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Title:

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Implementation of Model Predictive Control on a Hydrothermal Oxidation Reactor

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Abstract

This paper describes the model-based control algorithm developed for a hydrothermal oxidation reactor at the Pantex Department of Energy facility in Amarillo, Texas. The combination of base hydrolysis and hydrothermal oxidation is used for the disposal of PBX 9404 high explosive at Pantex. The reactor oxidizes the organic compounds in the hydrolysate solutions obtained from the base hydrolysis process. The objective of the model predictive controller is to minimize the total aqueous nitrogen compounds in the effluent of the reactor. The controller also maintains a desired excess oxygen concentration in the reactor effluent to ensure the complete destruction of the organic carbon compounds in the hydrolysate.

1. Introduction

Base hydrolysis is an alternative to combustion and open detonation for the destruction of energetic materials. In this process, the energetic material is hydrolyzed in a concentrated sodium hydroxide solution to yield non-energetic, water soluble compounds. The reaction product is an elevated pH solution that contains sodium carboxylic acid salts, amines, and nitrites. Base hydrolysis does not have the safety and environmental problems associated with combustion and open detonation, however, the resulting hydrolysate solution requires an additional treatment step before disposal to remove the organic carbon and aqueous nitrogen compounds.

One of the options for the environmentally benign treatment of the base hydrolysate is hydrothermal oxidation. This process oxidizes the organic compounds at elevated temperatures (400 to 450 deg C) and pressures (900 to 1000 bar) using hydrogen peroxide or oxygen as the oxidant. 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 hydrothermal oxidation reactor.

Since elevated concentrations of aqueous nitrogen compounds prevent the direct discharge of the aqueous effluent, the objective of the model-based controller is to minimize the total aqueous nitrogen in the reactor effluent while ensuring complete destruction of the organic carbon compounds. This objective must be achieved over the wide range of hydrolysate feed rate and concentration that is processed by the reactor. The controller uses a dynamic plug flow reactor model that incorporates a simplified kinetic model of the hydrothermal oxidation reactions. Using this model, the hydrogen peroxide injection rate required to minimize the total aqueous nitrogen compounds and maintain a desired excess oxygen concentration in the reactor effluent is determined.

2. Process Description

The hydrothermal oxidation reaction is carried out in a 780 foot long Inconel tubular reactor with a 0.188 inch inside diameter. The first 25 feet of the reactor length is used as the feed heat exchanger. The next 40 feet of the reactor is used to further heat the feed to the desired reaction temperature by electric resistance heating. Power is supplied by a 50 kilowatt variable power supply shorted across this reactor length. The following 690 feet of the reactor is the reaction section. The last 25 feet of the reactor length is used as the effluent heat exchanger. A heat transfer fluid pump-around system recovers heat from the reactor effluent in this heat exchanger to preheat the reactor feed in the feed heat exchanger. A schematic of the reactor is shown in Figure 1.

Hydrogen peroxide is injected with the feed at the reactor inlet and at a second injection point located 124 feet from the start of the reaction section of the reactor. Steady-state design calculations indicate a significant reduction in the effluent aqueous nitrogen compounds with the use of two peroxide injection points [1]. The feed flow rates are controlled by varying the speed of constant stroke piston pumps.

The reactor temperature is measured every twenty feet along the length of the reactor by thermocouples

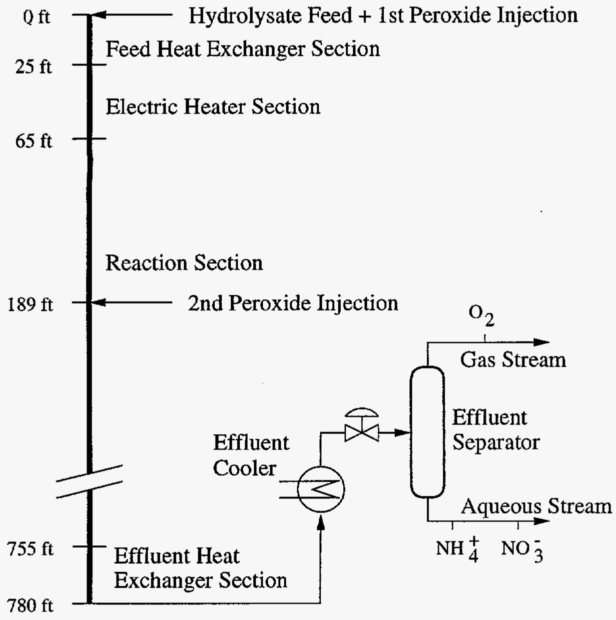

Figure 1: Hydrothermal oxidation reactor schematic.

brazed to the outside of the tube wall. The temperature measurements are performed in this manner to retain the integrity of the tubular reactor. Since there are no severe temperature gradients in the reaction section, these measurements are assumed to be representative of the fluid temperature inside the reactor. Average reaction section temperature is controlled by adjusting the power to the electrical resistance heater.

Since the reactor pressure drop is negligible, pressure is assumed to be constant along the reactor length. Reactor pressure is controlled by a Bafco control valve located after the reactor effluent cooler. In order to reduce the pressure drop across this valve, the effluent first passes through a series of capillary tubes.

The reactor effluent is separated into liquid and gas streams in a separator vessel. The aqueous nitrogen is measured by nitrate and ammonia sensors in the effluent liquid stream. Excess oxygen is measured by an oxygen sensor in the effluent gas stream.

3. Process Model

The hydrothermal oxidation reactor is modeled as a plug flow reactor with no axial diffusion. Since the Reynolds number for this system is on the order of 10^4 and the ratio of the reactor radius to average velocity is on the order of 10^{-3} seconds, radial variation of the concentration is neglected. The effect of axial diffusion is neglected since the contribution of the diffusive velocity is small compared to the convective velocity. This ratio is also on the order of 10^{-3} seconds. Further detail on the justification of these assumptions can be found in [2].

3.1. Kinetic Model

A simplified kinetic model of the oxidation reaction that lumps components with similar chemical behavior is used in the process model. Although this kinetic model is a gross simplification of the elementary reactions taking place in the reactor, it does capture the global reaction pathways through which organic carbon and nitrogen compounds are consumed in the reactor. It also provides an adequate representation of experimental data.

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 in the model.

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

$$\begin{aligned}
\mathcal{R}(\mathrm{TOC}) &= -k_1\rho_r[\mathrm{TOC}][\mathrm{NO}_x^-] - k_2\rho_r[\mathrm{TOC}][\mathrm{O}_2] && (1)\\
\mathcal{R}(\mathrm{NO}_x^-) &= -ck_1\rho_r[\mathrm{TOC}][\mathrm{NO}_x^-] && (2)\\
&\quad -k_3\rho_r[\mathrm{NO}_x^-][\mathrm{NH}_4^+] &&\\
\mathcal{R}(\mathrm{NH}_4^+) &= ak_1\rho_r[\mathrm{TOC}][\mathrm{NO}_x^-] + bk_2\rho_r[\mathrm{TOC}][\mathrm{O}_2] && (3)\\
&\quad -k_3\rho_r[\mathrm{NO}_x^-][\mathrm{NH}_4^+] &&\\
\mathcal{R}(\mathrm{O}_2) &= -dk_2\rho_r[\mathrm{TOC}][\mathrm{O}_2] && (4)
\end{aligned}$$

in which ρ_r is the reactor fluid density and the concentrations are in the units of mole/kg.

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

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.

on PBX 9404 hydrolysate solutions at temperatures between 350 C and 480 C. A more detailed discussion of the kinetic model development is contained in [3].

3.2. Reactor Model

The reaction system is modeled by a series of four partial differential equations, one for each of the chemical components discussed in Section 3.1, that describe the concentrations in a plug flow reactor. The partial differential equation for component c is

$$\frac{\partial[c]}{\partial t} + \frac{F\rho_f}{A_c\rho_r}\frac{\partial[c]}{\partial z} + \mathcal{R}(c) = 0 \qquad (5)$$

in which F is the 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, $[c]$ is the concentration of component c expressed in mole/kg, and $\mathcal{R}(c)$ is the rate of reaction from Eqs. 1 through 4.

The fluid density at reactor conditions is computed using the cubic form of the Peng-Robinson equation of state assuming the reactor fluid can be modeled as water.

$$\begin{aligned} P &= \frac{RT}{v-b} - \frac{a\alpha(T)}{v(v+b)+b(v-b)} \\ \alpha(T) &= \left(1 + c\left(1 - \sqrt{Tr}\right)\right)^2 \end{aligned} \qquad (6)$$

In this expression, P is pressure, T is temperature, v is molar volume, Tr is the reduced temperature, and $a = 5.908$, $b = 0.01893$, $c = 0.9732$ are functions of the critical properties of water.

The concentrations of TOC and NO_x^- in the hydrolysate feed are available from an analysis performed after the base hydrolysis reaction is complete. The O_2 concentration in the hydrogen peroxide feed is determined by assuming complete decomposition of the 30 wt% hydrogen peroxide before it enters the reactor. The reactor inlet concentration in mole/kg of a component, $[c]_i$, is determined from its feed concentration, $[c]_f$, volumetric feed rate, F_c, the hydrolysate volumetric feed rate, F_h, the first hydrogen peroxide volumetric injection rate, H_1, and the feed density.

$$[c]_i = \frac{F_c}{\rho_f(F_h + H_1)}[c]_f \qquad (7)$$

3.3. Reactor Operation

The optimal reactor operation is at the minimal total aqueous nitrogen concentration and a slight excess oxygen concentration. Figure 2 presents the predicted total aqueous nitrogen concentration as a function of the initial hydrogen peroxide injection rate with an effluent excess oxygen concentration target of 0.1 mol/kg, an average reactor temperature of 435C, a reactor pressure of 990 bar, and hydrolysate feed rates ranging from 150 to 300 gal/day. The reduction in the total aqueous nitrogen with reduced feed rate is due to the increased residence time in the reactor. In order to reduce the total aqueous nitrogen in the effluent, the reactor typically will be operated at the lower feed rates. As the hydrolysate feed rate is reduced, however, the effluent aqueous nitrogen concentration sensitivity to the initial hydrogen peroxide injection injection rate increases. For this reason, a model-based controller is developed.

The optimal reactor operation is achieved when the production of NH_4^+ from the TOC–O_2 reactions and the TOC–NO_x^- reactions balances the destruction of NH_4^+ from the NH_4^+–NO_x^- reaction. At low inlet peroxide injection rates, the TOC–NO_x^- reaction removes NO_x^- from the system resulting in a high NH_4^+ concentration. At high injection rates, the TOC–O_2 reaction predominates resulting in an elevated NO_x^- concentration in the effluent. Figure 3 presents the effluent nitrogen component concentrations for the 150 gal/day hydrolysate feed rate in Figure 2 as a function of the initial peroxide injection rate.

The concentration profile of TOC, NO_x^-, and NH_4^+ in the reaction section is shown in Figure 4 for the optimal initial peroxide injection rate of 5.75 gal/day at the 150 gal/day hydrolysate feed rate. The TOC concentration decreases rapidly at the reactor inlet and at the second peroxide injection point due to the reaction with O_2. The increase of NH_4^+ and the decrease of TOC and NO_x^- between the peroxide injection points is due to the oxidation of TOC by NO_x^-. The inlet O_2 is completely reacted with TOC at the beginning of this section. Following the destruction of the remaining TOC after the second peroxide injection point, NO_x^- and NH_4^+ are removed by the NO_x^-–NH_4^+ reaction.

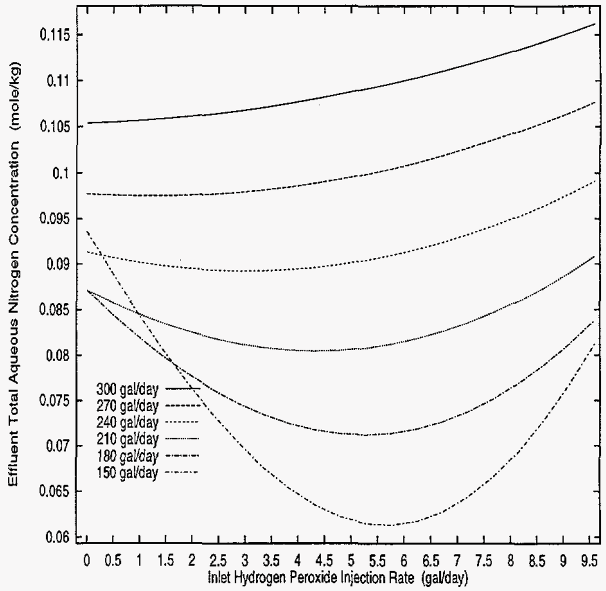

Figure 2: Total aqueous nitrogen effluent concentrations.

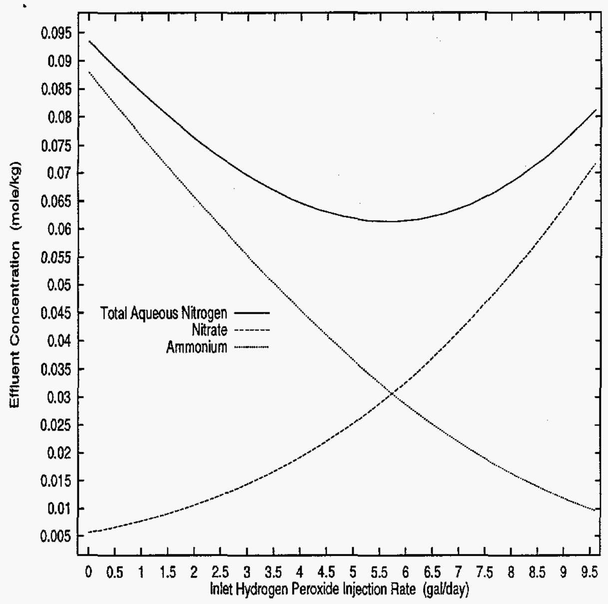

Figure 3: Effluent nitrogen component concentrations.

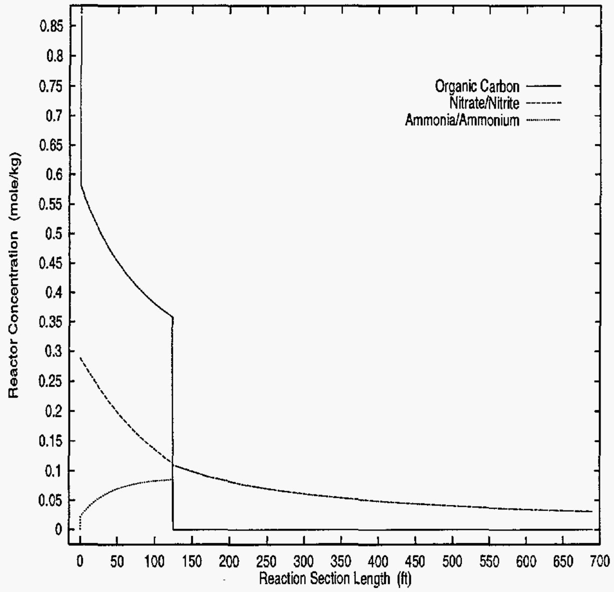

Figure 4: Reactor component concentration profiles.

4. Aqueous Nitrogen Minimization

The reaction system is described by a series of first order, nonlinear, hyperbolic partial differential equations as shown in Eq. 5. Previous work in the control of nonlinear hyperbolic distributed parameter systems considered modal approximation [4], method of characteristics [4], [5] and geometric control approaches [6] in which the controlled and manipulated variables are distributed in space.

In this work, the objective is to minimize the effluent total aqueous nitrogen and not to control the concentrations in the reactor at some target profile. As shown in Figure 2, the process is locally uncontrollable at the desired operating point since either the gain between the inlet peroxide injection rate and the effluent total aqueous nitrogen concentration is zero or the inlet peroxide injection rate is at a minimum constraint. In addition, process measurements are only available at the reactor outlet. For these reasons, a steady-state nonlinear optimization is performed to find the hydrogen peroxide injection rates that minimize the total aqueous nitrogen and bring the excess oxygen concentration to its target at the current hydrolysate feed rate and operating conditions. The optimization problem can be stated as

$$\min \quad [\mathrm{NO}_x^-]_e + [\mathrm{NH}_4^+]_e \tag{8}$$

$$\text{Subject To:} \quad \begin{aligned} \frac{F\rho_f}{A_c\rho_r}\frac{\partial[c]}{\partial z} + \mathcal{R}(c) &= 0 \qquad (9)\\ [\mathrm{O}_2]_e &= [\mathrm{O}_2]_t \qquad (10)\end{aligned}$$

in which $[c]_e$ is the effluent concentration of component c and $[\mathrm{O}_2]_t$ is the desired excess oxygen target. The excess oxygen concentration in the effluent can be determined from the following expression

$$[\mathrm{O}_2]_e = \frac{H_2([\mathrm{O}_2]_f/\rho_f) + (F_h + H_1)([\mathrm{O}_2] - d[\mathrm{TOC}])}{F_h + H_1 + H_2} \tag{11}$$

in which $[\mathrm{O}_2]$ and [TOC] are the model predicted oxygen and organic carbon concentrations in the reactor prior to the second peroxide injection point and H_2 is the second peroxide injection rate. The other variables are as defined previously. Feedback from the process is provided by on-line estimation of the model parameters which is discussed in Section 6.

5. Excess Oxygen Control

Excess oxygen in the reactor effluent is controlled by adjusting the second peroxide injection rate based on the effluent oxygen concentration determined by the oxygen analyzer in the gas effluent stream. A bias, which is difference between the model predicted effluent oxygen concentration, $[\mathrm{O}_2]_m$, and the concentration determined by the oxygen analyzer, $[\mathrm{O}_2]_a$, is computed as follows

$$B = [\mathrm{O}_2]_m - [\mathrm{O}_2]_a \tag{12}$$

in which $[\mathrm{O}_2]_m$ is a dynamic solution to the partial differential equation model. The adjustment to the second peroxide injection rate is determined from this bias using Eq. 11.

$$\Delta H_2 = \frac{B(F_h + H_1)\left([\mathrm{O}_2]_f/\rho_f - [\mathrm{O}_2] + d[\mathrm{TOC}]\right)}{\left([\mathrm{O}_2]_f/\rho_f - [\mathrm{O}_2]_t\right)^2 - B\left([\mathrm{O}_2]_f/\rho_f - [\mathrm{O}_2]_t\right)} \tag{13}$$

6. Model Update

In order to minimize the total aqueous nitrogen in the reactor effluent, the NO_x^- and NH_4^+ concentrations must be essentially equal after the second peroxide injection point to maximize the rate of destruction of both components. The determination of the hydrogen peroxide injection rates necessary to achieve these concentrations is based on the reactor model as shown in Section 4. Since the kinetic model is a simplified representation of the reactions taking place, it is reasonable to expect that there will be some modeling error over the normal operating range of the reactor. Therefore, nonlinear parameter estimation is used to update the model based on the measured NO_x^- and NH_4^+ concentrations in the effluent.

Since the limited number of process measurements available restrict the number of kinetic model parameters that can be reliably estimated, a sensitivity study was carried out to determine the model parameters that had the largest effect on the calculated NO_x^- and NH_4^+ effluent concentrations. Based on this study, the feed TOC and NO_x^- concentrations were selected. This choice can also be justified from an operational perspective since careful analysis of the hydrolysate feed may not always be performed in a process environment. The change in the predicted effluent concentrations as a function of the feed concentration of TOC and NO_x^- is shown in Figures 5 and 6.

Determination of the feed concentrations is performed by a moving horizon estimator using an initial estimate approach [7]

$$\min_{[TOC]_f,[NO_x^-]_f} \sum_{j=1}^{N} \Big(\big([NO_x^-]^m_{j\Delta t} - [NO_x^-]^a_{j\Delta t}\big)^2 + \big([NH_4^+]^m_{j\Delta t} - [NH_4^+]^a_{j\Delta t}\big)^2 \Big) \qquad (14)$$

in which $[c]^m_{j\Delta t}$ is the model predicted effluent concentration for component c at time $j\Delta t$, $[c]^a_{j\Delta t}$ is the analytical measurement of the effluent concentration at time $j\Delta t$, Δt is the sample time of the estimator, and N is the estimation horizon.

Acknowledgments

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References

[1] P. C. Dell'Orco, et. al. Hydrothermal treatment of high explosive hydrolysate. Part II: Reaction kinetics and process optimization. Submitted. *Ind. Eng. Chem. Res.*, 1998.

[2] A. H. Cutler, et. al. A critical evaluation of the plug-flow idealization of tubular-flow reactor data. *Ind. Eng. Chem. Res.*, 27:691–697, 1988.

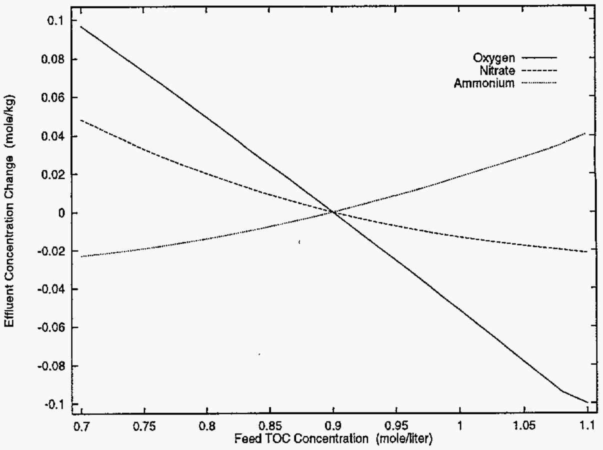

Figure 5: Effluent concentration change with feed TOC.

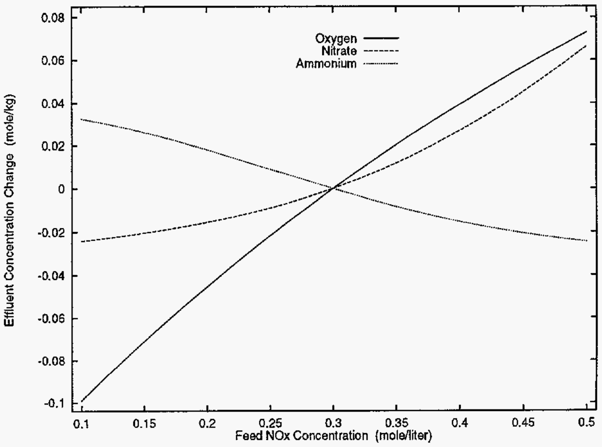

Figure 6: Effluent concentration change with feed NO_x^-.

[3] P. C. Dell'Orco, et. al. Demilitarization of high explosives. In *The Joint DoD/DOE Munitions Technology Development Program, Progress Report for FY96*, page 55, 1997.

[4] W. H. Ray. *Advanced Process Control.* McGraw–Hill, New York, 1981.

[5] B. O. Recke and S. B. Jorgensen. Nonlinear dynamics and control of a recycle fixed bed reactor. In *Proc. of the 1997 American Control Conference*, pages 2218–2222, 1997.

[6] P. D. Christofides and P. Daoutidis. Feedback control of hyperbolic PDE systems. *AIChE J.*, 42(11):3063–3086, 1996.

[7] K. R. Muske and J. B. Rawlings. Nonlinear moving horizon state estimation. In R. Berber, editor, *Methods of Model Based Process Control*, pages 349–365, 1995.