>15</td>
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<td>16</td>
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<td>975.0</td>
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