Spring 2016

Developing A Model Approximation Method and Parameter Estimates for Solid State Reaction Kinetics

William D. Arloff
Valparaiso University, william.arloff@valpo.edu

Karl Schmitt
Valparaiso University

Luke J. Venstrom
Valparaiso University

Developing A Model Approximation Method and Parameter Estimates for Solid State Reaction Kinetics

William Arloff [1], **Dr. Karl Schmitt**[1,2], **Dr. Luke Venstrom**[3]
[1] Department of Mathematics and Statistics, [2] Department of Computer Information Science, [3] Department of Mechanical Engineering

Abstract

The James S. Markiewicz Solar Energy Research Facility was built to research solar chemistry and currently being used to research the change in metal oxides such as iron or magnesium oxide that act as a medium for the production of hydrogen from water. This is significant because hydrogen can be used in vehicles equipped with appropriate fuel cells and due the decreased cost of producing hydrogen with this method.

The shrinking core model which governs this process has proved difficult to solve due to the high number of unknown constants and its non-linearity, we detail in this work the implementation of less common heuristics, mainly Particle Swarm Optimization. This technique was used because of its wide unbiased search for the possible constants. The development and method we are using to solve these unknown constants will be shown.

Figure 1:
James S. Markiewicz
Solar Energy Research Facility

Background

- Researchers at Valparaiso University are investigating the production of hydrogen as an alternative to fossil fuels.
- The Solar Furnace can provide the high enough temperatures to change the state of the metal oxides used in the production of hydrogen, while reducing the required electricity.
- The shrinking-core model [1] has been proposed for the reaction, but parameters can range over many orders of magnitude, with the vast majority being infeasible

$$\frac{d\alpha}{dT} = \frac{1}{\beta}\left[\frac{1}{10^{A_g}\exp\left(\frac{-E_{a,g}}{RT}\right)} + \frac{2\left((1-\alpha)^{-\frac{1}{3}}-1\right)}{10^{A_s}\exp\left(\frac{-E_{a,s}}{RT}\right)} + \frac{(1-\alpha)^{-\frac{2}{3}}}{3\times 10^{A_c}\exp\left(\frac{-E_{a,c}}{RT}\right)}\right]^{-1}$$

A_g, A_s, A_c are pre-exponential factors

$E_{a,g}$, $E_{a,s}$, $E_{a,c}$ are energies of activation

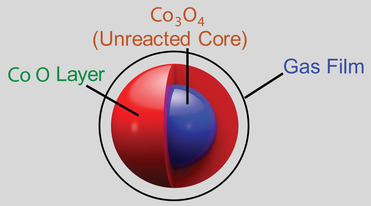
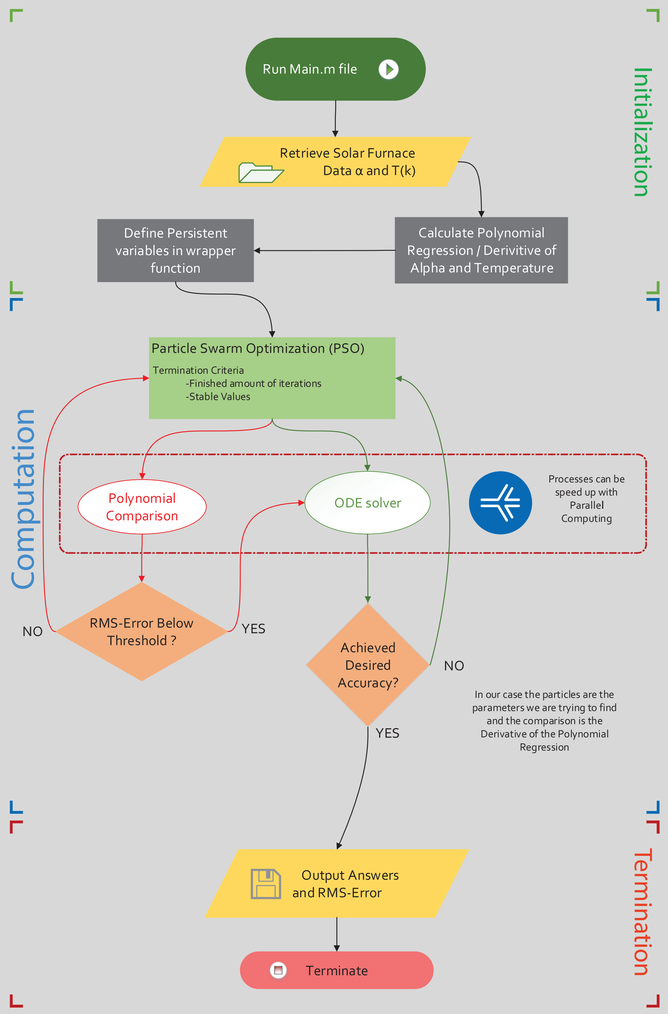


Figure 2:
Diagram of the Shrinking-Core Model

Flowchart For Parameter Fitting



- Code implemented in MATLAB
- Used Particle Swarm Optimization code from [3]

The Fitness Functions

- A fitness function determines the quality of potential solutions based on some predefined equation or criteria.
- Is a significant element of our system because it interacts with the PSO software's function handler by inputting the particles from PSO output and returning to the PSO software the fitness value after using one of our comparison techniques highlighted below.
  - → Potential Solution: Vector of model parameters.
  - → Criteria: RMS-Error of our current comparison technique.
- Two comparison techniques used are:
  - → Polynomial Approximation vs. Differential
    - ∗ A reasonably close estimate using the RMS-Error of the fitted polynomial's derivative vs. the model
  - → ODE solver: After a rough estimate is found by the PSO software, the ODE solver can solve the full model of the reaction.

Persistent Variables

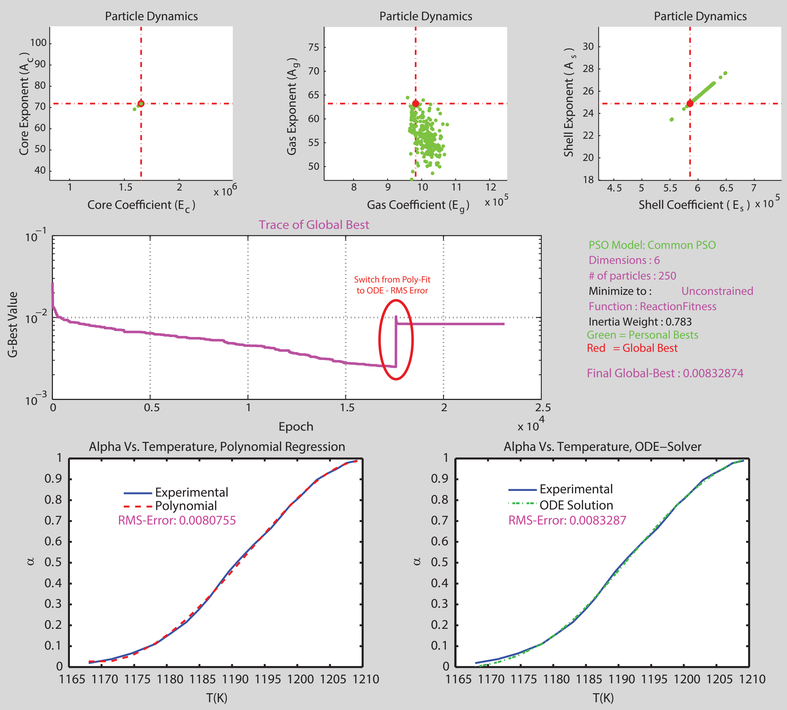
Persistent Variables are used in our Fitness Function to define the data objects that we use to compute our RMS-Error.

- Problem
  - → Fitness function is ran hundreds of times per iteration.
  - → Loading the comparison data each time significantly increases the run time.
  - → Introducing global variables can cause scoping and debugging issues.
- Solution: **MATLAB Persistent Variables**
  - → Can be load during a function initialization and maintain value for all future calls.
  - → Variable scope remains limited to function's workspace.
  - → Allows reduction of data-loads, and reduces overall run-time.

Results

- Both the polynomial approximation and ODE-based methods have provided parameters which closely match the experimental data.
- The closest parameters that we have found thus far are:

$E_{ac} = 1.65 \times 10^6$ $E_{ag} = 9.82 \times 10^5$ $E_{as} = 5.86 \times 10^4$
$A_c = 71.853$ $A_g = 63.214$ $A_s = 24.884$



Project Goals

- Develop code to fit parameters of recorded experimental data for conversion reaction, modeled by the shrinking-core differential equation.
- Ensure the robustness of this code for a wide range of parameters through good programming practices such as unit testing.
- Future Goals:
  1. Improve user interface.
  2. Implement an adaptive PSO to change swarm sizes based on the fitness function.

Unit Testing

Unit testing means defining strict requirements on output for a given set of input data which allows programmers to test the reliability of functions and sub functions.

- Allows us to ensure that complex sections of code were correct.
- Unit testing was used in the development of the differential equation function.
- To implement this programming practice our team wrote MATLAB script files that allowed us to call and test every possible instance of inputs.

Previous Work

- Prior to this faculty and undergraduate students manufactured and assembled parts of the solar furnace on-site. [4]
- Iron-Oxide and Magnesium-Oxide reductions have been investigated.
- Originally, data from an isothermal reaction was used to find model parameters .
  - → Using isothermal data significantly simplifies the model.
  - → Collecting isothermal data can only be done for a limited number of reactions.

References & Acknowledgements

[1] O. Levenspiel, *Chemical Reaction Engineering*. (2nd Ed.) Wiley, New York (1972)

[2] Kennedy, J. and Eberhart, R. C. "Particle swarm optimization". Proceedings of IEEE International Conference on Neural Networks, Piscataway, NJ. (1995)

[3] Birge, Brian. "Particle Swarm Optimization Toolbox", MATLAB central, 22 Apr 2005, File ID 7506. Access Date 09-2014

[4] Palumbo, Robert, R. B. Diver, C. Larson, E. N. Coker, J. E. Miller, J. Guertin, J. Schoer, M. Meyer, and N. P. Siegel. "Solar thermal decoupled water electrolysis process I: Proof of concept." Chemical Engineering Science 84 (2012): 372-380.

The data used in this work was collected under NSF Award 1334896.