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Submitted to:
1999 American Control Conference
June 2-4, 1999
San Diego, CA
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Parameter Identification and On-line Estimation for a Reduced Kinetic Model

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August 7, 1998

1 Introduction

Reduced kinetic models provide a means to characterize complex chemical reaction systems without the necessity of describing the chemical species and reaction kinetics of each component present in the system. Complexity in a chemical reaction system can occur from a wide variety of similar compounds in the feedstock or from a number of side and decomposition reactions occurring in the system. In this work, we describe the use of receding horizon identification and estimation techniques to determine the model parameters for a reduced kinetic model describing the oxidation–reduction reactions in a hydrothermal oxidation reactor. This model is used in a model predictive controller that minimizes the total aqueous nitrogen in the hydrothermal oxidation reactor effluent.

2 Process Description

The base hydrolysis process for the destruction of energetic or explosive materials results is a high pH hydrolysate solution with reaction products that include a series of carboxylic acid salts, glycolates, amines, and nitrites. The hydrolysate solutions obtained from this process contain from two to ten wt% of organic carbon and nitrogen compounds that must be further treated before disposal. Hydrothermal oxidation at elevated temperature (450°C) and pressure (14000 psi) was selected as the treatment process for the hydrolysate solutions obtained from hydrolysis of the high explosive PBX 9404 at the Department of Energy Pantex facility in Amarillo, Texas. This process is capable of complete destruction of the organic carbon compounds. Removal of aqueous nitrate is through reduction reactions with the organic carbon compounds and the ammonia generated as a by-product of the oxidation of organic carbon compounds.

A nonlinear model predictive controller was implemented on the hydrothermal oxidation reactor at Pantex to minimize total aqueous nitrogen (nitrate and ammonia) in the effluent of the reactor.
Aqueous nitrogen in the effluent is measured by nitrate and ammonia sensors in the liquid effluent stream. The nonlinear model used in this controller is a plug flow reactor model that incorporates a reduced kinetic model of the hydrothermal oxidation reactions.

3 Reduced Kinetic Model

The reduced kinetic model of the hydrothermal oxidation reactions lumps together components with similar chemical behavior and assumes the reactions are first order in both the oxidizing and reducing agent. The base hydrolysis reaction of PBX 9404 generates a number of organic carbon and nitrogen compounds in the resulting hydrolysate. Although it is possible to develop a detailed hydrothermal oxidation reaction model that distinguishes between each of the different nitrogen and organic carbon compounds, a kinetic model of this scale would result in a significant increase in complexity and computational requirements. Because of the difficulty in characterizing each of the components and reactions, this model would also provide limited improvement over the simpler reduced kinetic model in the prediction of aqueous nitrogen compounds. For these reasons, a reduced model was developed for the model predictive controller.

The reduced kinetic model contains four chemical species: total organic carbon, TOC, nitrate/nitrite, $\text{NO}_x^-$, ammonia, $\text{NH}_4^+$, and oxygen, $\text{O}_2$. There are three reactions considered in the model. The first two are the TOC-$\text{O}_2$ and TOC-$\text{NO}_x^-$ oxidation reactions and the third is the reduction of $\text{NO}_x^-$ by $\text{NH}_4^+$. The reaction rates for each component are as follows

\[
\begin{align*}
\mathcal{R}(\text{TOC}) &= -\rho k_1[\text{TOC}][\text{O}_2] - \rho k_2[\text{TOC}][\text{NO}_x^-] \\
\mathcal{R}(\text{NO}_x^-) &= -\alpha \rho k_2[\text{TOC}][\text{NO}_x^-] - \rho k_3[\text{NO}_x^-][\text{NH}_4^+] \\
\mathcal{R}(\text{NH}_4^+) &= \beta \rho k_2[\text{TOC}][\text{NO}_x^-] + c \rho k_1[\text{TOC}][\text{O}_2] - \rho k_3[\text{NO}_x^-][\text{NH}_4^+] \\
\mathcal{R}(\text{O}_2) &= d \rho k_3[\text{TOC}][\text{O}_2]
\end{align*}
\]

in which the concentrations are expressed in the units of mole/kg and $\rho$ is the density of the reactor fluid. Since the hydrogen peroxide is completely decomposed in the injection line before entering the reactor, hydrogen peroxide decomposition is not considered in the model. The initial reaction rate Arrhenius expressions and ratios were determined from pilot plant data on PBX 9404 base hydrolysate solutions.

4 Reactor Model

The hydrothermal oxidation reaction is carried out in a 780 foot Inconel tubular reactor. The reactor is modeled as a plug flow reactor that can be described by the following PDE for each of the four chemical components

\[
\frac{\partial c}{\partial t} = -\frac{F}{A_c} \frac{\partial c}{\partial \xi} - \mathcal{R}(c)
\]

in which $F$ is the volumetric flow rate and $A_c$ is the reactor cross-sectional area. Reactor temperature is measured approximately every twenty feet along the length of the reactor. Reactor pressure is measured at the reactor outlet. Since the reactor pressure drop is negligible, pressure is assumed to be constant along the length of the reactor. The fluid density is computed using the cubic form of the Peng-Robinson equation of state assuming the hydrolysate solution is represented by water. The volumetric flow rate is then determined from the density of the fluid.
5 Model Predictive Control

Two hydrogen peroxide injection points into the reactor are available to control the aqueous nitrogen and excess oxygen concentrations in the reactor effluent. The optimal operation is at the minimum total aqueous nitrogen concentration and a slight excess oxygen concentration. This minimum is achieved when the production of \( \text{NH}_4^+ \) from the TOC-O2 reaction and TOC-NO\(_2^-\) reaction balances the destruction of \( \text{NH}_4^+ \) from the NO\(_2^-\)-NH\(_2^+\) reaction. The model-based control algorithm used to determine the peroxide injection rates for the reactor is

\[
\text{min } [\text{NO}_2^-]_e + [\text{NH}_4^+]_e
\]

Subject To:

\[
\frac{F}{A_c} \frac{\partial [c]}{\partial z} + R(c) = 0
\]

\[
[O_2]_e = [O_2]_t
\]

in which \([c]_e\) is the effluent concentration of component \(c\) and \([O_2]_t\) is the desired excess oxygen target. The excess oxygen concentration in the effluent can be determined from the following expression

\[
[O_2]_e = \frac{H_2([O_2]_f/\rho_f) + (F + H_1) ([O_2] - d[TOC])}{F + H_1 + H_2}
\]

in which \([O_2]\) and \([\text{TOC}]\) are the model predicted oxygen and organic carbon concentrations in the reactor prior to the second peroxide injection point, \(H_1\) and \(H_2\) are the first and second peroxide injection rates, \(\rho_f\) is the feed density, and \([O_2]_f\) is the feed oxygen concentration. Feedback from the process is provided by on-line estimation of the model parameters.

6 On-line Parameter Estimation

Since the reduced kinetic model is a simplified representation of the reactions taking place in the system, it is reasonable to expect that there will be structural model error over the normal operating range. Therefore, a receding horizon nonlinear parameter estimator is used to update the model based on the measured NO\(_2^-\) and NH\(_4^+\) concentrations. Since the limited number of process measurements available restrict the number of kinetic model parameters that can be reliably estimated, a sensitivity study is carried out to determine those model parameters that provide the most effective feedback to the controller. Determination of these model parameters is performed by a moving horizon estimator using an initial estimate approach

\[
\text{min } \sum_{j=1}^{N} \left( ([\text{NO}_2^-]_{j\Delta t}^m - [\text{NO}_2^-]_{j\Delta t}^a)^2 + ([\text{NH}_4^+]_{j\Delta t}^m - [\text{NH}_4^+]_{j\Delta t}^a)^2 \right)
\]

Subject To:

\[
\frac{\partial [c]}{\partial t} + \frac{F}{A_c} \frac{\partial [c]}{\partial z} + R(c) = 0
\]

in which \([c]_{j\Delta t}^m\) is the model predicted effluent concentration for component \(c\) at time \(j\Delta t\), \([c]_{j\Delta t}^a\) is the analytical measurement of the effluent concentration at time \(j\Delta t\), \(\Delta t\) is the sample time of the estimator, and \(N\) is the estimation horizon.