Model Reduction and Parameter Estimation for a Semi-batch Reactor

Sankash V. Venkatesh
Department of Chemical Engineering, University of Wisconsin - Madison

1 Introduction

Scientific investigations involving data generally seek a rational model of observed phenomena, rather than a mere curve-fit of measured values. The investigation begins with a hypothesis (model), which might come from an analysis of existing information. To test this model, the model is fitted to the data obtained from experiments. This analysis may suggest a revised model. It might also suggest the additional data required to successfully estimate all the parameters in the model.

2 Model formulation

- Reaction

$$A + B \xrightarrow{k_1} C + B.HX$$
$$C + B \xrightarrow{k_2} D + B.HX$$

- Model

$$\frac{dV_R}{dt} = F(t)$$
$$\frac{dAV_R}{dt} = -k_1 ABV_R$$
$$\frac{dBV_R}{dt} = FB_{feed} - (k_1 AB + k_2 CB)V_R$$
$$\frac{dCV_R}{dt} = (k_1 AB - k_2 CB)V_R$$
$$\frac{dDV_R}{dt} = k_2 CBV_R$$

- Initial conditions $V_R(0)=V_{RO}$, $A(0)=A_O$, $B(0)=C(0)=D(0)=0$
- Assumptions
  - Isothermal, Negligible volume change, Perfect mixing, Negligible side reactions
- Parameters

$$p = (A_0, k_1, k_2)$$

3 Data explanation

- **Composition Analysis:**
  - Online **LC** which draws the sample every 8-10 mts and relays the **relative** amounts of C and D
  - LC detector wavelength set to detect the R-Vinyl bond The areas of the two peaks are related to the molar concentrations by

$$a_D = 2k_{lc}D$$
$$a_C = k_{lc}C$$

  - Normalised peak area

$$lc(t) = \frac{a_C}{a_C + a_D} = \frac{C}{C + 2D}$$

- **Feed rate of Base:** Micromotion mass flow meter that outputs a 4-20 mA logged once per minute by a Telog 2102 data recorder

4 Simulation studies

Sensitivity

Simulations were carried out to study the sensitivity of the lc with respect to each of the parameters.

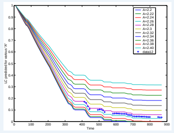

Figure 1:k_1 and k_2 fixed

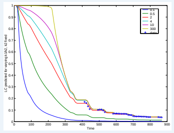

Figure 2:A_0 and k_2 fixed

- lc is very sensitive to A_0.
- lc is very sensitive to the ratio k_1/k_2, especially during the initial period where the data is missing

Objective function profiles

Objective function profiles were obtained by holding one of the parameters at a fixed value and varying the other two parameters.

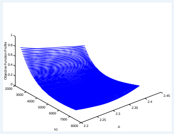

Figure 3:k_2 fixed , k_1 and A_0 varied

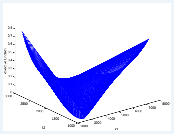

Figure 4:A_0 fixed , k_1 and k_2 varied

- It can be observed from figure 3 that, for a particular k_2 there is an optimal value of A_0 and k_1.
- No optimal point is found in figure 4. The optimum is a line which corresponds to a constant ratio of k_1/k_2.
- It can be inferred that the ratio of k_1/k_2 is a more important parameter than the absolute magnitudes of k_1 and k_2.

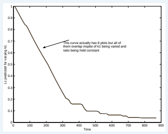

Figure 5:A_0 is fixed , k_1 is varied while k_1/k_2 is held constant

Figure 5 confirms that the absolute magnutudes of rate constants do not change profiles of lc predicted, as long as the ration of k_1/k_2 is held constant

5 Analysis

- **Objective function**

$$\phi = \sum_i \left(lc_{i(meas)} - lc_{i(model)}\right)^2$$

- **Optimization Problem**

$$\min_p \quad \phi(x(t), u(t); p)$$

subject to

$$\frac{dx}{dt} - f(x(t), u(t); p) = 0$$
$$x(0) = x_0$$

- Estimation Results
  - Estimates the parameter A_o, extremely well
  - Estimates the ratio of the rate constants $\frac{k1}{k2}$
  - Fails to estimate the absolute magnitude of the rate constants $k1, k2$
- Reasoning
  - Success
    - Parameter A_o can be estimated because the profiles of $\frac{C}{C+2D}$ vs. time are very sensitive to A_o
    - The profile of $\frac{C}{C+2D}$ vs. time are quite sensitive to the ratio of $\frac{k1}{k2}$, hence this can be estimated.
  - Failure
    - The absolute magnitudes of $k1, k2$ have no significant effect on the profile of $\frac{C}{C+2D}$ vs. time. It is the ratio which is more important

6 Observation

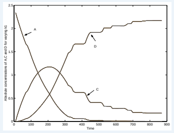

Figure 6:k_1/k_2 is fixed, k_1 is varied

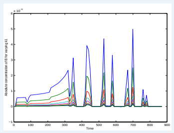

Figure 7:k_1/k_2 is fixed, k_1 is varied

- Figures 6 and 7 are the plots of concentrations of A,B,C and D for different absolute magnitudes of rate constants, but with a fixed ratio of k_1/k_2.
- From figure 7 it can be inferred that the amount of B left in the reactor is very small during the course of the reaction.
- Based on this we can make the assumption that B is consumed immediately and revise the model.

7 Proposal

Revise the model to eliminate the redundancy of the absolute magnitudes of the rate constants.

- Reaction

$$A + B \xrightarrow{extent\epsilon_1} C + B.HX$$
$$C + B \xrightarrow{extent\epsilon_2} D + B.HX$$

- Model

$$N_A = N_{A_0} - \epsilon_1$$
$$\frac{d(\epsilon_1 + \epsilon_2)}{dt} = FB_{feed}$$
$$N_C = N_{C_0} + \epsilon_1 - \epsilon_2$$
$$N_D = N_{D_0} + \epsilon_2$$
$$\frac{k_1}{k_2} = K$$
$$\frac{d\epsilon_1}{d\epsilon_2} = \frac{KN_A}{N_C}$$

8 Results

- New Model (with simulted data for initial part)

Parameter	Optimal Estimate	95% Confindence Interval
A_0	2.3502	±0.001
K	3.028	±0.021

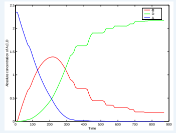

Figure 8:New Model predictions

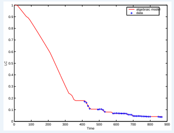

Figure 9: lc by new model

- Original Model

Parameter	Optimal Estimate	95% Confindence Interval
A_0	2.3501	±0.0021500
k_1	4466.8	±614.2
k_1/k_2	3.1296	±0.31

A_0(kmol),k_1(dm^3/kmol.min)

9 Conclusions

- The reactions are extremely fast when compared to the rate of available lc data.
- The rate constants can be estimated only by using suitable addition policy for B.
- The parameter estimates of the new model have good confidence intervals.
- Experimental data during the initial part of the reaction is required for better estimation of the parameters.