Optimization of Coupled Differential Equations for SrO2 Production

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Abstract

This report details a computational strategy for optimizing SrO_2 production through the adjustment of coupled differential equations, specifically targeting the flow rate of hydrogen peroxide (H_2O_2). Leveraging experimental temperature vs. time data, we develop a predictive model that aims to enhance the consistency and quality of SrO_2 batches. The challenge of maintaining the reaction within a narrow and critical temperature range is addressed through a novel approach that blends numerical methods, fundamental chemistry, and data science methodologies for modeling reaction kinetics.

1 Introduction

Producing strontium peroxide (SrO_2) requires meticulous control over the reactor's internal temperature, a challenge compounded by the reaction's exothermic nature and its sensitivity to changes in the concentration of reactants, especially with temperature. Traditional Proportional-Integral-Derivative (PID) control strategies fall short in managing this process due to the reaction's inherent volatility and the time-delayed response to modifications in the flow rate of hydrogen peroxide (H_2O_2). In response to these challenges, this report unveils a novel computational technique aimed at refining the regulation of H_2O_2 flow. At the core of this approach are coupled differential equations that model the kinetics of the SrO_2 production process and the heat transfer dynamics within the reactor. To align our model with the experimental observations, we employ the Nelder-Mead optimization

1

method, a powerful algorithm capable of fine-tuning the parameters of our differential equations to achieve an optimal fit with temperature versus time data gathered from several batches of production runs. This methodological innovation allows us to anticipate and precisely control the temperature trajectory of the reaction, ensuring the production of SrO_2 within the desired quality specifications found in MIL-S-612 Revision B:1975.

2 Materials and Methods

Materials and Process

For each batch the materials to be charged to the reactor are as follows:
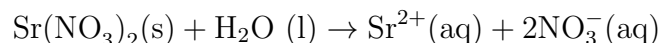
146 Liters of soft water

68 Kg of $Sr(NO_3)_2$ .... CAS # 10042-76-9

82 Kg of Aqua Ammonia .... CAS # 1336-21-6
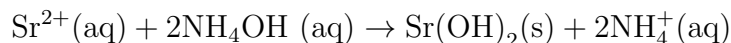
68 Kg of H_2O_2 .... CAS # 7722-84-1

The synthesis process involves the following chemical reactions:

1. Dissolving Strontium nitrate in soft water:

$$Sr(NO_3)_2(s) + H_2O\ (l) \rightarrow Sr^{2+}(aq) + 2NO_3^-(aq)$$

2. Reduction of aqueous Strontium nitrate with aqua ammonia to form Strontium hydroxide:

$$Sr^{2+}(aq) + 2NH_4OH\ (aq) \rightarrow Sr(OH)_2(s) + 2NH_4^+(aq)$$

3. The main reaction - Strontium hydroxide reacting with hydrogen peroxide in the presence of aqua ammonia to simultaneously form Strontium peroxide and ammonium nitrate:

$$Sr(OH)_2(s) + H_2O_2(aq) + 2NH_4OH\ (aq) \rightarrow SrO_2(s) + 2NH_4NO_3(aq) + 2H_2O\ (l)$$
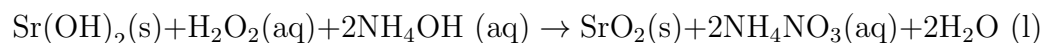
The filtered product will be washed outside the reactor with:

20 Liters of 10% H_2O_2

Which should yield around:

30 Kg of SrO_2 .... CAS # 1314-18-7

This synthesis process is a comprehensive approach to generating Strontium peroxide via this method. However, for the rest of the paper, only the 3rd reaction is analyzed as it is more technically complicated than the others owing to the fact that the specific conditions under which the reaction proceeds cause the formed SrO_2 to decompose to SrO and O_2. This highlights one of the main goals of the project - optimize the conditions of the reaction to reduce the decomposition of SrO_2.

2.1 Reactor Description

The experimental setup employs a 150-gallon jacketed Continuous Stirred Tank Reactor (CSTR) with a hemispherical bottom that transitions into a cylindrical top, both featuring a radius of 56 cm and a total depth of 76 cm. Certified by Brighton Corporation and crafted by Hamilton Kettels, the reactor bears the model number C-9066-1. Homogeneity within the reactor is maintained by an opposed arm mixing unit, regulated by a Variable Frequency Drive (VFD). A 35 KW chiller unit facilitates cooling by circulating coolant through the jacket, essential for managing the exothermic reaction. Although coolant temperature varies during the H2O2 charge, it is initially considered constant for simplification, with the intention of refining this parameter through optimization using the Nelder-Mead method alongside the development of our coupled differential equations. This setup assumes perfect mixing to focus our analysis on the temperature regulation and reactant concentration challenges.

3 Theoretical Model

Our theoretical model delves into the reactor dynamics involved in producing Strontium Peroxide (SrO_2) from Strontium Hydroxide ($Sr(OH)_2$) and Hydrogen Peroxide (H_2O_2). Starting from fundamental principles in chemical kinetics and heat transfer, the model is structured around coupled differential equations that represent the temperature and H_2O_2 concentration as state

variables. While the model's framework is intentionally simplified, capturing only a select set of crucial phenomena, it boasts a robust set of parameters. This design choice not only grants sufficient flexibility for fitting the model to empirical data but also means that the parameter values diverge from their direct, physical interpretations as this physical system is more accurately described by a more general family of equations.

3.1 Derivation of the Differential Equations

The derivation starts with fundamental principles of chemical kinetics, mass conservation, and energy balance within the reactor system, involving the reaction between Strontium Hydroxide and Hydrogen Peroxide.

3.1.1 Chemical Kinetics

The reaction kinetics are governed by the law of mass action, with the rate of reaction r given by:

$$r = k[\text{Sr(OH)}_2][\text{H}_2\text{O}_2],$$

where k is the rate constant, and $[\text{Sr(OH)}_2]$ and $[\text{H}_2\text{O}_2]$ are the molar concentrations of Strontium Hydroxide and Hydrogen Peroxide, respectively. The rate constant k is temperature-dependent, following the Arrhenius equation:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right),$$

where k_0 is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and T is the temperature. The main exothermic component of this reaction is between the ammonium and nitrate ions.

3.1.2 Mass Conservation and Energy Balance

The rate of change in the concentrations of the reactants due to the reaction and the temperature within the reactor can be described by the following set

4

of coupled differential equations:

$$\frac{\partial[\text{Sr(OH)}_2]}{\partial t} = -k\exp\left(-\frac{E_a}{RT}\right)[\text{Sr(OH)}_2][\text{H}_2\text{O}_2], \tag{1}$$

$$\frac{\partial[\text{H}_2\text{O}_2]}{\partial t} = F(t) - k\exp\left(-\frac{E_a}{RT}\right)[\text{Sr(OH)}_2][\text{H}_2\text{O}_2], \tag{2}$$

$$\frac{\partial T}{\partial t} = \frac{\Delta H \cdot k\exp\left(-\frac{E_a}{RT}\right)[\text{Sr(OH)}_2][\text{H}_2\text{O}_2] - hA(T - T_{\text{coolant}})}{C_p \cdot V \cdot \rho}. \tag{3}$$

Where:

- $[\text{Sr(OH)}_2]$ and $[\text{H}_2\text{O}_2]$ denote the concentrations of Strontium Hydroxide and Hydrogen Peroxide, respectively.

- k represents the pre-exponential factor of the reaction rate constant.

- E_a is the activation energy.

- R stands for the universal gas constant, and T is the temperature in Kelvin.

- $F(t)$ symbolizes the time-dependent flow rate of H_2O_2 into the reactor.

- ΔH indicates the heat of reaction.

- h is the heat transfer coefficient.

- A refers to the reactor surface area.

- T_{coolant} is the coolant temperature.

- C_p, V, and ρ are the specific heat capacity, volume, and density of the mixture, respectively.

These equations incorporate the Arrhenius equation for reaction kinetics, capturing the temperature dependence of the reaction rate. The flow rate $F(t)$ and the heat generated from the reaction, along with heat lost to the surroundings, determine the temperature changes within the reactor.

3.2 Parameters and Optimization

Key parameters—k, E_a, ΔH, h, A, C_p, alongside $F(t)$—are optimized against experimental temperature data to ensure the model accurately reflects the reactor's thermal behavior, facilitating precise reaction management.

Computational Methods Overview

The computational approach involves the use of Python for numerical solutions and optimizations. Key functions from the SciPy library, 'odeint' for solving differential equations and 'minimize' for optimizing parameters, are employed. The optimization process is guided by a cost function derived from polynomial-interpolated experimental temperature data.

3.3 Experimental Data

One of the greatest advantages of this model is that it may be custom fit to the specific equipment in use. The method requires fitting the parameters of the pair of differential equations to experimental data. While accurate data regarding the concentration of H_2O_2 over time is difficult obtain, the other state variable, temperature, is much easier. In order to obtain this data, the procedure for producing SrO_2 was completed several times using consistent flow rates of H_2O_2. Measurements of temperature were taken at specific times then averaged together to form a set of temperature, time points. The time t=0 is the starting point for each of the runs and is coincident with the time the H_2O_2 charge begins. The data points were then fit to a 4th order polynomial to form the function that the parameters will be fit to via Nelder-Mead. The temperature profile, modeled as a 4th order polynomial of time t, is given by:

$$y(t) = -2.14 \times 10^{-8}t^4 + 1.59 \times 10^{-5}t^3 - 3.92 \times 10^{-3}t^2 + .347t + 35.2 \quad (4)$$
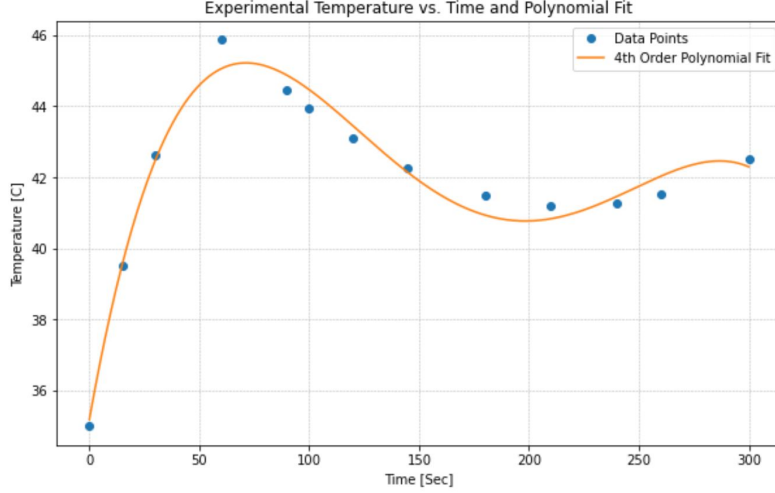
Which has the plot:

Figure 1: Comparison between polynomial fit and data points

3.4 Comprehensive Overview of the Nelder-Mead Method

The Nelder-Mead method is pivotal in optimizing multidimensional, nonlinear problems without the necessity for derivative computation. It utilizes a simplex, which is a polytope formed by $n + 1$ vertices in an n-dimensional space, adapting its structure to navigate towards the function's minimum. The method operates without requiring gradient information, making it suitable for a broad range of optimization problems.

The algorithm progresses through the following key steps:

1. **Initialization:** Formulate an initial simplex using a chosen starting point and a predefined step size.

2. **Ordering:** Arrange the simplex vertices $\{y_0, y_1, \ldots, y_n\}$ based on their objective function values f, ensuring $f(y_0) \leq f(y_1) \leq \ldots \leq f(y_n)$, with $f(y_n)$ being the highest.

3. **Transformation:** Depending on the ordered vertices' function values, execute one of the following actions:

   - **Reflection:** Create a new point by reflecting the worst vertex y_n across the centroid M of the remaining vertices to obtain $y_r =$

7

$M + \alpha(M - y_n)$, where $\alpha = 1$. If $f(y_0) \leq f(y_r) < f(y_{n-1})$, replace y_n with y_r.

- **Expansion:** If $f(y_r) < f(y_0)$, explore further in that direction to find $y_e = M + \gamma(y_r - M)$, where $\gamma = 2$. Replace y_n with y_e if $f(y_e) \leq f(y_r)$; otherwise, retain y_r.

- **Contraction:** Should reflection not yield improvement, opt for contraction by generating a point closer to the centroid. Distinguish between outside contraction $y_{oc} = M + \rho(y_r - M)$ if $f(y_r) < f(y_n)$ and inside contraction $y_{ic} = M - \rho(M - y_n)$ otherwise, with $\rho = 0.5$. Replace y_n accordingly or proceed to shrink if no improvement is observed.

- **Shrink:** In cases where other strategies fail to enhance, reduce the simplex size towards the best point, adjusting each vertex as $y_i = y_0 + \sigma(y_i - y_0)$ for $i = 1, \ldots, n$, where $\sigma = 0.5$.

Iteratively adjusting the simplex using these strategies, the method seeks convergence towards a minimum or satisfies a predefined termination criterion. Despite its heuristic approach and the potential for converging to non-stationary points, the Nelder-Mead method is acknowledged for its versatility and efficacy in handling problems where gradient calculation is unfeasible or cumbersome. [Ozaki et al. 2017]
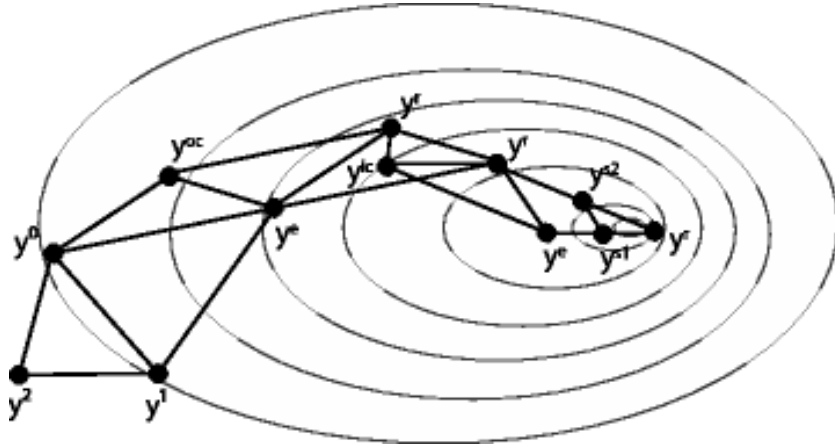

Figure 2: Illustration of successive applications of the Nelder-Mead algorithm

4 Optimized Parameters

The optimization process refined the parameters of the reactor model so as to align with the experimental data. The table below summarizes the initial and optimized values of these parameters, along with the percentage change resulting from the optimization process.

Parameter	Initial Value	Optimized Value	% Change
k (L/(mol·s))	5×10^{-5}	0.0001	80.39%
ΔH (J/mol)	200,000	11,083.0593	-94.46%
E_a (J/mol)	50,000	42,898.1039	-14.20%
C_p (J/(g·K))	4.18	1.2254	-70.68%
Ambient Temperature (K)	278	314.3616	13.08%
Initial Volume (L)	567.8115	208.3393	-63.31%
Heat Transfer Coefficient (W/(m²·K))	3,000	1,993.3151	-33.56%
Reactor Surface Area (m²)	1.5	2.9400	96.00%

Table 1: Comparison of initial and optimized parameters in the reactor model.

The optimized parameters can then be substituted into the model and solved for various initial values of non optimized parameters and, crucially, flow functions. For example, here is the fit to the experimental data polynomial for the flow function and initial values detailed in the procedure:
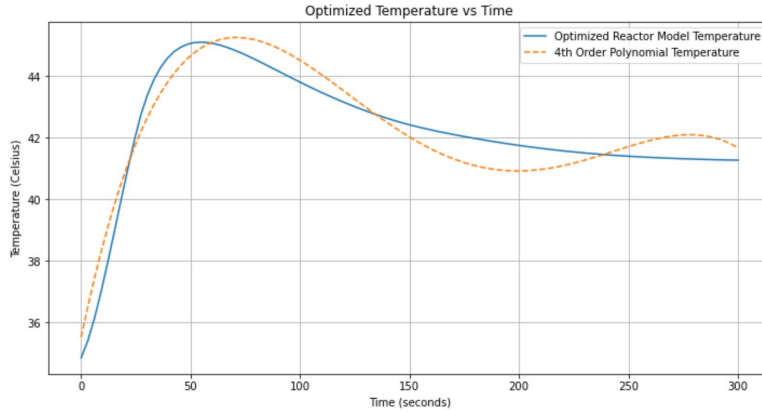

Figure 3: Comparison between the fitted model and experimental results

5   Results

The optimized model parameters were determined to significantly enhance the precision of H2O2 flow control, thereby improving the consistency of SrO2 batch quality. The flow function can be iteratively modified to produce an eigenfunction that represents some constant of a state variable. For example, here is a 4th order polynomial fit for a 42 C isotherm of the system:

$$F(t) = 2.66 \times 10^{-8}t^4 - 1.78 \times 10^{-5}t^3 + 4.29 \times 10^{-3}t^2 - 0.414t + 14.05 \quad (5)$$

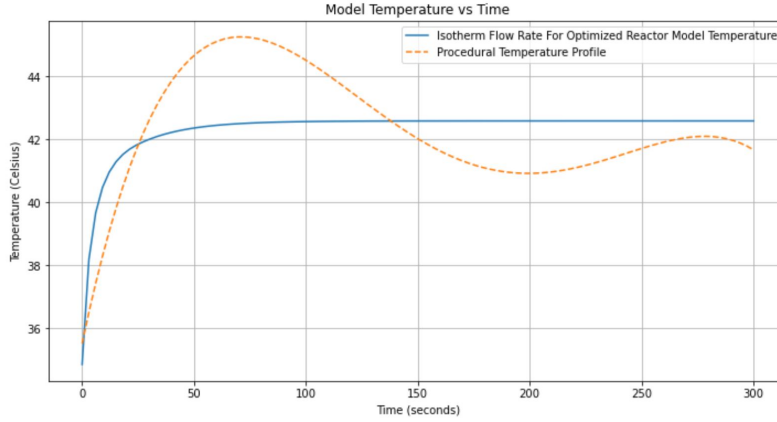Which would yield the following modeled temperature profile:

Figure 4: Comparison between the isotherm flow rate model a and procedural flow rate model

Here is that same eigenfunction plotted against the procedure flow function that has been created through trial and error:
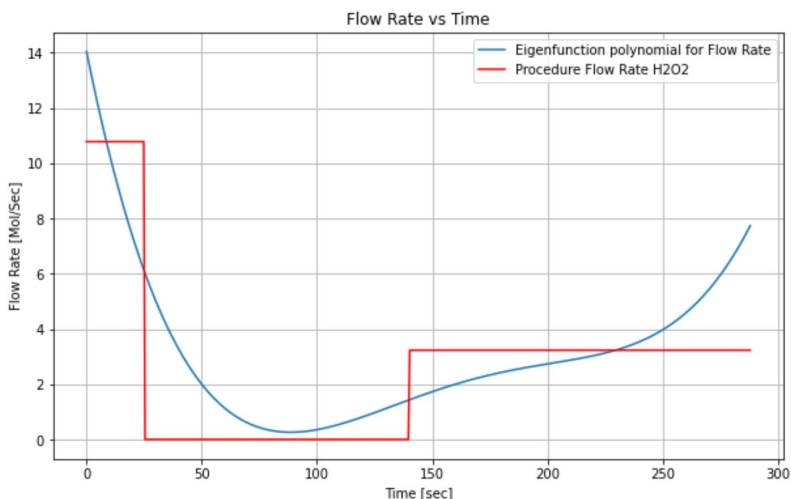
Figure 5: Comparison between the Eigenfunction approximation and procedural flow rate of H_2O_2

6 Conclusion

The refinement of the coupled differential equations and the subsequent optimization process have yielded significant insights into the production dynamics of SrO_2. The optimization of parameters not only demonstrates the capability of computational models to mirror complex chemical processes but also underscores the importance of precise control over the reactant flow rates and reactor conditions. Particularly, the adjustments in the H_2O_2 flow rate, as determined by the eigenfunction, suggest a strategic approach to maintaining the reaction within the desired temperature range, thereby mitigating the decomposition of SrO_2.

While we believe we have been successful in creating a numerical proof-of-concept of attaining arbitrary control of temperature via modeling the flow rate, discrepancies in the optimized parameter values from realistic values suggest that the set of differential equations themselves need to be made more general, encompass a greater number of effects and considerations, to accurately create flow functions worthy of experiment in production.

References

[1] Nelson, Mead. *Optimization Techniques for Chemical Processes.* Chemical Engineering Journal, Year.