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Parameter Identification and On-line Estimation of a Reduced Kinetic Model

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Abstract

In this work, we present the estimation techniques used to update the model parameters in a reduced kinetic model describing the oxidation-reduction reactions in a hydrothermal oxidation reactor. This model is used in a nonlinear model-based controller that minimizes the total aqueous nitrogen in the reactor effluent. Model reduction is accomplished by combining similar reacting compounds into one of four component groups and considering the global reaction pathways for each of these groups. The reduced kinetic model developed for this reaction system provides a means to characterize the complex chemical reaction system without considering each chemical species present and the reaction kinetics of every possible reaction pathway. For the reaction system under study, model reduction is essential in order to reduce the computational requirement so that on-line implementation of the nonlinear model-based controller is possible and also to reduce the amount of *a priori* information required for the model.

1. Introduction

The parameter estimation techniques used with a reduced kinetic model describing the hydrothermal oxidation of hydrolysate solutions obtained from base hydrolysis of the high explosive PBX-9404 are presented in the sequel. The combination of base hydrolysis and hydrothermal oxidation is used for the destruction of this material at the Pantex Department of Energy facility in Amarillo, Texas. In this process, the high explosive material is first hydrolyzed in a batch reactor using a concentrated sodium hydroxide solution to yield non-energetic, water soluble compounds. The result is a high pH base hydrolysate solution with reaction products that include a series of carboxylic acid salts, glycolates, primary and secondary amines, and nitrites. The hydrolysate solution contains from two to ten wt% of organic carbon and nitrogen compounds that must be further treated before disposal.

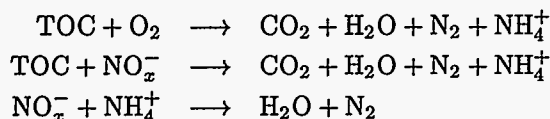
Hydrothermal oxidation is used to eliminate the organic compounds present in the base hydrolysate solution. The oxidation reaction is carried out in a tubular reactor in which hydrogen peroxide is injected with the feed and at a second injection point downstream. Hydrothermal oxidation is very effective at removing organic carbon compounds, however, aqueous nitrogen compounds tend to be more difficult to completely remove. The result is the presence of nitrate and ammonium ions in the aqueous effluent stream of the reactor. Since elevated concentrations of aqueous nitrogen compounds prevent the direct discharge of the aqueous effluent, a model-based controller is used to minimize the total aqueous nitrogen in the effluent while ensuring complete destruction of the organic carbon compounds.

The model-based controller contains a plug flow reactor model that incorporates the reduced kinetic model of the hydrothermal oxidation reactions. Using this model, the hydrogen peroxide injection rates required to minimize the total aqueous nitrogen compounds and maintain a desired excess oxygen concentration in the reactor effluent are determined. The effluent aqueous nitrogen concentration is measured by nitrate and ammonium ion-selective sensors. Excess oxygen is inferred from the oxygen concentration of the gas effluent stream. These measurements are used for on-line estimation of the model parameters.

2. Reduced Kinetic Model

The chemical components considered in the kinetic model are total organic carbon (TOC), nitrate/nitrite (NO_x^-), ammonia/ammonium (NH_4^+), and oxygen (O_2). TOC and NO_x^- are present in the base hydrolysis feed to the reactor. NH_4^+ is generated from the oxidation of the organic carbon compounds by both oxygen and NO_x^- . Oxygen is generated from decomposition of the hydrogen peroxide injected into the reactor. Since the hydrogen peroxide is completely decomposed in the injection line before it enters the reactor, only oxygen is considered. The following three

reactions are included in the reduced kinetic model.



Each reaction is assumed to be a second order oxidation-reduction reaction. The reaction rates for each of the chemical components are

$$\mathcal{R}(\text{TOC}) = -k_1\rho_r[\text{TOC}][\text{NO}_x^-] - k_2\rho_r[\text{TOC}][\text{O}_2] \quad (1)$$

$$\mathcal{R}(\text{NO}_x^-) = -ck_1\rho_r[\text{TOC}][\text{NO}_x^-] - k_3\rho_r[\text{NO}_x^-][\text{NH}_4^+] \quad (2)$$

$$\mathcal{R}(\text{NH}_4^+) = ak_1\rho_r[\text{TOC}][\text{NO}_x^-] + bk_2\rho_r[\text{TOC}][\text{O}_2] - k_3\rho_r[\text{NO}_x^-][\text{NH}_4^+] \quad (3)$$

$$\mathcal{R}(\text{O}_2) = -dk_2\rho_r[\text{TOC}][\text{O}_2] \quad (4)$$

in which ρ_r is the reactor fluid density and the concentrations are in the units of mole/kg. The fluid density at reactor conditions is computed using the cubic form of the Peng-Robinson equation of state.

The Arrhenius pre-exponential factor and activation energy for the reaction rate constants and the reaction ratios are shown in Table 1. These values were determined from hydrothermal oxidation experiments conducted at Los Alamos National Laboratory on PBX-9404 hydrolysate solutions at temperatures between 350 C and 480 C. A complete discussion of the kinetic model development and determination of the parameter values is contained in [1].

Rate Constant	A (lit/mole-sec)	E_a/R (K)
k_1	1.83×10^5	1.02×10^4
k_2	2.89×10^{42}	6.46×10^4
k_3	2.37×10^4	8.20×10^3

Ratio	Value
a	0.567
b	0.078
c	0.496
d	0.750

Table 1: Kinetic model parameters.

Although it is possible to develop a detailed hydrothermal oxidation reaction kinetic model that distinguishes between each of the different organic carbon and nitrogen compounds in the hydrolysate feed, a model of this scale would result in a significant increase in complexity and computational requirements. Since the hydrolysate composition can vary depending on the operation of the hydrolysis reactor, characterization of the feed components would

be necessary after each hydrolysis reaction in order to use this model. Due to the difficulties in accurately characterizing the hydrolysate feed at Pantex, this model would provide limited improvement over the simpler reduced kinetic model for the prediction of the effluent aqueous nitrogen compounds. In addition, the significant increase in the computational requirements would preclude the use of this model in the model-based controller. For these reasons, a reduced kinetic model was developed for this process.

3. Optimal Reactor Operation

The optimal reactor operation is achieved when the production of NH_4^+ from the TOC-O_2 reaction and the TOC-NO_x^- reaction balances the destruction of NH_4^+ from the $\text{NH}_4^+-\text{NO}_x^-$ reaction. At low peroxide injection rates, the TOC-NO_x^- reaction removes NO_x^- from the system resulting in a high NH_4^+ effluent concentration. At high injection rates, the TOC-O_2 reaction predominates resulting in an elevated NO_x^- effluent concentration. Figure 1 presents the effluent nitrogen component concentrations as a function of the initial hydrogen peroxide injection rate for an average reactor temperature of 435C, a reactor pressure of 990 bar, and a hydrolysate feed rate of 150 gal/day. A constant effluent excess oxygen concentration of 0.1 mol/kg is maintained by adjusting the second peroxide injection rate.

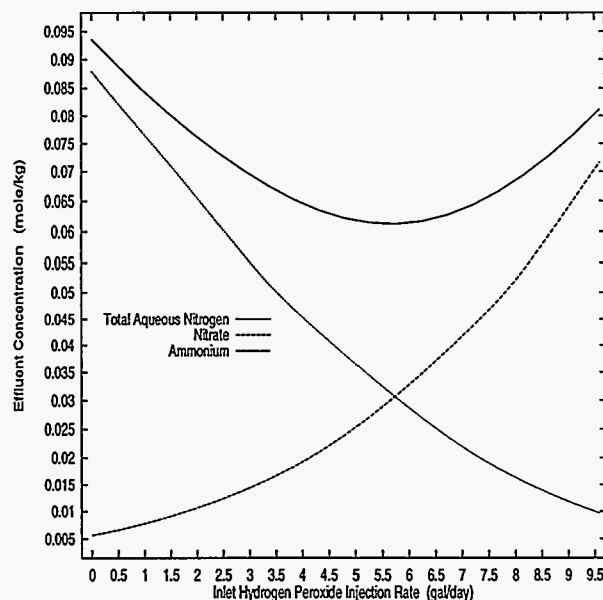


Figure 1: Effluent nitrogen component concentrations.

4. Model-based Controller

The model-based controller solves a steady-state nonlinear optimization problem to find the hydrogen peroxide injection rates that minimize the model predicted effluent total aqueous nitrogen at the desired

excess oxygen concentration target for the current hydrolysate feed rate and operating conditions. In this optimization, H_1 and H_2 are the first and second hydrogen peroxide volumetric injection rates, $[c]_e$ is the effluent concentration of component c , and $[O_2]_t$ is the excess oxygen target.

$$\min_{H_1, H_2} [\text{NO}_x^-]_e + [\text{NH}_4^+]_e \quad (5)$$

$$\text{Subject To: } \begin{array}{l} [O_2]_e = [O_2]_t \\ \text{Reactor Model} \end{array}$$

The reactor model consists of a series of four differential equations, one for each of the chemical components discussed in Section 2, that describe the steady-state concentration profile in a plug flow reactor

$$\frac{F\rho_f}{A_c\rho_r} \frac{d[c]}{dz} + \mathcal{R}(c) = 0 \quad (6)$$

in which F is the total volumetric feed flow rate, ρ_f is the feed density, ρ_r is the fluid density at reactor conditions, A_c is the reactor cross-sectional area, and $\mathcal{R}(c)$ is the rate of reaction of component c from Eqs. 1 through 4. The excess oxygen concentration can be determined from the following expression

$$[O_2]_e = \frac{H_2 [O_2]_f + (F_h + H_1) ([O_2] - d[\text{TOC}])}{F_h + H_1 + H_2} \quad (7)$$

in which $[O_2]_f$ is the concentration of oxygen in the peroxide feed, $[O_2]$ and $[\text{TOC}]$ are the model predicted oxygen and total organic carbon concentrations in the reactor prior to the second peroxide injection point, and F_h is the hydrolysate volumetric feed rate. The difference between the model predicted excess oxygen concentration, $[O_2]_e$, and the concentration determined by the oxygen analyzer, $[O_2]_a$, is used to make an adjustment to the second peroxide injection rate to control the effluent excess oxygen.

$$\alpha = [O_2]_e - [O_2]_a \quad (8)$$

$$\Delta H_2 = \frac{\alpha(F_h + H_1) ([O_2]_f - [O_2] + d[\text{TOC}])}{([O_2]_f - [O_2]_t)^2 - \alpha ([O_2]_f - [O_2]_t)} \quad (9)$$

Further detail on the model-based controller is presented in [2].

5. Parameter Estimation

The simplified hydrothermal oxidation reactions in the reduced kinetic model provide an adequate representation of the effluent aqueous nitrogen concentrations for the experimental data used to generate the model parameters [1]. However, the model must be adapted on-line to accurately predict the minimum effluent nitrogen concentration for the current reactor operating conditions. Due to the limited number

of analytical measurements on the process, it is not possible to update each of the parameters in the reduced kinetic model. Therefore, only the feed TOC and NO_x^- concentrations used by the model are estimated on-line. The effect of changes in these parameters on the calculated NO_x^- and NH_4^+ effluent concentrations are similar to the effect of changes in the kinetic parameters in Table 1 [2]. Accurate measurements of these concentrations are also not available for each hydrolysis batch.

Determination of the feed concentrations based on the measured aqueous nitrogen effluent concentrations is performed by steady-state batch estimation using an initial estimate approach [3]

$$\begin{aligned} \min_{[\text{TOC}]_f, [\text{NO}_x^-]_f} & w_c (\Delta [\text{TOC}]_f)^2 + w_n (\Delta [\text{NO}_x^-]_f)^2 \\ & + \sum_{j=1}^N ([\text{NO}_x^-]_e - [\text{NO}_x^-]_a^{j\Delta t})^2 \\ & + \sum_{j=1}^N ([\text{NH}_4^+]_e - [\text{NH}_4^+]_a^{j\Delta t})^2 \end{aligned} \quad (10)$$

$$\text{Subject To: } \begin{array}{l} [\text{TOC}]_{\min} < [\text{TOC}]_f < [\text{TOC}]_{\max} \\ [\text{NO}_x^-]_{\min} < [\text{NO}_x^-]_f < [\text{NO}_x^-]_{\max} \end{array}$$

in which $[c]_e$ is the predicted effluent concentration for component c at the current operating conditions, $[c]_a^{j\Delta t}$ is the measured effluent concentration at time $j\Delta t$, $\Delta[\text{TOC}]_f$ and $\Delta[\text{NO}_x^-]_f$ are the changes to the feed concentrations, Δt is the sample period of the estimator, N is the number of samples in the batch, and w_c and w_n are tuning parameters. The predicted effluent concentrations are determined from the steady-state plug flow reactor model in Eq. 6 using the nominal kinetic model parameter values in Table 1. Initial estimates of the feed concentrations are determined from analysis of the base hydrolysis solution.

The ion-selective sensors used to determine the effluent nitrate and ammonium concentrations measure the activity of these ions in solution. The activity coefficient of these ions is a function of the ionic strength and temperature of the solution [4]. The concentration measurements are therefore subject to error due to variation in the aqueous effluent stream temperature and ionic strength. Since it is not possible to estimate the activity coefficients from the ion-selective sensor readings and analytical corrections based on the Nernst and Debye-Hückel equations would not be reliable in the process environment, these sensor errors are not accounted for.

This omission has no effect on the model-based controller because minimizing the activity of the nitrate and ammonium ions is equivalent to minimizing their concentration. However, these errors do effect monitoring the performance of the reactor. In order to

address this issue, calibration of these sensors is performed prior to processing a hydrolysate batch using standard solutions at the expected ionic strength of the effluent. Sodium bicarbonate, the principal electrolyte in the effluent, is used to adjust the ionic strength of the standard solutions. Since the effluent nitrate and ammonium concentrations are so small, changes in their concentration have little effect on the ionic strength of the solution and, consequently, little effect on the activity coefficient.

6. Closed-loop Control

The estimated feed concentrations from Eq. 10 are used to provide feedback to the model-based controller in Eq. 5. After the feed concentrations are estimated, the controller uses these concentrations to determine a new set of hydrogen peroxide injection rates that minimize the model predicted total aqueous nitrogen. After a delay of one reactor residence time, the parameter estimation collects effluent sensor readings and then estimates updated feed concentrations. This cycle is continuously repeated during the operation of the reactor.

In order to determine the effectiveness of this feedback scheme, a Monte Carlo simulation study was first carried out before implementation on the reactor. The reactor operating conditions for this study were the nominal operating conditions at an average reactor temperature of 435 C, a reactor pressure of 990 bar, a hydrolysate feed rate of 150 gal/day, and feed compositions of 0.9 mol/kg total organic carbon and 0.3 mol/kg nitrate/nitrite. The effluent excess oxygen concentration target was 0.1 mol/kg. A series of process models were developed by randomly varying each of the reduced kinetic model parameters in Table 1 with normally distributed white noise. Table 2 presents the nominal values at the reactor operating conditions, standard deviations of the white noise sequences, and bias values for each of the model parameters.

Model Parameter	Nominal Value	Standard Deviation	Bias Value
k_1	0.108	0.025	0
k_2	742.6	250.0	50
k_3	0.222	0.05	0
a	0.567	0.10	0
b	0.078	0.025	0
c	0.496	0.10	0
d	0.750	0.10	0.01

Table 2: Kinetic model parameter variation.

Figure 2 compares the effluent total aqueous nitrogen concentration probability density between open-loop and closed-loop operation. The open-loop con-

troller implements the optimal hydrogen peroxide injections using the nominal model parameters and feed concentrations. The closed-loop controller uses the nominal model parameters with updated feed concentrations based on the parameter estimator in Eq. 10 with no penalty on the feed concentration changes. As shown in the figure, closed-loop operation results in a lower mean effluent total aqueous nitrogen concentration and a smaller variance. Feedback reduced the mean effluent concentration from 0.075 mol/kg to 0.065 mol/kg and the variance from 0.05 mol/kg to 0.03 mol/kg.

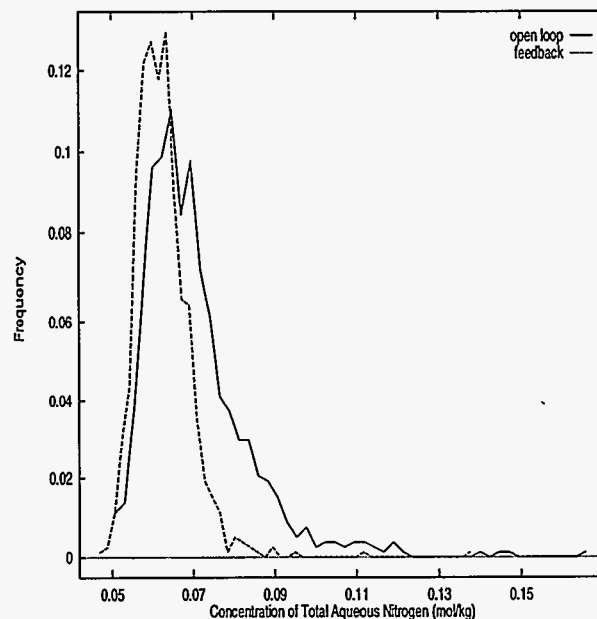


Figure 2: Open and closed loop effluent total aqueous nitrogen.

Figure 3 presents the probability density of the deviation from the minimum achievable effluent total aqueous nitrogen concentration for the open-loop and closed-loop operation. Open-loop operation shows a significant variation of this deviation. The closed-loop operation essentially achieves the minimum effluent concentration within the tolerance of the simulation for each of the runs. The result of feedback is a reduction in the average deviation from 0.01 mol/kg to 1×10^{-5} mol/kg. The number of iterations of the model-based controller and parameter estimation scheme is also an important consideration for closed-loop operation.

7. Conclusions

The reduced kinetic model in this work allows for the implementation of model-based control and on-line parameter estimation for a hydrothermal oxidation reaction system. A steady-state reactor model is used for the model-based control and parameter estimation because the computational requirements nec-

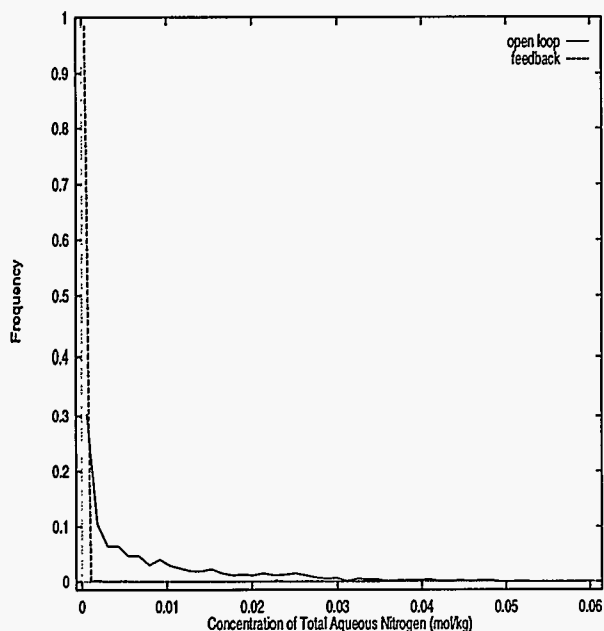


Figure 3: Open and closed loop deviation from minimum values.

essary for a dynamic reactor model exceed the limited computational resources available. Normal operation of the hydrothermal oxidation reactor is to process a single batch of hydrolysate solution at a given set of operating conditions. Under these conditions, steady-state algorithms are adequate since the reactor feed and operation remains constant for each hydrolysate batch processed.

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